#### STUDIES OF DISPERSION-HARDENING PARAMETERS

BY

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We accept this thesis as conforming to the standard required from candidates for the degree of MASTER OF APPLIED SCIENCE.

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#### ABSTRACT

Experiments were carried out with 1 micron copper powder compacts containing up to 7.5 vol % .018 micron alumina, and with various types of lead powder compacts containing up to 20 vol % of various other materials.

The results indicate that dispersion-hardened alloys should be divided into three groups on the basis of the nature of the second phase.

- i) particulate, adherent (not coherent) with matrix
- ii) particulate, non-adherent with matrix
- iii) semi-continuous

It is suggested that the room temperature strengthening of the second and third groups of alloys may be due primarily to a grain size effect as described by the Hall-Petch relationship.

The cell-like structure recently proposed for S.A.P. has been observed in the lead-lead oxide system by electron microscopy.

An explanation of the difference in properties between extruded and rolled dispersion-hardened alloys has been offered in terms of the directional deformation caused by rolling.

- i -

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## TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
II.	EXPERIMENTAL PROCEDURE	6
• •	A. Material	6
	B. Mixing	7
	C. Compacting	7
	D. Sintering	10
	E. Consolidation	10
	F. Cold Working	10
*	G. Annealing	. 10
	H. Tensile Specimens	11
	J. Tensile Testing	11
	K. Metallography	12
	L. Density Measurement	12
III.	RESULTS AND DISCUSSION	13
· .	A. Sintering of Copper-Alumina Compacts	13
	B. Strength of Sintered Copper-Alumina	20
	C. Elevated Temperature Strength of Copper-Alumina	22
	D. Grain Size Effects in Copper-Alumina	28
	E. Lead Results	32
	F. Summary of Discussion	37
IV.	CONCLUSIONS	40

- iii -

V. APPENDICES . . . .

### BIBLIOGRAPHY . VI.

**47** 

- iv

**41** 

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## LIST OF FIGURES

No.		Page
1.	The Effect of Temperature on the Strength of a Number of Aluminum Alloys at a Constant Strain Rate $\dot{\epsilon}$ = 5/hr (after Sherby <sup>7</sup> )	2
2	Typical Mixing Curve	8
3.	a) Typical Copper Powder before Mixing. 5000X	9
4.	Dimensions of Strip Tensile Specimens	11
5.	Sintering Curves	14
6.	Density versus vol. % Oxide	15
7.	Proposed Oxide Particle Motion during Sintering	16
8.	End Point Density and Calculated Curve	18
9.	Clusters in 2.5 vol % Alumina-Copper Compact. 30,000X	19
10.	Strength of Porous Compacts	21
11.	Room Temperature Tension Tests	23
12.	149 <sup>0</sup> C Tension Tests	2 <b>4</b>
13.	22,23 Room Temperature Creep Data.	-25
14.	0 149 <sup>°</sup> C Creep Data	26
15.	Graphical Interpretation of Ansell and Weertman's Creep Theory	27
16.	<ul> <li>a) As-sintered Cross-section</li> <li>b) Extruded Cross-section</li> <li>c) Rolled Cross-section</li> </ul>	28
17.	a) Standard Lead. In Extrusion Direction. 4000X	33
18.	a) -84. Melted and Cast. 300X	35
19.	Extrusion Equipment	.44

## LIST OF TABLES

			1.	•		
No.					•	Page
I.	Copper-Alumina Grain Size Re	sults .		• • • • •,	• •	30
II.	Lead Grain Size Results	• • • •			• •	34

#### **INTRODUCTION**

Since the discovery of S.A.P. (sintered aluminium powder)by Irmann<sup>1</sup> numerous studies have been made of this and other alloys produced by dispersing, artificially, a hard phase in a ductile metal matrix by powder metallurgical procedures. Among the artificial "dispersion hardened" systems which have received laboratory attention and, in some cases, commercial exploitation, are Al -  $Al_2O_3$ , Cu -  $Al_2O_3$ , Be -  $Be_2C$ , and Ni - ThO<sub>2</sub>. In such materials the dispersed phase has normally constituted less than 20 per cent by volume of the alloy, and interparticle spacings have been in the range of one-tenth to several microns.

Structurally there are apparent similarities between these artificial alloys and conventional age-hardened alloys in the overaged condition. Additionally, many natural two-phase alloys, including annealed and spheroidized steels, consist of a dispersed hard phase in a ductile matrix, and can therefore also be classified as "dispersion-hardened" systems.

Early theories of dispersed-particle strengthening were advanced by Orowan<sup>2</sup>, Fisher et al<sup>3</sup> and Mott<sup>4</sup> principally to explain experimental observations in age-hardening systems. Attempts to apply these theories to dispersion-hardened alloys in general have met with little success, especially in the case of artificially produced dispersions.

For the early and intermediate stages of age-hardening in suitable alloys, second phase zones, or "particles", are present which are coherent with the matrix. Strengthening in this case is most satisfactorily explained in terms of coherency strains in the matrix, and the effect of such strains on dislocation propagation. Systems involving a coherent second phase will not be considered as "dispersion-hardened" for purposes of the present work.

It has recently been demonstrated, to a large extent by conventional and thin-film transmission electron microscopy<sup>5</sup> that basic differences exist between the structures and behaviour of different dispersion-hardened systems, and it is thus possible that several different strengthening mechanisms may contribute to the overall strengthening.

There is now evidence that  $S_*A_*P_*$  differs basically from most other alloys in that it contains an almost continuous, porous network of alumina<sup>6</sup> rather than discrete particles of the hard phase. The mechanical properties of S.A.P. are quite different from those of other alloys. See Figure 1.



Figure 1. The effect of temperature on the strength of a number of aluminum alloys at a constant strain rate  $\dot{\epsilon} = 5/hr$ . (after Sherby<sup>7</sup>)

A unique characteristic of S.A.P. is its measureable creep resistance at a temperature 50-75°C above the melting point of aluminum. It is postulated that the porous alumina network is in the form of cells, elongated in the extrusion direction. It is easy to see how a network of this type could significantly alter strength and creep behaviour at elevated temperatures. The observed activation energy for creep of S.A.P. 865 (an alloy containing

- 2 -

7 vol % alumina) above the melting point of aluminum is 150 kilocal/mole<sup>o</sup> which is comparable to the reported activation energy for diffusion of oxygen in alumina of 152 kilocal/mole<sup>8</sup> or the reported activation energy for creep of alumina single crystals of 180 kilocal/mole<sup>9</sup>.

It has previously been suggested that the effect of incoherent but discontinuous hard particles in a ductile matrix is twofold. Firstly, by inhibiting dislocation motion in a general sense the particles cause a direct resistance to deformation. Secondly, by inhibiting grain growth and increasing the amount of dislocation climb required for a given amount of creep to occur, the particles increase temperature stability and creep resistance of the matrix.

Recent theories<sup>10,11</sup> which will be examined more closely in discussing results of the present work, deal specifically with incoherent particle dispersion, and satisfactorily explain elevated temperature properties of at least some such systems.

In dispersion-hardened systems, a distinction can be made (but has not by previous investigators) between those in which the dispersed phase "adheres" to the matrix and those in which it does not. "Adherence" is used here to imply that work is needed to separate the two solid phases at a flat interface, analogous to "wetting" of a solid phase by a liquid phase. The mechanism of adherence is not specified. It may involve local coherence at the interface arising from structural "fit" between the lattices of the two solid phases, or it may result from the formation, by chemical interaction and/or diffusion, of a layer which is coherent with both the dispersed phase and the matrix. Adherence would be said to exist if the second phase had a tendency to dissolve or increase in particle size during prolonged heating.

Overaged age-hardening alloys and natural carbide dispersions in

steels are examples of systems where adherence exists. Copper-alumina alloys prepared by powder metallurgical procedures are likely, by contrast, to involve no adherence, provided oxidation of copper has been prevented during consolidation<sup>12</sup>. It has been calculated thermodynamically<sup>13</sup> that in Ni at 1340° F a particle 200 Å in radius of Ni<sub>3</sub>Al, Fe<sub>3</sub>C, TiC, or TiN, would dissolve in several minutes whereas a similar particle of Al<sub>0</sub> would be  $^{23}_{23}$  stable for several years.

<sup>14</sup> There is evidence in the literature <sup>14</sup> that systems involving adherent dispersoids have quite different deformation and fracture behaviour characteristics from those involving non-adherent dispersoids. This is particularly true at ordinary temperatures and at strain rates normal to tensile testing or mechanical forming processes. For example, carbide dispersions in a ferrite matrix have a marked room temperature strengthening effect, whereas alumina dispersed in copper with a similar amount and degree of dispersion, gives much less relative strengthening and considerably greater embrittlement of the matrix. At elevated temperatures, the non-adherent dispersoid gives superior properties, presumably because it has less tendency to coarsen and/or cannot be dissolved by the matrix. There appears to have been no attempt previously to rationalize differences between the effects of adherent and non-adherent dispersoids.

Although internal strain originating from large scale coherency between dispersoid and matrix is not recognized as a "dispersion-hardening" mechanism herein, there is another source of internal strain which may be significant in any two phase alloy. Where the thermal expansion coefficient of an incoherent dispersed phase differs from that of the matrix, there will be residual elastic strain in both the particle and the matrix surrounding it at ordinary temperatures. The magnitude of the corresponding stresses in WC-Co (sintered carbide) has been investigated by Gurland<sup>15</sup>

- 4 -

and stresses from +50,000 to -100,000 psi were found in the WC , depending upon the per cent of Co present. This could be an important factor in dispersion-hardening systems, particularly those in which the volume fraction and particle size of the second phase are relatively large.

In view of evidence that all dispersion hardening systems are not alike in their deformation behaviour at ordinary and elevated temperatures, an attempt has been made, in the present work, to determine the origin of the observed differences. Initially it was assumed that only two categories of dispersion-hardened alloys existed; "natural" alloys such as overaged Al-Cuand spheroidized steel, and "artificial dispersed-phase alloys" produced from powders. For the first category, there is abundant reliable data in the literature and no further experimentation was warranted. For the second category, it was decided to re-examine the copper-alumina system, since reported data for this and similar systems was conflicting. In particular, there was considerable doubt as to the importance of processing variables (consolidation, sintering, etc.) on the properties of the dense alloys.<sup>17</sup> Also it was not certain whether adherence occurred between dispersoid and matrix in some or all cases. It was felt that it should be possible to prevent appreciable adherence in the Cu-Al<sub>2</sub>0<sub>3</sub> system, and thus to examine the importance of this variable more closely.

Later it became apparent that two categories of dispersion-hardened alloys were insufficient, and that perhaps S.A.P. should be considered as a category of its own. Room temperature tests on the lead-lead oxide system, which are effectively high-temperature tests since this is above the recrystallization temperature for lead, appeared to be qualitatively similar to results obtained for S.A.P. Studies of lead with oxide and other dispersions were therefore carried out in an attempt to determine the mechanisms of strengthening involved in this case.

#### II EXPERIMENTAL PROCEDURE

This is a general outline of the entire experimental procedure. Few specimens received the entire treatment. Some were tested in the green (unsintered) condition, some in the as-sintered condition, etc.

A. Materials

1. Alumina Powder. .018 micron alumina powder (Linde B) was obtained from the Linde Company of Chicago and was stated to be  $99.99^+$ % Al<sub>2</sub>0<sub>3</sub>. It was used in the as-received condition.

2. Copper Powder. 1 micron copper powder (NFIM) was obtained from Sherritt Gordon, Ltd., with an average particle size of 1.2 microns. The chemical analysis is as follows.

Cu	- balance
Ni	087%
Co	033%
Fe	007%
S	011%
Insol.	03%
H loss	40%
2 ann density	- 6/ 000/00

3. Lead powder. 3 types of lead powder were obtained from the Metalead Products Corporation.

(a) Superfine "S". Average particle size of 2.5 microns.
 99.575% lead with the major impurity being .2535% oxygen which is equivalent to 6.8%. Pb\_0

(b) Standard. Average particle size of 21 microns. 99.825% lead with .0035% oxygen which is equivalent to .1% Pb\_0

(c) -84 mesh. Average particle size of approximately 100 microns. This powder was at least as pure as the standard grade.

#### B. Mixing

Mixing of copper and alumina was done in a Waring blendor at approximately 13,000 rpm for five minute periods. The powder was allowed to cool between the mixing periods. The total mixing time varied from 10-60 minutes with 20 minutes being used as the standard total.

The copper powder used in this work originally had an apparent density of .64 gm/cc. Handling around the laboratory increased this to 1.2 gm/cc. However, upon mixing, the density increased further, to 2.6 gm/cc. See Figure 2. As it was known that the original powder particles were not spherical this suggested that some commutation took place during mixing. This was verified by electron photomicrographs. See Figure 3. Before mixing the copper powder appeared to be in clusters of up to 5 microns diameter, whereas, after mixing, the average particle diameter was estimated to be .2 microns. It was also observed that, after mixing, the powder particles had few re-entrant angles and more closely approximated a spherical shape.

Lead powders and additions were mixed in a modified Patterson-Kelly twin shell blendor for various lengths of times.

C. Compacting

(1) Die Compacting. Some copper specimens were compacted in a die measuring 2.5" x .375" under a pressure of 50,000 psi. This gave a compact with sufficient green strength to be easily handled.

(2) Hydrostatic Compacting. The majority of the copper compacts and all of the lead compacts were prepared in this manner. The blended powders were placed in an impermeable, thin, rubber container, which was then closed, and immersed in oil. A hydrostatic pressure of 30,000 psi was used to give cylindrical specimens 3 to 4" long by 1 to 1½" diameter.

- .7 -





Figure 3(a) Typical Copper Powder before Mixing .5000X.



Figure 3 (b) Typical Copper Powder after 20 minutes. Mixing. 20,000X.

#### D. Sintering

All copper compacts were preheated, sintered, and cooled under hydrogen. The sintering to precede consolidation was done in a small Nichrome resistance furnace at 1050-1070<sup>°</sup>C for 12-72 hours. Controlled sintering tests were carried out in a 15 KW Molybdenum resistance furnace at 900<sup>+</sup> 10<sup>°</sup>C. The larger capacity of the latter furnace was useful in permitting shorter heating times to be employed. Lead compacts were not sintered prior to consolidation.

#### E. Consolidation

(1) Extrusion. The extrusion press is described in Appendix I. Lead compacts were extruded at  $200^{\circ}$ F (93°C) under a pressure of 15-30,000 psi. The extrusion ratio was 45:1 and the extrusion speed approximately 2'/ min. The preheating was done under hydrogen and "Never-seez" was used as a lubricant.

(2) Hot Rolling. This applies to copper-alumina billets only. Hydrostatically compacted billets were preheated under hydrogen to  $800-900^{\circ}C$  and flattened to approximately 1/2" thickness to facilitate rolling. They were then hot rolled at 750-850°C to a thickness of .070-.090". A graphite slurry was used as a lubricant throughout this procedure. The square billets produced by die compacting were hot rolled in a similar manner but without, of course, the flattening operation.

#### F. Cold Working

The surface scale was removed from the hot rolled billets and they were cold rolled to approximately .030". This gave a smooth, highly polished surface.

#### G. Annealing

Cold rolled specimens were given an annealing treatment of 1 hour at 475  $\pm$  10<sup>o</sup>C in an atmosphere of hydrogen.

- 10 -

#### H. Tensile Specimens

Rolled billets (approximately .030" thick) were stamped into tensile specimens of the following dimensions.



Figure 4. Dimensions of Strip Tensile Specimens

Other copper specimens (green, as-sintered, etc.) were machined into tensile specimens of various shapes, depending upon the original shape.

Lead specimens were tested in the as-extruded shape.

J. <u>Tensile Tests</u>

(1) Copper at Room Temperature. Room temperature tests were carried out on an Instron Tensile Testing machine using a universal mounting<sup>19</sup> and friction grips designed for the specimens.

(2) Copper at High Temperature. Tests were made at  $149^{\pm} 1^{\circ}$ C using the same gripping arrangement in a stainless steel beaker containing silicon oil.  $149^{\circ}$ C was chosen because of the abundance of published data at  $149^{\circ}$ C. An immersion heater was used, and the temperature was controlled by a Precision Micro-Set Thermoregulator.

(3) Lead at Room Temperature. Sections of lead extrusion were cemented, with Shell Epon resin, into grips designed for the purpose, and tested in the same universal mounting.

#### K. Metallography

(1) Low Magnification. Specimens to be viewed were mounted in bakelite and polished on five, increasingly fine, emery papers. The copper specimens were then lapped on two alumina wheels. The lead specimens were both chemically polished and lapped to the final polish. The standard NH OH,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 2 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 10 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 2 & 10 \end{array}$ ,  $\begin{array}{c} H & 0 \\ 10 \end{array}$ ,  $\begin{array}{c} H & 0 \end{array}$ ,  $\begin{array}{c} H & 0$ 

(2) High Magnification. Electron microscopy was used when the resolving power of the optical microscope was insufficient. The carbon replica technique was used on polished surfaces, fracture surfaces, and loose powder. It was not possible to obtain replicas from green copper compacts. The replica procedure is outlined in Appendix II. Replicas were studied under an RCA microscope, type EMT, at 3000X, and under a Siemens Elmiskop I microscope at a variety of magnifications.

#### L. Density Measurement

The density of the loose powder was obtained in the following manner. A 50 ml. graduated cylinder was filled with powder and random tapping continued until no further densification took place. The density of all compacted material was obtained by geometrical measurement.

- 12 -

#### III RESULTS AND DISCUSSION

#### A. Sintering of Copper-Alumina Compacts

The results of  $900^{\circ}$ C sintering tests are shown in Figures 5 and 6. It can be seen that at any given time the density of the compact varies with the volume percent oxide and that the various compacts seem to reach a stable, end point density in 100 hours; i.e. at that time the slope of the curves is effectively zero.

Kuczynski<sup>20</sup> states that surface diffusion is the primary mechanism in the early stages of sintering, particularly for particles of submicron size. This process gives rise to a change in pore shape but no overall densification takes place. The driving force for this mechanism is a vacancy concentration gradient between concave and convex surfaces at, and adjacent to, the neck formed between particles. As the neck grows, the radius of curvature increases and the driving force diminishes. Finally this ceases to be the controlling process and volume diffusion to grain boundaries becomes the predominant mechanism. The neck surface is again the vacancy source and grain boundaries are the sinks. It is during this stage of sintering that most of the densification takes place. From Figure 5 it can be seen that extensive densification had occurred in the copper-alumine compacts before 0.4 hours and therefore the period during which only surface diffusion was occurring was extremely short.

Diffusion from necks to grain boundaries continues until stopped in some manner. This usually occurs when normal grain growth or secondary recrystallization results in the pores being no longer close to the grain boundaries.

In the presence of a second, non-adherent phase it is quite likely that the process may be slowed appreciably by the following mechanism.









#### Figure 7. Proposed oxide particle motion during sintering

The material transport is from the grain boundary to the neck. The neck continues to grow until it comes into contact with an oxide particle. Then, if there is no adherence between the two solid surfaces, the oxide is pushed along as the neck continues to grow. This causes an agglomeration of the oxide particles which ultimately fill the "pores" and prevent further shrinkage of the compact. If, on the other hand, the oxide and the expanding neck adhere, then, once contact between the two is established, this mechanism of sintering might effectively be slowed as vacancy concentration gradients would probably be reduced.

Calculations based on the above model will be made, using 6.25vol% alumina as an example. The end point density reached in this case was 6.58 gm/cc., which is 74% of the theoretical density of pure copper. Assuming a 1:1 ratio of the number of particles to the number of voids in the copper, the average pore radius would be 0.07 microns considering the average copper particle radius to be 0.1 micron. See Figure 3 (b). A pore of this size has a significant internal pressure given by the equation

 $P = 2\frac{8}{5}$ 

- 16 -

where  $\bigvee_{SV}$  is the surface tension at the solid-vapor interface, and  $r_p$  is the pore radius. This is equivalent to an external hydrostatic compacting pressure of 5400 psi, using  $\bigvee_{SV}$  for copper of 1300 dynes/cm.<sup>21</sup> The .018 micron alumina compacted at a pressure of 5500 psi has been found to have a bulk density of 0.65 gm/cc. However, due to the small number of particles of alumina per pore, in sintered copper compacts, packing would be further from the ideal, and a more reasonable effective density would be 0.6 gm/cc. Now 6.25 vol% alumina (2.5 Wt%) of effective density 0.6 gm/cc gives a predicted theoretical bulk density in the copper-alumina compacts of 6.64 gm/cc which is well within the limits of accuracy of the assumptions and the experimental data when compared to the observed end point density of 6.58 gm/cc.

A similar calculation for 1.25 vol% alumina gives the following results.

pore volume = 7%
pore radius = 0.042 microns
internal pressure = 9000 psi
density of alumina compacted at 9000 psi
= 0.8 gm/cc
modified(as above)to 0.75 gm/cc
theoretical bulk density = 8.48 gm/cc
observed end point density = 8.39 gm/cc

A plot of the observed end point densities and the calculated theoretical curve is shown in Figure 8.

The existence of this type of clustering and the approximate dimensions of clusters were verified by electron microscopy. See Figure 9.







Figure 9 Clusters in 2.5 vol % alumina-copper compact. 30,000X.

### B. Strength of Sintered Copper-Alumina

Tension tests were performed on copper-alumina compacts which had been sintered for different periods up to 100 hours at  $900^{\circ}$ C. The strength of the compacts is plotted in Figure 10 as a function of percent of theoretical density.

In view of the model of the structure of as-sintered compacts which was presented previously, one would not expect alumina content, per se, to have much influence on strength. Sintering behaviour indicated that adherence does not occur between copper and alumina under the present experimental conditions. Thus the mechanical properties of the sintered compacts would be expected to be determined largely by the relative volume and shape of the pores in the copper, even though these pores are filled with loosely compacted alumina powder. The results in Figure 10 support this expectation and, in fact, indicate that virtually no direct contribution to strength is provided by the alumina in the range of compositions considered.

The absolute values of the ultimate tensile strength attained in compacts of high sintered density (e.g. greater than 90% of the theoretical) are typical only of very fine-grained copper. This suggests that alumina clusters in the compacts may have the effect of preventing or impeding grain growth of the type commonly observed in pure metal compacts during the later stages of sintering, and that the alumina is therefore providing a secondary strengthening effect. Again, however, the amount of alumina present is not important in the range considered.



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#### C. Elevated Temperature Strength of Copper-Alumina

Sintered, rolled, and annealed specimens containing 0,2.5, and 7.5 vol % alumina were tested in tension at room temperature and 149<sup>°</sup>C at various strain rates. The results are shown in Figures 11 and 12. There is an increase in strength with increasing oxide content which is discussed in the following section as a grain size effect. There is a decrease in strength at the higher temperature as would be expected. It is the shape and slope of these curves which warrants discussion at this time.

It was observed (See Figures 13 and 14) that the pure copper results extrapolated directly onto the published creep data for OHFC copper at these temperatures. This is in agreement with the suggestion<sup>25</sup> that tension tests at constant strain rate are exactly equivalent to creep at constant stress. It was hoped that long-term creep data might be obtainable from short-term tension tests. This would be so, were it not for the change in slope of the curve occasioned by a change in creep mechanism. Frequently the change in slope occurs at a "strain rate" far too low to be determined by constant strain rate tests.

However, the results of this work are effectively "creep" data for the range of stresses encountered and, at this juncture, a look at the prevalent theory for creep of incoherent dispersions would be in order. It has been shown by electron microscopy<sup>5</sup> that dislocations do not pass through incoherent particles, provided that the particle is significantly harder than the matrix. Therefore, if a dislocation is to pass through the alloy, dislocation climb must occur in the vicinity of a particle. Ansell and 11 Weertman, considering climb to be the rate controlling process, arrive at the following greatly simplified equations for creep rate.

> 1) k  $\propto$  5 2) k  $\propto$  5<sup>4</sup>

at moderate stresses

at low stresses

- 22 -









3)  $k \propto \sigma^2 \exp(\sigma^2)$ 

at high stresses

These plot in the following manner.



Figure 15. Graphical Interpretation of Ansell and Weertman's Creep Theory

The slopes of these curves are in general agreement with the published data.

With a general knowledge of this creep theory an interpretation of the results discussed earlier can be given. The slope of the room temperature curves for 0 and 2.5 vol % alumina is approximately 60 which would place the points well into the high stress region, equation 3 above, as would be expected. The 7.5 vol % alumina curve has a greater slope placing it further into the parabolic region. Hence it would be logical to expect that the curve for this alloy would change to a slope of four at a lower creep rate and, hence, have greatly superior creep properties.

The pure copper data at  $149^{\circ}$ C are extrapolated onto the published data in Figure 14. Here the transition to the region of moderate stresses can be observed which is in agreement with Weertmans<sup>27,28</sup> theory of creep in metals, of which the dispersion hardening theory is merely a modification.

#### Grain Size Effects in Copper Alumina D.

It has been shown in Section IIIB that, in the porous sintered structure, the oxide does not appear to strengthen the alloy and a discussion of whether or not the oxide exhibits a direct strengthening effect under any conditions would seem to be in order at this juncture.

The porous alloy is usually consolidated into a fully dense alloy by either hot rolling or extrusion and, in each of these processes, the distribution of the oxide is obviously modified. Consider a specimen, the cross-section of which is to be reduced by a factor of 45:1. In extrusion the diameter would be reduced by a factor of 6.7. In rolling the horizontal dimension remains approximately unchanged and, therefore, the vertical dimension is reduced by a factor of 45. Pictorially this is as follows.







b) c)

Figure 16. (a) As-sintered Cross-section Extruded Cross-section Rolled Cross-section

Hence, the following situation pertains after consolidation. In · extruded material the effective inter-particle spacing for tension testing (transverse to the extrusion direction) has a diameter approximately  $\frac{1}{7}$ of the grain size of the as-sintered material. For hot rolled material the effective interparticle spacing for tension testing is a rectangle of

horizontal dimension equal to the as-sintered grain size and vertical dimension equal to  $\frac{1}{45}$  of this.

In discussing the strength of consolidated material, one usually speaks of the ability of the second phase particles to "pin" dislocations in some way, but there is no general agreement as to the most likely mechanism. It is felt, however, that a portion, if not a majority, of the observed strengthening may be due to a simple matrix grain size effect as described by the Hall-Petch<sup>29</sup> equation.

$$6 = 6_0 + k 1^{-\frac{1}{2}}$$

where1 = mean grain diameter

k is the slope of the plot of Sagainst 1<sup>-1/2</sup> So is a lattice friction stress opposing dislocation motion and S is the stress required to maintain plastic deformation at any given strain.

This means that to produce a given amount of deformation usually requires an increase in stress as the grain size is decreased. The reason for this, in greatly simplified terms, is that the stress required to produce deformation in any given grain is not just the applied stress. There are stress concentration factors in the adjacent grains in the form of dislocation pile-ups and the actual stress, acting on a given dislocation source, is the stress at the head of one of these pile-ups. The stress at the head of a dislocation pile-up increases with an increase in length of the pile-up, at a given applied stress and, since the maximum length of a pile-up depends upon the grain size, therefore the stress concentration due to these pile-ups is smaller in a fine grained material. Hence, the external applied stress, for a given amount of deformation, would be greater in a fine grained material.

The suggestion that grain size may have a significant effect in 30 dispersion-hardened alloys was made in 1953 but little work has been done

- 29 -

on the subject since.

The only data found in the literature for pure copper <sup>31</sup> gives, at 0.005 strain,  $5_0 = 2.6 \text{ Kg/mm}^2$  and k = .36 Kg-mm<sup>-3</sup>/<sub>2</sub>. It has also been suggested<sup>32</sup> that k is likely to decrease slightly with increasing strain for pure fcc metals.

Using typical results from this work and decreasing k from .36 .30 Kg-mm<sup>-3</sup>/ $_2$  because of the larger strains at which stresses were determined, the following table was compiled.

TABLE	1
-------	---

		Stress (psi)		
		.02 strain	.05 strain	
pure copper pure copper 15 pure copper .1 2.5 vol % alumina 7.5 vol % alumina	calc. obs. calc. obs. obs.	11,700 15,000 54,000 20,000 29,000	16,600 20,100 59,500 25,000 33,500	

All the specimens used for these calculations received identical processing, including annealing, etc.

The observed values are the average of at least three points and the results have been reduced to three significant figures for simplicity as this is a semi-quantitative argument. It is easily seen, however, that the results of this piece of work could be accounted for in terms of a grain size effect.

No actual grain sizes could be determined metallographically for specimens containing alumina, and the value used, 0.1 microns, was estimated on the basis of powder particle size as explained p viously. The reason that actual grain sizes could not be measured was that the oxide dispersion caused specimens to etch preferentially, and no successful technique for revealing grain boundaries was developed. Other workers have also experienced this problem and grain bound**aries** have yet to be observed in the metallic phase of S.A.P.<sup>6</sup>

17 It has been observed by other workers<sup>17</sup>, as mentioned in the Introduction, that the final properties of artificial dispersion-hardened alloys frequently depend upon the powder metallurgical and subsequent processing variables. In particular, properties of extruded materials seem to be significantly superior to the properties of rolled materials, even for the same reduction in area. This has never been satisfactorily explained by other investigators, but in view of the above discussion on grain size effects, an explanation is offered here.

In the Hall-Petch equation, "1" is usually considered to be the mean grain diameter but, at the same time, one is usually considering equi-axed grains. It could more suitably be defined as the "effective" grain diameter. Consider the size and shape of a grain after rolling and in the absence of recrystallization. Dislocation pile-ups in the horizontal direction (see Figure 16 (c)) can be as long as they were in the as-sintered compact, and deformation should proceed at a comparatively low applied stress. The "effective" grain size for rolled material is therefore approximately that of the as-sintered compact. In extruded material, on the other hand, the "effective" grain size would be 1/7 the as-sintered grain size and the necessary external applied stress required to produce a given amount of deformation should be correspondingly higher.

- 31 -

#### E. Lead Results

It can be seen in Figure 17 (a) that the cell-like structure proposed for S.A.P. by Meyers, et al, is present in this extruded lead-lead oxide alloy. This indicates that the oxide layer (approximately 0.3 vol %, calculated as  $Pb_2$  0) on the original particles is not broken up into discrete particles during consolidation, but instead remains as an elongated, semi-continuous, cellular network. Such would not appear to be the case for the superfine 'S' lead (see Figure 17 (b)) containing approximately 20 vol % oxide calculated as Pb 0. For this alloy the oxide layer would appear to have been disturbed extensively during consolidation and is much less continuous than in the standard lead alloy. The pressure required to extrude the superfine 'S' alloy was 30,000 psi as compared to 15,000 psi for the coarser alloys and, if one accepts that 50% of the applied pressure is used in overcoming friction, there was an effective pressure of 15,000 psi on the superfine 'S' alloy and only 7500 psi on the coarser alloys. Since 7500 psi is of the same magnitude as the strength of the material, it would be logical to suppose that the coarser materials deformed largely by slip. But 15,000 psi, on the other hand, is a stress at which the particles might fragment (fracture) together with their oxide surface layers; i.e. deformation of the superfine 'S' alloys may have occurred by a combination of slip and fracture. The metallographic evidence supports this suggestion.

A similar semi-quantitative analysis to that made in the last section can be made for the lead results, remembering that the alloys were extruded at a ratio of 45:1 in this case and the grain size (transverse to the extrusion direction) would be 1/7 of the original particle size. The results are summerized in Table II.

- 32 -



# Figure 17 (a) Standard Lead. In Extrusion Direction. 4000X.



Figure 17 (b) Superfine "S" Lead. In Extrusion Direction. 4000X.

- 33 -

TABLE II

MATER IAL	U.T.S. psi	ELON. %	PART.SIZ <b>E</b> micron	'1' micron
-84. Melted and cast	1980	35	-	40
-84. As received	2460	27	100	15
-84 + ½wt% kerosene	2800	28	100	15
Standard. As received	4740	5	21	3.5
Standard +½wt% kerosene	4400	5.2	21	3.5
Superfine 'S'. As received	6600	8	2.5	.37
Superfine 'S'. Oxidized 2 hrs.	6700	7.5	2.5	.37

The calculated "effective" grain size '1', was observed to be approximately correct, on the basis of metallography, as shown in Figure 18.

The results cannot be plotted as a single curve as the strain was far from constant. It was not possible to make dependable "offset" stress determinations from the stress-strain data obtained, owing to the lack of evidence of a linear elastic region. Also, no grain size data could be found in the literature for lead.

The three materials of larger grain size (that is, excluding the Superfine 'S') are found to lie on a straight line when plotted according to the Hall-Petch relationship and, extrapolating this line predicts that Superfine 'S' should have a strength of approximately 14,000 psi as compared to 6600 psi, the experimentally observed value. It must be remembered that

Figure 18 (a) -84. Melted and Cast. 300X.



Figure 18 (b) -84 + ½ wt.% Kerosene. 300X.

in this alloy, Superfine 'S', the oxide layer is substantially less continuous than the other alloys and is, in fact, almost a discrete particle second phase. Thus the properties would be comparable to those of copper-alumina and, since these are effectively high temperature properties, dislocation climb would allow deformation to proceed more readily than if the oxide were continuous.

It is interesting to note (See Figure 18 (b)) that little recrystallization occurred across the particle boundaries in the -84 mesh extrusion. It should be remembered that this alloy contained less than 0.1 wt %oxide, calculated as Pb 0, and that kerosene was the major semi-continuous  $^2$  second phase. This brings to light an interesting possibility; namely, that if the second phase is semi-continuous, it need not necessarily be harder than the matrix to improve the mechanical properties. It seems likely that even a softer second phase, having sufficient thermal stability, may effectively prohibit grain growth, particularly if it is semi-continuous. In the case of lead-lead oxide, there is no prior evidence that the oxide is harder than the matrix and kerosene is most certainly not harder than the matrix.

#### F. Summary of Discussion

It can be seen that there is now the need to divide dispersionhardening systems into three categories depending upon the nature of the second phase.

i) Discrete, adherent particles (i.e. in overaged alloys)

ii) Discrete, non-adherent particles (i.e. copper-alumina)

iii) Semi-continuous second phase (i.e. S.A.P.)

#### 1) Room Temperature Properties

For those alloys in which the second phase is distributed preferentially along the grain boundaries (as is believed to be the case with most artificial dispersion-hardened systems) low temperature strengthening may be due primarily to a grain size effect. The dispersed phase may be said to have a secondary strengthening effect in that it controls or limits the grain size. In S.A.P. type materials the limiting grain size is the original particle size. In copper-alumina type systems the dispersed phase limits grain growth and since the dispersed particles are frequently about as close together as the original particle size of the matrix metal permits, grain size might be expected to be initially of the same order as the matrix powder particle size. There is some experimental evidence that this is so.

In the case of overaged Al-Cu and similar alloys, where the dispersed phase may occur within the grains as well as on the grain boundaries, it may well be that the necessity for cross-slip to proceed past the dispersed particles is at least partially responsible for the strengthening observed. Cross-slip in the vicinity of CuAl particles in overaged aluminum-copper 2 alloys has been observed by Nicholson, et al, <sup>33</sup> using transmission electron microscopy.

At this point it is necessary to look at the currently accepted theory of yielding in dispersion-hardened materials. Ansell and Lenel in

1960<sup>10</sup> predicted that the yield stress should vary as  $\lambda^{-\frac{1}{2}}$ , where  $\lambda$  is the interparticle spacing. This theory is based on the assumption that permanent deformation occurs in the dispersed phase. Ansell and Lenel used results of S.A.P. experiments to verify this theory and found good agreement. Since that time, however, Thomas<sup>5</sup> has shown that dislocations do not pass through a non-adherent dispersed phase provided it is significantly harder than the matrix. This result alone would therefore appear to invalidate the Ansell-Lenel theory.

However, if the present model of the structure of S.A.P. is accepted, then the interparticle spacing becomes the grain size of the matrix and the yield stress should now vary as  $1^{-\frac{1}{2}}$ , where '1' is the mean grain diameter, and this is the familiar Hall-Petch relationship. Thus the Ansell-Lenel prediction is satisfied, but fortuitously on the basis of a different model and mechanism.

2) High Temperature Properties

It is in evaluating the elevated temperature properties that dissimilarities among the three types of dispersion-hardened alloys become strikingly evident.

For the first group (overaged alloys) a marked decrease in creep strength at elevated temperatures would be expected as the second phase coarsens by solution and reprecipitation and may even dissolve at sufficiently high temperatures. This is a well verified experimental observation.

The second group (discrete, non-adherent particles) would be expected to retain their strength to some moderate temperature and then to be fairly easily deformed as grain growth and dislocation climb in the presence of these particles becomes feasible.

S.A.P. type alloys, on the other hand, would not be expected to show a marked decrease in strength up to the melting point of the major (matrix)

phase, provided that the second phase remains stable. The hardness of the second phase is, in this case, of secondary importance, as any semi-continuous medium would act locally as an insurmountable obstacle to dislocation climb.

Figure 1 shows that these arguments are well supported by experimental data. The overaged 5% Al-Cu alloy shows a marked decrease in strength at a temperature of one-half the melting point, whereas S.A.P. undergoes no marked decrease in strength at any temperature.

- 39 -

#### IV. CONCLUSIONS

40

- Dispersion-hardening alloys can be divided into three categories depending on the nature of the second phase.
  - i) Discrete, adherent particles
  - ii) Discrete, non-adherent particles
  - iii) Semi-continuous

There is not necessarily a definite boundary between these three groups.

- Room temperature strengthening of the second and third groups may be due primarily to a grain size effect.
- 3. High temperature stability of these alloys, as reflected in creep properties, is better in the third group of alloys than in the second, which is in turn better than the first group.
- 4. The cell-type structure of S.A.P., proposed by Meyer, et al, has been observed for the lead-lead oxide system.
- Constant strain rate tension tests are equivalent to constant stress creep tests.
- Concerning the behaviour of porous copper-alumina compacts, the following conclusions were drawn.
  - i) Alumina particles tend to cluster during sintering.
  - ii) The strength of as-sintered copper-alumina compacts is independent of alumina content.

#### APPENDIX I

#### Extrusion Equipment Design

The original plan for this piece of research was to study the properties of extruded, dispersion-hardened alloys. However, copper extrusions were never obtained in sufficient quantities to become an experimental material. Lead with additives was extruded successfully.

The extrusion container design utilized an automated 100 ton press available in the Department of Metallurgy and the basic specifications were as follows;

> pmax = 200,000 psi Top = 500<sup>°</sup>C I.D. = 1.00"

The basic piece of information required is the outside diameter of the cylinder and, as it is proposed to operate the press above the yield strength of any practical material, this requires the use of plastic design equations. These allow for the inner wall of the cylinder being in plastic flow but having enough material in the elastic region to prevent the cylinder from failing. The boundary between the elastic and plastic regions is the critical radius,  $r_c$ . The basic equation for  $r_c$  is derived as follows. The maximum shear design theory is used as the materials will all behave in a ductile manner.

Sy	<pre>= yield strength of material at operating temp</pre>
Sr	= radial stress
St	= tangential stress
r1	= inside radius
r <sub>2</sub>	= outside radius
Pc	= pressure at boundary between elastic and plastic regions

P = internal pressure

- 41 -

## In the Elastic Region

 $S_r = A + B$  $r^2$   $S_t = A - B$  $r^2$ 

$$\begin{array}{l} \mathbf{\hat{q}} \quad \mathbf{r} = \mathbf{r}_2, \ \mathbf{S}_r = \mathbf{0} \\ \mathbf{\hat{q}} \quad \mathbf{r} = \mathbf{r}_c, \ \mathbf{S}_r = -\mathbf{P}_c \end{array}$$

$$S_{r} = \frac{r_{c}^{2} P_{c}}{r_{2}^{2} - r_{1}^{2}} \begin{bmatrix} 1 - r_{2}^{2} \\ - r_{2}^{2} \end{bmatrix}$$
$$S_{t} = \frac{r_{c}^{2} P_{c}}{r_{2}^{2} - r_{1}^{2}} \begin{bmatrix} 1 + r_{2}^{2} \\ - r_{2}^{2} \end{bmatrix}$$

$$\begin{array}{cccc} \mathbf{e} & \mathbf{r} = \mathbf{r}_{c} & \mathbf{s}_{s \text{ max}}^{=} & \frac{\mathbf{s}_{t} + |\mathbf{s}_{r}|}{2} & = & \frac{\mathbf{s}_{y}}{2} \end{array}$$

Therefore

Pc

$$s_{y} \left[ \frac{r_{2}^{2} - r_{c}^{2}}{r_{2}^{2}} \right]$$

(1)

42 -

In the Plastic Region

 $S_r = S_y \ln r + A$  $S_t = S_y (1 + \ln r) + A$ 

r<sub>1</sub>

$$(r = r_c, S_r = -P_c)$$
  
 $(r = r_1, S_r = -P_c)$ 

 $P_c = P - S_y \ln r_c$ 

Therefore

(2)

At the interface we can equate equations (1) and (2) giving

$$S_{y} \begin{bmatrix} \frac{2}{r_{2}^{2}} & -r_{c}^{2} \\ -r_{c}^{2} \\ r_{2}^{2} \end{bmatrix} = P - S_{y} \ln \begin{bmatrix} r_{c} \\ -r_{c} \\ r_{1} \end{bmatrix}$$

which is the basic design equation.

This is a transcendental equation in  $r_c$  and P, the effective internal pressure, which would be equal to the applied vertical pressure only if the extrusion billet behaved exactly as a fluid. It was finally decided that 10% of the wall thickness could be in plastic flow and a semi-arbitrary value assumed for the yield strength of a typical hot-work tool steel. A cylinder assembly was designed as shown in Figure 19.

The various dies were made of Rexalloy and a bottom, support plate was made for each size die with just enough clearance to allow passage of the extrusion.

It was proposed to preheat the press assembly to  $500^{\circ}C$  and the billet to  $900^{\circ}C$ . Unfortunately the press assembly reached only  $400^{\circ}C$  ( a Lepel induction unit was used) and the assembly yielded at a vertical pressure of 235,000 psi.





#### APPENDIX II

#### Electron Microscopy

It is assumed that the reader is familiar with the basic principles of electron microscopy and why replicas, of the surface to be studied, must be prepared. Replicas, in this project, were prepared in the following manner.

The surface to be studied was placed in a bell jar and evacuated to approximately .1 micron Hg. If shadowing was used, it was chromium evaporated on to the surface, at an angle of 45°, to a thickness of 50-100 Å. Carbon was then evaporated on to the surface from an electrode vertically above the specimen until a layer of the desired thickness (100 - 200Å) was produced. A thicker carbon layer than those reported as usual in the literature was found necessary as the alumina retained in the replicas caused them to be extremely brittle and difficult to handle.

The replicas were then removed from the surface by etching and it is at this point that individual techniqueshad tobe developed to suit individual materials. It was always difficult to produce good replicas because of the alumina content and impossible to produce them from green surfaces as the porosity caused the replicas to break up into particles too small to handle.

A standardized technique was finally adopted which gave reasonable replicas containing the alumina particles which are, of course, opaque to electrons and therefore appear as sharply defined black spots on a photograph.

- 1) "light" shadow with chromium
- 2) "heavy" carbon layer
- 3) approximately 1 minute in  $NH_4OH$ ,  $H_2O_2$ ,  $H_0$ , etch  $\binom{1}{10}$  the strength of etch) after scratching the surface in  $\frac{1}{16}$ " squares.
- 4) approximately  $\frac{1}{1}$  minute in very dilute HNO<sub>2</sub>.
- 5) completely dry specimen

- 45 -

## 6) release replica in distilled H $_2^{0}$ .

The method used for studying the shape of loose powders presents no difficulties. A dilute slurry of the powder to be studied is placed on an extremely clean glass slide and a carbon layer evaporated on to it. This layer can be released, retaining the powder, in distilled  $H_20$ .

## VI BIBLIOGRAPHY

1.	Irmann, R., Metallurgia <u>46</u> (1952) 125-133.
2.	Orowan, E., "Dislocations in Metals" (1954) AIME, New York.
3.	Fisher, J.C., Hart. E.W., Pry, R.H., Acta Met <u>1</u> (1953) 336.
4.	Mott, N.F., "Imperfections in Nearly Perfect Crystals" (1952) Wiley, New York.
5.	Thomas, G., Nutting, J., Hirsch, P.B., J. Inst. Met. <u>86</u> (1957) 7.
6.	Meyers, C.L., Shyne, J.C., Sherby, O.D., J. Aust. Inst. Metals <u>8</u> (1963) 171 - 183.
7.	Sherby, O.D., Acta Met <u>10</u> (1962) 138.
8.	Oishi, Y., Kingery, W.D., J. Chem Phys. <u>33</u> (1960) 48
9.	Chang, R.J. J. Appl. Phys. <u>31</u> (1960) 484.
10.	Ansell, G.S., Lenel, F.V., Acta Met <u>8</u> (1960) 612-616.
11.	Ansell, G.S., Weertman, J., Trans. AIME <u>215</u> (1959) 838-843.
12.	Misra, S.K., M.A.Sc. Thesis. University of British Columbia (1963).
13.	Cochardt, A.W., J. Metals <u>9</u> (1957) 434-437.
14.	Grant, N.J., Progress in Pow. Met. <u>16</u> (1960) 99-120.
15.	Gurland, J., Trans. ASM <u>50</u> (1958) 1063-1071.
16.	Zwilsky, K.M., Grant, N.J., Trans AIME 221 (1961) 371-377.
17.	Bonis, L.J., Grant, N.J., Trans AIME <u>218</u> (1960) 877-881.
18.	Roberts, D.H., Ratcliff, N.A., Hughes, J.E., Pow. Met. (1962) 10 132-158
19.	Snowball, R.F., M.A.Sc. Thesis, University of British Columbia (1961).
20.	Kuczynski, G.C., "Powder Metallurgy." (1961) Interscience, New York. 11-29.
21.	Adamson, A.W., "Physical Chemistry of Surfaces" (1960) Interscience, New York 252.
22.	Jenkins, W.D., Digges, T.C., J. Research, U.S. Bur.Stand. 45 (1950) 153.

- 47 -

- 23. Jenkins, W.D., Digges, T.C., J. Research. U.S. Bur. Stand. <u>47</u> (1951) 272.
- 24. ASTM. Spec. Tech. Pub. #181 (1956) 22-37.
- 25. Consolidated Mining and Smelting Co., private communication.
- 26. Goetzel, C.G., Bunshah, R.H., "Powder Metallurgy." Interscience (1961) New York, 253-266.
- 27. Weertman, J., J. Appl. Phys. 28 (1957) 362.
- 28. Weertman, J., J. Appl. Phys. 28 (1957) 1185.
- 29. Petch, N.J., J. Iron & Steel Inst., 174 (1953) 25.
- 30. Shaw, R.B., Shepard, L.A., Starr, C.D., Dorn, J.E., Trans ASM 45 (1953) 249.
- 31. Feltham, P., Meakin, J.D., Phil. Mag. 2 (1957) 105.
- 32. Armstrong, R., Codd, I., Douthwaite, R.M., Petch, N.J., Phil Mag 7 (1962) 45-58.
- Nicholson, R.B., Thomas, G., Nutting, J., Acta Met <u>8</u> (1960) 172-176.