SINTERING BEHAVIOUR OF CUPRONICKEL ALLOY POWDER

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

in the Department
of
METALLURGY

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA
July, 1976

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Date July 15, 1976
Studies have been made of both the solid state and supersolidus sintering characteristics of spherical cupronickel powders. Observations were made of the structural changes and shrinkage rates in specimens sintered in vacuum and in hydrogen.

It was concluded that the early stage of solid state sintering (up to one hour at 1200°C) was dominated by Nabarro-Herring creep. Calculations of the stresses at necks during sintering were consistent with the proposed mechanism. No solute segregation to necks occurred during sintering, contrary to earlier observations by Kuczynski with other copper alloys.

When pre-sintered cupronickel powder (68 μm) aggregates were heated to a temperature above the equilibrium solidus, melting was nucleated first at high angle grain boundaries (necks) and particle surfaces (voids). Most melting was intragranular, nucleated at interdendritic sites of above-average copper content. Solid-liquid equilibrium was established in less than one minute at the supersolidus temperature. The dihedral angle in the system was less than or equal to zero.
Growth of solid grains during supersolidus sintering obeyed a parabolic rate law consistent with a model of growth due to phase boundary reaction-controlled solution and precipitation.

Shrinkage during supersolidus sintering proceeded in several distinct stages. Prior to attainment of equilibrium; i.e. within the first minute above the solidus (Stage 1), contraction could be attributed to a melting and melt accommodation sequence, plus flattening by the local operation of solution and precipitation. Beyond this (Stages 2 and 3) all densification was attributed to solution-precipitation, including grain growth. In the final stage of shrinkage (Stage 3) the rate of contraction was controlled by the rate of escape of gas from closed pores.

Comparisons have been made between the supersolidus sintering of cupronickel and the liquid-phase sintering of iron-copper. The processes are seen to have little in common.
PART B

ABSTRACT

Porous cupronickel specimens with zero to 50 per cent porosity by volume have been prepared from loose prealloyed cupronickel powders by solid state and supersolidus sintering techniques. Young's Modulus (E) and strength values at low strains were determined in compression tests. Porosimetry and metallography were used to establish the continuity, size and shape of the pores.

In specimens sintered to > 93% of solid, the pores were essentially all closed and equiaxed, and the grains could not be identified with the original powder particles. In this density range, the elastic modulus varied with fractional porosity ($P_c$ for closed pores) according to

$$E = E_0(1 - 2P_c)$$

which for cupronickel is consistent with the predictions of several published theoretical analyses based on elasticity theory.

Between about 93 and 92% of solid density there was a drop in the elastic modulus associated with the appearance of major amounts of interconnected, irregular-shaped porosity. With decreasing density below 92
per cent of solid, pores increased in number but not in average size. For the range of 92 to 62% of solid, the elastic modulus was below that predicted from published analysis. However, over the whole range of density, the results fitted reasonably well to the relationship

\[ E = E_0(1 - 2P) \]

where \( P \) is the total fractional porosity. This is a special case of a Rule of Mixtures dependence wherein the loose powder aggregate prior to sintering has an initial porosity of 0.5 and has zero strength until sintered. The result is discussed in terms of the theoretical variation of the load-carrying neck area with porosity in sintered material. A similar approach is taken to analyse the results of offset strength measurements.
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ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Dr. John Lund for his advice and assistance during the course of this investigation. Helpful discussions with other faculty members and fellow graduate students, particularly the candidate's Ph.D. committee members, Dr. A.C.D. Chaklader, Dr. E.B. Hawbolt and Mr. R.G. Butters, are also gratefully acknowledged.

Special thanks are expressed for the generous assistance given by many members of the department technical staff, particularly Messrs. B.N. Walker, J. Walker, A. Lacis, E. Klassen and P. Musil.

Financial assistance was received in the form of an assistantship under National Research Council of Canada grant number A-2449, and is gratefully acknowledged.
PART A

STUDIES OF SOLID STATE AND SUPERSOLIDUS SINTERING
Chapter 1

INTRODUCTION

1.1 Solid State Sintering

The published literature is rich in reports of both experimental and theoretical studies of the sintering of metals in the solid state. The application of much of the previous theoretical work to practical sintering situations is not highly productive, however, for two major reasons:

a) The packing of particles and the internal pore morphology in real powder bodies deviate in important ways from those used in model experiments and analyses. This is particularly true for irregular shaped particles or for pre-compacted powders.

b) Most, and perhaps the best, of the prior work has been devoted to pure, single component metal systems. In practice, almost all powder metallurgical applications are to alloys of two or more major components, and impurities are also commonly involved.

1.1.1 Pure Metal Powders

Three successive, but overlapping stages have been distinguished in the course of sintering:
a) Formation of necks between particles, and neck growth. Particles bond together at contacts in the early stage of sintering without losing their identity and without moving closer together.

b) Further neck growth, accompanied by the approach of particle centres (densification), and progressive loss of particle identity.

c) Pores become isolated and spherical. In the proximity of grain boundaries, pores shrink and are eventually eliminated. In the absence of grain boundaries, further pore shrinkage stops.

Material transport mechanisms which have been cited for the sintering processes include: viscous creep, plastic flow, volume self-diffusion, grain boundary diffusion, surface diffusion, evaporation-condensation and recovery-recrystallisation. All of these mechanisms may either simultaneously or individually aid bonding and neck growth. Of these, viscous creep, plastic flow, volume diffusion and possibly grain boundary diffusion can account for the approach of particle centres; i.e. contribute to densification. In the case of metals, viscous flow can also be associated with self-diffusion in accordance with the "diffusional creep" model of Nabarro-Herring [1,2].

Since the important work of Kuczynski [3], several analytical approaches have been taken to predict neck growth and densification in powder aggregates as a function of sintering temperature and time. The approaches are based on different models of material transport.

The equations governing neck growth in model experiments are:

\[ \frac{x^n}{a^m} = F(T)t \quad \text{or} \quad \left(\frac{x}{a}\right)^n = F(T)t^{a^m-n} \]
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Equations for mid-point approach in the sphere-sphere model are as follows:

a) Viscous flow

$$\frac{\Delta L}{L_0} = -\frac{9n_1 \gamma^2 t^2}{16 a^2 \eta^2} \quad \text{(Kingery and Berg [6])} \quad (1.1)$$
b) Volume Diffusion

(i) Grain boundary as vacancy sinks

\[ \frac{\Delta L}{L_0} = \left( \frac{2 \gamma D_v \Omega}{RT a^3} \right)^{0.5} t^{0.5} \quad \text{(Coble [10])} \]  

\[ = -\left( \frac{\pi \gamma D_v \Omega}{3\sqrt{2} RT a^3} \right)^{0.4} t^{0.4} \quad \text{(Ichinose and Kuczynski [11])} \]  

\[ = -\left( \frac{10\sqrt{2} \gamma D_v \Omega}{RT a^3} \right)^{0.4} t^{0.4} \quad \text{(Kingery and Berg [6])} \]  

\[ = -\left( \frac{31 \gamma \Omega D_v}{\pi^2 RT a^3} \right)^{0.46} t^{0.46} \quad \text{(Johnson and Cutler [12])} \]  

\[ \frac{\Delta V}{V_0} = -\frac{3n_1}{8} \left[ \frac{80 \gamma \Omega D_v}{a^3 RT} \right]^{0.8} t^{0.8} \quad \text{(Kingery & Berg [6])} \]  

(ii) Particle Surface as vacancy sinks

\[ \frac{\Delta L}{L_0} = -\frac{n_1}{8} \left( \frac{40 \gamma D_v \Omega}{RT a^3} \right)^{0.8} t^{0.8} \quad \text{(Kingery & Berg [6])} \]  

\[ \frac{\Delta L}{L_0} = 0 \quad \text{(Ichinose and Kuczynski [11])} \]
c) Grain boundary diffusion

\[
\frac{\Delta L}{L_0} = -\left(\frac{50 w \gamma \Omega D_G}{\pi R T a^n}\right)^{0.31} t^{0.31} \quad \text{(Johnson and Cutler [12])} \tag{1.9}
\]

\[
= -\left(\frac{3 D_G \gamma \Omega w}{a^n R T}\right)^{0.33} t^{0.33} \quad \text{(Coble [10])} \tag{1.10}
\]

where

\(\Delta L\) = the change in length

\(L_0\) = the original length

\(a\) = the radius of the particle

\(n_1\) = the coordination number

\(\gamma\) = the surface free energy of the particle

\(\Omega\) = the atomic volume

\(w\) = the grain boundary thickness

\(n\) = the viscosity of the substance

\(R\) = the gas constant

\(T\) = the absolute sintering temperature

\(t\) = the isothermal sintering time

\(D_v\) = the lattice diffusion coefficient

\(D_G\) = the grain boundary diffusion coefficient

\(D_s\) = the surface diffusion coefficient

\(x\) = the neck radius

\(M\) = the molecular weight

\(k\) = Boltzmanns constant

\(\delta\) = the surface thickness

\(P_0\) = the equilibrium vapour pressure
Based largely on observations in wire, two-sphere and sphere-plate model experiments [13,14,15], it was concluded that surface diffusion was of primary importance in the earliest stage of sintering, that volume diffusion was more significant in the intermediate stage, and that grain-boundary diffusion was dominant in the final stage (isolated pore removal). Experiments with powder aggregates, rather than models, provide conflicting evidence of the general applicability of the above conclusions.

More recently, Johnson [16,17,18] has provided a more practical treatment of sintering in which he considers the operation of all mechanisms simultaneously rather than in isolation. Again, however, the quantitative predictions are strictly applicable only to regular arrays of particles of simple shape.

There are conflicting opinions about the participation of dislocations (plastic flow) in the densification of powder agglomerates during sintering. It has been suggested that the surface tension stresses at the neck region cause dislocation creep. However, Wilson and Shewmon [19] reached the conclusion that steady state creep by dislocation motion is impossible since the condition \(2\gamma > G_0 b\) (where \(b\) is Burgers vector and \(G_0\) is the shear modulus), for dislocation generation, can never be satisfied. Tikkanen et al. [20] noticed the existence of numerous twins in sintered nickel (from loose powder) and claimed that this observation strongly supported the theory that dislocations (plastic flow) are effective contributors to the densification process. In a study of sintering using hot stage electron microscopy Easterling and Thölen [21] concluded that dislocations play little or no part in sintering in the absence of an
external load. Similar observations were reported from previous work on the sintering of iron and aluminum spheres by Easterling and Thölen [22].

In a recent paper Ashby [23] has discussed the possibilities of dislocation involvement in sintering. He suggests that "all the dislocation segments in the neck region climb, becoming curved, until they reach a configuration such that they are in static equilibrium. In climbing, the dislocations release matter which joins the neck." Ashby described this as a "transient creep" mechanism which would be involved in the very early stage of sintering.

There is general agreement that if an external stress is applied then there is a significant contribution from dislocations to the densification process.

1.1.2 Prealloyed Powders

When a prealloyed powder mass of homogeneous composition is sintered in the solid state, neck growth and densification might be expected to proceed by mechanisms similar to those described above for a pure metal. However, the components of the alloy may not diffuse to the necks at the same rate, whether material transport is by surface or volume diffusion. Thus at least in the early stage of sintering, when the vacancy gradient is large due to the small neck radius, a greater concentration of the faster diffusing atoms may be generated in the neck area. Kuczynski et al. [24] observed this phenomenon occurring in the sintering of solid solution alloy wires. For Cu + 8 at. % In wire, indium diffused preferentially to the neck and formed an indium rich phase on the neck surface. In the case of Cu + 4.5 at. % Ag alloy wires, sintered at 920°C for 10 minutes and 2 hours, a silver rich area was found only in the specimens sintered for 10 minutes. It was argued that after longer times, there was
rediffusion of the solute atoms. Silver + 10 at. % Cu alloy wires sintered at 830°C for 10 minutes showed Cu rich neck regions. This may be attributed to the observation that in dilute solutions of copper and silver, the diffusion coefficient of the solute is greater than that of the solvent.

If the prealloyed powder particle contains two or more phases in equilibrium at the sintering temperature, the progress of sintering may be further influenced, e.g. by restrictions on grain growth or grain boundary mobility.

1.2 Liquid Phase Sintering

An alternative, and often effective approach to the manufacture of alloy parts by powder metallurgy is to sinter a powder mixture (a) above the melting point of one or more minor components of the mixture, or (b) at a temperature where some liquid will eventually form when alloy phase equilibrium is established. The technique is applied commercially to relatively immiscible systems such as copper-lead (for bearings) and tungsten-copper (for electrical switch contacts), and to partially-miscible systems such as iron-copper (for machine parts) and tungsten carbide-cobalt (cutting tools). In these cases, liquid is usually present throughout the sintering cycle. However, the procedure is also sometimes applied to a miscible mixture, in which case liquid is present only for the period during which the liquid species enters into solution in the more abundant solid. An example of the latter case is the sintering of a Cu - 10 wt. % Sn mixture at a temperature just above the melting point of tin. The tin rapidly diffuses into the copper to form a porous solid (bronze) body.
The structural and dimensional changes which take place under conditions of liquid-phase sintering are determined largely by the relative energies of the solid-vapour ($\gamma_{SV}$), liquid-vapour ($\gamma_{LV}$), solid-liquid ($\gamma_{SL}$) and grain boundary ($\gamma_{GB}$) interfaces in the system being sintered. Wetting of solid particles by the liquid is defined by the contact angle, $\theta$, which is given (from sessile droplet equilibrium) by:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}.$$

Systems for which $\theta > 90^\circ$, described as non-wetting, are of no practical interest since the liquid would be ejected from a solid-liquid aggregate. For $\theta = 0^\circ$ the liquid will spread throughout the aggregate, tending to cover all solid surfaces. At intermediate values of contact angle, the liquid tends to collect at solid-solid necks. For any system with $\theta < 90^\circ$, there will be a capillary pressure which acts as a hydrostatic compressive stress on the aggregate.

Equilibrium of surface tensions requires that the liquid makes an angle with the solid at a grain boundary given by

$$\phi = 2 \arccos \frac{\gamma_{GB}}{2\gamma_{SL}} = \text{Dihedral angle.} \quad (1.11)$$

In a system with a zero dihedral angle, the liquid will completely penetrate grain boundaries (at least those high angle boundaries for which $\gamma_{GB}$ is above a critical value). This condition correspond to $2\gamma_{SL} < \gamma_{GB}$; i.e. two solid-liquid interfaces can replace a solid-solid interface. When $\phi > 0$, grain boundaries are not completely penetrated. Thus, a solid network ("skeleton") must exist.
Several mechanisms [25] have been proposed to account for the dimensional (density) change in an aggregate which is sintered in the presence of a liquid phase.

1. **Rearrangement**

If solid particles are dispersed in a wetting (θ < 90°) liquid, they can slide past one another. The capillary stress which exists in a wetting system might tend to encourage particles to move into closer packed arrays. A substantial densification could occur by this mechanism alone if enough liquid were present. Kingery [26,27] has estimated that an array of spherical solid particles can be completely densified by rearrangement if 35 volume per cent of a completely wetting liquid is present.

It is important to note that it is a necessary condition for rearrangement that the dihedral angle be zero. Otherwise, a solid skeleton will exist. There are several systems of commercial interest in which this condition apparently prevails at least temporarily during sintering, including WC - Co and Fe - Cu.

Kingery has treated the rearrangement process in terms of viscous flow, and has predicted that the time dependence of shrinkage, \( \frac{\Delta V}{V_0} \), will be given by

\[
\frac{\Delta V}{V_0} \propto t^{1+y} \quad \text{where} \quad 0 < y \ll 1
\]  

(1.12)

\( (V_0 \text{ and } \Delta V \text{ are the original volume and change in volume of the powder aggregate.} ) \)
A more complex analysis was reported by Cech [28], but the predictions are similar to those of Kingery. There are several reported verifications of the above time-dependence of shrinkage, although some investigators [25,29] have reported much higher-order dependence.

2. Solution-Precipitation

Several mechanisms of shrinkage during liquid-phase sintering have been proposed which involve solution of the solid by the liquid at some locations followed by re-precipitation of solid at other locations. Price et al. [30] observed both rapid solid particle growth and rapid densification in the liquid phase sintering of W-Ni-Cu alloys. They attributed these effects to the selective dissolution of small particles (small radius of curvature) with precipitation onto the larger particles. While this process, which has become known as the Heavy Alloy mechanism [31], can adequately and quantitatively explain particle growth, it is not obvious that it can account for any densification. This criticism of the Price et al. model has been recorded by Parikh and Humeniak Jr. [32], and by Kingery [27].

An alternative solution-precipitation mechanism was proposed by Kingery [27]. At contacts, between solid particles, or at near contacts with a thin liquid film separation, there is a local concentration of the capillary stress in wetting systems. This increases the chemical potential of the solid, and thus its solubility in the liquid, at or near the contacts. Solid dissolves locally and is precipitated at less stressed regions. The mechanism predicts two effects; (a) densification associated with the approach of particle centres, and (b) shape changes of the solid particles.
such as to allow more efficient filling of space. Both of these effects are generally observed in wetting systems. From an analysis of his model, Kingery derived the following relationship for spherical particles:

$$\frac{\Delta V}{V_0} = C a^x t^z$$  \hspace{1cm} (1.13)

where 'a' is the mean particle radius and 'C' is a constant which includes $D_V$, $\gamma_{LV}$ and $T$.

For diffusion rate-control of the process, $x = -\frac{4}{3}$ and $z = \frac{1}{3}$. If the rate controlling step is a phase-boundary reaction, $x = -1$ and $z = \frac{1}{2}$. The constant is different for the two cases. Kingery also treated theoretically the case of prismatic shaped particles such as can develop during the sintering of WC-Co and TiC-Ni.

Attempts to verify experimentally the Kingery model of densification by solution-precipitation are complicated by the fact that the process is commonly preceded or accompanied by rearrangement. Kingery's analysis of his own experiments with Fe-Cu [33], WC-Co [34] and of published data for TiC-Ni-Mo [35] led him to conclude that solution-precipitation was diffusion rate-controlled in the three systems. Prill et al. [36] later reanalysed the same data and concluded that a phase boundary reaction was rate-controlling.

3. Coalescence

For systems with $\phi > 0$, solid state sintering mechanisms can operate within the solid skeleton even when a liquid phase is present.
Thus even in the absence of interfacial energy relationships which promote rearrangement or solution at contacts, densification of the aggregate can proceed.

Even in a wetting system with $\phi = 0$, some adjacent solid particles may be crystallographically oriented with respect to each other such that a low angle, low energy solid boundary is established which is not wetted by the liquid.

"Particle growth" is commonly observed during liquid phase sintering, in systems for which the dihedral angle is zero or positive. With zero dihedral angle, the growth can be largely attributed to the Heavy Alloy mechanism discussed above. However, there is experimental evidence that growth can also result from quite different processes described as "coalescence." Warren [37] distinguishes between two types of coalescence.

a) Agglomeration—particles retain their identity initially and are separated by contiguous boundaries. This process is essentially solid state sintering within a cluster of particles, with grain boundaries initially at necks. In the later stages of sintering of the agglomerate, the particles lose their identity, voids become isolated, and grain boundaries migrate. Thus an apparent particle "growth" has occurred. Agglomeration is expected to be important only in systems with positive dihedral angle.

b) "True" coalescence in which two or more single crystal particles of similar crystallographic orientation combine to form a single particle.

Coalescence processes are not as effective in producing net shrinkage (densification) of a powder mass as are rearrangement and particle
shape-change processes. Thus, in liquid phase sintering systems for which $\phi > 0$, densification proceeds at relatively low rates.

It should be noted that for some systems, dimensional changes during liquid phase sintering are complicated by other factors such as a) dissolution of liquid in the solid, causing progressive expansion of the solid particles and reduction in the amount of liquid available, and b) changing interfacial energies as a result of alloying during sintering. Only for the simplest of systems it is possible to characterise the progress of sintering in terms of the theoretical models described above.

1.3 Supersolidus Sintering

If an alloy powder mass is sintered at a temperature above the solidus of the alloy, liquid forms and equilibrium is more or less rapidly established. This process, described as supersolidus sintering [38], appears to be a special, or "ideal" case of liquid phase sintering. Liquid will be present throughout the sintering cycle. In general, it can be expected that the system will be completely wetting with a zero dihedral angle. Conditions are thus intrinsically favourable for rapid and effective densification of the powder mass by rearrangement and solution-precipitation processes.

As a means of fabricating alloy parts of high density from pre-alloyed powder, supersolidus sintering has an obvious potential, a fact which appears to have gone unrecognised until very recently. Preliminary studies of supersolidus sintering applied to high carbon steels and copper nickel alloy powders were reported by Cambal et al. [38] and Lund et al.
There are some recent indications that the process is being applied commercially to aluminium alloy powders [41], although no data have been reported to describe the amount of liquid used or the effect of the liquid on sintering kinetics. It is likely that the use of supersolidus sintering temperatures for aluminum alloys was at least partially motivated by the difficulty of breaking down oxide films between particles when solid state sintering was attempted.

1.4 Scope of the Present Research

Supersolidus sintering is of considerable engineering interest, yet has never previously been examined in depth. A primary objective of this investigation was to study the rates and mechanisms of contraction in the process, and to compare these with conventional liquid phase sintering. Some studies of solid state sintering of a solid solution alloy powder were also undertaken, for several reasons:

a) The sintering behaviour of solid solution powders has received little previous attention. Careful studies of structural changes are only reported for model experiments, notably in the work of Kuczynski [24] with wire models.

b) In the sintering of a solid solution, material transport may be manifested in behaviour which cannot be seen in a pure, single component system. Thus, further insight into solid state sintering mechanisms might be provided by examination of solid solution sintering.

c) Some solid state sintering inevitably occurs on heating to supersolidus temperatures. The structure developed at this stage can significantly affect the behaviour when liquid forms. Moreover, observations of the transition from subsolidus to supersolidus sintering may provide clues as to the sintering mechanisms involved.
Chapter 2

EXPERIMENTAL

2.1 Choice of Alloy for Experimental Work

Many binary solid solution systems were considered prior to choosing the alloy to be used in the present work. The following characteristics were desirable:

a) Low vapour pressure at the temperatures required for supersolidus sintering.

b) Low reactivity with air at ambient temperatures and with sintering atmospheres and containers at elevated temperatures. The oxides of the components should be readily reduced at moderate temperatures in hydrogen.

c) A solidus-liquidus temperature interval of 50 to 100°C [38].

d) Phase equilibrium data available in the literature.

e) No solid state transformations, or liquid-solid reactions which could obscure, on cooling, the structure present at the sintering temperature. A simple isomorphous system was preferred.

On the basis of these criteria, the copper-nickel alloy system was selected for the present study, and the specific alloy chosen for conversion to powder was 50% copper, 50% nickel by weight.
2.2 Preparation and Characteristics of Powders

A bulk alloy of nominal composition 50% copper, 50% nickel by weight was supplied to the Federal-Mogul corporation for custom atomisation. Inert gas was specified as the atomising medium in order to obtain a) dominantly spherical powder particles, and b) freedom from major oxidation or other contamination of the alloy. The as atomised powder all passed a 60 mesh (Tyler, 250 μm) screen, and was mostly minus 100 mesh.

The chemical analyses of several particle size fractions are shown in Table 2.1. All reported analyses for copper and nickel are the average of two or more determinations. Spectroscopic analysis on as-received powder revealed the presence of 0.001% Al, 0.001% Ag, 0.005% Mg, 0.01% Fe, 0.05% Co and 0.1% Si by weight. The silicon content, verified by chemical analysis (Table 2.1) reflects the use of silicon as a deoxidant.

Most of the powder particles were spherical, with small accretions as shown in Figure 2.1. Also, some agglomerates of the spherical
particles were seen. The surface of the particles was rough due to dendritic solidification of the melt, as shown in Figure 2.2. Optical metallography revealed a cored dendritic structure, and both large pores and microporosity as shown in Figure 2.3.

2.3 Cleaning and Homogenisation of Powder

Prior to use in sintering experiments, batches of powder were cleaned by heating in hydrogen or cracked ammonia for up to 12 hours at 600°C. Some re-oxidation of powders undoubtedly occurred during preparation of specimens for sintering. Where sintering was conducted in hydrogen, the low-temperature cleaning treatment was probably superfluous. In the case of vacuum sintering experiments, the amount of oxygen in the specimens at the start of heating was significant, as discussed in a later portion of the thesis. Above about 600°C in a reducing atmosphere the extent of sintering was such that the particles of powder could not be readily separated.

Preliminary experiments were conducted to establish conditions for homogenisation of the powders. It was found that the cored microstructure disappeared visually when the powder was heated for one hour at 900°C, and this procedure was applied as a "Presintering" treatment in all cases except where specifically noted otherwise.

2.4 Preparation of Cast Cupronickel Specimens

The coarsest screen fraction of the cupronickel alloy powders was melted under hydrogen in an alumina (alundum) crucible using induction
Figure 2.1. Scanning electron micrograph of 200 x 230 mesh (68 μm) cupronickel powder, x235.

Figure 2.2. Scanning electron micrograph of 68 μm cupronickel particle. (Rough surface due to dendritic solidification of the melt), x1000.
Figure 2.3. As-atomised powder. x250 (Cored dendritic structure, pores and segregation-free crust); (a) 68 μm powder, (b) 49 μm powder
heating in a graphite susceptor. The molten alloy was solidified in the crucible by applying a water cooled copper chill to the bottom end of the alundum crucible. In this manner, 1 cm diameter x 5 cm long bars were cast.

One of the as cast alloy specimens was analysed for microsegregation on the electron beam microprobe analyser, with the results shown in Figure 2.4.

Inhomogeneities of composition along any line through a cast structure can be approximated to a Fourier summation of sinusoidal variations. This yields, from the solution of Fick's second law, an expression [42]

$$\frac{c}{c_m} = e^{-\frac{\pi^2 D t}{\lambda^2}}$$

(2.1)

as an approximation for the redistribution of solute during an homogenisation anneal, where,

- $c$ = the variation from the average concentration at the point $\lambda$,
- $c_m$ = the initial maximum variation from the average concentration,
- $\lambda$ = the distance between a region of maximum concentration and an adjacent region of minimum concentration,
- $D_{\text{hom}}$ = the interdiffusion coefficient at the homogenising temperature,
- $t$ = the time for the desired degree of homogeneity.

Assuming the average composition to be 50 wt. % copper and using values of $4.8 \times 10^{-11}$ cm$^2$/sec. for $D_{\text{hom}}$ [43,44] at 1000°C and 0.01 cm for $\lambda$.  

---

21
Figure 2.4. Composition versus distance plots for as cast and homogenized cupronickel alloy (from Microprobe Analysis).
in Equation (2.1), a time of 270 hours was calculated to reduce the concentration variation to 0.01 of the maximum variation in the cast cupronickel at 1000°C. Accordingly, cast specimens were homogenised at 1000°C for 12 days.

The electron microprobe analysis of the as homogenised cupronickel revealed a composition variation of ±1 weight per cent of the average composition as shown in Figure 2.4. Also, average compositions of 49.9 wt. % Cu for the top portion and 49.8 wt. % Cu for the bottom portion of the homogenised casting indicated that the castings exhibited little or no macrosegregation along their length. The chemical analysis of as homogenised cupronickel is given below:

\[
\begin{align*}
\text{Cu} & : 49.46 \text{ wt. \%} \\
\text{Ni} & : 50.10 \text{ wt. \%} \\
\text{Si} & : 0.23 \text{ wt. \%} \\
\text{Al} & : 0.05 - 0.06 \text{ wt. \%} \\
\text{Co} & : 0.02 - 0.07 \text{ wt. \%} \\
\text{B} & : \sim 0.05 \text{ wt. \%} \\
\text{O} & : 0.0003 \text{ wt. \%}
\end{align*}
\]

(Can Test Ltd.)

2.5 Preparation of Powder Specimens

As-cleaned powders were poured into recrystallised alumina crucibles of 1.3 cm inside diameter. By adding approximately 25 gms of the powder in several increments, and tapping the crucibles between additions, a column of powder was obtained with 50.0 ± 0.02 per cent of the density of the
solid alloy. The maximum packing density that could be achieved by tapping 200 x 230 mesh powder was 53 per cent of the theoretical density. The loose powder columns were then pre-sintered for one hour at 900°C in a vacuum of $0.4 \times 10^{-5}$ torr. This treatment produced cylinders which were strong enough to sustain handling when removed from the crucibles.

2.6 Sintering Procedures

2.6.1 Vacuum Sintering

Homogenisation, solid state sintering and some supersolidus sintering experiments were done in a Centorr vacuum furnace. The furnace assembly consisted of a water cooled cylindrical copper chamber with internal tungsten screen heating elements located concentrically in the chamber. Two W/3% Re - W/25% Re thermocouples located close to the heating elements were connected to a temperature control unit. A Pt - Pt/10% Rh thermocouple was conducted to the specimen through a seal in the lid of the vacuum chamber.

The furnace chamber could be pumped to a vacuum of $10^{-7}$ torr. There was also an access for the controlled introduction of gases to the chamber.

Crucibles of dimensions 25 mm diameter x 100 mm tall could easily be accommodated inside the furnace. Several runs were made to calibrate the furnace for power settings and temperature control. It was possible to control the temperature at a desired level within ±3°C. A maximum temperature variation of ±2°C along the length of a 12 mm diameter x 38 mm long specimen was detected.
Cupronickel powder columns were presintered in the vacuum furnace with the thermocouple tip embedded in the top of the powder column. At the end of the presintering treatment the temperature was raised. The standard thermal cycle for a solid state sintering run is shown in Figure 2.5. After completion of a run, the power to the furnace was switched off and the sintered specimen was allowed to cool inside the furnace. A vacuum of \( \sim 10^{-5} \) torr was maintained throughout the cycle.

In the case of supersolidus sintering, the cupronickel powder columns were presintered in a split alumina crucible. They were further sintered isothermally at a supersolidus temperature for a desired interval of time. A vacuum of \( 10^{-2} \) torr was maintained during most of the thermal cycle, which is shown in Figure 2.6. However, when the furnace was switched off, helium gas was simultaneously introduced into the furnace chamber at one atmospheric pressure and the specimen was cooled with the helium atmosphere inside the furnace. For a few runs, the complete supersolidus sintering cycle was completed either in a vacuum of greater than \( 10^{-5} \) torr or in an atmosphere of argon gas instead of vacuum and helium.

2.6.2 Superkanthal Furnace Practice

The superkanthal furnace consisted of a vertical alumina tube heated externally by means of two molybdenum disilicide heating elements as shown in Figure 2.7. The bottom end of the alumina tube was immersed in a quenching medium. The top end of the tube could be closed with a water-cooled brass lid. The lid contained a gas inlet tube, two thermocouple access holes and a central hole to accommodate a wire supporting the specimen.
Figure 2.5. Thermal cycle for solid-state sintering in the Centorr furnace.

Figure 2.6. Thermal cycle for supersolidus sintering in the Centorr furnace.
Figure 2.7. Superkanthal furnace assembly. Radiation cage and specimen suspension shown separately (top right).
The upper ends of thermocouple and support wires were attached to a slide block. The thermocouple wires also supported a radiation cage.

The radiation cage consisted of two molybdenum sheet discs separated by three 50 mm long alundum thermocouple sheaths and molybdenum wires. The specimen was hung inside the cage by a molybdenum wire passing through a central hole in the top disc. The specimen could be lowered into the quench bath through a central hole, 18 mm in diameter, at the bottom disc of the cage. Since the specimen support wire and thermocouple wires were attached to the slide block, the cage along with the specimen could be lowered to, or raised from, the constant temperature-hot zone of the furnace.

The temperature control thermocouple, made up of Pt and Pt/13% Rh wires, was located at the high temperature zone of the furnace touching the outer surface of the alumina tube. The furnace was calibrated in preliminary runs. Any desired temperature could be obtained and maintained within ±2°C by controlling the power input and by using the temperature control. There was a constant temperature zone of greater than 35 mm length in the furnace tube.

A presintered cylinder from the vacuum furnace was removed from the split crucible. A hole, 1.5 mm in diameter was drilled radially near one end of a cylinder to allow a support wire to be fastened to the specimen. Alloying of the wire with the specimen was prevented by using an alumina thermocouple sheath. Another hole, 3 mm in diameter and 12 mm deep, was drilled axially at the top end of the presintered powder cylinder to act as a seat for the thermocouple hot junction. Contact
between the thermocouple and the specimen was prevented by using a closed-end alumina sheath.

The cage, along with the presintered powder cylinder, was hung at the colder top end of the furnace tube. The furnace tube was flushed with dry helium gas. After a few minutes, dry hydrogen was passed through the furnace at a constant rate and the helium flow was discontinued. The cage and specimen were lowered to the constant temperature zone. Specimens were sintered at the desired temperatures in hydrogen for various intervals of time. At the end of isothermal sintering the specimen was either raised to the colder top end of the furnace or lowered into the quench bath.

For quenching experiments, 10 mm diameter x 20 mm long presintered cupronickel cylinders were used. At the end of the isothermal sintering the wire supporting the specimen was cut to allow the specimen to fall freely into the iced-brine solution kept at the bottom of the furnace tube. Visible heat (colour) in the specimens was found to subside in less than 5 secs in the quenching medium. Also, as-homogenised cast cupronickel specimens, 10 mm in diameter x 25 mm long, were heated isothermally in an atmosphere of hydrogen and then quenched into iced-brine solution by the same procedure. The thermal cycle for superkanthal runs is as shown in Figure 2.8.

2.6.3 Thermocouple Calibration

For calibration of a Pt-Rh thermocouple the melting point of pure nickel was employed. Sherritt Gordon nickel powder, 99.90% pure, was melted in an alumina crucible using induction heating. Cooling of the nickel was followed with both a recorder and a potentiometer. In several runs,
the thermal arrests occurred at temperatures in the range of 1453 to 1455°C. The melting point of nickel can be taken as 1455°C [45].

The calibration of a W/3% Re - W/25% Re thermocouple was done in a similar way. In this case 99.999% pure copper was melted using the superkanthal furnace. Both melting and freezing arrests were observed with the results given in Table 2.2. An average of 1082°C was obtained as the melting point for copper compared with a published value of 1084°C [45]. The thermocouple was further calibrated against the Pt-Pt/10% Rh thermocouple between 1000 and 1500°C. The temperatures measured using W-Re thermocouple were within ±1°C of those measured using the Pt-Pt/Rh thermocouple.

Table 2.2
Thermocouple Calibrations Against Melting Point of Pure Copper
(W/3% Re - W/25% Re Thermocouple)

<table>
<thead>
<tr>
<th>Melting</th>
<th>Freezing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential, mV</td>
<td>Temp. °C</td>
</tr>
<tr>
<td>19.880</td>
<td>1083</td>
</tr>
<tr>
<td>19.885</td>
<td>1083</td>
</tr>
<tr>
<td>19.890</td>
<td>1083</td>
</tr>
</tbody>
</table>

2.7 Experimental Difficulties in Studies of Supersolidus Sintering

To follow the course of supersolidus sintering was intrinsically difficult for reasons which include the following:
a) Loose powder aggregates have low thermal conductivity.

b) Liquid forms over a range of temperature in an alloy.

c) The melting process is diffusion-controlled and hence a significant time is involved to establish phase equilibrium even at constant temperature.

d) The initial densification of a powder aggregate is the most rapid.

e) The equilibrium amount of liquid is very sensitive to temperature.

If the rate of heating is kept low the compact may heat uniformly but the amount of liquid will change over the interval between the solidus and any chosen isothermal supersolidus sintering temperature. This makes it impossible to analyse the kinetics of shrinkage for any given liquid content or temperature.

Conversely, if an attempt is made to reach the desired temperature quickly, two other problems arise:

a) Large temperature gradients are generated across the specimen and melting starts first near the surface.

b) The amount of liquid formed after short intervals of time is not the equilibrium amount.

2.8 Dilatometric Experiments

2.8.1 Description of the Apparatus

The dilatometer, shown in Figure 2.9, consisted of a quartz tube held vertically by means of a lava block pedestal at the bottom and a steel frame at the top. The top end of the quartz tube was closed with a water
Figure 2.9. The Dilatometer.
cooled, hollow brass collar. The brass collar supported a transducer (linear variable differential transformer, or LVDT) which could be held at any vertical position using a screw attached to the steel frame. An axial hole through the LVDT acted as a gas inlet tube to the quartz tube. The iron core of the LVDT was attached to a 20 cm long x 1.6 mm diameter alumina rod.

A thermocouple, made of W/3% Re - W/25% Re passed through a central hole in the ceramic (lava) pedestal block. The thermocouple projected approximately 6.3 mm above the top surface of a smooth silica disc placed on top of the pedestal block. The presintered specimen, with a central hole deep enough to accommodate the thermocouple hot junction, sat firmly on top of the silica disc. A second silica disc covered the top surface of the specimen. The alumina rod from the LVDT core was placed centrally on top of this silica disc. The iron core along with the alumina rod and the silica disc weighed roughly 9 gms. An alundum sleeve placed between the specimen and the quartz tube acted as a heat insulator and shield. A high frequency induction coil was located concentrically outside the quartz tube. The whole assembly of the dilatometer was supported on a screw jack and hence could be moved vertically for adjustment of specimen position relative to the induction coil.

The LVDT was connected to a Daytronic model - 300 BF signal conditioner and amplifier. The output of the amplifier was continuously recorded using a Honeywell chart recorder. The recorder was calibrated to give a maximum recording sensitivity of 0.0025 inch per inch of chart in the mV. direction using a feeler gauge of known thickness.
The thermocouple was connected to cold junction compensating leads and then to the Phillips induction furnace control unit. The control unit contained a thermocouple chart recorder with a full scale deflection of 25 mV. Separate measurements of the specimen temperatures were also made using a potentiometer with an accuracy of 0.01 mV. By further calibration of the potentiometer it was possible to measure the temperature at the thermocouple to an accuracy of ±0.5°C.

Hydrogen was employed for all cleaning and sintering in the dilatometer furnace. Bottled hydrogen was passed through a palladium catalyst chamber and then through "Drierite" and phosphorus pentoxide columns.

2.8.2 Procedures in Dilatometer Runs

Cupronickel powder was tapped into a small alumina crucible to obtain a powder column approximately 15 mm diameter by 20 mm high and with 50 per cent of the theoretical density. The crucible and contents were heated in a tube furnace at 1000°C for one hour in an atmosphere of hydrogen. This provided cleaning and some homogenisation. The presinters thus obtained were removed from the crucibles. Both ends of the cylinders were machined to be flat and parallel. The densities of the machined specimens were determined from weight and dimensions. An axial hole, 2.3 mm diameter x 9 mm deep, was drilled at one end of each cylinder to serve as the thermocouple well. The specimen was again weighed. The presinter was placed on the silica disc at the top of the pedestal block. It was then further cleaned and homogenised at 1000°C for one hour, in an
atmosphere of clean and dry hydrogen, using induction heating in the dilatometer. The specimen was cooled to room temperature and the weight and dimensions were again measured.

With the specimen returned to the dilatometer, the LVDT was zeroed and the recorder was calibrated. The specimen was heated to the sintering temperature in dry hydrogen in two steps according to the cycle shown in Figure 2.10. The initial power input was such that 1200°C was attained in approximately 4 minutes. At that moment the power input was increased to reach 1273°C rapidly. The input was thereafter controlled manually as necessary to maintain the temperature at 1273°C within ±1°C. The specimen was held at this temperature for varying times up to about 10 minutes. At the end of the sintering treatment the induction unit was switched off and the specimen was cooled to room temperature in the dilatometer itself. A typical dilatometric chart is shown as Figure 2.11.

After cooling, the weight and the length of the specimen were determined. The change in length during sintering, as measured by calipers agreed closely with the value recorded from the LVDT.

Calibration runs were also conducted to determine the contribution of expansion and contraction in the specimen support assembly members during a dilatometer experiment. A solid steel cylinder was used as a heat susceptor instead of a powder presinter. The alumina rod from the LVDT was passed, through an axial hole in the steel cylinder, to rest on the silica disc at the top of the pedestal block. The thermal cycle was typical of a dilatometer run, Figure 2.10. The thermal expansion curve obtained for the support assembly was used to correct the dilatometer curves obtained from powder specimens.
Figure 2.8. Thermal cycle for supersolidus sintering in the superkanthal furnace.

Figure 2.10. Thermal cycle for supersolidus sintering in the Dilatometer.
Figure 2.11. A typical continuous linear dimensional change curve obtained from a Dilatometer run.
During dilatometer runs, a copper deposit was formed on the silica discs at the ends of the specimen. Weight loss measurements indicated that up to 0.08 per cent of the specimen was lost by evaporation in the longest dilatometer runs. Even if this loss was assumed to be pure copper, it would not have produced a composition change of greater than 0.16 per cent in the copper and nickel contents of the alloy. Since this is well within the limits of accuracy of analytical determinations, no effort was made to correct for evaporation losses.

2.8.3 Advantages and Limitations of the Dilatometric Technique

The dilatometric technique employed in the present work had a number of advantages over that used for other studies of sintering (particularly liquid phase sintering):

a) By using direct HF induction heating the temperature gradients associated with the low thermal conductivity of a loose powder mass were partially reduced.

b) Heating and cooling rates were rapid using direct induction.

c) Continuous observation of shrinkage was provided.

However, data generated by the technique were of restricted quantitative significance for several reasons:

a) "Skin" heating effects occur in direct HF induction which introduce a radial gradient in temperature and in the sequence of melting across a specimen.

b) The linkages between specimen and dilatometer are heat sinks which contribute to an axial temperature gradient. The dilatometer "sees" dimensional changes at those locations where the heat-sink effects are greatest.
2.9 Optical Metallography

2.9.1 Mounting, Polishing and Etching

An epoxy resin mixture of 90 wt. % Epon 828 and 10 wt. % diethylenetriamine, was used for mounting specimens. Most of the porous sintered specimens were soldered to copper wires prior to mounting. They were then immersed in the resin and the assembly was placed inside a desiccator. The desiccator was evacuated using a forepump for five minutes to remove air from the pores of the specimens. When air was re-introduced into the desiccator the resin was forced into the continuous pores. This procedure was reasonably efficient in impregnating the pores with resin. The specimen, along with the resin, was poured into silicone rubber moulds with the copper wire projecting. After curing of the resin, specimens were ground and polished to 1 micron diamond.

Both chemical and electrolytic etching were practiced. Electrolytic etching was found to be superior since it removed some of the fine polishing scratches from the surface of the specimen. The chemical etchant used was Carapella's reagent [46];

- Ferric Chloride: 5 gms
- Conc. hydrochloric acid: 2 ml
- Ethyl alcohol: 99 ml
- Time at 20°C: 3 sec - 2 min

The composition and conditions of use for the electrolytic etch [47] were as follows:

- Chromic oxide: 25 gms
- Glacial acetic acid: 133 ml
- Distilled water: 7 ml
- Age: > 6 months
- Voltage: 6 volts
- Cathode: Stainless steel
- Temperature: 16°C
- Time: 2-15 minutes
2.9.2 Quantitative Metallography

Estimates of grain size were made using the linear intercept method [48]. For a composite containing gas (pores), liquid, and solid, the mean linear intercept $d_s''$ in the solid is given by

$$d_s'' = \frac{\ell p_s}{n_s}$$  \hspace{1cm} (2.2)

where $p_s$ = the proportion of solid

$n_s$ = the number of solid grains in an intercept of length $\ell$.

It has been pointed out that the mean linear intercept $d_s''$ is less than the true mean diameter of the grains in the plan of sectioning, $d_s'$, and that the mean diameter of the grains in a planar section, is less than the true mean diameter of the grains in the aggregate, $d_s$. According to derivations presented elsewhere [49,50]

$$d_s = 1.675 d_s''$$  \hspace{1cm} (2.3)

Woodhead [51] suggested that if the mean linear intercept is based on an observation involving $n$ grains, then the relative error, $\phi_1$, of the mean intercept can be given by

$$\phi_1 = \left(\frac{0.49}{n}\right)^{0.5}$$  \hspace{1cm} (2.4)

In the present work, lines 8.8 cm long were used to determine the mean intercept in micrographs of porous sintered specimens. The grain
size was estimated from counts of more than 500 mean intercepts using four
or more micrographs, and using the expression:

\[ d_s = \frac{1.675 \times \ell \times \rho}{n \times M_1} \]  

where \( \rho \) = the fractional density of the specimen

\( M_1 \) = the magnification of the micrograph.

The error involved in these determinations was approximately 3\% according
to Equation (2.4).

Estimates of "liquid" content in specimens were made using the
point count method [51]. The basic principle of the method is that the
volume fraction of a phase is given by that proportion of a regular array
of points, placed on a micrograph, that fall on the phase. It is impor­
tant that the spacing of the points on a rectangular grid be large with
respect to the microstructural features.

In sintered specimens regions which were liquid at the sintering
temperature were appreciably higher in copper content than those regions
which had remained solid. Conventional etching attacked the copper-rich
areas preferentially, giving them a dark appearance in the microstructure.
Since these areas could not always clearly be distinguished from porosity,
the point count method was used to evaluate the total dark area in photo­
micrographs, and the known porosity content was then deducted. A one inch
grid containing 36 points, regularly spaced, was superimposed on the micro
structure. The choice of magnification was such that the spacing of the
points on the rectangular grid was large compared to that of the dark
features. The volume fraction, \( p_d \), of the dark region is given by
\[ P_d = \frac{n_d}{n_2} \]  

(2.6)

where \( n_d \) is the number of points occurring in the dark region and \( n_2 \) is the total number of points in the microstructure.

The equation given by Gladman et al. [52] for the standard deviation of the volume fraction in relation to the number of points used in the point-counting method is

\[ \sigma_{P_d} = \left[ P_d (1 - P_d) / n_2 \right]^{0.5} \]  

(2.7)

Standard deviations of 0.0032-0.0061 were observed in the estimation of the liquid content in cupronickel.

The mean diameter, \( d_p' \), of spherical particles in a plane of section is related to the true mean volumetric diameter of the particles, \( d_p \), by [53]

\[ d_p' = \sqrt{\frac{2}{3}} d_p \]  

(2.8)

The value of \( d_p' \) was obtained directly by averaging the diameter of many particles seen in photomicrographs.

Some sintered specimens exhibited macroscopic variations in porosity content, associated with thermal gradients during sintering. In these cases, estimates of both porosity and liquid-phase content were made at localised regions of metallographic specimens or on photomicrographs of those regions, using the Quantimet instrument.
2.10 Microprobe Analysis

To study phase compositions and gradients in sintered specimens a JEOLCO JXA-3A electronprobe microanalyser was used.

a) A thin film of carbon was evaporated on to polished specimens to prevent charge build-up and to give better conductivity.

b) An operating voltage of 25 KV was used with an electron beam diameter of 1 μm.

c) A lithium fluoride crystal was used in the x-ray spectrometer.

d) Ni Kα and Cu Kα x-ray intensity counts for 10 seconds were recorded. Repeated 10-second counts were taken at the same specimen site, or after moving the specimens in steps of 1.25 μm.

e) Continuous scans were also made at a specimen speed of 100 μm per minute.

f) Background counts were obtained on specimens and standards by moving the spectrometer one degree off the peak being measured.

g) Intensity ratios were obtained from the counts obtained for the specimen and the standards after being corrected for "dead time" and background. The intensity ratio was further corrected for fluorescence enhancement. No correction for atomic number was necessary since copper and nickel are adjacent species in the Periodic Table. Similarly, no absorption correction was applied because the absorption coefficients for copper and nickel are closely similar.

Conversion of intensity ratio into weight fraction was performed directly by an IBM 370 computer using the MAGIC Programme [54]. The weight fraction could also be obtained from a back-calculation method using the MAGIC Programme. In this case assumed weight fractions of Cu and Ni were converted into corresponding intensity ratios corrected only for dead time and background. The intensity ratios obtained for 0.1, 0.2, 0.3, etc. up
to 0.9 weight fraction copper in nickel are given in Table 2.3. The variation of the ratio within an interval of 0.1 weight fraction was essentially linear. Thus all intensity ratios could be converted into weight fractions by simple interpolations within intervals of 0.1 weight fraction over the whole range of compositions.

Table 2.3

Intensity Ratios for the Cu-Ni System Obtained from the MAGIC Programme

<table>
<thead>
<tr>
<th>Weight Fraction</th>
<th>Intensity ratio (Kα-Ratios)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>0.9</td>
<td>0.8964</td>
</tr>
<tr>
<td>0.8</td>
<td>0.7936</td>
</tr>
<tr>
<td>0.7</td>
<td>0.6917</td>
</tr>
<tr>
<td>0.6</td>
<td>0.5905</td>
</tr>
<tr>
<td>0.5</td>
<td>0.4902</td>
</tr>
<tr>
<td>0.4</td>
<td>0.3906</td>
</tr>
<tr>
<td>0.3</td>
<td>0.2918</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1938</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0965</td>
</tr>
</tbody>
</table>

Probe calibrations were carried out using as standards homogeneous solid-state sintered or cast-cupronickel specimens, for each of which reliable chemical analyses had been obtained from an independent laboratory. In the acquisition and treatment of probe data, the following procedures were adopted:
a) Not less than five sets of 10-seconds counts were taken in the probe survey of a given specimen.

b) The mean concentrations of copper and nickel were adjusted proportionally to total 99.9 weight per cent. The justification for this procedure is that:

(i) copper and nickel x-ray counts were made simultaneously at any given specimen site; thus, fluctuations in such operating conditions as beam current would affect the counts for both species in the same direction,

(ii) chemical analyses showed that the copper plus nickel content of the materials under study was close to 99.9 per cent,

(iii) any residual segregation in homogenised specimens could alter the Cu:Ni ratio at a specific specimen site, but the average ratio over many sets of counts would be that of the bulk, as represented by the chemical analysis; and

(iv) no impurity phases were detected in the materials analysed.

The degree of reproducibility of the microprobe results was indicated by surveys on a single homogenised presinter specimen on seven different occasions (actually on 5 different days). The results are contained in Table 2.4 which also shows the application of the above-mentioned normalising procedure to the probe data. The averages of the seven copper and nickel determinations were compared with the chemical analysis also given in the table. The variance of the results is 0.6 per cent of the absolute value for each element.

Table 2.5 contains probe and chemical analyses from several sintered and cast cupronickel specimens of relatively high homogeneity.
Table 2.4
Microprobe and Chemical Analyses on a Presintered Cupronickel Powder Specimen
(sintered 900°C for 1 hour, from 200 x 230 mesh powder)

<table>
<thead>
<tr>
<th>Determination</th>
<th>Computed wt. % from Microprobe</th>
<th>Normalised wt. % Microprobe</th>
<th>Chemical Analysis* wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Ni</td>
<td>Cu</td>
</tr>
<tr>
<td>a</td>
<td>50.64</td>
<td>50.32</td>
<td>50.1</td>
</tr>
<tr>
<td>b</td>
<td>50.60</td>
<td>50.16</td>
<td>50.2</td>
</tr>
<tr>
<td>c</td>
<td>49.57</td>
<td>50.16</td>
<td>49.7</td>
</tr>
<tr>
<td>d</td>
<td>50.88</td>
<td>50.10</td>
<td>50.3</td>
</tr>
<tr>
<td>e</td>
<td>50.35</td>
<td>50.30</td>
<td>50.0</td>
</tr>
<tr>
<td>f</td>
<td>49.89</td>
<td>50.30</td>
<td>49.7</td>
</tr>
<tr>
<td>g</td>
<td>50.38</td>
<td>49.69</td>
<td>50.3</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>50.0</td>
</tr>
<tr>
<td>Variance</td>
<td></td>
<td></td>
<td>±0.6</td>
</tr>
</tbody>
</table>

*Can Test Ltd.

Combined with those in Table 2.4, these results indicate that a high proportion of individual probe analyses for copper and nickel can be expected to fall within a range of 1.2 per cent about the "true" analyses. Statistically, this is a simple, and conservatively high estimate of the variance in the data. A more rigorous treatment of the variance is neither justified by the size of the statistical sample, nor required for purposes of the present investigation. It should be noted that in some of the supersolidus sintering experiments to be discussed, progressive trends in
Table 2.5
Microprobe and Chemical Analyses on Relatively Homogeneous Cupronickel Specimens

<table>
<thead>
<tr>
<th>Material</th>
<th>Treatment</th>
<th>Microprobe Analysis, wt. %, Normalized</th>
<th>Chemical Analysis, wt. %*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>Ni</td>
</tr>
<tr>
<td>SPLS 2</td>
<td>Cast &amp; Homog.</td>
<td>49.9</td>
<td>50.0</td>
</tr>
<tr>
<td>SPLS 3</td>
<td>-do-</td>
<td>49.8</td>
<td>50.1</td>
</tr>
<tr>
<td>SPLS 4</td>
<td>-do-</td>
<td>50.0</td>
<td>49.9</td>
</tr>
<tr>
<td>Q22</td>
<td>sinter</td>
<td>49.9</td>
<td>50.0</td>
</tr>
<tr>
<td>Q1</td>
<td>sinter</td>
<td>49.9</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.1</td>
<td>49.8</td>
</tr>
<tr>
<td>R66</td>
<td>presinter</td>
<td>49.9</td>
<td>50.0</td>
</tr>
<tr>
<td>R67</td>
<td>-do-</td>
<td>50.3</td>
<td>49.6</td>
</tr>
<tr>
<td>R24</td>
<td>sinter</td>
<td>50.1</td>
<td>49.8</td>
</tr>
<tr>
<td>R14</td>
<td>sinter</td>
<td>49.8</td>
<td>50.1</td>
</tr>
<tr>
<td>R16</td>
<td>sinter</td>
<td>50.2</td>
<td>49.7</td>
</tr>
</tbody>
</table>

* Can Test Ltd., Vancouver.
composition change with changes in experimental conditions could be pre-
dicted from known phase equilibria in the copper-nickel system. In nearly
all cases, the results of microprobe analyses were consistent with the
predictions. These observations added confidence to the above estimates
of variability in the results of individual microprobe surveys.

2.11 Scanning Electron Microscopy

An ETEC autoscan scanning electron microscope coupled with an
ORTEC model 6200 multichannel analyser was used for both surface topology
studies and x-ray energy analyses.

2.12 Density Determinations

The lattice parameter of the cupronickel alloy powder was deter-
mined by the precise x-ray diffraction method [55]. Powder of 200 x 230
mesh, previously heated at 900°C in an atmosphere of cracked ammonia for
one hour, was used to obtain x-ray diffraction patterns. The value of
3.5630 Å obtained agreed closely with 3.5636 Å reported by Coles [56] for
an alloy of 50.09% Cu, 49.81% nickel by weight. From the present value of
the parameter, the theoretical density of the cupronickel alloy was cal-
culated to be 8.96 gm. cm^{-3}.

The density of a sintered specimen was obtained using two methods:

a) From accurate measurements of the weight and
dimensions of specimens.

b) By weighing oil-impregnated specimens in water
and in air [57].
A previously-weighed specimen was suspended in Dow Corning F-1-0173 fluid (dimethyl polysiloxane; specific gravity at 25°C = 0.968 gm. cc\(^{-1}\) and viscosity at 25°C = 100 centi stokes) using a fine thread. The specimen was heated in the fluid at 82 ± 5°C for 4 hours and cooled to room temperature while still immersed. The specimen was carefully wiped with filter paper to remove excess oil from the surface. The weight was then determined in air and in distilled water, and the density calculated in the usual manner.

Densities were measured on many compacts using both methods, and the results agreed to within ±0.5 per cent.

Densification during sintering can be represented in different ways; e.g.

a) as an absolute or fractional increase in density

b) as volumetric specimen shrinkage, \(\frac{\Delta V}{V_0}\) (\(\Delta V\) = the change in volume, \(V_0\) = the original volume),

c) as linear shrinkage, \(\frac{\Delta L}{L_0}\) (\(\Delta L\) = the change in length, \(L_0\) = the original length); valid only if shrinkage is isotropic),

d) as "densification parameter," [58] given by

\[
\text{densification parameter} = \frac{\text{sintered density} - \text{green density}}{\text{theoretical density} - \text{green density}}.
\]

The densification parameter can vary between zero and one and represents the densification which has occurred as a fraction of that theoretically possible. It is a useful property in situations where the initial ("green") density of the powder specimen is a variable in the experiments.
3.1 Phase Equilibria in Cupronickel

3.1.1 Published Phase Diagrams for Cu-Ni

Hansen [59] published in 1958 a copper-nickel equilibrium phase diagram derived from the thermal analysis results of earlier investigators. The solidus curve had been determined by several independent sets of cooling-curve data, which agreed reasonably well with each other. The Hansen diagram is shown with dashed lines in Figure 3.1.

Feest and Doherty [60] in 1971 redetermined the solidus and liquidus curves in the copper-nickel system using more sophisticated experimental and analytical techniques (described in Section 3.1.3 below) than had been available prior to 1958. The results are plotted in Figure 3.1 (with solid lines). In particular, the solidus curve was found to be substantially higher than indicated by Hansen, Feest and Doherty attributed the large discrepancies between their solidus temperatures and those in Hansen's diagram to errors inherent in dynamic thermal-analysis experiments when applied to systems that are subject to non-equilibrium solidification. It should be noted, however, that the solidus temperatures of
Figure 3.1. The Cu-Ni phase diagram according to Hansen and to Feest and Doherty.

Figure 3.2. The Cu-Ni phase diagram showing the predicted solid state miscibility gap.
Copper alloys are dramatically lowered by minor amounts of certain impurities, notably oxygen and sulphur. It is possible that some of the earlier studies were conducted with less pure raw materials.

Thermodynamic data predict that there is a tendency toward clustering in the solid state in the copper-nickel alloy system (Oriani et al. [61]), and the occurrence of some clustering was reportedly confirmed by x-ray and neutron diffraction experiments [62,63]. The solid miscibility gap shown in Figure 3.2 was calculated by Elford et al. [64], but has not been experimentally verified because of the low temperatures involved.

3.1.2 Effect of Impurities in Cupronickel

The major impurities in the cupronickel powder were (a) oxygen, originating mainly from superficial oxidation of the alloy powder particles in air, and (b) silicon, used as a deoxidant in melting prior to atomisation of the alloy. As indicated in Table 3.1, these impurities can have a significant effect on the melting temperatures of pure copper and pure nickel, and thus might be expected to lower the solidus and liquidus temperatures of a cupronickel alloy.

An attempt was made to establish the solidus temperature of the cupronickel powder by differential thermal analysis (DTA). A DuPont Model 900 Instrument was used with a 1600°C furnace cell. Since Pt-Pt/Rh thermocouples were involved, a hydrogen-rich atmosphere had to be avoided. Heating rates were 10 or 20°C per minute. Powders were cleaned in hydrogen prior to DTA work, but some oxidation undoubtedly occurred at ambient
Table 3.1
Effect of Oxygen and Silicon on the Melting Points of Copper and Nickel [59,46]

<table>
<thead>
<tr>
<th>Solute</th>
<th>wt. %</th>
<th>Lowering of Melting Temp. °C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>Ni</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquidus</td>
<td>Solidus</td>
<td>Liquidus</td>
</tr>
<tr>
<td>silicon</td>
<td>0.10</td>
<td>1.5</td>
<td>4.3</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>3.3</td>
<td>10.0</td>
<td>2.3</td>
</tr>
<tr>
<td>oxygen</td>
<td>0.001</td>
<td>0.05</td>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>0.2</td>
<td>18</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td>0.5</td>
<td>18</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>1.0</td>
<td>18</td>
<td>1.2</td>
</tr>
</tbody>
</table>

temperatures while the powders were handled and charged into the instrument. Initial runs were made with a helium atmosphere in the DTA cell. In several heating runs, the indicated solidus temperature of the alloy ranged from 1244 to 1250°C. While these temperatures are in good agreement with the solidus at 50 Cu - 50 Ni in Hansen's phase diagram, they are at least 20°C lower than the solidus in the Feest and Doherty diagram. The helium atmosphere in the DTA furnace cell was diluted with small concentrations of hydrogen for subsequent heating runs. Traces of hydrogen in the atmosphere increased the apparent solidus to 1255°C; with still more hydrogen the indicated solidus was 1266°C. At this juncture, it was apparent that the effective solidus temperature of the cupronickel alloy powder was a critical function of impurity content, particularly with respect to residual oxygen. The data in Table 3.1 suggest that 200 ppm
of oxygen could lower the solidus temperature of the alloy by 15 to 18°C. Separate gravimetric studies showed that superficial oxidation of pre-cleaned cupronickel powder could result in at least this level of oxygen contamination after only minutes of exposure to air at ambient temperatures.

Since it was impractical to duplicate in the DTA furnace the sintering atmospheres used in the present work, it was decided to evaluate the solidus and liquidus temperatures of the cupronickel alloy powder on the basis of quenching experiments in an actual sintering furnace, as described below.

3.1.3 Thermal Data from Quenching Experiments

Quenching experiments were conducted in conjunction with quantitative metallographic and microprobe analyses. This approach was essentially the same as that used by Feest and Doherty to establish complete solidus and liquidus curves in Figure 3.1; viz.

a) Presintered specimens were sintered (held for five or more minutes, usually 30 minutes) at a series of temperatures, some of which were above the solidus. The sintering was done in dry hydrogen, under conditions identical to those which applied to other sintering studies in the superkanthal-furnace.

b) The specimens were quenched into iced water from each of the sintering temperatures.

c) The compositions of the uniform nickel-rich regions of the quenched specimens; i.e. those regions which were solid at the sintering temperature, were determined by microprobe analysis for several experiments.

d) The volume fractions of nickel-rich and copper-rich regions in quenched specimens were assessed
by quantitative metallography on etched specimens or photomicrographs of the specimens. These fractions were related to the weight proportions of solid and liquid phase present at the sintering temperature.

The results are presented in Table 3.2 and have been used to prepare the phase diagram of Figure 3.3.

Figures 3.4 to 3.9 are photomicrographs of the structures typical of quenched specimens. Copper-rich areas were selectively attacked by the etchant and appeared darker in the microstructure. No evidence of melting could be found in specimens sintered at 1262 ± 2°C or lower temperatures, either visually in the microstructures or by microprobe analysis, Figure 3.4 and 3.10. Since a 1262°C specimen was cycled in the furnace between 1260 and 1264°C, it can be concluded that the solidus temperature of the homogeneous cupronickel alloy powder was > 1264°C. Melting had occurred in a 1264 ± 2°C specimen. The evidence for this was both metallographic (Figure 3.5) and analytical (Figures 3.11). Thus the solidus temperature for 49.9% copper was narrowly defined as 1265 or 1266°C.

The value of the solidus has two sources of uncertainty. The actual temperature of a specimen at the time of the quench was known only to ±2°C. Also, individual quantitative probe analyses are accurate to ±0.6 per cent (Section 2.10).

The solidus curve for the cupronickel powder (in dry hydrogen) was found to be at the lower limit of the range of scatter in Feest and Doherty's experimental data (Figure 3.1), and lay 7 to 8 degrees below the curve drawn by Feest and Doherty through their data points. It is unlikely that oxygen was present, after presintering and sintering in dry
Table 3.2
Quenching Experiments and Results

<table>
<thead>
<tr>
<th>Run</th>
<th>Quenching Temperature and Variation During Run °C</th>
<th>Time at Temp. min.</th>
<th>Composition* of Nickel Rich Areas (solidus) wt. % Ni</th>
<th>Estimated Liquid Content at Temp. **</th>
<th>wt. % Liquid Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q14</td>
<td>1260 ± 0.5 1.5</td>
<td>30</td>
<td>ND</td>
<td>NIL</td>
<td>NIL</td>
</tr>
<tr>
<td>Q22</td>
<td>1262 ± 2</td>
<td>30</td>
<td>50.0</td>
<td>NIL</td>
<td>NIL</td>
</tr>
<tr>
<td>Q20</td>
<td>1264 ± 2</td>
<td>30</td>
<td>50.2</td>
<td>V. small</td>
<td>0.9 ± 2</td>
</tr>
<tr>
<td>Q19</td>
<td>1266 ± 2</td>
<td>30</td>
<td>50.6</td>
<td>2.9</td>
<td>3.7</td>
</tr>
<tr>
<td>Q18</td>
<td>1268 ± 2</td>
<td>30</td>
<td>50.8</td>
<td>4.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Q47</td>
<td>1273 + 2.5 - 0.5</td>
<td>5</td>
<td>52.4</td>
<td>17.7</td>
<td>21.2</td>
</tr>
<tr>
<td>Q45</td>
<td>1273 + 2.5 - 0.0</td>
<td>15</td>
<td>52.9</td>
<td>20.7</td>
<td>21.7</td>
</tr>
<tr>
<td>Q42</td>
<td>1273 + 2.5 - 0.0</td>
<td>30</td>
<td>52.9</td>
<td>20.5</td>
<td>21.1</td>
</tr>
<tr>
<td>Q46</td>
<td>1273 + 2.5 - 0.5</td>
<td>5</td>
<td>ND</td>
<td>17.5</td>
<td>20.4</td>
</tr>
<tr>
<td>Q44</td>
<td>1273 + 2.5 - 1.0</td>
<td>15</td>
<td>ND</td>
<td>20.3</td>
<td>21.2</td>
</tr>
<tr>
<td>Q43</td>
<td>1273 + 2.5 - 1.0</td>
<td>30</td>
<td>ND</td>
<td>21.1</td>
<td>21.6</td>
</tr>
</tbody>
</table>

*Electron beam microprobe analysis, normalised 99.9% copper plus nickel.

**Quantitative Metallography.
Figure 3.3. The Cu-Ni phase-diagram derived from quenching experiments and probe analyses.
Figure 3.4. Specimen Q22, sintered at 1262°C for 30 min. in hydrogen and quenched. (Reveals the absence of liquid); (a) x120 and (b) x760.
Figure 3.5. Specimen Q20, sintered at 1264°C in hydrogen for 30 min. and quenched. (Reveals clearly the presence of liquid); (a) x120 and (b) x760.
Figure 3.6. Specimen Q19, sintered at 1266°C in hydrogen for 30 min. and quenched. Intraparticle liquid pools were revealed as shown at P; (a) x120 and (b) x760.
Figure 3.7. Specimen Q18, sintered at 1268°C in hydrogen for 30 min. and quenched, (a) x120 and (b) x760.
Figure 3.8. Specimen Q42, sintered at 1273°C in hydrogen for 30 min. and quenched. (Linear coalescences indicated at 'C'), (a) x120 and (b) x760.
Figure 3.9. Specimens sintered at 1273°C in hydrogen and quenched, x120; (a) Q47, 5 min. and (b) Q45, 15 min.
Figure 3.10. Copper and nickel x-ray intensity lines superimposed on the absorbed electron image of particle necks in Q22. (Reveals no noticeable liquid.) Scanning paths are: (a) through the neck, (b) across the neck, x1000.

Figure 3.11. Copper and nickel x-ray intensity lines superimposed on the absorbed electron image of particle necks in Q20. (Reveals the presence of liquid.) Scanning paths are: (a) through the neck, (b) across the neck, x1000.
hydrogen, in quantities sufficient to affect the solidus significantly. The lower curve for the present results can probably be attributed at least partially to the presence of approximately 0.1 weight per cent silicon in the alloy (see Section 3.1.2).

It was not possible to establish accurately the liquidus curve for the cupronickel alloy powder on the basis of the present data. However, it is reasonable to use the liquidus curve derived experimentally by Feest and Doherty, because: a) This liquidus differs little, in the composition range of interest, from that of Hansen's diagram, possibly indicating that it is relatively insensitive to minor impurity content, (b) within the limits of accuracy of quantitative metallography, the position of the liquidus is consistent with the amounts of liquid observed at several different supersolidus sintering temperatures, and (c) the effect of silicon on the liquidus temperature of cupronickel can be expected to be much less than its effect on the solidus based on the data for copper and nickel in Table 3.1.

It should be noted that the phase equilibria indicated in Figure 3.3 can be applied only to cupronickel powder which is sintered in dry hydrogen at one atmosphere. For vacuum and argon sintering experiments in the Centorr furnace, the effective solidus temperatures were substantially lower (as indicated in Section 3.3.2), probably due to the presence of a significant amount of residual oxygen in specimens at the sintering temperatures. However, no attempt was made to establish the solidus or liquidus curves quantitatively for these conditions of sintering.
3.2 Structure and Homogeneity of Presintered Cupronickel Powder Specimens

It was difficult to reveal the two dimensional microstructure of presintered specimens since the necks in such specimens were weak, and particles were pulled out of the mount while polishing. Since the density of the original powder column was increased from 50.0 to only 51.2 per cent of solid in the presintering treatment, the presintered structure can probably be assumed to be representative of the original packing. The distribution of powder particles in a section of the presinter is as shown in Figure 3.41.a. Clustering of powder particles and bridges are quite evident. Some homogenisation occurred in the powder particles during the presintering treatment and the cored structure was transformed to a uniform grain structure as shown in Figure 3.12. The mean grain size was 18 μm compared with a mean particle diameter of 68 μm. Each particle contained interdendritic microporosity and twins.

Figure 3.13 shows the results of microprobe surveys on the cupronickel powder as-received and after presintering for one hour at 900°C. Maximum concentration variations about the mean were reduced, by presintering, from about 10 per cent to one per cent by weight. Applying Equation (2.1) from Section 2.4, and using \( \lambda = 0.0004 \) cm (from Figure 3.13 for the as-received powder), the derived value of \( D \) is \( 1.04 \times 10^{-11} \) cm² sec⁻¹. This is in good agreement with the value of \( 9 \times 10^{-12} \) cm² sec⁻¹ obtained from data published by Brunel et al. [65]. It should be noted that further homogenisation of the alloy would have occurred in the course of heating to sintering temperatures in the range of 1200 to 1265°C. Moreover, in the previous determination of solidus and liquidus temperatures from quenching experiments, specimens had resided at 1260 to 1273°C for periods of 5 to 30 minutes. The amount of residual microsegregation in the solid after this treatment could not be detected within the limits of accuracy of individual probe analysis.
Figure 3.12. Internal structures of as-homogenised particles in a pre-sinter (R66) revealing grain boundaries, twins and microporosity, x270.
Cupronickel (68 μm) - Separate particles

○ As received
● Homogenised for one hour at 900°C

Figure 3.13. Composition versus distance plots for as-received and homogenised 68 μm cupronickel powder particles (Microprobe data).

3.3 Sintering Behaviour

3.3.1 Sintering at 1200°C

Table 3.3 contains the sintering conditions and results for experiments in which 68 μm cupronickel powder specimens were sintered in the solid state at 1200°C for varying periods up to 10 hours. Results for density versus time are plotted in Figure 3.14. Typical of the sintering behaviour of loose metal powders, the rate of sintering was initially rapid and decreased with increasing time.

Typical microstructures of specimens sintered at 1200°C are revealed in photomicrographs, Figures 3.15 to 3.18. The following observations are noted:
### Table 3.3
Data for Sintering Experiments at 1200°C

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Cleaning</th>
<th>Cleaning time</th>
<th>Time to reach 900°C</th>
<th>Time to reach 1200°C from 900°C</th>
<th>Sintering time</th>
<th>Density % of theoretical</th>
<th>Density variation %</th>
<th>Densification parameter</th>
<th>Densification parameter</th>
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<td>8.6</td>
<td>0</td>
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<td>0.5</td>
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<td>-</td>
<td>-</td>
<td>0</td>
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<td>16.3</td>
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<td>61.3</td>
<td>&lt;1.5</td>
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<td>12.7</td>
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<td>61.3</td>
<td>&lt;1.7</td>
<td>16.8</td>
<td>12.7</td>
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<td>44</td>
<td>21</td>
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<td>0</td>
<td>62.1</td>
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<td>18.5</td>
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<td>&lt;3.3</td>
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<td>&lt;1.3</td>
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<td>&lt;2.3</td>
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<td>67.2</td>
<td>-</td>
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<td>20.4</td>
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<td>56</td>
<td>17</td>
<td>10.0</td>
<td>0</td>
<td>66.3</td>
<td>-</td>
<td>27.5</td>
<td>19.3</td>
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<td>1</td>
<td>65</td>
<td>18</td>
<td>10.0</td>
<td>0</td>
<td>66.8</td>
<td>-</td>
<td>28.6</td>
<td>19.9</td>
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<td>45</td>
<td>13</td>
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<td>-</td>
<td>27.3</td>
<td>19.2</td>
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<td>H₂</td>
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<td>23</td>
<td>4⁺</td>
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<td>57.6</td>
<td>-</td>
<td>8.8</td>
<td>7.1</td>
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<td>H₂</td>
<td>12</td>
<td>23</td>
<td>5⁺</td>
<td>0.5</td>
<td>57.5</td>
<td>-</td>
<td>8.6</td>
<td>7.0</td>
</tr>
</tbody>
</table>

* time to reach 1200°C from 100°C
+ superkanthal practice

\(Δ\) in the calculation of densification parameter, the "green" density was taken as 53.5% of theoretical, corresponding to the density achieved when 1200°C was first reached (zero time)
Figure 3.14. Density, densification parameter and $\frac{\Delta V}{V_0}$ versus isothermal sintering time for 68 μm cupronickel powder sintered at 1200°C.
a) A marked increase in the grain size resulted from heating at 1200°C compared to 900°C (compare Figure 3.12 with 3.15). In specimens sintered for 5 or more hours, almost every particle had become a single crystal.

b) Annealing twins (revealed only by appropriate etching, as in Figure 3.18) were found in most grains.

c) Some of the necks which had developed between particles were large out of all proportion to others and were much larger than expected in relation to the bulk densification which had occurred (e.g. the necks at 'A' in Figures 3.16 and 3.17). This phenomenon was associated with relatively dense clusters (Figures 3.16 and 3.17).

d) No particles were ever observed which had a dimension greater than 74 μm (200 mesh) in the plane of polish. There is therefore no evidence of particle growth by complete coalescence of particles at 1200°C. Moreover the average particle diameter, determined by quantitative metallography on specimens sintered between 0 and 10 hours was 68 ± 2 μm.

The neck regions of several 1200°C sintered specimens were carefully surveyed in the microprobe analyser to determine if there was any evidence of segregation of one of the alloy components at the necks. Similar studies were performed on specimens which were sintered at 1200°C and quenched directly. No evidence of segregation was found in any specimen at any location. Figure 3.19 show typical x-ray intensity traces superimposed on absorbed electron image photographs for several necks.

3.3.2 Supersolidus Sintering in Vacuum

The first supersolidus sintering experiments were conducted at 1260°C in the Centorr furnace at pressures of $10^{-5}$ to $10^{-2}$ torr; Table 3.4.
Figure 3.15. Specimen R4, sintered at 1200°C for one hour in vacuum; (a) x270, (b) x740.
Figure 3.16. Specimen R14, sintered at 1200°C for 5 hours. (Reveals that all particles as essentially single crystals, very large necks at 'A' and dense clusters), (a) x270, (b) x740.
Figure 3.17. Specimen R16, sintered at 1200°C for 10 hours. Similar to Figure 3.16; (a) x270, (b) x740.
Figure 3.18. Microstructure of the section of R70 after etching with Carapella's reagent. Reveals annealing twins, x270.
Figure 3.19. Cu and Ni x-ray intensity lines superimposed on absorbed electron images in 68 μm cupronickel powder specimens sintered at 1200°C for one hour in hydrogen and quenched. (Scanning path is across the neck. Reveals absence of segregation); (a) Q1, x1000; (b) Q2, x1000; (c) Q3, x500.
<table>
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<td>R58 H₂</td>
<td>4</td>
<td>35</td>
<td>10⁻²</td>
<td>10.9</td>
<td>vac 10⁻² 0</td>
<td>He at 1 atm.</td>
<td>6.18 69.0</td>
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<td>R59 H₂</td>
<td>12</td>
<td>39</td>
<td>10⁻²</td>
<td>12.9</td>
<td>vac 10⁻² 0</td>
<td>He at 1 atm.</td>
<td>6.17 68.9</td>
</tr>
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<td>R52 H₂</td>
<td>4</td>
<td>34</td>
<td>10⁻²</td>
<td>12.7</td>
<td>vac 10⁻² 5</td>
<td>He at 1 atm.</td>
<td>7.64 85.3</td>
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<td>4</td>
<td>38</td>
<td>10⁻²</td>
<td>14.5</td>
<td>vac 10⁻² 5</td>
<td>He at 1 atm.</td>
<td>7.88 88.0</td>
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<td>37</td>
<td>10⁻²</td>
<td>14.7</td>
<td>vac 10⁻² 5</td>
<td>He at 1 atm.</td>
<td>7.60 84.9</td>
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<td>34</td>
<td>1.5 x 10⁻⁶</td>
<td>14.16</td>
<td>vac 0.2 x 10⁻⁵ 5</td>
<td>vac</td>
<td>7.87 87.9</td>
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<tr>
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<td>36</td>
<td>10⁻²</td>
<td>18.3</td>
<td>vac 10⁻² 10</td>
<td>He at 1 atm.</td>
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<td>37</td>
<td>10⁻²</td>
<td>20.7</td>
<td>vac 10⁻² 10</td>
<td>He at 1 atm.</td>
<td>8.63 96.4</td>
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<tr>
<td>R60 H₂</td>
<td>12</td>
<td>37</td>
<td>10⁻⁶</td>
<td>11.5</td>
<td>vac 0.4 x 10⁻⁵ 10</td>
<td>vac</td>
<td>7.44 83.1</td>
</tr>
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<td>0.4 x 10⁻⁵</td>
<td>12.5</td>
<td>vac 0.4 x 10⁻⁵ 15</td>
<td>He at 1 atm.</td>
<td>8.71 97.2</td>
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<td>10⁻²</td>
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<td>vac 10⁻² 15</td>
<td>He at 1 atm.</td>
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<td>vac 0.6 x 10⁻⁵ 15</td>
<td>vac</td>
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<td>He at 1 atm.</td>
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<td>8.45 94.4</td>
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<td>Ar.</td>
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<td>Ar. 760 30</td>
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<td>Ar.</td>
<td>8.08 90.1</td>
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Table 3.4
Data for Supersolidus Sintering Runs in the Centorr Furnace.
All Runs at 1260°C, with 200 x 230 Mesh Powder
The rate at which densification occurred at 1260°C suggested that a substantial amount of liquid had formed. It was subsequently revealed by DTA work (Section 3.1.2) that the solidus temperature of the alloy powder varied with the atmosphere in which it was heated and with the amount of residual oxygen in the system. Photomicrographs of typical sintered specimens are reproduced in Figures 3.20 to 3.23.

The following observations are significant: a) specimens sintered and cooled in a vacuum of $10^{-5}$ torr contained larger pores than those which were sintered in vacuum but cooled under 1 atmosphere of helium (compare Figures 3.20 and 3.22), b) specimens sintered and cooled in argon (at 1 atmosphere) did not achieve high densities, even after 30 minutes at 1260°C, and exhibited large pores after sintering (Figure 3.23), and c) owing to the slow cooling rate of specimens in the Centorr furnace, the boundaries between regions which had been liquid (copper-rich) and solid (nickel-rich) were not readily defined by metallography. It was therefore not possible to define quantitatively the amount of liquid which was present during sintering. However, there were qualitative indications that the amount of liquid formed was far from uniform for all the runs.

The above observations are consistent with the presence of sufficient oxygen in the vacuum sintering specimens to result in appreciable lowering of the solidus temperature of pure cupronickel and the evolution of oxygen gas at intraparticle voids during sintering. Although the powders were cleaned in hydrogen, they were exposed to air during the preparation of specimens, and they were not thereafter heated in a reducing atmosphere. Oxygen analyses were performed on a number of the sintered specimens. The results in Table 3.5 indicate that as much as 20-200 ppm of oxygen was
Figure 3.20. Cupronickel specimens sintered at 1260°C in a vacuum of \(-10^{-5}\) torr, for (a) 10 min. (R60) and (b) 30 min. (R62), x 120.

Figure 3.21. Cupronickel specimens sintered at 1260°C in a vacuum of \(-10^{-2}\) torr for (a) zero min. (R58) and (b) 5 min. (R52). Specimens helium treated at the end of the runs, x120.
Figure 3.22. Cupronickel specimens sintered at 1260°C in a vacuum of ~10^{-2} torr for (a) 10 min. (R57), (b) 30 min. (R51). Helium treated at the end, x120.

Figure 3.23. Cupronickel specimens sintered at 1260°C in Argon for 30 min. (a) as received powder (R63); (b) cleaned in hydrogen (R64), x120.
Table 3.5
Oxygen Content of Cupronickel Specimens Sintered at 1200 and 1260°C in the Centorr Furnace

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<td>13</td>
<td>R62</td>
<td>ss</td>
<td>17</td>
</tr>
<tr>
<td>R41</td>
<td>ss</td>
<td>36, 35</td>
<td>R63</td>
<td>ss</td>
<td>17</td>
</tr>
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<td>R42</td>
<td>ss</td>
<td>19, 15</td>
<td>R64</td>
<td>ss</td>
<td>36</td>
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<td>R43</td>
<td>ss</td>
<td>28, 14</td>
<td>R65</td>
<td>ss</td>
<td>33</td>
</tr>
<tr>
<td>R44</td>
<td>ss</td>
<td>15</td>
<td>R66</td>
<td>ps</td>
<td>27</td>
</tr>
<tr>
<td>R46</td>
<td>ss</td>
<td>14</td>
<td>R67</td>
<td>ps</td>
<td>25</td>
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<tr>
<td>R47</td>
<td>ss</td>
<td>21</td>
<td>R48</td>
<td>ss</td>
<td>12</td>
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</tbody>
</table>

*s* - solid state sintering at 1200°C

ss - supersolidus sintering at 1260°C

ps - presintered at 900°C
still present after sintering, and that there were appreciable differences in the amount of residual oxygen between specimens in the series.

For reasons indicated above, these early supersolidus sintering experiments, could not be interpreted quantitatively. However, they provided a basis for the design of later experiments. Metallography on the specimens also provided some early insight into the mechanisms of super-solidus sintering.

3.3.3 Sintering in Hydrogen at 1200-1273°C

As noted in Section 3.1.3, the solidus temperature of the cupro-nickel powder when heated in dry hydrogen was 1265 ± 1°C. A number of sintering experiments were conducted in the superkanthal furnace with a hydrogen atmosphere, and at temperatures in the range of 1200°C to 1273°C. All specimens were held for 30 minutes at temperature. Data and results for runs with 68 μm powder are in Table 3.6 and for runs with 81 μm powder are in Table 3.7.

The sintered densities and the densification parameters as a function of sintering temperature are plotted in Figure 3.24. The data show that:

a) Within the temperature regime where no liquid formed, densification during sintering was limited and was not strongly temperature dependent.

b) Specimens sintered at temperatures where liquid formed during the sintering cycle showed extensive densification, to a degree which depended strongly on the temperature (amount of liquid formed).

c) Under conditions of supersolidus sintering at a given temperature, there was little difference in the densification of 68 μm and 81 μm powder specimens. In the solid state, the coarser powder specimens densified slightly less for a given sintering treatment.

Figures 3.25.a and b are photomicrographs from specimens sintered at temperatures between 1230 and 1262°C.
Table 3.6
Data for 30-Minute Sintering Runs at 1200-1273°C in Hydrogen
Part I. 200 x 230 Mesh Powder
Density of the presinter = 51.2% of theoretical

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Sintering Temp. °C</th>
<th>Time to reach temp. min.</th>
<th>Temperature fluctuations °C</th>
<th>End Treatment</th>
<th>% theoretical density</th>
<th>Densification parameter %</th>
<th>Grain Size μm</th>
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<tbody>
<tr>
<td>Q49</td>
<td>1200</td>
<td>4.0</td>
<td>2.5 2.5</td>
<td>F</td>
<td>57.6</td>
<td>8.8</td>
<td>-</td>
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<tr>
<td>Q50</td>
<td>1200</td>
<td>5.0</td>
<td>2.5 2.5</td>
<td>F</td>
<td>57.5</td>
<td>8.6</td>
<td>71</td>
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<td>F</td>
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<td>13.1</td>
<td>75</td>
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<td>F</td>
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<td>12.9</td>
<td>-</td>
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<td>1260</td>
<td>5.0</td>
<td>2.5 3.0</td>
<td>F</td>
<td>63.1</td>
<td>20.7</td>
<td>-</td>
</tr>
<tr>
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<td>6.0</td>
<td>2.5 2.5</td>
<td>F</td>
<td>63.8</td>
<td>22.2</td>
<td>-</td>
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<td>23.0</td>
<td>73</td>
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<td>19.2</td>
<td>73</td>
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<td>62.8</td>
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<td>2.0 2.0</td>
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<td>86.2</td>
<td>70.3</td>
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<tr>
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<td>1268</td>
<td>5.0</td>
<td>2.0 2.0</td>
<td>Q</td>
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<td>62.6</td>
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<tr>
<td>Q63</td>
<td>1273</td>
<td>11.0</td>
<td>1.0 1.5</td>
<td>F</td>
<td>95.4</td>
<td>90.1</td>
<td>147</td>
</tr>
</tbody>
</table>

F = Furnace cooled
Q = Quenched into iced brine
* = Assuming solid and pores only
Table 3.7
Data for 30-Minute Sintering Runs in Hydrogen
Part II. 170 x 200 Mesh Powder
Density of the presinter = 51.2% of the theoretical density

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Sintering temp. °C</th>
<th>Temperature fluctuation °C</th>
<th>Time to reach the temp. min.</th>
<th>End Treatment</th>
<th>% theoretical density</th>
<th>Densification parameter %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>+</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q69</td>
<td>1250</td>
<td>1.5</td>
<td>3.0</td>
<td>4.25</td>
<td>F</td>
<td>58.1</td>
</tr>
<tr>
<td>Q70</td>
<td>1253</td>
<td>2.0</td>
<td>3.0</td>
<td>4.75</td>
<td>F</td>
<td>58.5</td>
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<td>1256</td>
<td>2.0</td>
<td>1.75</td>
<td>9.00</td>
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</tr>
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<td>F</td>
<td>59.9</td>
</tr>
<tr>
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<td>1262</td>
<td>2.0</td>
<td>0.5</td>
<td>8.25</td>
<td>F</td>
<td>67.5</td>
</tr>
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<td>1265</td>
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<td>1.5</td>
<td>5.92</td>
<td>F</td>
<td>73.4</td>
</tr>
<tr>
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<td>1268</td>
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<td>1.0</td>
<td>8.75</td>
<td>F</td>
<td>85.1</td>
</tr>
<tr>
<td>Q76</td>
<td>1270</td>
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<td>1.0</td>
<td>5.95</td>
<td>F</td>
<td>94.7</td>
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<tr>
<td>Q77</td>
<td>1273</td>
<td>1.0</td>
<td>1.0</td>
<td>8.60</td>
<td>F</td>
<td>97.5</td>
</tr>
</tbody>
</table>
Figure 3.24. Density and densification parameter versus sintering temperature for 30-minute runs in hydrogen.
a) Powder particles become single crystals after only 30 minutes at 1230°C or higher temperatures, whereas several hours at 1200°C were necessary to eliminate interparticle high angle boundaries.

b) Evidence was found for linear coalescence between some pairs of neighbouring particles (as at "C" in Figure 3.25), and the frequency of observations of coalescence increased with sintering temperature in the range 1230-1262°C. The types and significance of coalescence encounters are discussed later in the thesis.

c) The apparent size and size distribution of particles in specimens sintered at temperatures up to and including 1262°C did not increase with sintering temperature.

Typical optical microstructures of specimens which had been sintered at or above 1264°C are shown in Figures 3.26 to 3.28 and also in previous Figures 3.5 to 3.9. The following observations were made:

a) Liquid was present (at sintering temperatures) at two locations in the specimens;

(i) between near-neighbour solid particles; i.e. forming "necks" at locations corresponding to the high angle grain boundaries seen in solid state sintered specimens, and

(ii) as intraparticle "pools" of essentially spherical shape (at P in Figures 3.6 and 3.26, for example).

b) Liquid at particle surfaces remote from necks could not be detected by microprobe analysis (Figure 3.29) or by optical metallography.

c) Liquid had not completely penetrated all necks between solid particles. Different amounts of penetration are seen at B in Figure 3.26 and at D in Figure 3.27 and 3.28.

d) With increasing sintering temperature (amount of liquid present) for a fixed sintering time, the average grain size increased rapidly as shown in Table 3.6.

e) Coalescence encounters (solid necks) between neighbouring particles were frequently observed in specimens which were sintered at temperatures slightly above the solidus. Necks formed by coalescence were not penetrated by liquid at the end of the sintering cycle. Partial penetration of liquid at necks (see (c) above)
could result if coalescence was in progress when the specimen was cooled.

f) In the presence of a liquid phase at the sintering temperatures, there was a marked change in shape of the solid particles from spherical to polyhedral. Even at 1264°C, where very little liquid (0.9% by weight) had been formed, this shape change was observed at the more dense (liquid filled) clusters within the aggregate (e.g. Figures 3.26 and 3.27). After 30 minutes at 1273°C, when densification had progressed to an advanced degree, re-shaping of the solid particles was general (Figures 3.9 and 3.28).

3.3.4 Sintering at 1273°C in Hydrogen

In another group of experiments, the duration of sintering at a single supersolidus temperature, 1273°C, was varied from "zero" to 60 minutes in an effort to examine the kinetics of densification and the progress of structural changes. Again, all sintering was conducted with 68 μm powder in the superkanthal furnace, in a dry hydrogen atmosphere, according to the conditions in Table 3.8.

Results for densification are plotted in Figures 3.30 and 3.31. Essentially complete densification was obtained after one hour at 1273°C.

Figures 3.32 and 3.33 are photomicrographs typical of specimens from this series of runs. Using quantitative metallographic techniques, estimates were made of the size and distribution of copper-rich (liquid phase) and nickel-rich (solid) areas in the specimens. These results are collected in Table 3.9.

The observations can be summarised as follows:

a) At the sintering temperature, liquid was present both at interparticle and intraparticle sites.
Figure 3.25. Linear coalescences between particles, as shown at 'C', in specimens sintered (solid state) at (a) 1260°C, (Q14) and (b) 1262°C, (Q22) for 30 minutes, x385.

Figure 3.26. Liquid pools (P), interparticle liquid (as at B), and the shape change of particles at liquid filled clusters in cupronickel specimens at 1264°C for 30 min. (Q20); x385.
Figure 3.27. Specimen Q19, Sintered at 1266°C for 30 min. showing the presence of dense regions and different amounts of penetration of liquid (as at 'D'), x385.

Figure 3.28. Specimen Q18, sintered at 1268°C for 30 min. reveals the presence of large grains, linear coalescences and partial penetration of the liquid (as at 'D'), x385.
Figure 3.29. Absorbed electron images and x-ray intensity traces showing the presence of liquid at the neck region and the absence of liquid at particle surfaces and at the pore periphery, (a) Q47, x3600, (b) Q47, x1000, (c) Q20, x1000.
<table>
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<th>Spec. No.</th>
<th>Time to reach 1273°C min.</th>
<th>Temperature fluctuation °C</th>
<th>Sintering time min.</th>
<th>End Treatment</th>
<th>% theoretical density</th>
<th>Measured change in dimensions</th>
<th>Densification parameter</th>
<th>ΔL/L₀</th>
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</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Δd/d₀</td>
<td>ΔL/L₀</td>
<td>Using ρ₀ = 74.6%</td>
</tr>
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<td>Q37</td>
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<td>-</td>
<td>-</td>
<td>F</td>
<td>72.8</td>
<td>0.121</td>
<td>0.103</td>
<td>0</td>
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<tr>
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<td>11.0</td>
<td>-</td>
<td>-</td>
<td>F</td>
<td>76.4</td>
<td>0.098</td>
<td>0.085</td>
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<td>0.5</td>
<td>F</td>
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<td>0.139</td>
<td>0.110</td>
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<td>F</td>
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<td>0.137</td>
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<td>45</td>
<td>97.3</td>
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<td>-</td>
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<td>0.188</td>
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<td>1.0</td>
<td>30</td>
<td>97.5</td>
<td>-</td>
<td>-</td>
<td>0.078</td>
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F = Furnace cooled
Q = Quenched into iced brine
d = Diameter
L = Length
### Table 3.9

Quantitative Metallographic Data for Specimens Sintered at 1273°C in Hydrogen

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Sintering time min.</th>
<th>Liquid pool diameter $d_p$ μm</th>
<th>Grain size* $d_p = d_s$ μm</th>
<th>Average planar diameter, μm</th>
<th>No. of pools counted</th>
<th>Wt. % liquid as pools $N d_p^{1/2}$ **</th>
<th>Wt. % liquid at grain boundary</th>
<th>True grain size*** $d_s$ μm</th>
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<td>17.1</td>
<td>194</td>
<td>14.0</td>
<td>158.0</td>
<td>59</td>
<td>18</td>
<td>182</td>
</tr>
<tr>
<td>Q32</td>
<td>5</td>
<td>84</td>
<td>84</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>83</td>
</tr>
<tr>
<td>Q30</td>
<td>10</td>
<td>115</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>114</td>
</tr>
<tr>
<td>Q35</td>
<td>30</td>
<td>146</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14</td>
<td>140</td>
</tr>
</tbody>
</table>

* Grain size assuming pore and solid only (uncorrected).

** The number of grains, $N$, counted are 22.

*** Grain size assuming liquid, solid and pore. True grain size.
Supersolidus Sintering
(68 µm, 1273 °C)

Figure 3.30. Density versus time for supersolidus sintering at 1273°C in hydrogen.

Figure 3.31. Densification parameter versus time for supersolidus sintering at 1273°C in hydrogen.
Figure 3.32. Cupronickel specimens sintered at 1273°C in hydrogen for (a) zero min. (Q38), (b) 5 min. (Q31), (c) 10 min. (Q33) and (d) 15 min. (Q29). Clustering is evident in (a), x120.
Cupronickel specimens sintered at 1273°C in hydrogen for
(a) 30 min. (Q28), (b) 45 min. (Q36) and (c) 60 min. (Q66). Coalescence is evident at 'C' in (a), x120.

Figure 3.33.
b) After "zero" time at 1273°C; i.e. liquid present during only the interval of time required to heat from 1265 to 1273°C, most of the liquid was evidently present as intraparticle pools. At high magnifications, there was evidence of liquid between adjacent particles, but more liquid was in the pools. Owing to galvanic effects in etching, the copper-rich (liquid) regions are attacked selectively and can be expected to appear disproportionately large in the microstructure. However, this effect applies to both interparticle and intraparticle regions.

c) With increasing time at 1273°C, the intraparticle pools increased slowly in size but decreased rapidly in number, and eventually represented only a minor fraction of the total amount of liquid present at the sintering temperature (Figure 3.34).

d) The mean planar spacing of nearest neighbour intraparticle pools after zero minutes at 1273°C was 13 μm within a given particle. After longer sintering times the pools were concentrated near the volumetric centres of the solid particles (Figure 3.33).

e) The size of the solid particles which existed at the sintering temperature increased steadily with time at temperature (Table 3.9 and Figure 3.34).

f) Solid particles underwent substantial shape change, from spherical to polyhedral, with increasing time at 1273°C. Within particle clusters, some particles had already begun to change shape when 1273°C was reached on heating; i.e. after zero time at temperature.

g) There was evidence of coalescence (formation of solid necks) between some pairs of particles after all times at 1273°C (as at 'C' in Figures 3.3.a or 3.8.a).

h) After zero time at 1273°C, pronounced clustering of the solid particles in high-density regions was evident (Figure 3.32.a). Voids were present which were at least as large as those which existed in the original loose powder aggregate or which existed after sintering in the solid state (compare Figures 3.4.a and 3.32.a). Scanning electron micrographs which support several of the above observations are reproduced in Figures 3.35 and 3.36.
Supersolidus Sintering
(68 µm, 1273 °C)

Figure 3.34. The amount of liquid as pools, and the real grain size, versus time of sintering at 1273°C in hydrogen.
Figure 3.35. Scanning electron micrographs of cupronickel specimens sintered at 1273°C in hydrogen for (a) zero min. (Q38), (b) 5 min. (Q31), (c) 10 min. (Q33) and (d) 15 min. (Q29), x120.
Figure 3.36. Scanning electron micrographs of specimens sintered at 1273°C in hydrogen for (a) 30 min. (Q28), (b) 45 min. (Q36) and (c) 60 min. (Q66), x120.
### 3.3.5 Sintering at Temperatures Above 1273°C

A few specimens were sintered in hydrogen at 1280°C and 1285°C, for which the phase diagram (Figure 3.3) indicates that the amount of liquid present was 29 and 38 per cent by weight, respectively. Densification proceeded rapidly, but problems were encountered with sagging of the specimens under their own weight and some physical segregation of liquid at the highest temperature (Figure 3.37). The following observations are noted:

a) Specimens achieved ≥ 96 per cent of solid density after 5 minutes or less of sintering at 1280 or 1285°C.

b) Appreciable particle growth occurred in only 5 minutes at 1285°C.

c) The intraparticulate liquid pools formed at 1285°C were larger than those formed at lower super-solidus temperatures.

### 3.4 Dilatometer Results

#### 3.4.1 Qualitative Observations on the Progress of Shrinkage

A typical continuous linear dimensional change curve obtained from a dilatometer run is presented in Figure 2.11. The curve clearly shows

a) initial thermal expansion during the course of heating to the solidus temperature,

b) rapid net shrinkage for a short period after reaching the solidus temperature, followed by slower net shrinkage at a steadily decreasing rate, and

c) final thermal contraction during the course of cooling the specimen to room temperature.
Figure 3.37. Bottom section of the specimen sintered at 1285°C for 5 min. in hydrogen reveals the segregation of liquid, (a) x12, (b) x145.
This last component of the dilatometer curve includes solidification shrinkage.

From the previous results for the effect of temperature on densification it follows that:

(i) solid state sintering shrinkage during the course of heating to the solidus temperature is negligibly small and

(ii) rapid net shrinkage starts to occur at the solidus temperature even though the temperature at the centre of a specimen was noted to be about 10°C below the solidus at that stage in a dilatometer run.

On this basis shrinkage curves were calculated by adding the appropriate thermal expansions to the observed decrease in length of the specimens. Corrected shrinkage curves thus obtained for a number of dilatometer runs are given in Figure 3.38.

The times at which the final sintering temperature was reached at the thermocouple are indicated on the curves. Actual times to attain the isothermal sintering temperature from the start of observed net shrinkage are given in Table 3.10.

Some specimens held for more than about 12 minutes (e.g. LVDT 62, curve 12 in Figure 3.38) exhibited "sagging." This is believed to be the consequence of overheating of specimens. The thermocouple wires became alloyed with cupronickel and thus their thermoelectric properties were altered.
Figure 3.38. Corrected $\frac{\Delta L}{L_0}$ versus time plots for 81 μm cupronickel powder (dilatometer runs).
Table 3.10
Measured Shrinkage Values for Dilatometer Specimens

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Total Shrinkage Time min.</th>
<th>Measured Average $\frac{\Delta L}{L_0}$</th>
<th>Measured Average $\frac{\Delta d}{d_0}$</th>
<th>Corrected Maximum $\frac{\Delta L}{L_0}$ from LVDT</th>
<th>Shrinkage Time at 1273°C min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVDT 54</td>
<td>0.025</td>
<td>0.0214</td>
<td>0.0247</td>
<td>0.0012</td>
<td>-</td>
</tr>
<tr>
<td>LVDT 49</td>
<td>0.125</td>
<td>0.0613</td>
<td>0.0742</td>
<td>0.0234</td>
<td>-</td>
</tr>
<tr>
<td>LVDT 53</td>
<td>0.200</td>
<td>0.0597</td>
<td>0.0808</td>
<td>0.0324</td>
<td>0.140</td>
</tr>
<tr>
<td>LVDT 59</td>
<td>0.200</td>
<td>0.0847</td>
<td>0.0972</td>
<td>0.0456</td>
<td>0.180</td>
</tr>
<tr>
<td>LVDT 58</td>
<td>0.300</td>
<td>0.0871</td>
<td>0.0962</td>
<td>0.0442</td>
<td>0.190</td>
</tr>
<tr>
<td>LVDT 55</td>
<td>0.550</td>
<td>0.0980</td>
<td>0.1093</td>
<td>0.0651</td>
<td>0.125</td>
</tr>
<tr>
<td>LVDT 57</td>
<td>0.850</td>
<td>0.1072</td>
<td>0.1232</td>
<td>0.0633</td>
<td>0.180</td>
</tr>
<tr>
<td>LVDT 56</td>
<td>3.350</td>
<td>0.1222</td>
<td>0.1260</td>
<td>0.0866</td>
<td>0.190</td>
</tr>
<tr>
<td>LVDT 61</td>
<td>5.150</td>
<td>-</td>
<td>-</td>
<td>0.1036</td>
<td>0.160</td>
</tr>
<tr>
<td>LVDT 29</td>
<td>10.280</td>
<td>0.1519</td>
<td>0.1490</td>
<td>0.1201</td>
<td>0.260</td>
</tr>
<tr>
<td>LVDT 35</td>
<td>11.430</td>
<td>0.1450</td>
<td>0.1490</td>
<td>0.1176</td>
<td>0.330</td>
</tr>
<tr>
<td>LVDT 62</td>
<td>21.10</td>
<td>-</td>
<td>-</td>
<td>0.1809</td>
<td>0.190</td>
</tr>
</tbody>
</table>
3.4.2 Anisotropy of Shrinkage in Dilatometer Runs

The vertical specimen surfaces and corners were the first regions to be heated in the high frequency induction furnace. Temperature gradients were generated in the early stages of supersolidus sintering, aggravated by the relatively low heat transfer rate through the porous bodies. The early gradients caused non-uniform dimensional changes, and the initial cylindrical shape of a specimen became and remained distorted. Using calipers, the final dimensions of a sintered specimen were measured at a number of positions, as indicated in Figure 3.39.

Ratios of the average change in length and diameter to the original dimensions are given in Table 3.10. Also, the maximum linear shrinkages obtained from dilatometer plots are given in the same table.

The following observations may be made from the data:

a) Dimensional changes during supersolidus sintering are not isotropic; in nearly all runs there was more net diametral shrinkage than length shrinkage.

b) The net average decrease in length measured on sintered specimens was significantly greater than that detected by dilatometry. The dilatometer observed changes in specimen length only at the centre of the long axis of the specimen, which was the last part of the specimen to attain the sintering temperature.

From both of the above observations it was clear that shrinkage data derived directly from dilatometer plots were of restricted quantitative value. However, the nature of the anisotropy and non-uniformity of sintering shrinkage in the dilatometer were comparable from one run to another. Thus, the trends observed in shrinkage with variations in time, temperature, particle size, and other factors in the dilatometer experiments were significant.
3.4.3 Calculated Versus Measured Density Changes

Finally densities of sintered dilatometer specimens were determined by (a) the oil-impregnation method, and (b) measurements of weight and average dimensions. Owing to the non-cylindrical shape of the specimens after sintering (Figure 3.39), the values from impregnation tests were the more accurate.

Results are given in Table 3.11, together with values of density calculated from the dilatometer data, on the assumption of homogeneous and isotropic shrinkage in the specimens, using the relationship:

$$p\% = \frac{1}{1 - \frac{3\Delta L}{L_0}} \rho_0 \times 100$$

where

- $\rho_0$ = the initial density of the presinter,
- $\rho$ = the final sintered density,
- $\Delta L$ = the change in length,
- $L_0$ = the initial length at $\rho_0$.

The results are compared in Figure 3.40, from which it may be observed that:

a) The degree of densification indicated by dilatometric measurements of linear shrinkage is consistently lower than that which actually occurred.

b) The absolute discrepancy does not change appreciably with time of sintering, indicating that it probably has its origins in the very early stages of supersolidus sintering.
Figure 3.39. Sintered dimensions of specimen LVDT 56.
Table 3.11

Density and Grain Size of Dilatometer Specimens as a Function of the Temperature Attained During the Run

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Time of Sintering* min.</th>
<th>Derived (from dilatometer data) Density I % theoretical</th>
<th>Measured</th>
<th>Temperature at the termination of run °C</th>
<th>Grain size μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVDT 60</td>
<td>0</td>
<td>54.2</td>
<td>54.2</td>
<td>ND</td>
<td>81</td>
</tr>
<tr>
<td>LVDT 54</td>
<td>0.025</td>
<td>54.3</td>
<td>60.4</td>
<td>60.8</td>
<td>-</td>
</tr>
<tr>
<td>LVDT 49</td>
<td>0.125</td>
<td>58.6</td>
<td>68.0</td>
<td>68.0</td>
<td>1258</td>
</tr>
<tr>
<td>LVDT 53</td>
<td>0.200</td>
<td>60.2</td>
<td>69.0</td>
<td>71.3</td>
<td>1264</td>
</tr>
<tr>
<td>LVDT 59</td>
<td>0.200</td>
<td>62.9</td>
<td>72.6</td>
<td>72.8</td>
<td>1276</td>
</tr>
<tr>
<td>LVDT 58</td>
<td>0.300</td>
<td>61.6</td>
<td>71.6</td>
<td>72.4</td>
<td>1273</td>
</tr>
<tr>
<td>LVDT 55</td>
<td>0.550</td>
<td>66.8</td>
<td>75.0</td>
<td>75.6</td>
<td>1273</td>
</tr>
<tr>
<td>LVDT 57</td>
<td>0.850</td>
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<td>78.8</td>
<td>80.5</td>
<td>1274</td>
</tr>
<tr>
<td>LVDT 56</td>
<td>3.350</td>
<td>72.7</td>
<td>80.8</td>
<td>83.6</td>
<td>1274</td>
</tr>
<tr>
<td>LVDT 61</td>
<td>5.150</td>
<td>78.9</td>
<td>ND</td>
<td>89.5</td>
<td>1273</td>
</tr>
<tr>
<td>LVDT 29</td>
<td>10.280</td>
<td>84.6</td>
<td>88.0</td>
<td>90.1</td>
<td>1273</td>
</tr>
<tr>
<td>LVDT 35</td>
<td>11.430</td>
<td>81.2</td>
<td>87.1</td>
<td>88.4</td>
<td>1273</td>
</tr>
<tr>
<td>LVDT 62</td>
<td>21.100</td>
<td>ND</td>
<td>ND</td>
<td>96.6</td>
<td>1274</td>
</tr>
</tbody>
</table>

I - Calculated from \(\Delta L/L_0\) obtained from dilatometer
II - Calculated from weight and average dimensions
III - Measured by oil impregnation method
* - Zero time was taken at the start of shrinkage
ND - not determined
Figure 3.40. Density versus time for dilatometer runs.
3.4.4 Metallography and Microprobe Analyses on Dilatometer Specimens

Dilatometer specimens were sectioned for their full length along a diameter and through the thermocouple well (Figures 3.41 and 3.42).

As noted earlier, cooling in the dilatometer was rapid, and it could be assumed that little adjustment of composition in the solid portion of a specimen occurred during cooling. This assumption was justified by comparisons of probe results for specimens which had been quenched from 1273°C in the superkanthal furnace (Section 3.1.3) with those for specimens cooled in the dilatometer from the same temperature after sintering for times sufficient to ensure that equilibrium had been established prior to cooling.

Both metallographic examination and microprobe analysis were carried out at various locations in the specimens along the two lines M and C as shown in Figure 3.41.d. The "solid" (nickel-rich) regions in the microstructure were analysed in the probe at 500 µm intervals along each line, with the results plotted in Figures 3.43 to 3.46. Each plotted composition is the result of averaging five sets of counts in the probe taken at 1.5 µm intervals within a single solid particle.

At low magnifications, Figures 3.41 and 3.42, it was evident that at the top and bottom of the specimens, adjacent to the ceramic discs in the assembly, densities were lower than elsewhere. Additionally, for times up to 0.2 minutes from the start of observed shrinkage, there were density gradients between the outer surface of a specimen and the thermocouple well. Higher magnification photomicrographs revealed that there were substantial gradients in the amount of liquid present in specimens
Figure 3.41. Portion of the longitudinal sections of dilatometer specimens (81 μm powder), x7. Revealing presintered and inhomogeneous sintered structures. The lines C and M show the paths of electron probe microanalyses; (a) LVDT 60 (as homogenised); (b) LVDT 54; (c) LVDT 49; (d) LVDT 59; (e) LVDT 55.
Figure 3.42. Portion of the longitudinal sections of dilatometer specimens, x7 (particle size 81 μm except (e)), revealing the sintered structures; (a) LVDT 56; (b) LVDT 61; (c) LVDT 29; (d) LVDT 62; (e) LVDT 32 (49 μm).
Figures 3.43 to 3.46. Results of microprobe surveys across dilatometer specimens shows composition of nickel-rich solid versus distance from centre (thermocouple well).
Figure 3.44.
Figure 3.45.
Figure 3.46.

Thermocouple Well

Outside of Specimen

LVDT 29-M

LVDT 29-C

LVDT 62-M

LVDT 62-C

Nickel, Weight %

Distance, 500 μm. Intervals
heated for shorter periods in the dilatometer. These gradients alone could account for the above mentioned discrepancy between the densification of specimens indicated by LVDT data and that found by direct measurements of bulk density (Table 3.11).

Microprobe analyses further revealed that substantial gradients in liquid content existed in the short-term specimens (Table 3.12). Moreover, it was evident that constitutional equilibrium had not been established through these specimens. The temperatures reached at the thermocouple when the runs were terminated are given in Table 3.11. Specimen LVDT 59 had reached 1273°C at the thermocouple, and at equilibrium there would be ~16 per cent liquid present at this temperature; yet both metallography and the probe surveys showed that very little liquid was present near the centre of the specimen (Figures 3.47 and 3.48).

The scatter bars shown in Figures 3.43 to 3.45 represent two sources of error in the probe analyses:

a) The error in individual probe analyses previously established as ±0.6 per cent.

b) A "sampling" error associated with inhomogeneity in the solid particles, estimated as ±1% (of the absolute composition) for short run specimens, but negligible for long-time specimens such as LVDT 29 and LVDT 62.

Gradients in the composition of solid across a dilatometer specimen arise from two sources:

1) Temperature gradients associated with induction heating and with the relatively low heat transfer rate through a porous specimen.

2) Differences in the time available for diffusion in the solid to approach equilibrium.
Table 3.12
Liquid Distribution in Dilatometer Specimens

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Central hole</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
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</thead>
<tbody>
<tr>
<td>LVDT 54</td>
<td>0-10</td>
<td>0-5</td>
<td>0-8</td>
<td>0-5</td>
<td>0-5</td>
<td>4-14</td>
<td>0-10</td>
<td>16-26</td>
<td>5-15^M</td>
<td></td>
<td></td>
<td></td>
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<td>0-5</td>
<td>0-8</td>
<td>0-5</td>
<td>0-5</td>
<td>1-11</td>
<td>0-8</td>
<td>11-21</td>
<td>22-32</td>
<td>7-17^M</td>
<td></td>
<td></td>
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<td>0-5</td>
<td>0-5</td>
<td>1-11</td>
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<td>0-5</td>
<td>11-21</td>
<td>5-15</td>
<td>13-23^M</td>
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<td></td>
</tr>
<tr>
<td>LVDT 59</td>
<td>5-15</td>
<td>0-8</td>
<td>0-5</td>
<td>0-5</td>
<td>0-5</td>
<td>0-5</td>
<td>0-8</td>
<td>1-11</td>
<td>5-15</td>
<td>0-5</td>
<td>16-26</td>
<td>5-15</td>
<td>11-21</td>
</tr>
<tr>
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<td>1-11</td>
<td>1-11</td>
<td>5-15</td>
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<td>4-14</td>
<td>13-23</td>
<td>5-15</td>
<td>11-21^M</td>
</tr>
<tr>
<td>LVDT 61</td>
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<td>9-19</td>
<td>19-23</td>
<td>21-35</td>
<td>27-29</td>
<td>27-29</td>
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<tr>
<td>LVDT 62</td>
<td>16</td>
<td>16</td>
<td>18</td>
<td>14</td>
<td>20</td>
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<td>27</td>
<td>27C</td>
<td>27C</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.47. Microstructure of LVDT 59 on the diametrical axis (line M) shown in Figure 3.41.d, at locations: (a) surface, (b) 2 mm from the surface, x760.
Figure 3.48. Same as Figure 3.47, for locations (a) 4 mm from the surface, (b) near the central hole, x760.
It is not possible to isolate the contributions of these two effects in short time specimens. If a nickel content of 52.5 wt. % indicated by probe analysis, this corresponds either to equilibrium at 1273°C or failure to reach equilibrium at a temperature higher than 1273°C.

With the exception of the extreme top and bottom regions, there were no significant composition gradients in specimens LVDT 29 and LVDT 62 heated for 10 and 21 minutes respectively beyond the start of observed shrinkage. Since all specimens were heated selectively from the outside, it can be inferred not only that the temperature had been relatively uniform in these specimens, but also that constitutional equilibrium had been established.

From photomicrographs of the structures (Figures 3.49 and 3.50) at point 'A' in Figures 3.41 and 3.42 the following observations may be made:

a) In regions where liquid phase had just begun to form, there was a preference for intergranular nucleation of melting (Figure 3.49.a).

b) Particles underwent significant and progressive shape change from spherical to polyhedral with increasing time in the presence of liquid. Some shape change took place in regions where only small volume fractions of liquid (< 5%) were present and in times substantially less than one minute after liquid had first been observed at interparticle boundaries (Figures 3.49.d and 3.50).

c) With increasing time at supersolidus temperatures, smaller pores became progressively closed. However, large pores remained even in the 20 minute specimen (LVDT 62, Figure 3.42.d) which had attained a density of 96 per cent of theoretical.
Figure 3.49. Microstructures at region A in Figure 3.41: (a) LVDT 49, (b) LVDT 59, (c) LVDT 53 (not in Figure 3.41), (d) LVDT 55, x67.
Figure 3.50. Microstructures at region A in Figure 3.42; (a) LVDT 56, (b) LVDT 61, (c) LVDT 29, (d) LVDT 62, x67.
3.4.5 Effect of Powder Particle Size

In Figures 3.51 and 3.52 corrected dilatometric shrinkage curves are compared for specimens made from three particle size fractions of cupronickel powder; 49, 68 and 81 μm. In the early stages of shrinkage, the effect of particle size was apparently insignificant. After about 4 minutes from the start of contraction, however, the rate of shrinkage was high for the finer powders. At this same stage of a run, the pore size was also smaller in the specimens made from finer powders, as shown in Figure 3.42.e.

3.5 Behaviour of Cast Cupronickel

3.5.1 Structure of Cast and Homogenised Specimens

Figures 3.53 and 3.54 show the microstructure of cast cupronickel specimens before and after an homogenising anneal. Interdendritic segregation in the cast alloy (Figure 3.53) was reduced by the annealing to a level at which it could not be detected metallographically. Microprobe analysis (Section 2.4 and Figure 2.4) had shown that composition variations were approximately ±2% of the mean in homogenised specimens. The average planar dendrite spacing was found to be 33 μm.

Microporosity was evident in the homogenised alloy (Figure 3.54). The spacing of the pores indicated that they were interdendritic in origin, and their spherical shape suggested that gas evolution as well as shrinkage was involved in their creation. The volume content of porosity, based on density measurements on machined specimens was 2.0 per cent.
Figure 3.51. Linear shrinkage versus time from start of contraction, for runs 29, 32, 34.
Figure 3.52. Linear shrinkage versus time from start of contraction, for runs 30, 31, 35.
Figure 3.53. As cast cupronickel alloy, (a) x26, (b) x120; showing dendritic segregation.
The average grain size of the cast cupronickel was ~ 1.2 mm, and was not affected by homogenisation. No annealing twins were observed in any grains in the specimens as shown in Figure 3.54.

3.5.2 Liquid Formation on Heating Above the Solidus

Table 3.13 reports data for experiments in which cast and homogenised specimens were heated in the superkanthal furnace to 1273 ± 2°C for periods ranging from zero to 30 minutes, and then quenched. The heating cycle was described in Section 2.6.2. Metallography and microprobe analyses were conducted on the specimens, with the quantitative results collected in Table 3.13. Typical microstructures are presented in Figures 3.55 to 3.57.

Based on the composition of the nickel-rich regions in those specimens which were heated for 15 and 30 minutes at 1273°C, it was indicated that the solidus of the cast cupronickel alloy was lower than that of the cupronickel powder by approximately 8°C. This was not unexpected, since there was 0.23 wt. % silicon in the cast alloy compared with ~ 0.10 wt. % silicon in the powder. From previous experience, it was assumed that the effect of this additional silicon on the liquidus temperature could be neglected. On this basis, the weight fraction of liquid in equilibrium with solid at 1273°C was estimated as ~27 per cent. Data in Table 3.13 thus suggest that equilibrium had probably been established after 15 minutes or less at 1273°C.

Microprobe analysis on the "zero-time" specimen revealed that constitutional equilibrium had not been established. From the average composition of the nickel-rich regions, and assuming that there was
Table 3.13
Data for Experiments with Cast Cupronickel

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Treatment</th>
<th>Isothermal Heating</th>
<th>Composition* of Ni rich phase</th>
<th>Normalised** composition</th>
<th>Weight per cent liquid (phase diag.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temp. °C</td>
<td>Temp. fluctuations</td>
<td>Cu wt. %</td>
<td>Ni wt. %</td>
</tr>
<tr>
<td>SPLS-2</td>
<td>H</td>
<td>1000</td>
<td>5, 5, 288</td>
<td>50.27</td>
<td>50.31</td>
</tr>
<tr>
<td>SPLS-2</td>
<td>Q</td>
<td>1273</td>
<td>-</td>
<td>48.15</td>
<td>52.42</td>
</tr>
<tr>
<td>SPLS-3</td>
<td>H</td>
<td>1273</td>
<td>5</td>
<td>49.57</td>
<td>49.92</td>
</tr>
<tr>
<td>SPLS-3</td>
<td>Q</td>
<td>1273</td>
<td>5</td>
<td>50.27</td>
<td>50.31</td>
</tr>
<tr>
<td>SPLS-3</td>
<td>Q</td>
<td>1273</td>
<td>5</td>
<td>49.57</td>
<td>49.92</td>
</tr>
<tr>
<td>SPLS-4</td>
<td>H</td>
<td>1273</td>
<td>5</td>
<td>50.27</td>
<td>50.31</td>
</tr>
<tr>
<td>SPLS-4</td>
<td>Q</td>
<td>1273</td>
<td>5</td>
<td>50.27</td>
<td>50.31</td>
</tr>
</tbody>
</table>

H - Homogenised
Q - Quenched from temperature indicated
* - Composition obtained from probe analyses
** - Composition normalised to 100 per cent
+ - Took 6 minutes and 36 seconds to reach 1273°C from 1265°C
++ - Took 6 minutes and 38 seconds to reach 1273°C from 1265°C
Figure 3.54. As homogenised, cast cupronickel alloy, (a) x26, (b) x120. Note large grains and microporosity.

Figure 3.55. Cast cupronickel specimen SPLS 2, heated at 1273°C for "Zero" minutes in hydrogen and quenched. This reveals liquid pools, discontinuous grain boundary liquid and pool-free zones (as at 'Z'), (a) x26, (b) x120.
Figure 3.56. Cast cupronickel SPLS 3, heated at 1273°C for 15 min. and quenched, revealing elongated liquid pools, (a) x26, (b) x120.

Figure 3.57. Cast cupronickel SPLS 4, heated at 1273°C for 30 min. and quenched; revealing spheroidised liquid pools and concentration of liquid at triple points, (a) x26, (b) x120.
complete mixing in the liquid when 1273°C was attained, the estimated volume fraction of liquid in this specimen was ~14 per cent. Again, this was in good agreement with the results of quantitative metallography.

The initiation and progress of melting on heating the cast and homogenised alloy to 1273°C could be followed by examining photomicrographs of the type represented by Figures 3.55 through 3.57. The important observations as follows:

a) The average grain size of the specimens was not altered by heating for up to 30 minutes at 1273°C.

b) Liquid had formed at many intragranular sites in the course of heating between the solidus and 1273°C (zero time at 1273°C), Figure 3.55.

c) The volume of liquid formed at intragranular sites ("pools") was many times greater than that which had formed at grain boundaries.

d) The grain boundaries did not appear to be completely penetrated by liquid.

e) Near some grain boundaries there were "pool-free zones" extending up to 60 μm from a boundary (as at Z in Figure 3.55).

f) The liquid pools in the zero-time specimen were mostly of regular and equiaxed shape, and their mean planar spacing was ~37 μm. This can be compared with the average dendrite spacing of 33 μm in the as-cast alloy and micropore spacing of 47 μm in the homogenised alloy.

g) With increasing time at 1273°C,

(i) Intraparticule pools grew in size, decreased in number, and increased in total volume. 
There was, however, little change in the total volume of pools beyond 15 minutes, consistent with the previous indication that constitutional equilibrium had been established in less than 15 minutes at 1273°C.
(ii) The pools changed from regular and equiaxed to irregular shapes. Between 15 and 30 minutes there was a tendency for pools to assume more rounded contours.

(iii) More liquid became concentrated at grain boundaries (particularly at triple points). However, even after 30 minutes at 1273°C, the ratio of intergranular to intragranular liquid had remained very low.
4.1 Solid State Sintering Behaviour of Loose Powders

4.1.1 Sintering in Real Systems versus Model Systems

In attempting to identify the mechanisms responsible for densification during the sintering of powder aggregates, the usual approach has been to compare the experimental time and/or temperature dependence of density or dimensional change with that predicted from various mass transport models singly and in combination (see Section 1.2.1). In the case of model experiments this approach has enjoyed some success. However, real powder aggregates of practical interest differ physically from the models in respect to regularity of packing, uniformity of particle size and shape, and initial interparticle contact (which is affected by compaction).

To a limited extent, it is possible to anticipate the effects of particle shape, size distribution and initial neck geometry on the progress of sintering and to modify the models appropriately. However it is also possible, as in the present work, to minimise these effects experimentally by using loose (uncompacted) powders of essentially spherical shape and uniform particle size. In such experiments it may be possible
to isolate the effect of the initial packing of particles in the powder aggregate.

4.1.2 Observations of Early Sintering Kinetics

It is a general observation that loose or lightly compacted powder aggregates undergo more rapid early shrinkage than either heavily compacted powders or model systems when sintered at a given homologous temperature. Typical of this behaviour are the results by Tikkanen and Yläsaari [66] for fine spherical carbonyl nickel powders, reproduced in Figure 4.1. At any given sintering time, the rate of densification (slope of the plots) was higher for specimens of lower initial density. Uncompacted (loose powder) specimens exhibited the highest rates of shrinkage.

Calow and Tottle [67] sintered loose spherical copper powders (20-90 μm particles) with the results plotted in Figure 4.2. A large degree of densification had occurred in specimens after the smallest sintering interval of 30 minutes. Data from the present work with cupronickel powder are plotted with the Calow and Tottle results, and exhibit similar characteristics.

As described in Section 1.2.1 most models of mass transport in sintering predict a simple power law time dependence of shrinkage; i.e.

\[ \frac{\Delta V}{V_0} \propto t^p \]  

(4.1)

in which the value of \( p \) can be an indicator of the dominant transport mechanism.

Few data are available from experiments with loose aggregates of uniform and spherical metal powder particles. Results reported by
Figure 4.1. Relative density versus sintering time at 1000°C for fine spherical carbonyl nickel powder, from Tikkanen and Yläsaari [66].
Figure 4.2. Relative Density $\rho/\rho_T$ versus sintering time for solid state sintering. Data of Calow and Tottle [67] for copper, and present data for cupronickel.
Clark, Cannon and White [68] for 37.5 μm copper powders are plotted as log \( \frac{\Delta V}{V_0} \) versus log time in Figure 4.3, together with results from the present work for cupronickel powder. Up to a volume shrinkage of roughly 10 percent the slopes of the plots (p) are in the range of 0.7 to 1. Beyond this degree of sintering the time dependence of shrinkage decreases markedly (p \approx 0.2). Short time sintering data from Tikkanen and Mäkipirtti [69] for copper and nickel powders are plotted in Figure 4.4. The parameter used to describe shrinkage in this case is different, but the slopes of the plots correspond to values of p in the range 0.55 to 0.9.

Shumaker and Fulrath [70] followed the early stage of sintering of compacted copper and nickel powders in a scanning microscope. Their results, which exhibit considerable scatter, are given in Figure 4.5. The average slopes of the log plots are 0.71 for copper powders and 0.73 for nickel powders.

4.1.3 Structural Changes During Sintering

That sintering shrinkage in real powder systems is initially concentrated at the most close-packed or clustered regions in the original aggregate has been amply demonstrated both previously and in the present work. Barrett and Yust [71] described "centres of densification" in three-dimensional aggregates, examples of which are also clearly evident in Figures 3.4, 3.16 and 3.17 (also Figures 3.3 and 3.4 in Part B) from the present work.

Eloff and Lenel [72] observed rearrangement of the particles within some regions of planar arrays of powders in the very early stages of
Figure 4.3. Volumetric shrinkage versus sintering time for copper (Clark et al. [68]) and for cupronickel (present results).

Figure 4.4. Volumetric shrinkage data for copper and nickel (Tikkanen and Makipirtti [69]) and for cupronickel (present results). (Plotted as \( \log \frac{V_a - V}{V - V_T} \) versus log time).
<table>
<thead>
<tr>
<th>Material</th>
<th>Run No.</th>
<th>Size (μm)</th>
<th>Temp.°C (Tm)</th>
<th>Green Density % pth</th>
<th>Slope log Δl/10 vs. log t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>Ni-A</td>
<td>-30+20</td>
<td>1200</td>
<td>43% (C)</td>
<td>0.69</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni-B</td>
<td>-30+20</td>
<td>1195</td>
<td>72% (C)</td>
<td>0.78</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni-C</td>
<td>-30+20</td>
<td>1110</td>
<td>40% (D)</td>
<td>0.73</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-A</td>
<td>-44+37</td>
<td>950 (0.80)</td>
<td>43% (C)</td>
<td>0.36</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-B</td>
<td>-30+20</td>
<td>810 (0.90)</td>
<td>43% (D)</td>
<td>1.08</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-C</td>
<td>-44+37</td>
<td>950 (0.90)</td>
<td>42% (C)</td>
<td>0.67</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-D</td>
<td>-30+20</td>
<td>810 (0.80)</td>
<td>40% (D)</td>
<td>0.83</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-E</td>
<td>-44+37</td>
<td>950 (0.90)</td>
<td>28% (C)</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Figure 4.5. Linear shrinkage data of Shumaker and Fulrath [70] for the solid state sintering of Cu and Ni powder compacts in the S.E.M. (Experimental data in Table, plotted in figure.)
sintering. The local repacking caused a net densification of the array even before interpenetration of particles had occurred at the necks. Exner et al. [73] observed contraction in some areas and expansion in other areas of planar arrays of copper powder particles, and suggested that a type of rotation was occurring at some necks. Rotations at two-particle necks during sintering have also been observed in scanning microscope studies by Gessinger et al. [74], Haímrlé and Angers [75], and Nii [76].

The observation of annealing twins in his sintered nickel powder agglomerates was taken by Tikkanen [20] as an indication that plastic flow, followed by recrystallisation, occurred at the necks at some early stage. In all sintered cupronickel specimens in the present work, annealing twins were found in almost every grain. However, when individual particles of cupronickel powder were heated at 900°C, twins were also produced in most grains. It must therefore be concluded that solidification shrinkage stresses within as-atomised particles were alone sufficient to induce flow and recrystallisation.

Occasional linear coalescences between powder particles were observed in all cupronickel specimens that had been sintered at 1200°C or higher. The incidence of coalescence was distinctly greater in specimens sintered at higher temperatures up to the solidus. By linear coalescence is meant the formation of a coherent interface [77] between two particles. Coalescence-type encounters occur between particles which have closely similar crystallographic orientations at their mating surfaces, or which assume similar orientations as a consequence of annealing twin formation, or which have relative orientations (described by Kronberg and Wilson [78]) that produce a significant density of coincident lattice sites at the
interface. In the case of F.C.C. metals, for example, the Kronberg-Wilson (K-W) orientations include rotations of 22°, 30°, and 38° about a common [111] pole. Observations of coalescences are important to an interpretation of sintering mechanisms for two reasons:

   a) they may be an indication that relative particle rotations have occurred at necks during sintering, and

   b) the growth of a neck between a coalesced particle pair must proceed without the aid of a high angle grain boundary as a vacancy sink for diffusion. (The role of coalescence in supersolidus sintering is discussed separately below.)

If coalescence encounters were purely statistical; i.e. related only to the relative orientations of neighbouring pairs in the original aggregate, it would not be expected that an increase in sintering temperature would affect the incidence of coalescence. It therefore appears likely that some of the observed encounters were aided by particle rotations, and that the rotations were more prevalent at higher temperatures. No direct metallographic evidence for rotation at necks was found in any of the sintered cupronickel specimens. Such evidence would be hard to find, however, since surface diffusion acts rapidly to influence neck profiles.

4.1.4 Possible Mechanisms of Early Sintering Shrinkage

Of the many transport mechanisms which have been suggested and identified in the sintering of metal powders, it is recognised that only five types can contribute to shrinkage:
a) Volume diffusion, driven by vacancy concentration gradients

b) Grain boundary diffusion
c) Dislocation glide or creep, under the action of external and/or internally-generated stresses
d) Diffusional creep; i.e. volume diffusion driven by external and/or internally generated stresses
e) Rearrangement (repacking), involving particle rotation at necks and possibly grain-boundary sliding as a cooperative process

4.1.4.1 Diffusion Mechanisms

There are several models for those transport processes which involve primarily diffusion along vacancy concentration gradients (Section 1.2.1). Of these, only the one due to Kingery and Berg [6] predicts a value of \( p > 0.5 \) in the relationship \( \frac{\Delta V}{V_0} \propto t^p \). Both in the present experiments and in the more reliable of the previous kinetic studies of loose powder sintering, \( p \) was found to lie in the range of 0.6 to 1.1 for the earliest stage of sintering, with most values > 0.7.

Kingery and Berg [6] predicted \( p = 0.8 \) for one model of transport by volume diffusion with grain boundaries acting as vacancy sinks (see 1.2.1). They argued that this could explain the experimental results obtained by Clark et al. [68] with loose copper powder (Section 4.1.2, Figure 4.3). However, it has been pointed out by Tikkanen et al. [20] that the model is unsound on fundamental grounds. In the early stage of sintering, the total area of grain boundaries rapidly increases with time (this is both expected and observed metallographically). This cannot be
reconciled thermodynamically with annihilation of vacancies at the boundaries during the same time interval. However, the Kingery-Berg model would predict an increase in the rate of shrinkage as more and larger necks became established, which is contrary to observation.

The arguments presented above also apply to those models of grain-boundary diffusion which predict shrinkage. While they may be relevant to later stages of sintering, it is unlikely that they apply to the earlier stage.

A quantitative comparison can be attempted between Kingery and Berg's prediction [6] of volume shrinkage, due to volume diffusion with dislocations and grain boundaries as vacancy sinks, and the experimental values for cupronickel. A value of 3.3 contacts per particle \( n_1 \) in the density range 53-61% of theoretical density was obtained from plots of De Hoff et al. [79], of the number of contacts per particle versus sintered density. An average value of 1800 ergs/cm\(^2\) was assumed for \( \gamma \) based on values of 1640 ergs/cm\(^2\) [80] for Cu and 1900 ergs/cm\(^2\) [80] for Ni. The atomic volume, given by

\[
\Omega = \frac{\text{atomic weight of the alloy}}{\text{Avogadro's number} \times \text{theoretical density}}
\]

was found to be \( 1.13 \times 10^{-23} \) cm\(^3\). A value of \( 6.1 \times 10^{-10} \) cm\(^2\)/sec was obtained for the diffusion coefficient of 47.8 atom % Cu cupronickel alloy, \( D_v \), at 1200°C, by extrapolating the log \( D_v \) versus \( \frac{1}{T} \) plot of Brunel et al. [65] and others [43,81], in Figure 4.6. Using these values in the Expression (4.2), a value of \( \frac{\Delta V}{V_0} = 1.4 \times 10^{-3} \) was obtained for a sintering interval of 30 minutes. The experimental volume shrinkage was \( 6.5 \times 10^{-2} \); i.e. 50 times as great. The
Figure 4.6. Interdiffusion coefficient versus $\frac{1}{T}$ for 50-50 weight % cupronickel alloy.
necessity for participation of dislocations as sources or sinks has been disputed [15]. Thus, Expression (1.6) reduces to the form of Expression (1.4), which predicts $\frac{\Delta V}{V_0}$ values still lower, with $p = 0.4$.

Kingery and Berg derived an expression for $\frac{\Delta L}{L_0}$, by a volume diffusion mechanism with the particle surface as a vacancy sink, which yielded $p = 0.8$. However, Ichinose and Kuczynski [11] predicted $\frac{\Delta L}{L_0} = 0$ for volume diffusion with particle surface as vacancy sinks.

4.1.4.2 Creep Mechanisms

There are some experimental indications that plastic flow occurs, at least during the earliest stages of sintering of metal powders, without the external application of stress. These include observations of inert markers [82,83] and crystallographically oriented particle pairs [84].

Several approaches have been used to estimate the stresses induced by surface tension at a neck during sintering. Probably the most rigorous of these is due to Leary [85], and is based on a virtual work argument. For a two sphere model (Figure 4.7), the compressive stress at the neck is given by

$$\sigma_1 = \frac{P_1 \gamma}{a} \approx \frac{\gamma}{h}$$

(4.3)

where $P_1$ is a dimensionless coefficient related to the geometry of the neck, and $h$ is the centre-to-centre approach of particles (related to $\Delta L$). Leary states that the analysis applies only for $h/a \leq 0.05$; i.e. for $\frac{\Delta L}{L_0} \leq 5\%$. For the cupronickel powder of the present work $a = 3.4 \times 10^{-3}$ cm and $\gamma = 1800$ ergs cm$^{-2}$, from which the neck stresses given in Table 4.1 have been calculated for different levels of fractional interpenetration.
Table 4.1

Compressive Stresses at the Neck for Various Fractional Interpenetration, According to Leary [85], \([a = 3.4 \times 10^{-3} \text{ cm}, \gamma = 1800 \text{ erg cm}^{-2}\)]

<table>
<thead>
<tr>
<th>Fractional Interpenetration (\frac{h}{a})</th>
<th>The Compressive Stress (\sigma_1) MN • m(^{-2})</th>
<th>Fractional Interpenetration (\frac{h}{a})</th>
<th>The Compressive Stress (\sigma_1) MN • m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 \times 10^{-4}</td>
<td>535</td>
<td>6 \times 10^{-3}</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>268</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>135</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>108</td>
<td>0.01</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>91</td>
<td>0.015</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>77</td>
<td>0.02</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>68</td>
<td>0.025</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>60</td>
<td>0.03</td>
<td>1.8</td>
</tr>
<tr>
<td>1 \times 10^{-3}</td>
<td>55</td>
<td>0.035</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>27</td>
<td>0.04</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>0.045</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>14</td>
<td>0.05</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Assuming that the volume of material undergoing deformation in response to the compressive stress is equal to the volume of the neck, then the mean true strain associated with an increment of particle approach, $dh$, is

$$d\varepsilon = \frac{1}{2} \frac{dh}{h}.$$  

The velocity of centre-to-centre approach is then

$$\frac{dh}{dt} = 2h \frac{d\varepsilon}{dt} = 2h\dot{\varepsilon} \quad , \tag{4.4}$$

where $\dot{\varepsilon}$ is the instantaneous strain rate.

The stress dependence of the steady-state strain rate of metals at a given high homologous temperature can be described by a power law:

$$\dot{\varepsilon} = C \sigma^n \quad , \tag{4.5}$$

For stress levels in the range of $10^{-4}$ to $10^{-3}$ $G_0$ ($G_0$ = the shear modulus), a value of $n = 4$ to 5 has been observed experimentally for a wide range of metals [86]. Weertman [87] predicted $n = 4.5$ for steady-state creep on the basis of a model in which dislocation climb was the process controlling the rate of deformation. Creep data for many metals, as presented by Sherby [88], are also found to confirm closely to this prediction.

Ashby [89] has derived "deformation-mechanism maps" for metals, of which the one for nickel of 32 $\mu$m grain size is presented as Figure 4.8. If any two of the variables stress, strain rate and temperature are known,
Figure 4.7. Two-sphere model for solid-state sintering with complete penetration (Lenel et al. [85]).

the map identifies the dominant deformation process and the level of the unknown variable. Thus for nickel, at stress levels between $10^{-3}$ and $10^{-4} G_0$, and at high homologous temperatures, dislocation creep is indicated as the dominant deformation mechanism. This prediction is consistent with many experimental observations, as noted above.

Reference to Equation 4.3 and Table 4.1 reveals that neck stresses in excess of $10^{-3} G_0$ are likely to be encountered in the very early stages of sintering of loose powders (corresponding to $\frac{\Delta L}{L_0} < 0.001$). Stresses in the range $10^{-3}$ to $10^{-4} G_0$ might be experienced for a penetration ratio (linear shrinkage) of up to 0.005. In fact, this degree of shrinkage, and corresponding neck development at particle contacts, would occur heating a specimen to the sintering temperature; i.e. a period during which the kinetics of shrinkage could not be followed experimentally. In the present
work with cupronickel powder, specimens underwent 0.008 linear shrinkage when presintered at 900°C. Throughout the rapid "initial" stage of sintering at 1200°C, therefore, the stresses at necks (other than at those new contacts established as a consequence of shrinkage) were likely to have been substantially below $10^{-1} \sigma_0$.

At temperatures > 0.9 $T_m$ and at stresses < $10^{-4} \sigma_0$, Ashby's map predicts that deformation will proceed by Nabarro-Herring Creep, a type of viscous deformation in response to stress-directed diffusion. That such behaviour is exhibited by copper alloys was recently demonstrated by Burton and Bastow [90] in experiments with wires.
Theoretical treatment of the viscous creep process [1,2] indicates a linear relationship should exist between applied stress and steady state strain rate. Specifically:

\[ \dot{\varepsilon} = \frac{B \sigma_1 \Omega D_v}{d_s^2 kT} \]  

(4.6)

where \( B \) is a constant related to grain geometry, \( \Omega \) is the atomic volume, \( d_s \) is the grain [1,2] or sub-grain diameter [2,91], and other quantities were defined previously. In placing constant strain-rate contours on Figure 4.8, Ashby has used a value of 14 for the constant \( B \), and has taken \( d_s \) to be the grain size.

It is possible to predict the rate of linear approach of a particle pair due to the action of Nabarro-Herring creep. From Equations 4.4 and 4.6,

\[ \frac{dh}{dt} = 2h \dot{\varepsilon} = 2 \frac{\gamma}{\sigma_1} = \frac{2B \Omega D_v \gamma}{d_s^2 kT} \]  

(4.7)

On integration this yields

\[ h = \frac{2 B \Omega D_v \gamma}{d_s^2 kT} t + C \]

The constant of integration \( C \) would be zero if \( h = 0 \) at \( t = 0 \). Thus volume shrinkage is given by

\[ \frac{\Delta V}{V_0} = \frac{3 \Delta L}{L_0} = \frac{3h}{a} = \frac{6 B \Omega D_v \gamma t}{d_s^2 a kT} \]  

(4.8)
This predicts that the rate of shrinkage is independent of stress, and that the fractional amount of shrinkage varies linearly with time \((p = 1\) in Equation (4.1)). This prediction is in good agreement with the observed kinetics of the early shrinkage behaviour of cupronickel powder at 1200°C in the present experiments \((p \approx 0.9)\).

For the present experiments, calculations can be made from Equation (4.8), using \(B \approx 10\), \(\Omega = 1.13 \times 10^{-23}\) cm³, \(D_v = 6.1 \times 10^{-10}\) cm²/sec [65], \(\gamma = 1800\) ergs/cm², \(k = 1.38 \times 10^{-16}\) ergs/°K, \(a = 3.4 \times 10^{-3}\) cm and \(T = 1473^\circ\)K. When values of \(\frac{\Delta V}{V_0} = 0.065\) and 0.125 are taken with the corresponding sintering times of 0.5 and 1 hour, \(d_s\) is found to be \(1.7 \times 10^{-4}\) and \(1.75 \times 10^{-4}\) cm. This is much smaller than the grain size of cupronickel specimens.

According to Pines [91] dislocation substructure boundaries within a crystal act as vacancy sources and sinks. Thus the dimension which defines the vacancy concentration gradient should be the size of substructure unit \(\ell\) rather than the grain size. Mosaic blocks of 2 μm diameter are not unreasonable for cast and annealed metals.

Alexander et al. [92] stated that the radius of curvature at the "neck" between a wire and a plate is usually < 10⁻⁴ cm while sintering. If viscous flow occurs only in the neck region, then the effective diffusion distance could be identified with this radius, and the result is again consistent with the above calculations.

It is known that transport mechanisms such as surface diffusion and evaporation and condensation can contribute to neck growth and decrease the stresses at the neck. This might account for slopes of less than unity in the experimental plots (Figure 4.3).
4.1.4.3 Rearrangement

Other processes which could contribute to shrinkage in the sintering of loose powders can be grouped under the title "Rearrangement." As noted in Section 4.1.3, there is reported experimental evidence that particles can actually rotate [74,75,76] or slide past one another at a neck under the influence of unbalanced stresses [76] (e.g. asymmetric necks). Such motion could not contribute to net shrinkage in a model or close-packed powder array, but might produce at least localised densification in a less regular aggregate.

There are two ways in which shrinkage may be augmented by rearrangement in principle; (a) more efficient packing may be produced, and (b) the relative motion of particles may allow new contacts to be established. It is difficult to verify (a) experimentally; the clusters or "centres of densification" observed in the present and in previously reported [73] sintering studies can have their origin in the original localised packing of the loose powder particles. Metallographic observations support the latter suggestion in the present work; i.e. there was no direct evidence that densification of clusters with time at 1200°C occurred by other than the linear approach of centres of neighbouring particles.

The creation of new interparticle contacts can occur as a natural consequence of linear interpenetration at particle necks by mechanisms other than rearrangement. Moreover, there is no experimental evidence that an increase in the number of contacts will result in an instantaneous increase in the rate of bulk shrinkage. To the contrary, shrinkage is commonly found to be faster in aggregates of looser packing. DeHoff et al. [79] used
vibration to increase the initial number of contacts per particle in loose powder specimens, and found that this decreased the rate of densification.

There are other reasons to suggest that rearrangement processes contribute little to sintering shrinkage. For example, rotation or grain boundary sliding at a given neck requires cooperative motion at other necks in a three dimensional aggregate. It was noted by Exner et al. [73] that a given rotation or shear is as likely to produce expansion as it is to produce contraction. A particle which has only one contact could rotate without the restraint of other necks, but its rotation could produce no increase in density, even locally.

4.1.5 Segregation of Solute During Sintering

Menon et al. [93] presented a theoretical analysis of diffusional creep in binary metallic solid solution polycrystals subjected to an uniform uniaxial stress. Equations were derived for the strain rate and the distribution of the components at quasi-steady state for both grain boundary and volume diffusion paths. Their analysis showed that diffusional creep should cause segregation to occur whenever the diffusivities of the components were unequal. Following Herring and others they assumed that the behaviour of a uniformly stressed, initially spherical grain would approximate the behaviour of grains in a uniformly stressed, initially equiaxed polycrystalline material. Diffusion by a vacancy mechanism was assumed in determining the strain rate and the segregation due to diffusion creep.

The steady state creep rate due to volume diffusion was derived to be
\[ \varepsilon = \frac{4 \sigma_1 \Omega}{3 kT r_s^2} \left( \frac{D_1 D_2}{N_1^0 D_2 + N_2^0 D_1} \right) \] (4.9)

which is roughly a factor of 2 smaller than the Nabarro-Herring creep rate from Equation (4.6) with \( B = 10 \). The compositions of the components at steady state were given by

\[ N_i = \frac{v_i^0}{v_i^*} N_i^0 \exp \left[ -\frac{A_{i2}}{kT} r^2 \right] \] (4.10)

for \( \theta' = 0 \) (where \( \theta' \) is the angle subtended at the centre of the spherical grain between the direction of applied stress and any position on the grain boundary)

\[ A_{i2} = \frac{(-1)^i 12 \sigma_1 \Omega (1 - N_i^0)(D_1 - D_2)}{3r_s^2 (N_1^0 D_2 + N_2^0 D_1)} \] (4.11)

Subscripts 1 and 2 = the component 1 and 2,

- \( i \) = the component 1 or 2,
- \( r \) = any radial distance inside the grain,
- \( r_s \) = the grain radius,
- \( v_i^0 \) = the activity coefficient for solid solution with composition \( N_i^0 \),
- \( v_i^* \) = the activity coefficient for the solid with composition \( N_i \),

and \( N_i^0 \) = the original concentration of component \( i \) in the alloy.
It was shown previously that there exists a compressive stress at the neck. It can also be shown that a tensile stress \( \sigma_1 = \frac{Y}{\rho} = \frac{Y}{h} \), exists at the neck. Thus the segregation at the neck due to unequal flow of two kinds of atoms could be predicted using Expression (4.10). Multiplying the expression for \( A_{i_2} \) by 2, assuming \( v_i = v_i^0 \) and \( r = r_s \), the values of \( N_{Cu} \) for various values of \( h \), \( (\sigma_1 = \frac{Y}{h}) \), were calculated using Expression (4.10).

The values of intrinsic diffusion coefficients \( D_1 = D_{Cu} \) and \( D_2 = D_{Ni} \), at 1200°C, were calculated from reported tracer self diffusion coefficients [94] for Cu and Ni at an alloy composition of 45.4 at % Cu and the interdiffusion coefficient [65] \( D_V \) at a composition of 47.8 atom % Cu. The values are given in Table 4.2.

**Table 4.2**

Diffusion Data for Cupronickel Alloy at 1200°C

<table>
<thead>
<tr>
<th>Alloy Composition at % Cu</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{Cu} ) [94]</td>
<td>45.4</td>
</tr>
<tr>
<td>( D_{Ni} ) [94]</td>
<td>45.4</td>
</tr>
<tr>
<td>( D_V ) [65]</td>
<td>47.8</td>
</tr>
<tr>
<td>( \phi ) (Thermodynamic factor)</td>
<td>45.4-47.8</td>
</tr>
<tr>
<td>( D_{Cu} )</td>
<td>~ 47.8</td>
</tr>
<tr>
<td>( D_{Ni} )</td>
<td>~ 47.8</td>
</tr>
</tbody>
</table>
Values of $N_{Cu}$ and $(N_{Cu} - N_{Cu}^0)$ were calculated and are plotted versus $\frac{h}{a}$ values on a log-log scale in Figure 4.9. It is seen that for linear shrinkages of $2.2 \times 10^{-2}$ and $4.2 \times 10^{-2}$ (after 0.5 and one hour at 1200°C respectively) the excess concentrations of Cu are $10^{-4}$ and $4 \times 10^{-5}$ atomic fractions. This segregation is far too small to be detected by microprobe analysis. For segregation which is at the limit of detection of $6 \times 10^{-3}$ atomic fraction in the probe, the linear shrinkage would be $3.4 \times 10^{-4}$ cm, which is achieved at an extremely early stage of sintering. Moreover, the penetration $(h)$ at this stage, which is approximately equal to the neck radius, is only $10^{-6}$ cm. This is two orders of magnitude smaller than the beam diameter in the microprobe analyser, and is thus clearly beyond the resolution of the instrument. It is also well below the limits of resolution of optical microscopy.

Kuczynski et al. [24] considered two spherical particles of the same radius, $a$, of a well homogenised binary alloy containing $N_A$ and $N_B$ atom fractions of atoms A and B respectively. If these particles were brought together and heated they would form a neck, which would grow according to the predictions of a volume diffusion model. If $D_A > D_B$, where $D_A$ and $D_B$ are the coefficients of self diffusion of atoms A and B respectively, the unequal diffusional flow of the two species would cause an excess concentration $\delta N_A$ of atoms A to build up in the neck area. The excess of A atoms over B, $\Delta J$, at the neck is given by [24]

$$\Delta J = \frac{D_A - D_B}{kT} \nabla \mu + \left( \frac{D_A}{kT} \frac{\delta N_A}{\nabla N_A} - \frac{D_B}{kT} \frac{\delta N_B}{\nabla N_A} \right) \nabla N_A$$

(4.12)

where $\nabla \mu$ = the gradient of the chemical potential of vacancies at the neck.
Figure 4.9. $N_{Cu} - N_{Cu}^0$ versus $\frac{h}{a}$ plot for cupronickel alloy powder.
\( \mu_A \) and \( \mu_B \) = the chemical potentials of A and B respectively.

The second term of the right side of Expression (4.12) represents the flux of atoms A diffusing back into the alloy due to the concentration gradient \( \nabla N_A \) produced by the greater flux of A atoms. According to Equation (4.12) \( \delta N_A \) would increase initially, reach a maximum corresponding to a certain critical radius of curvature of the neck, \( \rho_c \), and then decrease because of the outflow of atoms A caused by the gradient \( N_A \). The value of \( \rho_c \) obtained from Expression (4.12) by equating \( \Delta J \) to zero is given by:

\[
\rho_c = \frac{2(D_A - D_B) \gamma \Omega}{\left( \frac{D_A}{N_A} + \frac{D_B}{N_B} \right) \frac{\partial \mu_A}{\partial N_A} \delta N_A}
\]

(4.13)

But,

\[
\frac{\partial \mu_A}{\partial N_A} = \frac{kT}{N_A} \left( 1 + \frac{d \ln \gamma_A}{d \ln N_A} \right)
\]

(4.14)

\[
\rho_c = \frac{2(D_A - D_B) \gamma \Omega N_A}{kT \delta N_A \left( 1 + \frac{d \ln \gamma_A}{d \ln N_A} \right)}
\]

(4.15)

where \( \left( 1 + \frac{d \ln \gamma_A}{d \ln N_A} \right) \) is the thermodynamic factor equal to

\[
\left( \frac{D_V}{N_A D_A^* + N_B D_B^*} \right).
\]
Using appropriate values in Expression (4.15) and a value of $6 \times 10^{-3}$ atom-fraction for $N_A$ (the lower limit at which it can be detected by probe analysis), a value of $5 \times 10^{-6}$ cm was obtained for $\rho_C$. Again therefore, any segregation which might occur in the cupronickel aggregates would be beyond the capabilities of microprobe analysis or optical metallography to detect.

4.2 Melting Behaviour of Cupronickel

4.2.1 The Partial Melting of Metals and Alloys

When a metal or alloy begins to melt at a clean surface, it is found that the liquid which is formed completely "wets" (covers) the surface of the solid; i.e.

$$\gamma_{SV} \geq \gamma_{SL} + \gamma_{LV}$$

(contact angle $\theta \leq 0$).

Thus melting is nucleated at a surface without the need for any superheating above the equilibrium solidus temperature. Indeed, if $\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$, a condition which might prevail locally at a curved solid surface of small radius, melting can be nucleated below the equilibrium solidus.

What happens at a grain boundary is less obvious, and is not as well-documented experimentally. In metals and in some alloys, the relation $\gamma_{SL} \leq \frac{1}{2} \gamma_{GB}$ is satisfied at high angle grain boundaries, in which case the replacement of a solid boundary by two solid-liquid interfaces is
thermodynamically favourable. For $\gamma_{SL} = \frac{1}{2} \gamma_{GB}$, melting can be nucleated at the boundary without superheat.

Again, in principle, it is also possible for $\gamma_{SL} < \frac{1}{2} \gamma_{GB}$, in which case "grain boundary melting;" i.e. selective melting [95] at high angle grain boundaries in a polycrystal below the equilibrium solidus, will result. Direct experimental evidence for grain boundary melting is somewhat ambiguous. Theoretical predictions have been made by Li [96] for the lowering of the melting point at grain boundaries, but there are insufficient thermodynamic and physical data available to make the predictions quantitative.

In experiments with a series of aluminium-tin alloys, which were heated above their equilibrium solidus temperatures, Smith [97,98] obtained the dihedral angle data shown in Figure 4.10. Dihedral angles were measured directly from photomicrographs of the alloys after they had been solidified. It is noted that a value of $\phi = 0$ was observed at Al - 30 at % Sn. For alloys containing less tin, $\phi > 0$; i.e. grain boundary melting would not occur without superheat. For alloys of < 30 at % Sn, extrapolation of Figure 4.11 suggests values of $\gamma_{SL} < \frac{1}{2} \gamma_{GB}$, and the corresponding possibility

![Figure 4.10](image-url)

**Figure 4.10.** Relative interfacial energy as a function of composition in the Al-Sn system (Ikeuye et al. [98]).
of grain boundary melting. Direct evidence of such behaviour was not obtained from the original experiments. Probably the best experimental indication that grain boundary melting may occur at high angle boundaries was the study of the high temperature fracture behaviour of bicrystals by Weinberg and Teghtsoonian [99].

For a pure metal, not only is melting nucleated at surfaces and grain boundaries without superheat, but melting proceeds to completion without superheat. For a solid solution alloy, melting is initiated at the equilibrium solidus or slightly below, at surfaces and (only if $\gamma_{SL} \leq \frac{1}{2} \gamma_{GB}$) at grain boundaries. But for melting to continue, the temperature must be increased. Moreover, if the equilibrium amounts and compositions of phases are to be attained as the temperature is increased, diffusion must occur in both the solid and the liquid.

At rapid rates of heating, it is therefore possible to obtain substantial superheating of a solid solution. This may permit melting to be nucleated at internal locations, either homogeneously or (with less superheat) at "defects" of many possible types. It can thus be explained why intracrystalline "pools" of liquid can form when a solid solution alloy is heated above its solidus. The frequency and spacing of such pools would be expected to depend on

a) diffusion rates in the solid and liquid phase,
b) rate of heating and highest temperature attained,
and
c) effectiveness and density of pre-existing defects which might be active as nuclei for melting.

For most alloy systems, it can be expected that the liquid which forms above the solidus will occupy substantially more volume than the
solid from which it forms. At surfaces and at grain boundaries when $\phi = 0$, this expansion meets little or no resistance. However, the formation of intragranular pools or discontinuous grain-boundary liquid ($\phi > 0$) must be accommodated (in the absence of internal holes) by flow of the solid.

4.2.2 The Partial Melting of Cast Cupronickel:

When cast cupronickel was heated to $1273^\circ C$ and held, both intragranular and grain-boundary melting occurred (Figures 3.55 to 3.57). The majority of the liquid formed as intragranular pools. Although the grain boundaries did not appear to be uniformly and completely penetrated with liquid, the microstructures were consistent with a zero dihedral angle. If $\phi$ were $> 0$, only grain edges would have been extensively wetted, and few such edges are seen in a metallographic section.

The fact that so much liquid formed intragranularly in the presence of wetting grain boundaries reflects the large diffusion distance between grain-boundaries (i.e. very large grain size). In specimens heated for relatively short times at $1273^\circ C$, a "pool-free zone" was observed adjacent to the grain boundaries. This is evident in Figure 3.55. This zone can only be satisfactorily explained if grain boundary melting preceded intragranular melting. Had melting been simultaneous at both types of site, then the mean planar spacing of nearest neighbour pools should be comparable to the average distance between the grain boundary liquid film and the nearest pools. As noted in the next section, there was other evidence that in sintered specimens grain-boundary liquid formed before intraparticle melting occurred.
It seems probable that each of the pools of liquid was nucleated heterogeneously at an intragranular defect. Metallography revealed that the cast alloy specimens contained appreciable interdendritic shrinkage porosity (Figure 3.54) which was not unexpected in the light of the casting practice. Moreover, microsegregation was present in the alloy specimens. Even after homogenisation, composition gradients of as much as ± 1 % Ni were present.

The average spacing of secondary dendrites, which was indicated in probe surveys (Figure 2.4), was 33 microns. This is in close agreement with the planar spacing of nearest-neighbour pools in the specimen heated to 1273°C for zero minutes. The observations are consistent with the following:

a) intragranular melting was nucleated at shrinkage pores, adjacent to copper-rich interdendritic regions,

b) the small pools formed initially by melting between secondary dendritic arms grew as more liquid formed, and then eventually united to form larger and more irregular-shaped pools between primary dendrite arms,

c) once equilibrium was established, pools no longer grew but tended to spheroidise to reduce their surface area-to-volume ratio, and

d) the interdendritic shrinkage pores, provided space to accommodate net expansion associated with the melting process, as well as providing solid-vapour interfaces at which melting could be nucleated.

4.2.3 The Partial Melting of Sintered Cupronickel

In several respects the melting behaviour of sintered cupronickel powder was markedly different from that of the cast alloy. Moreover, in the case of powder specimens, rapid and important microstructural changes
followed the introduction of liquid into the system, and these changes made it difficult to describe the process of melting itself.

As in the case of the cast alloy, melting started first at grain-boundaries (interparticle mecks). Evidence for this was of two types:

a) the microstructures in those regions of dilatometer specimens (e.g. LVDT 54, 49, 59) which had spent very short times above the solidus indicated that only intergranular liquid had formed (see result, Section 3.4.4), and

b) intragranular pools were found to be clustered more densely near the centres of grains (particles) than near surfaces or grain boundaries, following the "pool-free zone" argument, applied to cast cupronickel in Section 4.2.2 above (see Figure 3.32).

Although it would be expected that melting was nucleated actively at particle surfaces (voids), neither optical microscopy nor microprobe examination revealed that a film of liquid had been present at such surfaces (see results, Section 3.3.3). The liquid film may have been too thin to be resolved. Figure 4.11 shows how the thickness of a uniformly melted layer varies with the volume fraction of a solid sphere of 68 μm diameter that has melted. If 5 per cent of the particle has melted at the surface, the liquid film will be only one micron thick. Moreover, capillary forces tend to hold liquid at an interparticle neck (Figure 3.32). Thus, if only a small volume fraction of liquid is formed at particle surfaces, it will tend to be drawn and held in the neck region, leaving an extremely thin layer on the surface remote from the neck.

The dendrite spacing, and thus the spacing of shrinkage micropores and copper-rich concentration centres, is roughly 6 times smaller in the sintered powder than in the cast alloy. However, the mean planar spacing of liquid pools was about 3 times smaller in the sintered powder than in
Figure 4.11. Thickness of the melted shell on a 68 micron spherical particle as a function of the volume fraction melted.
the cast cupronickel. This could be explained if some of the pools coalesced since the interdendritic spacing of 5 μm is comparable to the pool radius of 5 μm. Following the description of intragranular melting in Section 4.2.2, it is therefore not surprising that the size and spacing of the pools which formed above the solidus in the powder specimens were also about 3 times less than those of cast cupronickel (compare Figure 3.32.a and 3.55.b).

Metallographic examination revealed that in the early stages of supersolidus sintering there was more liquid in intragranular pools than at intergranular sites. Further, the proportion of the liquid inside the grains decreased with time above the solidus. These observations are in contrast to those made for cast cupronickel, which the proportion of intragranular liquid remained large and essentially constant with time beyond that necessary to achieve alloy equilibrium. The differences in behaviour can be explained as follows:

a) Powder specimens had a very large specific surface area at which melting would be actively nucleated (internal pores, with convex solid surfaces).

b) Powder specimens had a very small grain size, and a large grain boundary area.

c) Melting was nucleated first (and probably with some undercooling) at grain boundaries and free surfaces. Since melting is diffusion controlled it follows from a) and b) that a larger volume fraction of the solid in a powder specimen could melt at these locations before intragranular melting started.

d) At necks in the powder specimens above the solidus, the solid would be subjected to compressive stress by the local concentration of capillary forces (see Kingery's model of solution-precipitation in Section 1.2). This might tend to increase locally the rate of melting at the interparticle necks (and possibly depress the solidus). No comparable situation would exist in the cast alloy.
e) As a result of solution-precipitation effects in the later stages of supersolidus sintering, discussed in Section 4.3.1, some of the grains in the powder specimens were selectively dissolved and reprecipitated on other grains to give net grain growth. When a grain was dissolved, its intragranular liquid was released to the intergranular liquid network. Thus a decrease in the proportion of intragranular liquid would be expected to accompany grain growth. No similar process occurred at detectable rates in cast cupronickel. This is not surprising, if only because grain growth would be much slower in view of the much larger initial grain size (smaller driving force) of the cast alloy.

4.2.4 Attainment of Solid-Liquid Equilibrium

Rough estimates of the time required to reach equilibrium between solid and liquid at 1273°C in both cast and sintered cupronickel can be made using the model of "Diffusion out of a Finite Slab" (Jost [100]). The following assumptions are essential in the calculations:

a) Liquid nucleates at residual copper concentration centres (interdendritic sites).

b) The mean linear planar spacing between the pool edges at "zero" time is identifiable with the thickness, 2%, of the slab, and is assumed not to change during isothermal heat treatment.

c) The liquid pool size does not change with time.

d) The rate-controlling step is diffusion in the solid.

e) Impingement effects are negligible.

Interdendritic spacings were estimated from probe analyses (Figures 2.4 and 3.13). The mean planar spacing between pools was calculated using Edelson and Baldwin's [101] relationship
\[ L_s = \left( \frac{2d^2}{3f} \right)^{0.5} (1 - f) \]  

(4.16)

where  
\[ L_s = \text{the centre to centre planar spacing} \]

\[ f = \text{the volume fraction of the second phase, i.e. liquid or pores} \]

Also,
\[ L_{\lambda} = L_s - d_p' \]

where  
\[ L_{\lambda} = \text{the mean planar edge-to-edge spacing, and } d_p' = \text{the mean planar diameter of the pools or pores. The values of dendrite spacing, pool spacing, pool diameter and edge-to-edge mean planar spacing of pools for both cast cupronickel and sintered cupronickel are given in Table 4.3.} \]

The model for diffusion out of a finite slab of thickness \( 2\lambda \) is shown in Figure 4.12. The fixed composition at the solid/liquid interface is 47.5 wt. % Cu (equilibrium composition, at 1273°C, of the solid). Because the variance of probe analyses is ± 0.6%, equilibrium is assumed to be attained at 47.8 wt. % Cu. Figure 4.13 shows a theoretical plot [102], which is applicable to the present case, of \( \frac{C - C_0}{C_1 - C_0} \) versus \( \frac{x_1}{\lambda} \) for the carburisation of a sheet of steel of thickness \( 2\lambda \) for various values of \( \frac{D_t}{\lambda^2} \), where \( C_0 \) is the uniform composition of the solid at \( t = 0 \) (50 wt. % Cu in the present case), \( C_1 \) is the surface composition (interfacial equilibrium composition of the solid: 47.5% Cu), \( C \) is any composition at time \( t \), and \( x_1 \) is the distance given by \( -\lambda < x_1 < \lambda \). In the present case \( C \) is assumed to be 47.8% Cu, at which time equilibrium is attained between solid and liquid. Thus an approximate value of \( \frac{D_t}{\lambda^2} = 1 \) for a value of \( \frac{C - C_0}{C_1 - C_0} = 0.9 \) was used to calculate the time interval to reach equilibrium.
Table 4.3
Dendrite Spacings, Pool Diameter and Pool Spacings of Cast Cupronickel and Sintered Cupronickel

<table>
<thead>
<tr>
<th></th>
<th>Cast Cupronickel cm</th>
<th>Sintered Cupronickel cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrite spacing</td>
<td>$3.3 \times 10^{-3}$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Homog. pore diameter</td>
<td>$8.4 \times 10^{-4}$</td>
<td>-</td>
</tr>
<tr>
<td>Homog. pore spacing</td>
<td>$4.7 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>Vol. fraction porosity</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>Vol. fraction liquid</td>
<td>0.13</td>
<td>0.244</td>
</tr>
<tr>
<td>Pool diameter, $d_p$</td>
<td>$1.9 \times 10^{-3}$</td>
<td>$1.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Pool diameter, $d'_p$</td>
<td>$1.6 \times 10^{-3}$</td>
<td>$0.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>Pool spacing, $L_s$ (centre-to-centre)</td>
<td>$3.7 \times 10^{-3}$</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Pool spacing, $L_\xi$ (edge-to-edge)</td>
<td>$2.1 \times 10^{-3}$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Using a value of $\sim 10^{-9}$ cm$^2$/sec for $D$ at 1273°C (obtained from extrapolation in Figure 4.6), and the edge-to-edge pool spacings ($L_\xi = 2\xi$) from Table 4.3, values of 18 min and one minute were calculated as times to reach equilibrium at 1273°C in the case of cast cupronickel and sintered cupronickel respectively.

For powder specimens, this estimate is consistent with microprobe analyses on dilatometer specimens (see Figures 3.43 to 3.46, and Section 3.4.4).
Figure 4.12. Composition profile in a finite slab due to diffusion out of the slab.

Figure 4.13. Concentration distributions at various times in the sheet \(-\lambda < x_1 < \lambda\) with initial uniform concentration \(C_0\) and surface concentration \(C_1\). (Numbers on curves are values of \(Dt/\lambda^2\)).
Metallographic observations and estimates of liquid contents also indicated that equilibrium was established within one minute of the attainment of 1273°C at the centre of specimen LVDT 55 (Table 3.12).

4.3 Grain Growth During Supersolidus Sintering

4.3.1 Mechanisms of Growth

The coarsening of solid particles (grains) which are dispersed in a wetting liquid may occur in two ways:

a) By the linear coalescence of groups of particles.

b) By selective dissolution of smaller particles and growth (by reprecipitation) of larger particles.

According to Ostwald [103] the solubility $S$ at the surface of a particle of radius $r$ is related to the solubility $S_0$ of the same material at a flat surface by

$$\ln \frac{S}{S_0} = \frac{2 \gamma_{SL} \Omega}{r RT}$$  \hspace{1cm} (4.17)

In the present studies, the contribution of coalescence can be considered minor, because

i) little or no grain growth occurred at high temperatures in the solid state; e.g. 30 minutes at 1262°C (Figure 3.4). By contrast, large grains were formed with very little liquid present; e.g. 30 minutes at 1264°C (Figure 3.5). The frequency of linear coalescences was not much different at 1262°C than at 1264°C, and

ii) new coalescence encounters were neither observed nor expected to continue to occur beyond the earliest stage of supersolidus sintering (e.g. the first 0.6
minutes), yet grain growth was observed to progress steadily with time to high sintered densities.

Growth of solid particles by solution and precipitation was the subject of an extensive and systematic study by Ostwald [103] in 1900, and has become known as "Ostwald Ripening." The literature of the phenomenon was reviewed by Fischmeister and Grimvall [104].

Two mass-transport models for growth have been analysed previously. In one model, diffusion of atoms between particles is assumed to be the slowest step in the process. The analyses of Wagner [105], Lifshitz and Slyozov [106] and Greenwood [107] all yield a prediction of diffusion-controlled growth of the form

$$ r_s^3 - r_0^3 = k_1 t $$

where $r_0$ and $r_s$ are the initial and final mean grain radii, respectively. Slight differences in the analysis yield different values of $k_1$, which according to Wagner [105] is given by

$$ k_1 = \frac{8 \gamma_{SL} \Omega^2 D_v C_0}{9 RT} $$

where $D_v$ is the coefficient of diffusion of solute in the liquid.

In the second model, the rate of growth is controlled by solution or deposition of atoms at the particle surfaces; i.e. by a "phase-boundary reaction." Wagner's analysis of this case yields

$$ r_s^2 - r_0^2 = k_2 t $$
where \( k_2 = \frac{64 \gamma_{SL} \Omega^2 k_r C_0}{81 RT} \) and \( k_r \) is a rate constant for the phase-boundary reaction involved.

It is interesting to compare Equation (4.20) with the law derived by Burke [108] for solid state grain growth. Burke assumes that growth is driven by the curvature of the grain boundary, which is inversely proportional to the average grain size, i.e.

\[
\frac{dr_s}{dt} \propto \frac{1}{r_s^2} \quad \text{or} \quad r_s^2 - r_0^2 = k_3 t
\]

Exner and Fischmeister [109] used a different assumption than Wagner to describe the original distribution of particle sizes. For phase boundary reaction-controlled growth, they then predicted

\[
(r_s^2 - r_0^2)^2 = k_4 t
\]

Smith and Spencer [110] studied the growth of nickel grains in the presence of intergranular liquid in the Ni-S system, and their data followed the relation \( r_s^4 = k_5 t \) (initial grain size was assumed to be negligibly small). This was attributed tentatively to a surface diffusion-controlled mechanism.

Exner et al. [111] found that growth data for VC in liquid nickel and cobalt could be fitted with equal statistical significance to either of Equations (4.18) or (4.20). Comments about the difficulty of obtaining unique fits of growth data to one or other relationship were also made by Exner and Fischmeister [109] and by Warren [37]. Where ambiguity was present, attempts have sometimes been made to analyse results in terms of
grain size distribution after growth, and in terms of the apparent activation energy of the growth process.

The activation energy for diffusion in liquid metals is rarely reported to be above 20 Kcals per mole. However, the value derived by Warren [37] from his growth results with NbC - Co assuming diffusion controlled growth, was 95 Kcals per mole. Similarly, Lay [112] found a good graphical fit with Equation (4.18) for his data from the UO2 - Al2O3 system, but the apparent activation energy was 93 Kcals per mole.

Exner and Fischmeister [109], in studies of liquid phase sintering in WC-Co claimed that the growth results fitted Equation (4.22), and were consistent with phase boundary reaction control. The apparent activation energy was reported to be $142 \pm 25$ Kcals/mole, which was in good agreement with an estimate by Skolnick [113] for the activation energy of solution of WC in Co.

A difficulty with previous analyses of growth is that they do not consider quantitatively the effect of particle interactions when the particles are close together as is the case for small volume fractions of liquid. The kinetics of phase boundary reaction controlled growth should not depend on particle spacing, since a sharp concentration change is expected at the boundary. However, for the diffusion-controlled case, the liquid thickness could markedly affect growth by influencing the interactions between diffusion "fields" around the particles. No solution to this problem is available.
4.3.2 Growth Law for the Present Results

Table 3.9 and Figure 3.34 present data for the increase of grain size with time at 1273°C for specimens sintered in the superkanthal furnace. Taking $d_0$ to be 74 $\mu$m, the mean grain diameter of the zero-time specimen, plots have been made of $(d_S - d_0)^2$, $d_S^2 - d_0^2$, $d_S^3 - d_0^3$, and $d_S^4 - d_0^4$ versus time, and appear as Figures 4.14 to 4.17.

The most accurate grain size measurements are on specimens sintered for the longest times, for which corrections for liquid content are minor. Accordingly, lines have been drawn from the origin to the 60-minute points in Figures 4.14 to 4.17, to illustrate that the growth results are best fitted by the relationship in Figure 4.14; i.e.

$$r_s^2 - r_0^2 = kt$$

The results are thus consistent with a phase boundary reaction-controlled process of solution and precipitation.

Using the grain growth data for four different sintering temperatures compiled in Tables 4.4 and 4.5, it was possible to evaluate an apparent activation energy for growth. The data were plotted according to

$$K = C \exp \frac{-Q}{RT}$$

(4.23)

where $K$ = an "apparent" rate constant

$$r_s^n = \frac{r_s^n - r_0^n}{t}$$

Plots for $n = 3$ and 2 are shown in Figure 4.18.
Figure 4.14. Grain size data for 1273°C sintering runs plotted as $(d_s^2 - d_0^2)$ versus time.

Figure 4.15. Grain size data for 1273°C sintering runs plotted as $(d_s^3 - d_0^3)$ versus time.
Figure 4.16. Grain size data for 1273°C sintering runs plotted as \((d_s - d_0)^2\) versus time.

Figure 4.17. Grain size data for 1273°C sintering runs plotted as \((d_s^4 - d_0^4)\) versus time.
Table 4.4
Grain Size Values for Supersolidus Sintered Specimens at Temperatures Other than 1273°C
(From Quantitative Metallography)

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Total amount of liquid wt. %</th>
<th>Average planar diameter, μm</th>
<th>No. of pools</th>
<th>No. of grains</th>
<th>( \frac{n d_p^1}{\sum N d_p^1} )</th>
<th>wt. % interparticle liquid</th>
<th>Grain size μm</th>
<th>Real Grain size μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q18</td>
<td>6</td>
<td>6.5</td>
<td>94</td>
<td>109</td>
<td>1.7</td>
<td>4.3</td>
<td>115</td>
<td>113</td>
</tr>
<tr>
<td>Q57</td>
<td>32</td>
<td>11.7</td>
<td>87</td>
<td>158</td>
<td>9.5</td>
<td>22.5</td>
<td>105</td>
<td>97</td>
</tr>
<tr>
<td>Q56</td>
<td>42</td>
<td>13.2</td>
<td>92</td>
<td>222</td>
<td>15.0</td>
<td>27.0</td>
<td>113</td>
<td>102</td>
</tr>
</tbody>
</table>

* assuming solid and pore only

** assuming solid, pore and liquid
Table 4.5
Experimental Data Used In Arrhenius Plots of Figure 4.18

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Sintering time min.</th>
<th>Temp. °C</th>
<th>$\frac{1}{T}$ ($^\circ$K)$^{-1} \times 10^4$</th>
<th>$d_s$ μm</th>
<th>$d_0$ μm</th>
<th>$\frac{r_s^3 - r_0^3}{t}$ μm$^3$/sec.</th>
<th>$\frac{r_s^2 - r_0^2}{t}$ μm$^2$/sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q18</td>
<td>30</td>
<td>1268</td>
<td>6.489</td>
<td>113</td>
<td>71</td>
<td>75</td>
<td>1.07</td>
</tr>
<tr>
<td>Q35</td>
<td>30</td>
<td>1273</td>
<td>6.468</td>
<td>140</td>
<td>74</td>
<td>163</td>
<td>1.96</td>
</tr>
<tr>
<td>Q28</td>
<td>30</td>
<td>1273</td>
<td>6.468</td>
<td>139</td>
<td>74</td>
<td>158</td>
<td>1.92</td>
</tr>
<tr>
<td>Q31</td>
<td>5</td>
<td>1273</td>
<td>6.468</td>
<td>92</td>
<td>74</td>
<td>156</td>
<td>2.50</td>
</tr>
<tr>
<td>Q32</td>
<td>5</td>
<td>1273</td>
<td>6.468</td>
<td>83</td>
<td>74</td>
<td>69</td>
<td>1.18</td>
</tr>
<tr>
<td>Q57</td>
<td>5</td>
<td>1280</td>
<td>6.439</td>
<td>97</td>
<td>78</td>
<td>183</td>
<td>2.77</td>
</tr>
<tr>
<td>Q56</td>
<td>5</td>
<td>1285</td>
<td>6.419</td>
<td>102</td>
<td>82</td>
<td>212</td>
<td>3.07</td>
</tr>
</tbody>
</table>

When the data were plotted according to the assumption of diffusion-controlled growth ($n = 3$), an apparent activation energy of $\sim 270$ Kcal per mole was indicated. This is an order of magnitude larger than the activation energy normally associated with diffusion in liquid metals.

When surface reaction-control of the growth process was assumed, an apparent activation energy of $280$ Kcal mole$^{-1}$ was obtained. Unfortunately, no other published data are available with which this result can be compared directly, and no specific phase-interface reaction can be suggested which could be expected to have the large activation energy indicated.

The grain growth observed during the supersolidus sintering of cupronickel powder is thus consistent with a model in which material transport
Figure 4.18. Arrhenius plots of grain growth data, log K versus reciprocal absolute temperature.

Upper plot, \( K = (r_S^3 - r_0^3) t^{-1} \)

Lower plot, \( K = (r_S^2 - r_0^2) t^{-1} \)
occurs from smaller to larger particles by solution and precipitation, with a phase-boundary reaction (possibly dissolution at the solid surfaces) as the rate-controlling step.

4.4 Shrinkage During Supersolidus Sintering

Figure 4.19 shows the typical three-stage shrinkage-time behaviour of cupronickel powder specimens heated through the solidus and sintered at a supersolidus temperature. In Stage 1 about 18 per cent volumetric contraction of a specimen occurred in only half a minute. During the first part of Stage 1, identified as la in Figure 4.19, the centre of the specimen was increasing to 1273°C; i.e. conditions were far from isothermal. During Stage 1b there were substantial temperature gradients in the specimen, and the amount of liquid was steadily increasing in response to solid state diffusion.

In Stage 2, specimens typically increased in density from ~ 70% to ~ 90% of solid in 10 minutes, the rate of shrinkage steadily decreasing during the interval.

Stage 3 was characterised by slow contraction to full density. Only those specimens which were sintered while suspended provided data which permitted Stage 3 to be defined. In dilatometer experiments, specimens deformed inhomogeneously (sagged) in the late stages of densification (see Section 3.4.1).
Figure 4.19. Log plot of linear shrinkage versus time data for 1273°C sintering experiments (time origin is start of contraction). Different "stages" of sintering revealed by slope changes.
4.4.1 Possible Stage 1 Shrinkage Mechanisms

It is suggested that one or more of four transport processes could operate to cause the rapid shrinkage observed in Stage 1.

a) Rearrangement
b) Accommodation of isotropic melting
c) Accommodation of neck melting
d) Solution-precipitation at contacts

a) **Rearrangement**

On the assumption that viscous flow was the rate-controlling mechanism in rearrangement, Kingery used the relationship [27]

\[
\frac{\Delta L}{L_0} = kt^{1+y}
\]

(4.24)

where \( y \ll 1 \) (see Section 1.2). Several investigators of liquid phase sintering claim to have found good agreement of their shrinkage-time data with Equation (4.24). Other reported results, however, reveal time exponents of up to 5 for the early stage of sintering (Eremenko [25]).

Huppmann and Riegger [114] observed particle repacking in model experiments with planar arrays of copper-coated tungsten particles. Froschauer and Fulrath [115] also reported direct observations of rearrangement at the surface of a WC-Co specimen, while it was being sintered, in a scanning electron microscope. Because there are constraints to particle motion in a three dimensional network which have no counterpart in two-dimensional arrays, these observations can be misleading.
In the particular case of supersolidus sintering, it is here argued that rearrangement is of doubtful importance as a process of densification, for several reasons:

i) Direct evidence of repacking is not available; in fact, bridges between clusters clearly do not break down in Stage I (see Figure 4.20).

ii) There is no obvious reason why the capillary forces in a three-dimensional solid-liquid network would act to slide solid particles over one another and into closer packed arrays. In fact, it seems more reasonable that the forces would resist such motion. If unbalanced stresses were present at the liquid necks between particles, they could equally well act to produce movement into a less dense arrangement. A similar argument was used in Section 4.1.4 to rule out a major contribution from rearrangement processes to solid state sintering shrinkage.

iii) In the present experiments, the amount of interparticle liquid increased substantially with time within Stage I. This would be expected to produce a corresponding increase in the rate of shrinkage by the rearrangement process (decrease in viscosity), which was not observed.

The first two of the above arguments could also be used to question the role of rearrangement in all liquid phase sintering system. It is possible, however, that some particle sliding and repacking might result from the longer-range motion of liquid which can occur when one component of a two-component powder mixture is melted.

b) Accommodation of Melting

If it is assumed, as in Figure 4.21, Model A, that (a) surface and grain boundary melting are coincident and isotropic, and (b) solid particles attempt to maintain contact in response to surface tension forces, then linear shrinkage given by
Figure 4.20. Optical micrographs showing the formation of clusters in dilatometer specimens: (a) LVDT 49, (b) LVDT 55; x24.
\[
\frac{\Delta L}{L_0} = 1 - \left(1 - f\right)^{1/3}
\]  

will occur within a simple cubic array, where \( f \) is the volume fraction of alloy melted. Calculations of shrinkage for different amounts of melting are given in Table 4.6.

However, in the early stage of melting, most surface liquid will be drawn into the capillaries at particle "contacts." Assumption (b) may not be valid; i.e. there may be a liquid film of finite thickness at contacts even with \( \phi = 0 \). No theoretical treatment of this question is available, and metallographic observations on short-run specimens are inconclusive. However it is clear from Figure 3.50 that there were stable liquid films of substantial thickness at all solid-solid "contacts" in Stage 2.

It is therefore not obvious that isotropic melting can produce shrinkage at all. Moreover, in view of the small amounts of interparticle liquid present during Stage 1 (Table 4.6), this process can at best account for only a fraction of the shrinkage observed.

If there is preferential nucleation of melting at necks, shrinkage will be more positive. In Model B, Figure 4.21, the volume melted is seen to take the form of a spherical segment. Calculations of shrinkage for different amounts of melting and for 81 \( \mu \)m powder are given in Table 4.6. Two cases are treated; one - in which it is assumed that the solid particles maintain contact, and one - in which a 2-micron thick stable film of liquid is assumed to exist at contacts. Even in the latter case, a relatively small amount of melting can account for a substantial amount of shrinkage.

It should be noted that selective melting at necks produces contact-flattening, a phenomenon which was observed after very short times.
Table 4.6
Shrinkage Produced by Melt-Accommodation Models A and B in Figure 4.21
(Simple cubic packing of solid spheres)

| Fraction of solid particles which has melted at surfaces and boundaries (f) | Linear shrinkage, $\frac{AL}{L_0}$ |
|---|---|---|---|
| | Model B assuming $t_f = 0$ | Model B assuming $t_f = 2 \mu m$ | Model A assuming $t'_f = 0$ |
| $\frac{AL}{L_0} = \sqrt{\frac{4}{3}} f$ | $AL = 0.001$ | $AL = 0.0002$ |
| 0.0005 | 0.026 | 0.011 | 0.0003 |
| 0.001 | 0.036 | 0.027 | 0.0007 |
| 0.002 | 0.052 | 0.057 | 0.0017 |
| 0.005 | 0.082 | 0.091 | 0.0033 |
| 0.010 | 0.116 | 0.116 | 0.0050 |
| 0.015 | 0.141 | 0.138 | 0.0067 |
| 0.020 | 0.163 | 0.175 | 0.0101 |
| 0.030 | 0.200 | 0.206 | 0.0135 |
| 0.040 | 0.231 | 0.233 | 0.0170 |
| 0.050 | 0.258 | 0.258 | 0.0204 |
| 0.060 | 0.283 | 0.281 | 0.0239 |
| 0.070 | 0.306 | | 0.0345 |
| 0.100 | | | 0.0527 |
| 0.150 | | | 0.0717 |
| 0.20 | | | 0.112 |
| 0.30 | | | 0.157 |
| 0.40 | | | 0.206 |
| 0.50 | | | |
Accommodation models.

Local melting at neck (grain boundary)
\[ \theta = \phi = 0 \] (particle = grain)

Isotropic melting at surfaces and neck
\[ \theta = \phi = 0 \]

Figure 4.21. Accommodation models.

Model (B): Local melting at neck (grain boundary)
\[ \theta = \phi = 0 \] (particle = grain)

Model (A): Isotropic melting at surfaces and neck
\[ \theta = \phi = 0 \]
above the solidus temperature, and with very small volume fractions of liquid (Figures 4.22).

c) Solution-Precipitation of Contacts

Kingery [27] has suggested that at the contacts between wetted particles as in Figure 4.22 there is a localised stress induced in the solid by capillary forces. This increases the activity, $a$, of the solid locally according to

$$\ln \frac{a}{a_0} = \frac{\Delta P \Omega}{RT} = \frac{2k \gamma_{LV} \Omega}{r_p RT}$$

(4.26)

where

- $\Omega$ is the molecular volume
- $k$ is a constant relating the maximum contact area pressure to the overall hydrostatic pressure
- $r_p$ is the radius of the pores

The increase in activity acts as a driving force for material transport, involving solution of the solid at the contacts, and reprecipitation at less-stressed locations. As shown in Figure 4.22, the operation of this process leads to a flattening of the contacts and an approach of particle centres.

If the solution of solid occurs as spherical segments, then the resulting shrinkage is related to the volume fraction of solid transported in the same way that shrinkage is related to the volume fraction of solid melted at necks in the accommodation process, Model B (Figure 4.21).

Many previous investigators of liquid phase sintering have accepted that the particle-flattening mechanism accounts for much observed shrinkage.
Figure 4.22. Contact flattening and shrinkage by solution-precipitation.

(a) Contact after melting and accommodation only.

A) Region of high chemical potential where solution is favoured.

B) Low-activity surface where reprecipitation occurs.

(b) Contact after extensive local solution and reprecipitation has occurred to cause contact flattening and shrinkage.
However it was argued by Kingery [27], and has not since been disputed in the literature, that this type of shrinkage occurs only after a rearrangement stage is essentially completed. This seems unreasonable, since high stresses at contacts are encountered when the solid-liquid-solid contacts are first established, and the contact areas are at a minimum. It is therefore suggested that important shrinkage from this source takes place within Stage 1 and continues into Stage 2.

4.4.2 Role of Coalescence and Bridging

More coalescences were observed to have occurred above the solidus temperature than below (Section 3.3.3). Therefore it is possible that the presence of liquid facilitated coalescence by allowing particles to rotate (at "contacts") into more favourable orientations relative to one another. Coalescences could then be the purely statistical consequence of random rotations of dispersed particles. After coalescence, however, any particle in a coalesced pair or group is not free to rotate. The above process can therefore not lead to the formation of a continuous network of particles. However, it is possible to visualise the creation of coalesced chains or groupings, the extent of which would be difficult to detect metallographically.

The act of coalescence between two particles produces some shrinkage since a liquid film is eliminated. Subsequent growth of the solid neck between the particles is not likely to be able to produce shrinkage at a rate which is any higher than would have prevailed without the coalescence. The higher the frequency of coalesced contacts, the fewer are the contacts at which shrinkage by accommodation and solution-precipitation must occur to account for any observed bulk contraction.
Coalesced groupings of particles would severely restrict rearrangement, further reducing the likelihood that rearrangement contributes to supersolidus sintering shrinkage.

Powder specimens consist of more or less dense clusters. Within clusters, particles group to form stable "bridges" which enclose large pores. The clusters themselves are also bridged. Two-dimensional representations of these effects are shown in Figures 4.23 and 4.24, in which the large pores A and C are the result of bridging. Three-dimensional equivalents of these groupings can be visualised.

It has been argued earlier that packing in the aggregate is not the result of rearrangement processes; rather it represents the arrangement which loose particles assumed when they were tapped into a crucible. An original tap density of 50 per cent of solid represents the average of more and less dense groupings.

Close-packed groupings of particles can, with the aid of little interparticle liquid, be fully densified by the operation of the melt accommodation process, Model B (Figure 4.21), or the stress-induced solution-precipitation process. If 10 per cent of the solid melted preferentially at necks in a simple cubic array of spherical particles, complete densification of the aggregate (~ 20% linear shrinkage) could be accomplished by melt accommodation alone. For the same array with a very small volume fraction of liquid present at capillaries densification could be achieved by the transfer of 10 per cent of the mass of the particles by solution at contacts and reprecipitation nearby. Even smaller amounts of mass transport are required to fully densify the closer-packed arrays of particles that occur (and are seen) in some clusters.
Figure 4.23. Pores within clusters (B) and at bridges (A).

Figure 4.24. Contribution of grain growth to closure of large pores.
Grain 1 smaller than 2 or 3. Grain 1 dissolves and re-precipitates on 2 and 3. Grains 2 and 3 approach.
However, bridges between particles and clusters cannot be eliminated without the transport of comparatively large amounts of material. Figure 4.25 illustrates in two dimensions the shrinkage of an array of bridged particles which could result due to either of the mechanisms just discussed above. Even when substantial particle approach has occurred, a large void remains. To close this type of void requires either a large amount of liquid to be provided, or a more extensive operation of solution-precipitation effects than was visualised in Stage 1. It must be realised that as the contact areas between the particles in a bridge grow, the forces at the contacts decrease; i.e. the driving force for selective solution precipitation decreases.

Stage 1 is seen as a period during which the closest-packed groupings within the original aggregate become fully densified. Once these centres are filled with liquid, the shrinkage of less-dense groupings and of bridged arrays is necessary to produce macroscopic contraction. Stage 2 involves a steadily declining rate of contraction, during which progressively larger voids become successively eliminated by mass transport. This is consistent with metallographic observations (Figure 3.50).

4.4.3 Possible Shrinkage Mechanisms in Stages 2 and 3

a) Solution-precipitation of contacts

There was strong metallographic evidence of continuing contact-flattening (particle shape change) in Stage 2 culminating in the development of obvious polyhedral shapes (see Figure 3.50).
Figure 4.25. Shrinkage of bridged array of particles.

Dashed lines: Particle positions after solid-state sintering (assume high angle boundaries at all necks).

Solid lines: Particle positions after supersolidus sintering. Equivalent to ~ 5% by volume of solid transported either by melting at necks alone (accommodation model B) or by solution-precipitation at contacts.
b) **Particle (Grain) Growth**

During Stage 2, the average diameter of grains increased by approximately 30% (Tables 3.9 and 3.11) corresponding to more than a doubling of the volume of each particle. Considerable further grain growth occurred in Stage 3.

Kingery [27] has argued that particle growth, without shape change at contacts, does not produce contraction in liquid phase sintering. However, it is believed that there are two ways in which particle growth can independently contribute to densification, the first of which is unique to supersolidus sintering, but the second of which should apply equally well to liquid phase sintering.

i) Release of intraparticle liquid and its subsequent accommodation within capillaries. Experiments with cast cupronickel revealed that intraparticle liquid was stable; i.e. there was no apparent transfer of liquid to or from grain boundaries with increasing time at 1273°C. However, in sintered specimens there was a marked decrease in the number of intraparticle pools with time at 1273°C. As shown in the sequence of Figures 3.32 and 3.33, pools became concentrated at the centres of particles during Stages 2 and 3. This is clearly what will result from the dissolution of some particles and growth of others. Liquid pools from those particles which dissolved would be released and accommodated in capillaries. The solid which reprecipitated on to larger particles would be free of liquid pools. Thus, the average volume per particle doubles if slightly more than half the particles dissolve, and the amount of intragranular liquid per particle is reduced by approximately 50 per cent. The metallographic data
of Table 3.9, within the limits of experimental accuracy, are reasonably consistent with this explanation.

ii) Breakdown of bridged particle arrays. Figure 4.24 illustrates how the selective dissolution of one particle within a bridged array can allow neighbouring particles in the array to approach. The repetitive operation of this process will, in effect, allow a rearrangement of particles into close packed arrays where bridges once existed. Thus grain growth may contribute significantly in those stages of sintering in which the closing of large pores is necessary to produce appreciable densification.

4.4.4 Transition from Stage 2 to Stage 3

At the start of Stage 3 specimens were found to contain pores which were:

a) relatively large and few in number (Figure 3.7 in Part B)

b) equiaxed in shape (compare Figures 3.6 and 3.7 in Part B)

c) nearly all closed (Section 3.1 and Figures 3.7 to 3.9 in Part B)

There is abundant metallographic evidence that the solution-precipitation process described in the previous section operated continuously through Stages 2 and 3. Thus material transport mechanisms are available in Stage 3 to close pores. However, when pores become isolated from the surface in late Stage 2, the sintering atmosphere is trapped inside them. Closure of the pores, and thus bulk shrinkage of the specimens, could become controlled by the rate of escape of gas by diffusion. Cech
[28,25] analysed this problem using Fick's law and assuming that the external gas pressure was small compared to that inside the pores. The gas concentration gradient was given by

$$\frac{dC}{dx_1} = \frac{2\gamma}{r_2 x_1(1 - 2 r_2 n)}$$  \hfill (4.27)

where \( n \) = the number of pores in length \( x_1 \),

\( r_2 \) = the pore radius

The quantity of gas diffusing from a sphere of radius \( x_1 \) is

$$dp_1 = -D 4\pi x_1^2 \frac{2\gamma}{r_2 x_1(1 - 2 r_2 n)} dt$$  \hfill (4.28)

where \( D \) = the diffusion coefficient of gas

If \( V_0 \) is the original volume of gas in a pore, then

$$dp_1 \approx \frac{3V_0}{r_1} dr_2$$  \hfill (4.29)

Performing suitable transformations and integrating from \( r_1 \) to \( r_2 \) (\( r_1 \) was calculated for the case of the closing of pores at the corresponding sintering time \( t_3 \), while \( r_2 \) corresponds to time \( t \)), the following expression was obtained.

$$t_3 - t = \frac{1}{D} \frac{V_0 N_1}{4\pi\gamma} (r_2^3 - r_1^3)$$  \hfill (4.30)
where \( N_i \) = the number of pores per unit length.

If sintering proceeds up to \( r_2 = 0 \), then from Equation (4.30) it follows that

\[
\frac{\Delta L}{L_3} = A(t - t_3)^{1/3}
\]

where \( A \) is a constant.

4.4.5 Kinetics of Shrinkage

Previous investigators of sintering have used the slopes of different "straight-line" portions of log-log plots such as Figure 4.19 to define kinetics and to deduce sintering mechanisms. This practice can lead to misleading conclusions, particularly if mechanisms of shrinkage are overlapping in time, and if it is impossible to define the dimensional or time origin of each mechanism. Kingery's analysis of liquid-phase sintering data for Fe-Cu [33] and TiC-Ni-Mo [35] was specifically criticised on these grounds by Prill et al. [36].

In the present experiments, Stage la was characterised by non-isothermal conditions, and it is inappropriate to attempt to analyse the shrinkage-time data quantitatively. However, only about 0.02 linear shrinkage occurred in this stage, the duration of which was only ~ 0.2 minutes. It is not likely that a large error is introduced, therefore, if it is assumed that the mechanisms responsible for shrinkage in later stages did not start within Stage la. Accordingly, the data have been replotted in Figures 4.26 to 4.28 (upper curves and open symbols only) with the
Figure 4.26. Replots of linear shrinkage data from dilatometer runs: 29, 35, 62. Origin taken as end of stage 1a.

Upper plots (open symbols) are experimental data.

Plots through half-filled symbols are solution-precipitation contribution to shrinkage based on assumptions in text.

Plots through filled symbols are contributions to shrinkage from other than solution-precipitation processes.
Figure 4.27. Same as Figure 4.26, for dilatometer runs 30 and 34.
Figure 4.28. Same as Figure 4.26, for dilatometer runs 31 and 32.
origin taken as the start of Stage lb; i.e. where the specimen centre first reached 1273°C. Slopes of the corrected plots are compiled in Table 4.7.

From earlier arguments, the following assumptions can be made in analysing the corrected shrinkage-time data:

a) Solution-precipitation process of shrinkage proceeds throughout all stages,
b) solution-precipitation processes are phase-boundary reaction controlled, consistent with the analysis of grain growth data in 4.3.2,
c) rearrangement and melt accommodation processes are not possible beyond Stage lb,
d) closed pores become prevalent only at the end of Stage 2 (consistent with porosimetry results in Part B, Figure 3.1), and
e) diffusion of gas from closed pores controls the rate of shrinkage in Stage 3.

Thus the total shrinkage observed in Stages lb and 2 is the sum of two contributions as shown schematically in Figure 4.29. Solution-precipitation gives shrinkage according to curve J and

\[
\frac{\Delta L}{L_T} = B \left(t - t_T\right)^{1/2}
\]  \hspace{1cm} (4.32)

Curve fitting within Stage 2 allows B to be evaluated, with the results in Table 4.8 for the present experiments. A typical example of such fitting, for LVDT 35, is shown in Figure 4.30.

Curve K in Figure 4.29 represents the sum of other contributions to shrinkage, and can be found by difference. If only solution-precipitation processes operate in Stage 2, then \( \frac{\Delta L}{L_T} \) in curve K becomes constant.
Table 4.7
Slopes Obtained by the Linear Regression Method for Different Stages of Sintering at 1273°C, Using the Log-Log Plots of Corrected Data in Figures 4.26 to 4.28

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Particle size μm</th>
<th>Slope Stage 1b</th>
<th>Slope Stage 2</th>
<th>Slope Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVDT (all)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short Runs</td>
<td>81</td>
<td>-</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>LVDT 29</td>
<td>81</td>
<td>0.89</td>
<td>0.30</td>
<td>-</td>
</tr>
<tr>
<td>LVDT 35</td>
<td>81</td>
<td>0.78</td>
<td>0.40</td>
<td>-</td>
</tr>
<tr>
<td>LVDT 62</td>
<td>81</td>
<td>0.86</td>
<td>0.34</td>
<td>-</td>
</tr>
<tr>
<td>Q (all) S.K. Runs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>-</td>
<td>0.54</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>LVDT 30</td>
<td>68</td>
<td>0.90</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>LVDT 34</td>
<td>68</td>
<td>0.96</td>
<td>0.42</td>
<td>-</td>
</tr>
<tr>
<td>LVDT 32</td>
<td>49</td>
<td>0.96</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>LVDT 31</td>
<td>49</td>
<td>0.97</td>
<td>0.41</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4.29. Schematic plot showing contribution of components J (due to solution-precipitation processes) and K (due to other mass transport mechanisms) to total linear shrinkage observed in supersolidus sintering after stage la.
Figure 4.30. Experimental data from stage 2 of LVDT run 35 plotted as linear shrinkage versus square root of time, corrected to make origin coincide with end of stage la.
(at a value A) at the end of Stage 1 as indicated. Stage 2 shrinkage is represented by

\[ \frac{\Delta L}{L_T} = A + B \left( t - t_T \right)^{1/2} \]  \hspace{1cm} (4.33)

A can also be found by extrapolation of plots of \( \frac{\Delta L}{L_T} \) vs \( (t - t_T)^{1/2} \) to \( t = t_T \) (Figure 4.30). These values of A from the present experiments are compiled in Table 4.8. Expression (4.33) could also be used for Stage 1b. In Stage 1b A values vary with time as shown in Figure 4.29 (Curve K).

The log-log equivalents of curves J and K for the experimental data are superimposed on Figure 4.26 to 4.28 (filled and half-filled symbols). The results are consistent with the assumptions (a) to (d) above. The considerable scatter in values of A probably reflects gradients in temperature and liquid content, plus anisotropy of shrinkage in Stage 1b, see Section 3.4.2.

An attempt was also made to fit corrected Stage 2 data to a \( (t - t_T)^{1/3} \) relationship; i.e. on the assumption of diffusion-controlled solution-precipitation. Fits as good as Figure 4.30 (LVDT 35) could not be obtained. Moreover, the extrapolation of all such plots to \( t = t_T \) yielded negative values of A. This result was considered to be excellent further validation of assumption (b) above and of the conclusions regarding grain growth in Section 4.3.

Following assumptions (d) and (e) a log-log plot of corrected Stage 3 data has been made (Figure 4.31). The results are described by

\[ \frac{\Delta L}{L_3} = K \left( t - t_3 \right)^{0.25} \]  \hspace{1cm} (4.34)
Table 4.8
Experimental Values of A and B in the Assumed Relation

\[
\frac{A}{L_T} = A + B(t - t_T)^{0.5}
\]

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>B, min-0.5</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVDT 29</td>
<td>0.022</td>
<td>0.023</td>
</tr>
<tr>
<td>LVDT 35</td>
<td>0.024</td>
<td>0.003</td>
</tr>
<tr>
<td>LVDT 62</td>
<td>0.023</td>
<td>0.017</td>
</tr>
<tr>
<td>LVDT 30</td>
<td>0.024</td>
<td>0.015</td>
</tr>
<tr>
<td>LVDT 34</td>
<td>0.029</td>
<td>0.007</td>
</tr>
<tr>
<td>LVDT 31</td>
<td>0.031</td>
<td>0.008</td>
</tr>
<tr>
<td>LVDT 32</td>
<td>0.036</td>
<td>0.004</td>
</tr>
</tbody>
</table>

This time-dependence of shrinkage is in reasonable agreement with that predicted by Cech [28,25] and discussed in Section 4.4.4. No other rate-controlling process can be suggested which is consistent with the observed kinetics. Unfortunately, there is a lack of gas diffusion data from which a more quantitative check on the Cech model might be attempted.

4.4.6 Summary

The above results and discussion indicate that dimensional changes during supersolidus sintering are dominated by three processes:

a) Melting and melt accommodation: Allow particle centres to approach without any change in packing mode (i.e. rearrangement unnecessary). Account for rapid linear
Figure 4.31. Log plot of stage 3 shrinkage data corrected to make origin coincide with slope change between stages 2 and 3.
shrinkage of between 0.02 and 0.04 during Stage I of the present experiments. Not operative beyond Stage I.

b) Solution-precipitation: Starts in Stage I, and overlaps melt accommodation as a process of shrinkage. Continues throughout supersolidus sintering to full density. Accounts for 0.12 to 0.14 linear shrinkage. Dominates Stage 2.

c) Gas escape from closed pores: Limits rate of shrinkage due to solution-precipitation when pores become closed (Stage 3).

It is believed that melting is nucleated first at grain boundaries (necks). The formation of very little liquid preferentially at necks allows substantial shrinkage to occur by melt accommodation. However, melting quickly becomes more isotropic; the shrinkage available from accommodation of liquid formed at all surfaces is more limited.

Solution-precipitation causes shrinkage both by contact-flattening and by grain growth, the former being an important contribution to both Stage 1 and Stage 2 shrinkage. Grain growth is believed to be important in Stages 2 and 3, where its principal effect on shrinkage derives from the release of intragranular liquid. It is believed that both solution-precipitation mechanisms are phase-boundary reaction controlled.

4.5 Comparisons of Supersolidus and Liquid-Phase Sintering

Supersolidus sintering has been described as a special case of liquid phase sintering. However, the present work has shown that there are major differences between the two processes, and a comparison is of interest.

Not all liquid-phase sintering systems behave identically. However, iron-copper has been selected for the present comparison, because
i) it is of appreciable practical interest, ii) it has been the subject of extensive previous study, and iii) it is believed to be typical of several of the more important systems.

In the supersolidus sintering of cupronickel powder:

a) no particle completely melts,
b) all particles partially melt,
c) all solid particles are expected to decrease in size as a consequence of partial melting,
d) liquid probably does not move over distances larger than a particle diameter,
e) equilibrium is very rapidly established between solid and liquid phases; i.e. the amount and composition of the phases do not undergo change beyond the first minute at the sintering temperature, and
f) the dihedral angle is zero at all stages.

By contrast, in the liquid-phase sintering of an Fe-Cu powder mixture:

a) copper particles completely melt; clusters of copper particles also melt,
b) iron particles do not melt at all,
c) solid particles (iron) do not decrease in size as a direct result of melting (a small decrease in particle size follows soon after melting due to the dissolution of some iron in the liquid copper),
d) in response to capillary forces, liquid copper may move through the aggregate over distances which are large compared to a particle diameter,
e) equilibrium between solid and liquid phases is slow to be achieved. Copper diffuses into iron at sintering temperatures, but for typical powder particle sizes (e.g. 100 μm diameter) hours may be required to reach equilibrium. During this period the amounts of the phases are changing, the composition of the solid
is changing, and there is a continuing flux of copper across solid-liquid interfaces, and

f) the dihedral angle may be zero in the early stages of sintering [116], but becomes greater than zero as equilibrium is approached or reached.

As a result of these differences, the mechanisms responsible for dimensional change in the two processes also differ appreciably throughout the sintering period:

a) Rearrangement can contribute to early densification in Fe-Cu, since solid particles can be swept into closer-packed positions by the long-range movement of the liquid. This mechanism is unlikely to be operative at all in supersolidus sintering.

b) Since all particles decrease in size when melting occurs in supersolidus sintering, the accommodation of liquid between particles allows particle centres to approach. There is no equivalent shrinkage in liquid-phase sintering.

c) Solution-precipitation processes can operate early and effectively to produce contact-flattening and rapid shrinkage in the case of supersolidus sintering. However, the flux of copper across solid-liquid interfaces interferes with solution-precipitation in the Fe-Cu system during the early stages of sintering. Moreover, when equilibrium is approached in Fe-Cu, solution-precipitation processes cannot contribute to dimensional change because the dihedral angle becomes greater than zero and the system agglomerates.

d) A major source of shrinkage in the sintering of Fe-Cu can be the approach of particle centres which accompanies agglomeration when the dihedral angle becomes greater than zero [116]. No equivalent mechanisms is involved in supersolidus sintering of cupronickel.

It is probably during only the final stage of sintering that similar mechanisms control the density changes in the two processes; i.e. the escape of gas from closed pores may become the rate controlling process.
However, the dominant mass-transport mechanism during the final stage will be solid-state diffusion in the case of Fe-Cu and solution-precipitation in the case of cupronickel.
CONCLUSIONS

Solid State Sintering of Loose Cupronickel Powder

1) The initial stage of shrinkage (up to 1 hour at 1200°C) is dominated by Nabarro-Herring creep. This conclusion is consistent with observations of sintering kinetics, and with calculations of the stresses at necks due to surface tensions.

2) In contrast to the observations of Kuczynski [24] with several other copper and silver alloys, no detectable segregation of solute at necks occurs during the solid state sintering of cupronickel.

3) Clusters, or centres of densification, do not form during sintering due to relative particle motions, as concluded by previous investigators from observations of surfaces and two-dimensional arrays. Rather, all such clusters in three-dimensional aggregates have their origin in the initial packing of the loose powder particles.
Melting Behaviour of Sintered Cupronickel Powder when Heated Above the Solidus

4) Melting is nucleated at necks (high angle grain boundaries) and at particle surfaces; at less than the equilibrium solidus temperature. Subsequent melting occurs intragranularly at interdendritic sites of above-average copper concentration.

5) The dihedral angle in solid-liquid cupronickel is ≤ zero.

6) Constitutional equilibrium is attained within one minute after reaching the supersolidus temperature (for 68 μm powder).

Grain Growth During Supersolidus Sintering

7) The growth of solid cupronickel grains during supersolidus sintering proceeds according to the relation

$$r_s^2 - r_0^2 = kt.$$  

This is consistent with the predictions of an Ostwald Ripening model in which growth is assumed to be due to solution-precipitation with phase boundary reaction control.

Shrinkage in Supersolidus Sintering

8) A period of very rapid shrinkage (Stage 1) occurs while a specimen is being heated above the solidus temperature to the final sintering
temperature, and prior to the attainment of constitutional equilibrium. This period is dominated initially by a melting and melt-accommodation sequence of shrinkage, followed by contact-flattening due to localised solution-precipitation.

9) Beyond the attainment of constitutional equilibrium (Stages 2 and 3), a specimen continues to shrink to full density. Solution-precipitation processes account for most or all of the contraction. Grain growth is important because it is accompanied by the release of intragranular liquid.

10) When sintered specimens reach approximately 92-93% of solid density, all pores are closed. The rate of shrinkage beyond this density (in Stage 3) is controlled by the rate of escape of gas from the pores.

Comparisons Between Supersolidus and Liquid Phase Sintering

11) Contrary to previously reported conclusions about the early stages of liquid-phase sintering, rearrangement is not believed to make a significant contribution to shrinkage in supersolidus sintering.

12) Solution-precipitation processes are responsible for most of the shrinkage observed during supersolidus sintering; contrary to the conclusions of Kingery [27] and others, however, it is believed that solution-precipitation plays a minor role in some liquid-phase sintering systems, including iron-copper.


77. Nielsen, P.J., "Recrystallisation, Grain Growth and Textures," Papers presented at a seminar of the ASM, ASM, 1965, Chapter 4, p. 141.


PART B

MECHANICAL PROPERTIES OF SINTERED CUPRONICKEL
Chapter 1

INTRODUCTION

1.1 Review of Previous Work

1.1.1 Elastic Constants for Porous Materials

The expressions compiled in Table 1.1 are among many proposed to describe the elastic properties of porous solids as a function of the volume fraction of porosity, P. Most of the relationships in the table are the result of modifications to analyses of the properties of two-phase composite materials, in which one phase has been replaced by pores. The analyses are based on the application of linear elasticity theory to different models of the structure and elastic deformation of composites. Most of the solutions represented by Table 1.1 are "upper bounds."

For an isotropic solid, the elastic constants are related by

\[ E_0 = \frac{9K_0G_0}{3K_0 + G_0} \quad (1.22) \]

and

\[ \nu_0 = \frac{E_0}{2G_0} - 1 \quad (1.23) \]
Table 1.1
Predictions of Elastic Constants for Porous Materials

<table>
<thead>
<tr>
<th>Author</th>
<th>Nature of Expression</th>
<th>Proposed Relationship</th>
<th>Equation Number</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dewey</td>
<td></td>
<td>$E = E_0 \left[1 - 3E_0(9p_1 + 4E_0)^{-1}p\right]$</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\nu = \nu_0\left[1 - 3E_0(9p_1 + 4E_0)^{-1}p\right]$</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>MacKenzie</td>
<td></td>
<td>$K^{-1} = [K_0^{-1}(1-P)]^{-1} + 3P[4G_0(1-P)^{-1} + \text{terms of order } P^3]$</td>
<td>1.3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G = G_0\left[1 - 5P(3K_0 + 4G_0)(9K_0 + 8G_0)^{-1} + \text{terms of order } P^2\right]$</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>MacKenzie I*</td>
<td></td>
<td>$K^{-1} = [K_0^{-1}(1-P)]^{-1} + 3P[4G_0(1-P)]^{-1}$</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G = G_0\left[1 - 5P(3K_0 + 4G_0)(9K_0 + 8G_0)^{-1}\right]$</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>MacKenzie II**</td>
<td>Analytical</td>
<td>$K^{-1} = [K_0^{-1}(1-P)]^{-1} + 3P[4G_0(1-P)]^{-1}$</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>Kerner</td>
<td></td>
<td>$G = G_0(7 - 5\nu_0)(1-P)[(7 - 5\nu_0) + (8 - 10\nu_0)P]^{-1}$</td>
<td>1.9</td>
<td>3</td>
</tr>
<tr>
<td>Hashin</td>
<td></td>
<td>$K = 4G_0K_0(1-P)[4G_0 + 3K_0P]^{-1}$</td>
<td>1.10</td>
<td>4</td>
</tr>
<tr>
<td>Stropppe</td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Hashin and</td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Shtrikman</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gatto</td>
<td></td>
<td>$E = E_0(1 - 2.36P)$</td>
<td>1.11</td>
<td>7</td>
</tr>
<tr>
<td>Weil</td>
<td></td>
<td>$G = G_0\left[1 - 15(1 - \nu_0)P(7 - 5\nu_0)^{-1}\right]$</td>
<td>1.12</td>
<td>8</td>
</tr>
<tr>
<td>Hashin</td>
<td></td>
<td>$K = K_0\left[1 - 3(1 - \nu_0)P(2 - 4\nu_0)^{-1}\right]$</td>
<td>1.13</td>
<td>9</td>
</tr>
<tr>
<td>Skorokhod</td>
<td></td>
<td>$K = K_0(1-P)[3K_0P(4G_0)^{-1} + 1]^{-1}$</td>
<td>1.14</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5G_0(3G + 2G_0)^{-1}\theta_S + (7G + G_0)G_0[2(3G + G_0)G]^{-1}\theta_C = 1$</td>
<td>1.15</td>
<td></td>
</tr>
</tbody>
</table>
**Table 1.1 (Continued)**

<table>
<thead>
<tr>
<th>Author</th>
<th>Nature of Expression</th>
<th>Proposed Relationship</th>
<th>Equation Number</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hasselman</td>
<td>Semi</td>
<td>( E = E_0 {1 + AP[1 - (A + l)P]^{-1}} )</td>
<td>1.16</td>
<td>11</td>
</tr>
<tr>
<td>Chung</td>
<td>Empirical</td>
<td>( EE_0^{-1} = GG_0^{-1} = KK_0^{-1} = 1 - aP + bP^2 )</td>
<td>1.17</td>
<td>12</td>
</tr>
<tr>
<td>McAdam</td>
<td></td>
<td>( E = E_0(1 - P)^{3.4} )</td>
<td>1.18</td>
<td>13</td>
</tr>
<tr>
<td>Spriggs</td>
<td>Empirical</td>
<td>( E = E_0 \exp(-bP), E = E_0 \exp(-bP_b) \exp(-b_cP_c) )</td>
<td>1.19, 1.20</td>
<td>14</td>
</tr>
<tr>
<td>Hasselman and Fryxell</td>
<td></td>
<td>( E = E_0(1 - bP) )</td>
<td>1.21</td>
<td>15, 16</td>
</tr>
</tbody>
</table>

*obtained by dropping the terms of the order of \( P^2 \) and \( P^3 \) in MacKenzie equations.

**terms of the order of \( P^2 \) is ignored and terms of the order of \( P^2 \) are taken as \( AP^2 \). \( A \) was then evaluated to be -0.883 by setting \( G/G_0 = 0 \) when \( P = 1 \).
Table 1.1 (Continued)

where

\[ E, G, K, \nu = \text{the Young's, rigidity and bulk modulus and Poisson's ratio of porous material} \]

\[ E_0, G_0, K_0, \nu_0 = \text{the Young's, rigidity and bulk modulus and Poisson's ratio of bulk material} \]

\[ p_i = \text{the gas pressure in the pores} \]

\[ P = \text{the volume fraction porosity} \]

\[ g = \frac{G}{G_0} \]

\[ \theta_S = \text{volume fraction spherical material} \]

\[ \theta_C = \text{volume fraction cylindrical material} \]

\[ A, a, b = \text{the material constants} \]

\[ b_b, b_c = \text{the constants depending on open and closed porosity} \]

\[ P_b, P_c = \text{volume fraction of open and closed porosity} \]
where \( E_0 = \) Young's modulus
\( G_0 = \) Shear modulus
\( K_0 = \) Bulk modulus
\( \nu_0 = \) Poisson's ratio

Probably the most widely-tested predictions of elastic behaviour are those due to MacKenzie [2] and to Skorokhod [10]. In MacKenzie's model, a relatively small volume of isolated holes is assumed to be distributed through an homogeneous and isotropic solid. The application of MacKenzie's equations should probably be restricted to \( P \leq 0.1 \). Skorokhod depicts the solid part of the porous structure as a mixture of spherical and cylindrical "phases." If the origin of the solid structure is irregular, flake-shaped, or fibre-like particles, then for a given density there will be a higher proportion of the cylindrical phase present than if the origin was equiaxed particles. Moreover, with increasing density the proportion of the spherical phase increases, regardless of the original shape of the particles. Using a statistical method, Skorokhod calculated the volume fractions of the two phases for different fractional porosity contents with the results shown in Table 1.2. He then applied elasticity theory to predict how the bulk and shear moduli should vary with fractional porosity and "phase" distribution with the results shown in Equations (1.14) and (1.15) of Table 1.1. Calculated values of the relative shear modulus, \( G/G_0 \), are also presented in Table 1.2.b.

Hashin's analysis [9] reduces to the simple predictions

\[
E = E_0(1 - k'P)
\]  
(1.24)
Table 1.2
Quantities Used in Skorokhod's Model

a) Relative Fractions of "Spherical" and "cylindrical" Phases in Porous Bodies

<table>
<thead>
<tr>
<th>Type of body</th>
<th>P</th>
<th>0.9</th>
<th>0.8</th>
<th>0.7</th>
<th>0.6</th>
<th>0.5</th>
<th>0.4</th>
<th>0.3</th>
<th>0.2</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>$\theta_s$</td>
<td>0.90</td>
<td>0.80</td>
<td>0.69</td>
<td>0.58</td>
<td>0.45</td>
<td>0.32</td>
<td>0.21</td>
<td>0.14</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>$\theta_c$</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
<td>0.08</td>
<td>0.09</td>
<td>0.06</td>
<td>0.015</td>
</tr>
<tr>
<td>Fibre</td>
<td>$\theta_s$</td>
<td>0.67</td>
<td>0.48</td>
<td>0.34</td>
<td>0.23</td>
<td>0.15</td>
<td>0.09</td>
<td>0.05</td>
<td>0.02</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>$\theta_c$</td>
<td>0.23</td>
<td>0.32</td>
<td>0.36</td>
<td>0.37</td>
<td>0.35</td>
<td>0.31</td>
<td>0.25</td>
<td>0.18</td>
<td>0.095</td>
</tr>
</tbody>
</table>

b) Relative Shear Moduli of Porous Bodies of Various Densities

<table>
<thead>
<tr>
<th>Type of body</th>
<th>P</th>
<th>0.9</th>
<th>0.8</th>
<th>0.7</th>
<th>0.6</th>
<th>0.5</th>
<th>0.4</th>
<th>0.3</th>
<th>0.2</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>$G$</td>
<td>0.83</td>
<td>0.67</td>
<td>0.50</td>
<td>0.35</td>
<td>0.24</td>
<td>0.17</td>
<td>0.11</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Fibre</td>
<td>$G_0$</td>
<td>0.85</td>
<td>0.72</td>
<td>0.60</td>
<td>0.49</td>
<td>0.39</td>
<td>0.30</td>
<td>0.21</td>
<td>0.13</td>
<td>0.06</td>
</tr>
</tbody>
</table>
$G = G_0(1 - k''P)$ (1.25)

Rossi [17] adopted these relationships and identified $k'$ and $k''$ as "stress intensity factors." On the basis of experimental results he then assigned values to these factors for porosity of different degrees of orientation.

Hasselman [11] proposed Relationship (1.16) in Table 1.1 as a result of his attempts to fit experimental data to Equations (1.14) and (1.15) derived by Hashin.

Chung [12] reported experiments which indicated that Young's modulus varied with the size and shape of pores. He used the form of MacKenzie's Equations (1.3) and (1.4) and proposed the semi-empirical relationship in Equation (1.17).

Several purely empirical expressions have been proposed. That due to McAdam [13] in Equation (1.18) was based on published experimental data for a wide range of sintered porous alloy products. Spriggs' equations [14], based on studies of the effect of porosity on the elastic modulus of polycrystalline aluminum oxide [14,18] have been criticised since they predict finite values of $E$ when $P = 1$. The other empirical equations are essentially of the form

$$E = E_0[1 - k'P]$$

i.e. consistent qualitatively with the predictions of one of Hashin's analysis [9].
1.1.2 Strength of Porous Materials

Porous materials on which attempts have been made to correlate mechanical properties with pore content are characteristically brittle. Accordingly most theoretical and experimental work has been concerned with ultimate tensile strength rather than with any yield or flow property.

Theoretical predictions of the tensile strength of porous bodies have been attempted by Eudier [19], Haynes [20,21] and Gallina and Mannone [22] with the results shown in Table 1.3.

Eudier [19] treated a sintered body as a solid containing spherical holes. Tensile strength was calculated by considering each cube of material containing a spherical hole. The strength of such a cube is equal to the product of the minimum cross-section times a load \( R_0 \) falling between the maximum practicable load and the true breaking load. If the cube is of unit volume containing a spherical hole of radius \( r_2 \), the surface area of minimum section is \( (1 - \pi r_2^2) \). The volume of the hole, which is numerically equal to the porosity, is \( P = \frac{4}{3} \pi r_2^3 \), from which the relative strength is given by

\[
\frac{\sigma}{\sigma^0} = 1 - \pi r_2^2 = 1 - \pi \left( \frac{3}{4\pi} \right) p^{2/3} = 1 - kP^{2/3} = 1 - 1.2 p^{2/3}
\]  

(1.26)

where \( \sigma^0 \) is the strength of pore free material.

Haynes [20,21] used Hashin's expression [9] for elastic modulus, which is given by

\[
E = E_0(1 - K_p P)
\]  

(1.27)
### Table 1.3
Empirical Expressions for the Tensile Strength of Porous Materials

<table>
<thead>
<tr>
<th>Authors</th>
<th>Expressions for Tensile Strength</th>
<th>Equation No.</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balshin</td>
<td>( \sigma = \sigma^0 (1 - p)^n )</td>
<td>1.41</td>
<td>25</td>
</tr>
<tr>
<td>Ryshkevitch</td>
<td>( \sigma = \sigma^0 e^{-bp} ), ( \frac{\sigma}{p} = \frac{\sigma_0^0 e^{-bp}}{\rho (1-p)} )</td>
<td>1.42, 1.43</td>
<td>26, 27</td>
</tr>
<tr>
<td>Duckworth</td>
<td>( \sigma = \sigma^0 (1 - \frac{3}{2} p) )</td>
<td>1.44</td>
<td>23</td>
</tr>
<tr>
<td>Pines et al.</td>
<td>( \sigma = \sigma^0 )</td>
<td>1.40</td>
<td>24</td>
</tr>
<tr>
<td>Knudsen</td>
<td>( \sigma = \sigma^0 d_s^{-a} e^{-bp} )</td>
<td>1.45</td>
<td>23</td>
</tr>
<tr>
<td>Eudier</td>
<td>( \sigma = \sigma^0 k \cdot p^{2/3} )</td>
<td>1.45</td>
<td>23</td>
</tr>
<tr>
<td>Eudier</td>
<td>( \sigma = \sigma^0 (1 - 1.2p^{2/3}) )</td>
<td>1.26</td>
<td>19</td>
</tr>
<tr>
<td>Hasselman</td>
<td>( \sigma = \sigma^0 \left[ 1 - \frac{AP}{1 + (A-1)p} \right] ) or ( \sigma = \sigma_0^0 \frac{(1 - p)}{(1 + AP)} )</td>
<td>1.46</td>
<td>28, 8</td>
</tr>
<tr>
<td>Weil</td>
<td>( \sigma = \sigma^0 \left[ 1 - \frac{3(1-v_o)(5v_o + 9)p}{2(7 - 5v_o)} \right] (1 - p)^{2/3} )</td>
<td>1.38</td>
<td>22</td>
</tr>
<tr>
<td>Gallina and Mannone</td>
<td>( \sigma = \sigma^0 \left[ \frac{1 - P}{1 + BP} \right] )</td>
<td>1.34</td>
<td>20, 21</td>
</tr>
</tbody>
</table>

\( \sigma \) = the tensile strength of porous material  
\( \sigma^0 \) = the tensile strength of bulk material  
\( a, b, A, B, k \) = the constants  
\( d_s \) = the grain diameter  
\( n \) = an exponent
to obtain a stress concentration factor $K_p$, which can be given by

$$K_p = \frac{1 - E_{\text{Rel}}}{1 - \rho_{\text{Rel}}} = \frac{1 - E_{\text{Rel}}}{1 - \rho_{\text{Rel}}}$$

where $E_{\text{Rel}} = E/E_0$ and $\rho_{\text{Rel}} = \rho/\rho_T$.

By analogy with the effect of notches on fatigue properties, the reduction in the tensile strength due to pores was given by a reduction factor $K_{TS}$, which is defined as

$$K_{TS} = \frac{\sigma_{TS}^0 (1 - P)}{\sigma_{TS}} = \frac{1 - P}{\sigma_{\text{Rel}}}$$

This is a ratio of the tensile strength of porous material in which pores have no stress-raising effect, to the observed tensile strength of material of the same porosity content. Usually, the effect of the pores is less than that predicted by the use of the theoretical stress concentration factor. Thus, a factor, $q_p$, which defines "pore sensitivity" (or the degree to which the theoretical effect is felt) is used, and defined by:

$$q_p = \frac{K_{TS} - 1}{K_p - 1}$$

As a first approximation it is assumed that

$$q_p \propto P \quad \text{or} \quad q_p = AP$$

where $A$ is an arbitrary constant.
From Equations (1.29) and (1.32)

\[
\sigma_{\text{Rel}} = \frac{\sigma_{TS}}{\sigma_{TS}^0} = \frac{1 - P}{1 + A(K_p - 1)P} = \frac{1 - P}{1 + BP}
\]  

(1.34)

Good agreement has been reported between experimental results and the predictions of both Eudier and Haynes in the case of sintered compacts [19, 21, 23], but only for low porosity contents (< 10%).

Gallina and Mannone [22] used MacKenzie [2] and Hashin's [9] theories to predict the tensile strength of porous materials. It was assumed that the theory would apply up to 30% porosity. Based on the assumption the following approximate expression was derived:

\[
\frac{E}{E_0} \approx 1 - \frac{3(1 - \nu_0)(5\nu_0 + 9)P}{2(7 - 5\nu_0)}
\]  

(1.35)

According to the Griffith theory of the instability condition for cracking in brittle materials,

\[
\sigma_f = kE
\]

where \(\sigma_f\) is the fracture stress and \(k\) is a proportionality constant depending on the particular material.

If \(\sigma_f^0\) and \(\sigma_f\) are the stresses required to produce a certain type of fracture in a dense wrought material and in the corresponding sintered one with porosity \(P\), then

\[
\sigma_f = \sigma_f^0 \frac{E}{E_0}
\]

(1.36)
It should be noted that $\sigma_f$ is the actual stress applied. The apparent stress, $\sigma_f^1$, i.e., the applied load divided by the geometrical cross section, could be obtained by a simple introduction of the factor $(1 - P)^{2/3}$ in Equation (1.36). Thus

$$\sigma_f^1 = \sigma_f^0 \frac{E}{E_0} (1 - P)^{2/3} \quad (1.37)$$

This in turn gives the following relationship

$$\sigma_{TS} = \sigma_{TS}^0 \left[ 1 - \frac{3(1 - \nu_0)(5\nu_0 + 9)P}{2(7 - 5\nu_0)} \right] (1 - P)^{2/3} \quad (1.38)$$

Agreement with experimental results for sintered iron [22] is poor.

Knudsen [24] proposed a semi empirical relationship between strength and porosity for sintered materials. He suggested that the load-carrying ability was related to the total contact area at particle junctions. He calculated the contact areas per unit volume for coalesced arrays of particles with different initial packing geometry (Figure 1.1.a). The corresponding relative strength values are plotted in Figure 1.1.b. In the region of 0 to 10 per cent porosity, the calculated strengths fitted the relation

$$\sigma = \sigma^0 \exp(-bP) \quad (1.39)$$

Knudsen further suggested that $\sigma^0$ should be a function of grain size, $d_s$, according to a type of Hall-Petch relationship; i.e.
Figures 1.1. a) Contact area versus porosity plots.  
b) Relative strength versus porosity plots for ideally packed sintered spheres as calculated by Knudsen [24].

\[ \sigma = \sigma_0 d_s^{-a} \exp(-bP) \]  

(1.40)

Several other strength-porosity relations proposed by previous investigators, and included in Table 1.3, have no theoretical basis.

1.2 Scope of the Present Work

Most experimental determinations of the elastic properties of porous bodies have been conducted on ceramic materials. Few reliable data appear in the literature which describe the elastic behaviour of porous sintered metals or alloys. With conventional powder processing techniques, it is difficult to produce bodies which contain uniform distributions of pores, yet which span a wide range of densities. Compacting tends to produce density gradients and directionality in pore geometry, neither of
which is effectively eliminated by sintering. If loose powders are used it is difficult by solid state sintering alone to obtain densities approaching theoretical. Good property data in the high density range are thus particularly scarce.

In the present work, it has been possible to produce relatively homogeneous and isotropic metal specimens with zero to 50 per cent porosity (by volume), by employing a combination of:

a) loose, solid solution alloy powders,
b) spherical powders of narrow particle size distribution,
c) solid state sintering to produce up to 90 per cent of theoretical density, and
d) supersolidus sintering to produce densities up to 100 per cent of theoretical.

The elastic deformation of these specimens could thus be compared, over a wide porosity content range, with that predicted from theoretical analyses. By using compression instead of tension loading, it was possible to observe plastic stress-strain behaviour up to small total strains without problems of early and unpredictable fracture of specimens.
Chapter 2

EXPERIMENTAL PROCEDURE

2.1 Compression Test Specimens and Technique

Porous sintered cupronickel specimens were prepared by the solid state sintering and supersolidus sintering procedures described in Part A of the thesis. None of the specimens used in dilatometric studies was employed for mechanical testing. Densities below 58% of theoretical could be obtained by using powder which had been allowed to oxidise slightly after the original hydrogen cleaning (Section 2.3, Part A) but before sintering.

Sintered specimens were machined with small cuts to minimise surface deformation, and to produce specimens of 0.33 inch diameter by one inch length. Eight machined specimens at a time were mounted in a jig, and surface ground at each flat end until the two ends were closely parallel. Densities of the specimens were then determined from weight and dimensions.

Compression tests were conducted on an Instron testing machine between adjustable anvils as shown in Figure 2.1. One of the anvils was bolted to the cross-head and the other was fastened to the platform of a compression load cell with a maximum capacity of 10,000 lbs.

Teflon tape was used as a lubricant at specimen ends. A strain gauge extensometer of \( \frac{1}{2} \) inch gauge length and 10 per cent elongation was mounted on the specimen (as shown in Figure 2.1). The outputs of the
Figure 2.1. Apparatus for compression tests on porous sintered cupronickel. Shows specimen, anvils, load cell and extensometer strain gauge mounted directly on the specimen.
compression load cell and the extensometer were fed into an X-Y recorder. For each specimen tested, elastic loading-unloading cycles were completed with the extensometer mounted initially at 0° to a reference position then at 90°, 180°, and 270°. The strain was measured to 0.0005 accurately with an initial strain rate of 0.01 min⁻¹. Only if the unloading cycle retraced closely the loading load-strain curve on the X-Y chart was it assumed that deformation had been purely elastic.

Young's modulus, E, was calculated from the elastic load-strain curve for each cycle. If the average E for the 0° and 180° positions was not within 3% of the average for the 90° and 270° positions, the test was rejected and the specimen ends were reground for improved parallelism. In most cases, sets of E values agreed within one per cent. The accuracy of the absolute values of E was checked by carrying out compression tests on hot rolled mild steel and on both annealed and hard drawn commercial purity copper; standard tension tests were performed to establish the modulus values. Close agreement was observed in all cases.

Upon completion of the elastic test, the specimen was completely unloaded. It was subsequently re-loaded to produce approximately one per cent total strain (elastic plus plastic) to study the yielding and flow behaviour. From the load-strain curve, flow strengths at 0.02, 0.2 and 0.6% offset strain were determined.

2.2 Heat Treatment and Retesting

2.2.1 Homogenisation

On the basis that concentration gradients in supersolidus-sintered specimens could affect both elastic and plastic properties, a few of the
specimens were homogenised and retested in compression. The composition variation was initially as shown in Figure 2.2.

An estimate of the time required for a given degree of homogenisation was made following the analysis of Singh and Flemings [29] for a binary alloy containing a nonequilibrium eutectic. In this model dendrite arms are assumed plate like, and solute distribution within them is sinusoidal as shown in Figure 2.3. It is also assumed that the interdendritic region is of constant composition. The solution to the diffusion equation is similar to that for homogenisation of a cast structure (Part A, Section 2.4), except for a factor of 4 in the denominator of the exponent as given in the following expression:

\[ \frac{C}{C_m} = e^{-\frac{\pi^2 \tilde{D} t}{4\lambda^2}} \]  

(2.1)

For supersolidus sintered specimens, assuming the average composition to be 50 wt. % copper and using values of \(4.8 \times 10^{-11} \text{ cm}^2/\text{sec}\) [30] for \(\tilde{D}\) at 1000°C and 0.01 cm for \(\lambda\) (\(\approx \) half the grain size) in Equation (2.1), a time of 45 days was obtained to reduce the concentration gradient to 0.01 of maximum variation in the as-sintered specimen. Accordingly, a few of the supersolidus sintered specimens were homogenised at 1000°C for 45 days in cracked ammonia, machined, remeasured for density determination and retested in compression.

2.2.2 Resintering

During homogenisation treatments, it was observed that low density specimens underwent a substantial increase in density. In order to evaluate
Figure 2.2. Cu and Ni x-ray intensity lines superimposed on absorbed electron images of supersolidus sintered cupronickel specimen (Q42) showing the variation in composition. The scanning paths were: (a) across the grain boundary, and (b) across the liquid pools, x1000.

Figure 2.3. Schematic diagram of the composition distribution in supersolidus sintered cupronickel, showing the sinusoidal distribution of composition in the intradendritic region (Ni rich).
the possible effect of the "method" of sintering (i.e. solid state versus supersolidus) on mechanical properties, two solid-state sintered specimens were resintered at 1200°C for 115 hours in cracked ammonia to increase their densities into the range usually obtained only by supersolidus sintering. Resintered specimens were machined, their densities were measured and they were retested in compression.

2.3 Estimation of Open and Closed Porosity

A Xylene-impregnation technique due to Arthur [31] was applied to all the sintered specimens to evaluate the amounts of open (interconnected) and closed pores. The weighed specimens were immersed in xylene and placed in a desiccator. The desiccator was pumped to $10^{-1}$ to $10^{-2}$ torr in 30 minutes. A gas trap, immersed in liquid nitrogen, was connected between the desiccator and the fore pump. The function of evacuation was to remove air or gas from the interconnected pores and thus allow xylene enter into the pores. At the end of the treatment air was let into the desiccator. The specimens were removed from the xylene and excess liquid on the surfaces was wiped off using a filter paper. The specimens were then weighed in air and in water. This procedure was carried out quickly in order to minimise the error from evaporation of the xylene while handling. The amount of total porosity, $P$, and the open porosity, $P_o$, are given by the following expressions:

$$ P = \frac{(B - C) - A/\rho_T}{B - C} \quad (2.2) $$
and

\[ P_b = \frac{B - A}{(B - C)\rho_x} \]

where

- \( A \) = the weight of the original specimen in air
- \( B \) = the weight of the specimen impregnated with xylene, in air
- \( C \) = the weight of the specimen impregnated with xylene, in water
- \( \rho_T \) = the theoretical density of the cupronickel
- \( \rho_x \) = the specific gravity of the xylene

The specific gravity of the commercial xylene used was determined using a pyknometer to be 0.862 gm/cc.

Appropriate corrections were made for the weight of the fine copper wire used to suspend the specimens in water for weighing. The reliability of these tests was checked using highly porous specimens (porosity > 40%) with known porosity obtained from their weight and dimensions. The amount of porosity calculated from the xylene impregnation technique was regularly within ±1% of the known value.

The amount of closed porosity was obtained from the difference between the total and the open porosity.
3.1 Microstructure Versus Density

Results of xylene-impregnation tests, showing open and closed porosity as a function of density, are plotted in Figure 3.1 (also refer to Table 3.1). These data may be compared with those of Arthur [31] as reproduced in Figure 3.2.

Photomicrographs of unetched sections of typical cupronickel specimens are reproduced in Figures 3.3 to 3.9. Observations from metallography and impregnation tests may be summarised as follows.

a) In specimens containing > 13% pores by volume, the porosity was virtually all interconnected and was highly irregular in shape (Figures 3.3 to 3.6).

b) In specimens containing < 7% porosity by volume, nearly all the pores were closed, and were mostly equiaxed in shape (Figures 3.8 and 3.9).

c) There was a relatively homogeneous distribution of pores on a macroscopic scale in all the specimens. However, the distribution of finer pores (microporosity) depended on the sintering conditions.

d) For supersolidus-sintered specimens, the number of pores decreased markedly with increasing density in the range of about 69 to 92 per cent of a solid.
Table 3.1
Data for Compression and Xylene-Impregnation Experiments

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Density % theor.</th>
<th>Treatment</th>
<th>( P_b )%</th>
<th>( P_c )%</th>
<th>( E ) ( 10^{-6} ) psi</th>
<th>Stress at 0.02% offset ( 10^{-3} ) psi</th>
<th>Stress at 0.2% offset ( 10^{-3} ) psi</th>
<th>Stress at 0.6% offset ( 10^{-3} ) psi</th>
<th>Stress at 1% strain ( 10^{-3} ) psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>R6</td>
<td>51.1</td>
<td>I</td>
<td>47.7</td>
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<td>1.9</td>
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<td>3.7</td>
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<td>I</td>
<td>44.8</td>
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<td>-</td>
<td>-</td>
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<td>4.4</td>
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<td>6.4</td>
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<td>I</td>
<td>43.5</td>
<td>0.1</td>
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<td>I</td>
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<td>-</td>
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<td>-</td>
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<tr>
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<td>-</td>
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<td>7.9</td>
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### Table 3.1 (Continued)

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Table 3.2
Treatment Numbers and the Symbols Used in the Figures
(Figures 3.1, 3.15, 3.17, 3.18, 3.20, 3.21, 3.22 and 3.23)

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Figure 3.1. Amount of open and closed porosity versus density for sintered cupronickel specimens. (Meaning of symbols for plotted points given in Table 3.2.)
Figure 3.2. Amount of open and closed porosity versus total porosity for copper powder (Arthur [31]). a) -300 mesh, loose sintered and b) 240 x 300 mesh, compacted and sintered.
Figure 3.3. Specimen sintered in solid state to density of 61.4% of solid (structure typical of specimens with densities less than about 62% of solid) (R4), x73.

Figure 3.4. Specimen sintered in solid state to density of 65.5% of solid (R14), x73.
Figure 3.5. Specimen sintered in solid state to 85.4% of solid density (sintered twice, once before and once after a first compression test), (R36), x73.

Figure 3.6. Specimen sintered above solidus to 86.6% of solid density (Q31), x73.
Figure 3.7. Specimen sintered above solidus to 92.3% of solid density (Q30), x73.

Figure 3.8. Specimen sintered above solidus to 97.4% of solid density (Q28), x73.
Densification was associated primarily with a reduction in number of pores rather than with a reduction in their size. Only in the closed-pore range (0 to 7 per cent porosity) did the pore size diminish rapidly with increasing density. However, in the density range 62 to 85% of solid, solid state sintering had the effect of decreasing the size of the pores, rather than the number of pores, and thus increasing the density (Figures 3.4 and 3.5). This can also be seen by comparison of the microstructures of supersolidus sintered and solid state sintered specimens of comparable density (Figures 3.6 and 3.5).

e) In the range of 51 to about 62 per cent of solid density, changes in pore structure were not evident. The particle coordination appeared to remain constant.

f) For a given density, pores in supersolidus sintered specimens were larger on average than pores in solid-state resintered specimens. However, the shape of the pores did not seem to be appreciably affected by the method of sintering.

g) Spheroidised pores were found only in high density specimens which had been subjected to long solid-state homogenising anneals (Figure 3.9).

Etched microstructures of specimens which were homogenised or re-sintered after a small compressive plastic strain are shown in Figures 3.10 to 3.14. The grain size after these treatments was very large compared to the original powder particle size. Accurate determination of the average grain diameter was not attempted, but would have been difficult since twin boundaries were in many cases difficult to distinguish from grain boundaries in these specimens.

3.2 Young's Modulus

3.2.1 Elastic Modulus Versus Density

Results of elastic compression tests on sintered specimens are presented in Table 3.1 and in Figure 3.15 as Young's modulus versus density.
Figure 3.9. Specimen sintered above solidus, then homogenised 45 days at 1000°C. Final density 96.7% of solid (R49), x73.

Figure 3.10. Supersolidus sintered and homogenised structure (R59), x80.
Figure 3.11. Supersolidus sintered and homogenised without prestrain. Reveals large grains (Q75), x80.

Figure 3.12. Supersolidus sintered and homogenised without prestrain. Reveals large grains (Q77), x14.
Figure 3.13. Same as Figure 3.5, revealing grain shape (R36), x80.

Figure 3.14. Supersolidus sintered and resintered after a prestrain. Reveals large grains (Q39), x14.
All experimental stress values are based on the full cross section of the specimens. No consistent effect of grain size or homogeneity on the modulus was observed.

Reported values [32] are available for the elastic modulus of dense polycrystalline pure copper, pure nickel, and for a 55 wt. % copper-45% nickel alloy. It is also possible to calculate the elastic constants for isotropic polycrystalline alloys in the copper-nickel system from published elastic compliance data of the pure metals [33]. A summary of these experimental and calculated constants is given in Table 3.3 and Figure 3.16. The value of Young's modulus thus estimated for the 50 wt. per cent nickel alloy of the present work, from Figure 3.16, is $24.4 \times 10^6$ psi ($1.69 \times 10^5$ MNm$^{-2}$). This compares very closely with the value of the modulus, $24.3 \times 10^6$ psi, measured in the present work on specimens which were sintered to full density.

Using elastic constants derived from Figure 3.16 it is also possible to apply the theoretical relationships in Table 1.1 to porous cupronickel. Values of the elastic modulus thus calculated for different theories and for different porosity contents are compiled in Table 3.4 and have been plotted in Figure 3.17.a for comparison with the experimental results.

There is excellent agreement between experiment and the predictions of most theories for densities in excess of about 92 per cent of solid. This agreement has not been well documented previously for sintered metallic specimens, probably because of the experimental difficulty of obtaining suitable high-density metal specimens by sintering. The region of good fit with theory is one in which only closed pores were found in the specimens;
Figure 3.15. Young's modulus versus density for porous sintered cupronickel. Experimental data and theoretical "rule of mixtures" line (assuming elastic constants zero at 50% density).
### Table 3.3

Elastic Constants for Cu-Ni Alloys, at Room Temperature, From Elastic Compliance Data and Reported Experimental Values

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* Values for 90.9 9.1 composition are approximate.
Figure 3.16. Elastic constants for Cu-Ni alloys (from Table 3.3).
Table 3.4

Predicted Values of E for Sintered Cupronickel, Assuming Elastic Constants are Zero at Zero Density

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<td>(15.1)*</td>
<td>(15.1)*</td>
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<td>(14.3)*</td>
<td>15.8</td>
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<td>-</td>
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<td>(10.7)</td>
<td>(13.0)</td>
<td>(8.3)</td>
<td>11.3</td>
<td>17.1</td>
</tr>
<tr>
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<td>(9.3)</td>
<td>(6.2)</td>
<td>(10.5)</td>
<td>-</td>
<td>7.8</td>
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<tr>
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<td>(6.8)</td>
<td>(1.6)</td>
<td>(8.7)</td>
<td>-</td>
<td>5.1</td>
<td>12.2</td>
</tr>
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*The extension of theoretical analysis to porosity contents > 0.1 is probably unjustified in view of the assumptions in the models.
Figure 3.17. Young's modulus versus density for porous sintered cupronickel. Experimental data and theoretical predictions.

a) Theoretical predictions of MacKenzie -2 [2], Skorokhod [10], and Hashin and others [3,6] (assuming elastic constants zero at zero density).

b) Predictions from Knudsen's model [24].

c) Hashin's plot [3,6] (assuming elastic constants zero at 50% density) and best-fit-plot.
i.e. the internal morphology of the specimens was consistent with most of the models used to treat elastic behaviour analytically.

Below about 92 per cent of solid density, a marked discrepancy is observed between experimental values of the moduli and those predicted from any theory. This is typical also of the observations reported in the literature for other porous materials. However, the sharp decrease in modulus (associated with a discontinuity in the $E$ versus density plot) which accompanies a transition from closed to open porosity as shown in Figure 3.18 has not heretofore been reported, and is a particularly interesting feature of the present results.

Although some of the homogenised and resintered specimens had a very large grain size relative to powder particle size, no effect of grain size on modulus values could be detected.

3.2.2 Interpretation

In view of the good agreement between theory and experiment at high densities, several of the analyses discussed in Section 3.2.1 can be said to describe reliably the elastic behaviour of porous sintered cupronickel when the pores are all isolated and dispersed. However, no available theory is consistent with the results obtained for specimens with interconnected porosity, and most available theories predict much higher modulus values than were observed.

In a sintered powder aggregate, an applied load must be borne at the necks between particles. It is possible to pack uniform spherical particles into a rhombohedral array which fills ~ 74 per cent of space with
Figure 3.18. High density portion of Figure 3.15 and 3.17.
solid. Until this array of particles sintered, it has no load carrying capacity at all; i.e. its elastic modulus is zero, yet its porosity content is only 0.26. If the array is even very lightly sintered, necks form and the modulus of the aggregate becomes finite. To a first approximation, it might be assumed that when the array is further sintered, its capacity to support a load will increase linearly with increasing density due to neck growth with particle-centre approach. That is,

\[ E = E_0 \frac{(P_i - P)}{P_i} \]  

(3.1)

where \( P_i \) is the porosity in the loose-powder aggregate (unsintered).

Equation (3.1) plotted in Figure 3.15 is a "Rule of Mixtures" which recognises, in marked contrast to most of the theoretical equations collected in Table 1.1, that the elastic modulus of a sintered body can be zero even when the porosity is considerably less than unity. If values of \( P \) are replaced by \( P/P_i \) in the derived equations, a correction is made in effect for the fact that the elastic strength is zero when \( P = P_i \). Moreover, no assumption about the type of particle packing is required in making this correction.

Hashin equations [3,4,5,6] (Table 1.1) have been thus treated to calculate \( E \) versus \( P \) for cupronickel, with the results shown in Figure 3.17.c. Agreement with the experimental results is poor, which suggests that Hashin's model (which is similar to that of Kerner and others) cannot apply to systems with interconnected porosity.
Clearly the Rule of Mixtures in Equation (3.1) cannot give accurate predictions of modulus variations with porosity if the load-carrying neck elements do not grow linearly with increasing density during sintering, as was assumed in deriving the equation. As noted in Section 1.1.2, Knudsen [24] has treated quantitatively the growth of contact (neck) areas between coalescing arrays of uniform spherical particles, assuming several different ideal packing arrays. The calculated relation between contact area and porosity is shown in Figure 1.1.a.

On the assumption that the elastic stress-bearing capacity is directly related to neck contact area, Young's modulus versus porosity predictions can be made from the results of Figure 1.1.a, as was done for ultimate strength versus porosity by Knudsen [24]. Similar approaches were taken by Spriggs [14,18]. However, it is necessary to choose an appropriate model for particle packing. In the present work with cupronickel, the initial loose-powder porosity was ~ 0.50, which is slightly larger than that calculated for the ideal simple cubic array (0.48) and is widely different from those calculated for any other ideal array of uniform spheres. Metallography has shown (Section 3.2, Part A) that the packing is far from uniform in powder specimens, there being randomly oriented groupings with different types of dense packing joined by bridges. However, the forms of the curves in Figure 1.1.a for different packing modes are so similar that it seems reasonable to assume that the average neck growth in the aggregate will vary with density in a manner closely parallel to that predicted for the simple cubic model (Table 3.5).

On this basis, the derived plot of E versus P in Figure 3.17.b was made and may be compared with the experimental results.
### Table 3.5
Contact Area, Density, and Young's Modulus for Ideal Cubic Packing of Spherical Cupronickel

<table>
<thead>
<tr>
<th>Density</th>
<th>( \pi x^2 ) Area of contact without meniscus</th>
<th>( E \times 10^{-6} ) psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.36</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>53.15</td>
<td>0.012</td>
<td>0.3</td>
</tr>
<tr>
<td>55.57</td>
<td>0.048</td>
<td>1.2</td>
</tr>
<tr>
<td>59.75</td>
<td>0.110</td>
<td>2.7</td>
</tr>
<tr>
<td>65.94</td>
<td>0.198</td>
<td>4.8</td>
</tr>
<tr>
<td>74.39</td>
<td>0.314</td>
<td>7.7</td>
</tr>
<tr>
<td>79.50</td>
<td>0.397</td>
<td>9.7</td>
</tr>
<tr>
<td>85.09</td>
<td>0.493</td>
<td>12.0</td>
</tr>
<tr>
<td>90.84</td>
<td>0.613</td>
<td>15.0</td>
</tr>
<tr>
<td>95.94</td>
<td>0.776</td>
<td>18.9</td>
</tr>
<tr>
<td>96.51</td>
<td>0.804</td>
<td>19.6</td>
</tr>
<tr>
<td>100.00</td>
<td>1.000</td>
<td>24.4</td>
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</table>
It should be noted that the plot is based on Knudsen's calculation for ideal cubic packing and should therefore have its origin at $E = 0, \rho_0 = 52.4$ per cent. However, it has been shifted to $\rho_0 = 50$ per cent in Figure 3.17.b to reflect more accurately the starting density of cupronickel specimens.

Discrepancies between the measured modulus values and those predicted from the neck-area argument might be interpreted as follows:

a) The model of contact-area growth used to calculate the predicted moduli in Figure 3.17.b assumes that when particle centres approach the particles adopt the shape of truncated spheres. Essentially this type of contact development will arise when spheres are pressed together, and material transport is by plastic flow only. However, if contact development proceeds by diffusional processes as in sintering, a neck with the familiar rounded meniscus is formed. This type of neck has a larger relative contact area for a given approach of particle centres than that assumed in the Knudsen [24] model. Thus the effective load bearing areas and elastic moduli of sintered specimens will be higher, for a given porosity content, than the above analysis predicts. Knudsen attempted to make allowance for the neck meniscus (dashed lines in Figure 1.1.a), but his approach involved arbitrary assumptions.

b) Neck growth is also caused by non-densifying mass transport mechanisms such as evaporation-condensation and surface diffusion. In the earliest stages of sintering it is possible that more neck growth occurs from these sources than from processes which contribute to a decrease in the volume of porosity (e.g. volume diffusion mechanisms). This could explain why, in the lowest density region of the plots (Figures 3.15 and 3.17) modulus values were higher than those predicted from contact-area growth based on the approach of particle centres. Following this argument, the slow rise of $E$ with density between 50 and 60 per cent of theoretical suggests that a mechanism such as surface diffusion has established necks in very short sintering times or at low sintering temperature, and that subsequent approach of particle centres (for densification) has somehow proceeded with little growth of the original
necks up to a density of about 60 per cent of solid. It is difficult to visualise how this could occur, and some doubts are therefore cast on the above argument.

An alternate approach to describing the modulus-porosity relationship is as follows:

a) Use a relationship for the region of closed porosity (high density) from the MacKenzie [2] or similar analyses. Equation (1.35) reduces to

$$E = E_0(1 - K_c P)$$

(3.2)

b) As a first approximation, use a Rule of Mixtures for the open porosity region; i.e.

$$E = E_0 \left( \frac{P_i - P}{P_i} \right)$$

c) To obtain a general equation for the full range of porosity, combine

$$E_c = E_0(1 - K_c P) \frac{P_c}{P}$$

(3.3)

plus

$$E_b = E \frac{(P_i - P) P_b}{P_i}$$

(3.4)

from which

$$E = E_0 \left[ \frac{P_b}{P} - \frac{P_b}{P_i} + \frac{P_c}{P} - K_c P_c \right]$$

$$= E_0 \left[ 1 - \frac{P_b}{P_i} - K_c P_c \right]$$

(3.5)
Using an appropriate value of $v_0$ for cupronickel, $K_c$ has been evaluated from Equation (1.35) and found to be 2.0. Also, since $P_i = 0.50$ in the present experiments, Equation (3.5) becomes

$$E = E_0 \left[1 - 2(P_b + P_c)\right] = E_0 \left[1 - 2P\right]$$

(3.6)

with $P_i = 0.50$, the Rule of Mixtures is identical (Figure 3.15).

A test has been made of the empirical expressions proposed by Hasselman [15] and by Fryxell and Chandler [16], Table 1.1. When the exponential term in Spriggs' [14] relation is replaced by a series expansion, and second order or higher terms are dropped, it is equivalent to Hasselman's [15]; i.e.

$$E = E_0 (1 - bP)$$

(1.21)

This becomes a statement of the simple Rule of Mixtures by $b = P_i^{-1}$. When the present experimental data are "fitted" to this relationship by linear regression analysis, $E_0$ is found to be $24.6 \times 10^6$ psi with $b = 2.1$ (which is very close to $P_i^{-1}$). The best-fit plot is presented in Figure 3.17.c.

3.3 Plastic Flow Behaviour

Engineering stress-strain curves were derived from X-Y load-elongation plots. Examples are shown in Figure 3.19. From these curves were obtained flow stress values for 0.02, 0.2 and 0.6 per cent offset strain and for 1 per cent total strain (slightly < 1 per cent plastic strain).
Figure 3.19. Typical stress-strain curves for sintered cupronickel powder specimens.
Results are collected in Table 3.1, and plotted versus porosity in Figures 3.20 to 3.23.

The large scatter in the flow stress values can be attributed to the following:

a) Variations in shapes and distribution of pores, composition gradients in as-sintered specimens, and differences in neck composition between sintered and homogenised specimens.

b) Variations in grain size due to differences in previous history of specimens. These variations are likely to be most evident in the higher density specimens, which is when the greatest experimental scatter was observed.

c) Plastic buckling of the compression specimen. Beyond the proportional limit, if the load applied exceeds a critical, load, \( W_{\text{crit.}} \), there will be buckling of the specimen in a compression test. The critical load, according to Tangent Modulus theory [34], is given by

\[ W_{\text{crit.}} = \frac{\pi^2 E_T I}{L^2} \]  

where \( E_T \) is the tangent modulus at any \( W \), \( L \) is the length of the specimen, \( I \) is the moment of inertia for the specimen. The moment of inertia,

\[ I = \frac{\pi d^4}{64} \]

for a simple cylinder of diameter \( d \). For porous sintered cupronickel buckling was probably important only in specimens with densities higher than 96% of theoretical and at total strains exceeding 0.9%. 
Figure 3.20. 0.02% offset flow stress in compression versus density. Line drawn is least squares fit.
Figure 3.21. Same as Figure 3.20 but for 0.2% offset flow stress.
Figure 3.22. Same as Figure 3.20, but for 0.6% offset flow stress.
Figure 3.23. Flow stress at 1% total strain versus density. (Solid line is a least squares best fit plot.)

Flow Stress at 1% Total Strain, lb/in^2 x 10^-3

Density, % Theor.
In view of the large scatter, there was no merit in attempting to describe the results in terms of analytical expression such as those suggested in the literature. The data have been fitted to a Rule of Mixtures; i.e.

\[ \sigma = \sigma^0 (1 - b' P) \]  

(3.8)

Using regression analysis, values of \( \sigma^0 \) and \( b' \) for different offset strains were obtained as given in Table 3.6.

<table>
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<th>Strain %</th>
<th>( \sigma^0 ) Ksi</th>
<th>( b' )</th>
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<td>0.02 plastic</td>
<td>15.1</td>
<td>1.9</td>
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<tr>
<td>0.2 plastic</td>
<td>18.6</td>
<td>1.8</td>
</tr>
<tr>
<td>0.6 plastic</td>
<td>20.7</td>
<td>1.8</td>
</tr>
<tr>
<td>1.0 (total)</td>
<td>22.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Following the arguments of the previous section, a value of \( b' = 2 \) would indicate that \( b' = 1/P_i \) and the Rule of Mixtures would have the physical meaning already discussed in relation to Young's Modulus.
Chapter 4

CONCLUSIONS

1. In porous sintered cupronickel specimens containing only closed porosity (density > 93% of solid), the dependence of elastic modulus on density is adequately described by several of the published analyses based on the application of elasticity theory. These analyses approximate to

\[ E = E_0 (1 - K_C P_c) \]

where \( K_C \) is a function of Poisson's Ratio and is equal to 2.0 for cupronickel.

2. For lower-density sintered cupronickel specimens (density < 92% of solid), in which interconnected porosity is dominant, modulus-porosity results cannot be closely fitted to any single theoretical or empirical relationship. However, over the whole range of density, an approximate fit is provided by

\[ E = E_0 \left( 1 - \frac{P}{P_i} - K_C P_c \right). \]

For the present experiments, \( P_i = 0.5 \), and this relationship reduces to
\[ E = E_0 (1 - 2P), \text{ where } P = P_b + P_c. \]

This dependence is consistent with a model of the powder aggregate in which no strength is available until necks are established by sintering, and the load-carrying neck area after sintering is linearly related to the density.
BIBLIOGRAPHY


