PHASE TRANSFORMATIONS IN TITANIUM-RICH ALLOYS WITH IRON AND NICKEL

by

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We accept this thesis as conforming to the standard required from candidates for the degree of Doctor of Philosophy

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THESIS

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Phase transformations have been studied in titaniumrich binary alloys with iron and nickel. Particular attention has been given to the formation and decomposition of metastable phases in powder specimens. All alloys were prepared by a levitation melting technique and precautions were taken throughout the experimental work to minimize contamination.

In the Ti-Fe system martensitic a' is produced when powder specimens containing up to 12% iron are quenched from 1000°C. The hardness of hypoeutectoid specimens increases with iron content to a maximum at 12% Fe. The eutectoid temperature for the system has been reassessed at 625 \pm 10°C. During tempering the decomposition rates of retained β phase are slow but the appearance of FeTi is accompanied by an increase in slope of the β /log time curve. The hardness of tempered alloys increases as the FeTi content increases. Contrary to the results of other investigators Ti₂Fe has been found to exist in sensibly oxygen-free alloys. This phase forms at 1000°C in crushed powder specimens but decomposes below the eutectoid temperature.

In the Ti-Ni system the constitution of quenched alloys is found to depend on both composition and cooling rate from the β range. An 'inverse stabilization' of the β phase has been observed and the 100% β phase exhibits two types of sub-structures which have been attributed to polygonization and stacking faults. The hardness of quenched alloys is higher for higher nickel contents and for faster cooling rates. Orientation relationships were observed between β and α° and a shear mechanism suggested by Burgers for Zr is proposed for this system.

Decomposition studies have shown that α breaks down by a growth-controlled process similar to that described by Johnson and Mehl. An activation energy of 84000 cal/mole has been determined and a model has been proposed which involves planar interfaces of Ti₂Ni advancing into α regions to produce a Widmanstätten-type microstructure. The self-diffusion of titanium is believed to be the growth controlling factor. Hardness values decrease with longer tempering times and higher tempering temperature.

Retained β decomposes on tempering by a two stage process:

$\beta \rightarrow \alpha'' \rightarrow \alpha + Ti_{PNi}$

X-ray diffraction data indicate that α'' has the same drystal structure as α' . The β - α ' reaction appears to be a diffusion process although reaction curves are similar to those observed for isothermal martensite formation in steels. During the first stage of the reaction ($\beta \rightarrow \alpha$ ") the hardnesses and x-ray diffraction line breadths initifally show a sharp increase, probably due to coherence between β and α'' . The reaction $\alpha'' \rightarrow \alpha$ + TioNi proceeds in a similar way to the decomposition of a : ; but with a shorter induction period for Ti2Ni formation. Further, the activation energy for the $a'' \rightarrow a$ + TipNi growth process (71000 cal/mole) is lower than that for α' decomposition. These observations suggest that Ni-rich regions exist in the a" phase and accelerate the nucleation and growth processes.

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ABSTRACT

Phase transformations have been studied in titanium-rich binary alloys with iron and nickel. Particular attention has been given to the formation and decomposition of metastable phases in powder specimens. All alloys were prepared by a levitation melting technique and precautions were taken throughout the experimental work to minimize contamination.

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X-ray diffraction data indicate that \ll'' has the same crystal structure as \ll' . The $\beta \rightarrow \ll'''$ reaction appears to be a diffusion process although reaction curves are similar to those observed for isothermal martensite formation in steels. During the first stage of the reaction ($\beta \rightarrow \ll''$) the hardnesses and X-ray diffraction line breadths initially show a sharp increase, probably due to coherence between β and \ll'' . The reaction $\ll'' \rightarrow \ll' + \text{Ti}_2\text{Ni}$ proceeds in a similar way to the decomposition of \ll'' ; but with a shorter induction period for Ti₂Ni formation. Further, the activation energy for the $\ll'' \rightarrow \swarrow' + \text{Ti}_2\text{Ni}$ growth process (71000 cal/mole) is lower than that for \ll'' decomposition. These observations suggest that Ni-rich regions exist in the \ll'' phase and accelerate the nucleation and growth processes.

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FOREWORD

Many recent studies have been carried out on the constitution of binary alloys of titanium with the transition metals. Phase diagrams for these systems are still subject to revision since slow diffusion rates are involved in most cases and it is therefore uncertain whether equilibrium has been achieved. Some isothermal decomposition curves have been developed for selected commercial titanium alloys of doubtful purity and complex composition. However, most previous workers on titanium systems have devoted little attention to metastable phases and the mechanism of their decomposition during tempering.

Non-equilibrium conditions and rate processes warrant careful quantitative study in titanium alloys since equilibrium conditions are rarely achieved in practice and, in most cases, are probably not desired. In previous work the interpretation of results has been based almost entirely on optical metallography with very little X-ray evidence to support the conclusions which have been made. In the present work extensive X-ray diffraction studies have been made and new techniques have been used for detailed analysis of transformations in Ti-Fe and Ti-Ni alloys. The occurrence of martensitic α' and retained β have been studied with particular emphasis on the effects of cooling rate and composition. Further, the decomposition kinetics of these phases have been studied quantitatively and analysed in terms of current nucleation and growth theories.

D. H. P.

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PHASE TRANSFORMATIONS IN TITANIUM-RICH

BINARY ALLOYS WITH IRON AND NICKEL

INTRODUCTION

Pure titanium undergoes an allotropic transformation at 882°C (1). The stable structure above this temperature is body centred cubic β and at lower temperatures hexagonal close-packed \checkmark . The temperature range over which each of these structures is stable can be altered by alloy additions and depends on both types and quantity of solute present (2,3). In addition, the rate of temperature change produces some interesting variations in transformation products. Three important types of phase diagrams are encountered in the study of titanium alloys; these are the eutectoid, peritectoid and beta isomorphous types. The eutectoid-type systems offer the most interesting properties from the viewpoint of heat treatment and fundamental phase transformation studies; Ti-Fe and Ti-Ni alloys fall into this classification.

The transformation of $\beta \rightarrow \alpha$ can proceed either by diffusion or diffusionless means. If a specimen is cooled quickly enough from the β range the α' phase may form from β by a shear process without observable diffusion; it is therefore considered to be a martensitic transformation. On the other hand, slower cooling may enable nucleation and growth reactions to occur in the manner characteristic of diffusion processes. In the presence of alloying elements the $\beta/\alpha + \beta$ phase boundary may be raised or lowered from 880° depending on the added elements; however in eutectoid systems the type solute always lowers the boundary. For example, oxygen raises this boundary whereas iron and nickel lower it. The presence of these elements has a marked effect on the Ms temperature and the critical cooling rate necessary to effect a martensite reaction. In some alloys of titanium the transformed β products may be formed by both shear and diffusion if cooling is not sufficiently rapid. This phenomenon is commonly observed in eutectoid systems when procutectoid phases tend to form by diffusion on cooling hypo- or hypereutectoid alloys. In some systems (e.g. Ti-Fe and Ti-Mn) the β phase will tend to be retained on quenching to room temperature if sufficient alloying element is present and if the cooling rate is fast enough. Further, proeutectoid products may exist with retained β if cooling is not rapid enough.

It is important to note that retained β , martensitically transformed β , and procutectoid constituents are all non-equilibrium phases at room temperature. The phase diagram is virtually valueless in considering these structures, because it represents only the conditions which exist at equilibrium. Equilibrium can be achieved only by infinitely slow cooling to the prescribed temperature or by prolonged holding at temperature. Even when diffusion reactions appear to be complete there may be some concentration gradients and structural imperfections still existing. It is therefore very important to use phase diagram information with a great deal of caution and to realize that it cannot tell how quickly or by what means equilibrium is approached.

Previous work (2,3) has shown that phase transformations in the various eutectoid-type titanium systems bear many similarities to one another. Some significant observations are summarized as follows:

(1) With increasing amounts of alloying element there is an increasing tendency for β to be retained at least partially on rapid cooling from the β range. At low solute contents the β may transform completely to α' (hexagonal-close-packed) by shear.

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(2) Definite orientation relationships have been observed between \checkmark and retained β in several systems.

(3) The eutectoid reaction in most systems is very sluggish, presumably due to the slow diffusion rates and large composition changes involved. In some cases, notably the Ti-Mn system (2), the intermetallic phase nearest the Ti end of the diagram does not form even after prolonged heat treatment at temperatures only slightly below the eutectoid.

(4) At cooling rates slower than critical diffusion processes may occur which will result in formation of proeutectoid constituents.

(5) The eutectoid composition and temperature vary considerably, depending on the alloy system; for example, in Ti-Fe alloys the eutectoid is at 625°C and 16% Fe, whereas in Ti-Ni alloys it is at 770°C and 5% Ni (2).

(6) Both the \checkmark' and retained \checkmark' phases are metastable and decompose on tempering to approach the constitution indicated by the phase diagram for the particular tempering temperature. The mechanisms of these processes have not been previously studied in titanium alloys. Most of the previous work in kinetics has involved quenching specimens from the \checkmark range to a lower temperature, holding at this temperature for various times, and examining the resulting structures at room temperature. In the previous work phase ratios were estimated from metallographic observations and, in some cases, qualitative X-ray checks were also made.

PART I

TTTANIUM-IRON SYSTEM

GENERAL

The titanium-iron system was selected for an initial study in order to test newly developed experimental techniques (Appendices I-IV) and to examine the suitability of the system for a detailed kinetic analysis. Early phase diagram work on this system was done by Wallbaum and associates (4,5,6) who used relatively impure titanium and encountered considerable contamination. Subsequent work on the heat treatment and constitution of titanium-rich alloys was done by Worner (7,8) who used Kroll sponge as the base for his alloys. Van Thyne, Kessler and Hansen (9) studied the phase diagram by using iodide titanium for alloys up to 30% Fe and Kroll sponge for higher iron alloys; part of their diagram is shown in Figure 1. Other work on this system has included Ms temperature determinations on Kroll spongebase alloys by Duwez (10) and an investigation of the controversial phase TigFe by Rostoker (11).

In the present investigation the constitution of quenched powders and lumps and the decomposition rates of quenched powders (-200 mesh⁴) were studied. Further, some parts of the phase diagram were re-investigated by using high temperature X-ray diffraction methods (Appendix IV). Most of this work was performed on powder specimens obtained by filing alloy ingots since they are more amenable to X-ray studies and, in addition, diffusion reactions are often more rapid in powdered specimens than in lumps. It is realized, however, that the practice of relating phase constitutions in powders to the properties of lump specimens is questionable. Powder specimens and lumps which

A Particles smaller than 74 microns were obtained by using 200 mesh Tyler screens which have openings of 74 microns. Tyler standard screens were used throughout this work for particle sizing.

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Figure 1. <u>Ti-Fe Phase Diagram after Van Thyne</u>, <u>Kessler, and Hansen (9)</u> have similar phase constitutions can have quite different appearances under the microscope (12).

EXPERIMENTAL

A series of alloys ranging in composition from 0.2 to 49.6 ^A Fe were prepared by levitation melting of iodide titanium and Johnson Matthey electrolytically prepared vacuum-melted iron. The experimental techniques including levitation melting, heat treatment, phase ratio estimation etc. are discussed in detail in the Appendices. Most heat treatments were performed on -200 mesh powders. X-ray studies of similarly heat treated powders revealed no difference in constitution for various particle sizes.

CONSTITUTION, MICROSTRUCTURE AND HARDNESS OF QUENCHED HYPO-EUTECTOID ALLOYS

Powder specimens (-200) of a series of hypoeutectoid alloys were heated to 1000°C and quenched by a blast of cold argon (Appendix II) to yield martensitic \prec' and/or retained β . The powders tended to sinter lightly at 1000°C and in order to obtain a much faster cooling rate the specimens were agitated during heat treatment to prevent sintering. There was no difference in structure between sintered and unsintered quenched specimens and hence most powders were quenched in the sintered form since this technique was much simpler. In order to compare the constitution of quenched powders with that of lump specimens a series of small alloy lumps was also quenched from 1000°C by a blast of cold gas.

Figure 2 shows the representative microstructure of \ll in a 0.2% Fe alloy powder quenched from 1000°C. The structure shows a Widmanstätten pattern of strain lines characteristic of martensite observed

a Atomic percentages are used throughout unless otherwise stated.

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Figure 2. - Photomicrograph showing $100\% \propto'$ (martensite) in a 0.2% Fe alloy powder (-200 mesh) which was quenched from 1000° C - Mag. 800X.



Figure 3. - Photomicrograph showing representative martensitic structure of a lump specimen of 0.2%Fe alloy which was quenched from $1000^{\circ}C$. - A very slight trace of β is also present. - Mag. 800X.

Etchant: Both of the above were etched in 1% HF, 1% H₂O₂ in H₂O.

in other titanium systems (13,14). Figure 3 shows the structure of \checkmark in a quenched lump specimen of 0.2% Fe content. It is evident that the structures are quite similar except that the martensite needles are slightly coarser in the lump specimen than in the small particle.

Quenched powder specimens showed 100% \prec' at iron contents less than 1%; higher alloys showed a progressively increasing tendency to retain the B phase, which agrees with general observations in other eutectoid systems (1). Figure 4 shows the variation of \prec' phase with iron content for alloy powders and lumps quenched from 1000°C. The phase ratios in lump specimens had to be visually estimated from X-ray diffraction films and, hence, are only approximations. Fairly reliable values were obtained for the constitution of quenched powders from spectrometer intensity measurements. Worner, in his work on heat treatment of Ti-Fe alloys (8), reported that quenched specimens containing more than 4% iron 'appear to consist of retained eta ' although they 'may not be strictly unaltered solid solutions' . In addition, he obtained a maximum hardness at a composition of about 4% iron. The small lump specimens $(1/8 \times 1/8 \times 1/20)$ which were quenched from 1000°C in the present work yielded similar results (see Figure 4) except that a higher maximum hardness was obtained than that reported by Worner. Further, & was detected in quenched alloy powder specimens containing up to 12% iron and hardness values increased very gradually to a much lower value than the maximum observed for lump specimens.

The difference in hardness between similarly treated powders and lumps appears to be a characteristic of specimen size. The effects of specimen size on phase transformations are controversial and it was felt that investigations on other systems than titanium alloys would be more

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Figure 4. - Constitution and Hardness of Ti-Fe Alloys Quenched from 1000°C.

fruitful; therefore the subject was not pursued in the present work.

CONSTITUTION OF HYPER-EUTECTOID ALLOYS

Several hypereutectoid alloys were heat treated at 1000°C and examined by X-ray diffraction and microscopic techniques. Both 20% and 25% alloys showed β + Ti₂Fe with larger amount of Ti₂Fe at the higher iron content. A 50% Fe alloy showed FeTi + Ti₂Fe. No quantitative estimate could be made of the amount of FeTi₂ because its complex structure is not accurately known. Due to the controversy over the existence of Ti₂Fe in the absence of interstitials a detailed investigation of this phase was carried out and is reported later in this thesis.

Information about the phase FeTi was reported by Worner (7) and some points are given here merely to supplement his information. The lattice parameter was found to be 2.978 Å \pm .001 as compared to Worner's value of 2.97 Å. The density, as determined from the above lattice parameter for a body-centred cubic structure and Avogadro number of 6.023 x 10^{23} , should be 6.52 gms/cm³. The density, as measured by a water displacement method, is 6.50 gms \pm .03. No ordering was observed in FeTi produced in slowly cooled powders.

EUTECTOID TEMPERATURE

It is valuable to know the eutectoid temperature with reasonable accuracy since it is the maximum temperature at which quenched structures can be safely tempered. A 12% as-cast iron alloy containing $\beta + \alpha'$ was studied by high-temperature X-ray methods. This alloy was selected because it was near the eutectoid composition and would, therefore, yield sufficient FeT⁴ for easy detection by X-ray diffraction. Reflections of FeTi were first detected at about 500°C on heating and subsequent observations were made by measuring the intensity of the 110 reflection. The observed amount of FeTi increased with a corresponding decrease of intensity of α_{101} and β_{110} . At 625°C an equilibrium condition was reached whereby the phase quantity did not change over a three hour period. At higher temperature the FeTi line began to disappear.

The transformations of the same alloy were studied on cooling from 1000°C where the structure is initially $100\%\beta$. The Θ range over which the FeTi₁₁₀ would be expected was repeatedly scanned. A broad, low intensity reflection was observed after 20 minutes at 600°C which resolved into a fairly sharp peak after two hours at temperature. It is evident that 600° must be below the eutectoid temperature. The slowness of the reaction is a further indication of the low diffusion rates in the Ti-Fe system.

BECOMPOSITION OF \checkmark AND β

Since diffusion reactions in the Ti-Fe system were found to be extremely slow, detailed studies of the decomposition of \checkmark and β were not attempted. Subsequent work on Ti-Ni alloys revealed this system to be much more satisfactory for kinetic studies. Consequently detailed discussion of the kinetic approach in studying tempering reactions is reserved until later in the report of Ti-Ni work. Some useful information was obtained for partial decomposition of quenched Ti-Fe powders and this is presented here.

The quenched powder specimens were tempered at 570°C for various periods of time in order to study the rate of decomposition of retained β . The $\#\beta$, # FeTi and combined $\#(\propto + \propto')$ as determined from X-ray line intensities are shown in Figure 5 for a series of tempered alloys. The reactions involved in tempering are as follows:

It can be seen from Figure 5 that the slope of the β breakdown curves increases with increasing iron content, which can probably be attributed to the higher percentage of β present in the quenched form. Alloys containing below 6% Fe display discontinuities in their β decomposition curves when FeTi is first detected. This is probably due to the incubation period required for the formation of FeTi nucleii during which the growth reaction is not detectable. Subsequently, the growth of these FeTi nucleii proceeds with the accompanying formation of \ll ; both of these reactions proceed at the expense of the β phase which decomposes. Accordingly, the percent β decreases more rapidly with the increase of $\% \ll$ and % FeTi.

The ratio of FeTi: \propto after 1000 hours tempering is much higher than would be expected from the phase diagram. This seems not unreasonable since the presence of β and \propto' means that the system is out of equilibrium and, hence, further tempering would favour the formation of \propto from these metastable forms to produce equilibrium phase ratios.

Hardness measurements made on alloys tempered for 1000 hours are plotted in Figure 6. Note that the hardness increases quite regularly with iron content and also increases consistently with % FeTi which is also shown on the graph.

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Figure 5. - Constitution of Ti-Fe alloys tempered at 570°C. The alloys contained from 0.2 to 15.31%iron. The rates of breakdown of β and rates of formation of FeTi are indicated.



Figure 6. - Hardness of alloys tempered at 570°C for 1000 hours.

THE PHASE Ti2Fe IN Ti-Fe ALLOYS

Introduction

Previous work has created some controversy over the existence of the phase Ti₂Fe in binary Ti-Fe alloys. In early work, Wallbaum and co-workers (4,5,6) reported a phase Ti₂Fe which was face-centred-cubic with 96 atoms per unit cell. In later work Duwez and Taylor (15) supported Wallbaum's results and found the lattice parameter to be 11.305 kx. Worner (7) in his investigations failed to produce the phase Ti₂Fe. It is significant that all of these investigations utilized relatively impure titanium. In the more recent work on the Ti-Fe system by Van Thyne et al (9) both high purity iodide titanium and Kroll sponge were used. Ti₂Fe was not produced and hence, Worner's contention that the phase Ti₂Fe occurs only in the presence of oxygen and proposes a composition range Ti₄Fe₂O to Ti₃Fe₃O.

In a preliminary study of hypereutectoid Ti-Fe alloys the present author observed the phase Ti₂Fe by means of X-ray diffraction methods on heat treated specimens. High temperature diffraction studies indicated that the phase occurs between the eutectoid and eutectic temperatures. Examination of an as-cast 25% Fe alloy failed to reveal Ti₂Fe but the phase did appear in crushed powders of the same alloy after heat treatment in purified argon, purified helium or in vacuo at 1000°C. Identical heat treatments performed on pure titanium indicated insignificant amounts of oxygen contamination. Rostoker determined the 1000°C isothermal section of the Ti-Fe-O system and maintains that at least 2% O is necessary for the co-existence of Ti₂Fe with β and FeTi. This contention led to a detailed study of the characteristics of the phase.

Experimental

An alloy corresponding to the composition Ti₂Fe was prepared by levitation melting from pure iodide titanium stock and pure iron. Powder specimens were prepared by crushing and the -200 mesh fractions were used in subsequent heat treatments. Heat treated powder specimens were remelted by supporting the sintered specimen in an induction field on a molybdenum wire.

The maximum amount of contamination due to heat treatment was established as 0.07% (atomic) oxygen by hardness measurements made on identically treated Ti-Fe filings. Scratch hardness tests, which were performed on numerous specimens, failed to reveal any variation of hardness from edge to centre of particles. Any oxygen-rich surface layers would be detectable by this test.

Discussion of Results

X-ray diffraction examination of the as-cast alloy (crushed to powder) revealed FeTi and β phases. In spite of the brittle nature of the alloy, diffraction peaks were very broad, implying considerable internal strain in the powder. Microscopic examination of the powder showed massive primary dendritic FeTi and a eutectic of FeTi and β (see Figure 7). Reference to Worner's phase diagram for the system indicates that this structure would be expected in the 33.3 atomic Fe alloy.

After heat treatment at 1000°C for three hours crushed powders of the as-cast alloy showed new X-ray diffraction lines of Ti₂Fe. The phase had formed at the expense of some β and FeTi. The quantity of the new phase could not be measured from line intensities because of its complex crystal structure. Microscopic examination revealed a coarse structure (Figure 8) in which only two phases were discernible. However, much of the

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eutectic seemed to have disappeared due to coagulation and the grain boundaries of FeTi etched heavily.

It therefore appeared that although TigFe was not produced in an as-cast structure, it could be formed by heat treating a crushed powder. To check this surmise, the heat treated powder specimen (containing TigFe) was remelted, crushed and examined. X-ray spectrometer plots showed that the phase TigFe had almost completely disappeared. As the experimental techniques merely allowed the material to be brought just to the fusion point and then cooled, it is not surprising that a trace of TigFe remained, for the centre of the sample may not have melted. A photograph of a particle of the remelted and crushed material is shown in Figure 9.

While heat treated crushed powders (-200 mesh) produced the phase Ti₂Fe, small lumps broken from the as-cast ingot did not show Ti₂Fe diffraction lines after 24 hours annealing at 1000°C. The microstructure (Figure 10) shows that the eutectic has disappeared, presumably due to the diffusion of FeTi to the dendrites.

It is believed that the difference in behaviour of lumps and powders can be attributed to one of two reasons:

(a) The powder is susceptible to oxidation and the phase Ti_4Fe_2O could be formed, as suggested by Rostoker (11). A lump sample having a smaller surface-to-volume ratio may be less likely to react with oxygen so readily.

(b) The powder is strained and hence is in a more susceptible condition for reaction between FeTi and β . If the driving force of the reaction FeTi + $\beta \rightarrow \text{Ti}_2\text{Fe}$ is insufficient to surmount the activation barrier it may be necessary to induce the reaction by strain. Such a mechanism is believed to exist for example in the system Fe-Ni where metastable γ can only be





Figure 7. - Microstructure of crushed powder of 33.3% Fe alloy, as-cast - Mag. 800X

Figure 8. - Microstructure of crushed 33.3% Fe alloy after heat treatment for 3 hours at 1000°C - Mag. 800X



Figure 9. - Microstructure of 33.3% Fe alloy which was heat treated at 1000°C, remelted, and crushed. - Mag. 800X



Figure 10. - Microstructure of crushed powder taken from lump specimen which was heated 24 hrs. at 1000°C. - Mag. 800X.

Etchant: Etched in 1% HF, 1% H2O2 in H2O.

transformed to the stable \checkmark phase by cold work in addition to appropriate heat treatment.

The first possibility of oxidation is ruled out on the following grounds:

(1) Checks made on titanium powder (see section headed 'Contamination') showed insignificant oxygen pick-up. Further hardness tests showed that a small lump of titanium acquired as much oxygen as the 200 mesh powder.

(2) If the heat treated powder samples contained Ti_4Fe_2O , the oxygen would remain in the specimen on remelting. This remelted material was heat treated in lump form at 1000°C for one day - a treatment which is known to produce Ti_4Fe_2O if sufficient oxygen is present. Therefore, if the Ti_2Fe in the original heat treated powder is, in fact, the oxygen-containing phase then no less of this phase should appear in the remelted lump, heat treated at 1000°C. However, only a small trace of the phase was produced under these circumstances and this can be attributed to incomplete fusion during the remelting operation. The cycle of operations including melting, crushing, heat treating to produce Ti_2Fe , remelting, and re-annealing in lump form was made on several samples with similar results.

The second possibility, described in (b) above, was confirmed by stress-relieving the as-cast crushed powder just below the eutectoid temperature for 65 hours. Even after this period, the structure remained in some state of strain, as indicated by broad diffraction peaks. However, on subsequent heat treatment at 1000°C for three hours the relieved powder showed considerably less Ti₂Fe than the unrelieved powder which had been held at 1000°C for three hours. An approximate estimation indicated that the amount of Ti₂Fe produced in the stress-relieved powder was about one half that in the unrelieved specimen.

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Margolin's Work

Recent work by Margolin (16) on lump specimens has confirmed the existence of Ti_2Fe in the absence of significant interstitial contamination. His results offer sufficient agreement with the present work to refute the conclusions of previous investigators that Ti_2Fe exists only in the presence of greater than 2% oxygen at 1000°C.

TI-Fe SYSTEM, SUMMARY AND CONCLUSIONS

(1) Martensitic $\not\ll'$ is produced in Ti-Fe alloys containing up to 12% iron which have been argon-quenched from 1000°C.

(2) Retained β decomposes very slowly at 50°C below the eutectoid but the rate increases with higher iron contents. The slope of the β versus log time curve increases as the presence of FeTi is detected.

(3) The tempering curves at 570°C indicate a very slow rate of formation for FeTi. Hence complete decomposition of β would involve extremely long heating times even at the eutectoid temperature. For this reason it was decided not to make a more detailed kinetic analysis on the Ti-Fe alloys. It has been suggested by Jaffe (17) that the early appearance of FeTi reported by the present work (18) may explain the brittleness encountered in commercial Ti-Fe alloys subjected to moderately high operating temperatures.

(4) The hardness of tempered alloys increases with FeTi content.

(5) High temperature X-ray diffraction studies have established the eutectoid temperature at $625^{\circ} + 10^{\circ}C$.

(6) The density and parameter of FeTi have been determined to be $6.50 \text{ gms/cm}^3 \pm 0.03$ and $2.978 \text{ \AA} \pm 0.001$. No ordering has been found.

(7) Ti₂Fe is produced in sensibly oxygen-free specimens which are coldworked and heat treated in the range between eutectoid and eutectic temperatures. Unstrained material does not appear to produce Ti₂Fe and this is in accordance with some results of previous investigators. However, Ti₂Fe cannot be nucleated from the melt and hence it appears difficult to amend the phase diagram. It appears that Ti₂Fe cannot be distinguished microscopically from FeTi and β when customary etching reagents are used.

(8) The effect of specimen size on the-martensite reaction has been studied. The hardness of as-quenched alloys appears dependent on particle size since Worner's results for lump specimens were confirmed. The hardness maximum of powders and lumps appears at a composition where the formation of \ll' has all but ceased. Appearance of the martensitic structure is essentially similar in both powders and lumps. It is significant that the martensite structure in Ti-Fe alloys is not a hard phase like the martensite observed in steels. The hardness of Ti-Fe quenched structures is greater when there is a great deal of internal strain which will be the case when the \ll' reaction is on the verge of occurring. It therefore appears that these strains are relieved at least partially by the shear transformation.

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PART II

TITANIUM-NICKEL SYSTEM

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GENERAL

In view of the slow decomposition rates observed in Ti-Fe alloys and the similar behaviour reported for the Ti-Mn system (19) it was decided to work on a system with a higher eutectoid temperature and lower eutectoid composition. Work by other investigators (1) suggested that metastable phases in such systems experience fairly rapid decomposition in tempering or interrupted quenching. The Ti-Ni system was selected for this study since it has a eutectoid temperature of 770°C, a eutectoid composition of 5% Ni, and, in addition, the phase diagram is known with reasonable certainty (1).

Previous investigations of Ti-Ni alloys were devoted primarily to phase diagram studies; relatively little attention was given to metastable phases and tempering processes. Early work by Wallbaum (4,5,6) on alloys prepared by powder metallurgical techniques and later efforts by Long et al (20) who used Kroll sponge titanium resulted in tentative phase diagrams. However these did not represent true binary conditions since their alloys were contaminated by oxygen and nitrogen. The most recent diagram (Figure 11) is due to Margolin et al (21) and a slight modification of the $\propto +\beta/\beta$ transus (shown dotted in Fig. 11) has been proposed by McQuiilan (22).

Margolin et al (21) reported the formation of a martensite phase (close-packed hexagonal \checkmark') in rapidly cooled lump specimens of titanium-nickel alloys of low nickel content. With increasing nickel content an increasing tendency to retain the β phase (body-centred cubic) was observed and at 7% nickel 100% β was retained. McQuillan (22) has studied the effect of delay time before quenching on the microstructure of a hypo-eutectoid alloy. This delay time results in slow cooling from the β to $\checkmark + \beta$ zone before rapid quenching to room temperature. He has included a series

- <u>2</u>4 -



ATOMIC · PERCENT Ni

Figure 11. - Phase Diagram of the Ti-Ni System after Margolin et al (21).

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of micrographs in his paper which show the formation of increasing quantities of precipitated alpha due to progressively greater delay times before quenching. McQuillan also pointed out that the $\propto + \beta /\beta$ transus reported by Margolin et al is higher than it should be due to the inherent delay involved in the quenching method used in their phase diagram investigation.

In the present work on Ti-Ni alloys similar techniques to those used in the Ti-Fe work have been used to study the formation and decomposition of metastable phases.

EXPERIMENTAL

Alloys ranging from .25% Ni to 18% Ni were prepared by levitation melting from iodide titanium and Johnson Matthey spectrographic grade nickel. Most of the subsequent work was performed on powder specimens ranging from +65% to -200 mesh by using techniques described in the Appendices. X-ray diffraction and microscopic studies of screened specimens which received a common heat treatment revealed no difference in constitution for particle sizes ranging from -48 to -200 mesh.

Specimens of -200 mesh compacted quite readily during heat treatment at 1000°C unless they were continuously rotated to inhibit sintering (see Appendix II). Filings of +65 mesh did not sinter readily and, consequently, were quenched more rapidly since individual particles were contacted by the quenching gas. During the course of heat treatments on each alloy above 2% nickel it was observed that the constitution of powders quenched in helium differed from that of powders quenched in argon. This difference was found to be caused by the different quenching rates. Specimens of -200 mesh and +65 mesh were quenched in the sintered and unsintered condition by

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⁺⁶⁵ mesh powder corresponds to oversize material from 65 mesh screens (openings of 208 microns).

both argon and helium. This work revealed that the difference in constitution is definitely due to cooling rate and not due to particle size effects. The different quenching rates and measurement of relative rates are discussed in Appendix II.

CONSTITUTION, MICROSTRUCTURE, AND HARDNESS OF QUENCHED ALLOYS

A series of alloy powder specimens in the composition range up to the solid solubility limit of Ni in β titanium (approximately 11%) were quenched from the β range and examined by X-ray diffraction and metallographic methods. Alloys were heated to 1000°C prior to quenching with the exception of some of the hypereutectoid compositions which required slightly lower soaking temperatures to avoid incipient melting. No differences were observed in the quenched products for a given alloy when the soaking time was increased from one minute or when the holding temperature was varied within the β range.

Samples containing less than 2% nickel showed a completely hexagonal close-packed transformed- β structure after either argon or helium quenching. This structure is believed to be martensitic and is designated α' , as in other titanium systems. Compositions greater than 2% Ni showed differences in constitution with varying quenching rate. Argon quenched sintered specimens (i.e. the slowest quenching rate used) produced $100\% \alpha'$ in alloys up to 6% nickel. However, the more rapid helium quench of sintered and unsintered powders retained increasing amounts of β in alloys containing more than 2% nickel (Fig. 12). $100\% \beta$ could be retained by helium-quenching an unsintered specimen containing 6% nickel.

Figure 13 shows a typical Widmanstätten pattern of strain lines in a structure consisting entirely of \checkmark' . The microstructure becomes progressively finer with increasing nickel content - an observation

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ATOMIC PERCENT NICKEL

Figure 12. - Graph of V.P.M. Hardness versus composition for as-quenched sintered alloy powders; and percentage retained β versus composition for the helium quenched specimens. that has been made in the Ti-Cu system (23).

Investigation of alloys in the vicinity of 11% nickel (the limit of solubility of nickel in β titanium) showed that Ti₂Ni precipitated in powders regardless of the quenching speed from 950°C. Presumably the diffusion rates are quite rapid at the temperature of the β/β + Ti₂Ni boundary. High temperature X-ray goniometry studies (Appendix IV) confirmed the existence of 100% β at 950°C in an 11% nickel alloy. The following reactions were observed during heating and holding at 950°C.

100% β was produced within a few seconds at 950°C and after approximately one minute at temperature the base of the β peak broadened and the intensity gradually decreased, suggesting that incipient melting occurred.

Water quenching a lump of the 11% alloy retained a completely β structure; this suggests that the precipitation of Ti₂Ni is more rapid in powders than in lumps since the gas quenching of powders is considerably faster than water quenching of lumps.

Stabilization of the β phase was not observed in either hypoeutectoid or hyper-eutectoid alloys when cooling rates slower than the argon quench were employed. The retained β phase in a 6% Ni alloy remained untransformed on subsequent cooling to liquid oxygen temperature; nor could a martensitic transformation be induced by cold working powders at room temperature prior to sub-zero quenching.

Hardness measurements were made on powder specimens quenched in argon and in helium. A Bergsman microhardness tester with 10 gm. loads was used. The variation of microhardness with composition for -200 mesh alloy powders quenched by helium and argon in the sintered condition is shown in

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Figure 13. - Photomicrograph showing 100% \checkmark structure in a 1% Ni alloy powder which was quenched from 1000°C - Mag. 800X.

Etchant: Etched in 5% HF in H20 - HNO3 rinse.

Figure 12. The % retained β in the helium quenched specimens is also shown on the graph and it is apparent that this more rapid quench retains β more readily and produces higher hardness values than the argon quenched powders. In alloy powders containing 6% Ni and above, it was possible to completely suppress the transformation of β by quenching in the unsintered form. The results indicate that the presence of a mixed structure $\alpha' + \beta$ leads to higher hardness values at a given composition. For example, in the 6% alloy a helium quenched sintered specimen contains $80\% \alpha'$ and $20\% \beta$; it has a hardness of 475 V.P.N. The unsintered specimen, with a correspondingly faster quenching rate, shows 100% retained β and has a hardness of only 390 V.P.N. An argon quenched sintered specimen (slowest quench) of the same alloy contains 100% α' and has a hardness of 430 V.P.N.

CONSTITUTION OF RETAINED β Phase

Sub-boundaries

A photomicrograph of retained β in a quenched 6% Ni alloy is reproduced in Figure 14. In this structure a pronounced network of subboundaries which occurred in many grains is visible. Figure 15, which was taken at high magnification (1500 X) shows adjacent β grains in another 6% quenched powder; one grain contains marked intra-crystalline boundaries and the other is completely free from any sub-structure. The sub-crystals appear to have fairly regular shapes - which suggests a regular orientation relationship among them. Tempering the retained β structure eliminates the sub-structure at an early stage of β decomposition.

Ogden et al (19) have previously observed sub-boundaries in the β phase of a Ti-Mn-N alloy; but this structure was attributed to nitrogenrich \propto precipitation. The nitrogen content of the Ti-Ni alloys does not



Figure 14. - Photomicrograph of 100% β in a quenched 6% Ni alloy powder - Note the substructure within the β grains.- Mag. 800X



Figure 15. - Photomicrograph showing two adjacent grains of 100% retained β in a quenched 6% Ni alloy; one grain exhibits subboundaries but the other is apparently free from any sub-structure - Mag. 1500X

Etchant: - Etched in 5% HF in H20 - HNO3 rinse

exceed .02% and, in addition, the quenching rate was sufficiently rapid to suppress precipitation reactions. Further, X-ray diffraction results have confirmed the absence of any second phase which might account for this phenomenon. Therefore it seems unlikely that this phenomenon is explicable in terms of nitrogen content.

At the present time it is possible only to conjecture an explanation for this sub-boundary phenomenon since very little work has been reported on sub-structures resulting from phase changes. It is believed that the present phenomenon is due to polygonization resulting from unrelieved stresses set up during the $\prec \rightarrow \beta$ transformation on heating. Since some Ti₂Ni is also present, the reaction on heating is:

$$\alpha + \mathrm{Ti}_2\mathrm{Ni} \rightarrow \beta$$

In hypereutectoid Ti-Ni alloys the $\prec \rightarrow \beta$ reaction possibly proceeds before Ti₂Ni starts to decompose. If the $\prec \rightarrow \beta$ reaction is fairly rapid strains may be induced in the β grains which could lead to polygonization during soaking. A similar type of process is believed to cause the 'alpha veining' observed in ferrite (24). Subsequently when Ti₂Ni decomposes, nickel atoms diffuse into the β phase and the vacancy flow involved could assist in the movement of dislocations necessary to form low angle boundaries. The mechanism of polygonization is believed to involve climbing of edge dislocations out of their slip planes in order to change their grouping (25) - a process which involves vacancy diffusion and which can only occur at high temperatures where self diffusion is rapid.

Faulting

A second type of sub-structure has been observed in retained β during the course of this work. This structure has a twin-like appearance

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Figure 16. - Photomicrograph of retained β showing the twin-like sub-structure observed in some grains and attributed to clusters of stacking faults - Mag. 800X

Etchant: - Etched in 5% HF in H2O - HNO3 rinse

(Figure 16) and does not occur in all specimens. It usually appears in grains which do not show the previous type of sub-boundaries. A similar type of structure, observed by Barrett (26) in Cu-Si alloys, has been attributed to clusters of faults separated by relatively perfect crystal layers. Such a structure indicates the presence of internal strains caused by quenching stresses.

The appearance of faults in a body-centred cubic structure is rather unusual but not impossible. Stacking faults in this system are believed to occur along $\{112\}$ planes (27) and could conceivably cluster to give the twin-like microscopic appearance. Faults are generally expected when a transformation is on the verge of occurring or has just started. It is pointed out in the next section of this thesis that the Burgers shear mechanism for the transformation of a hexagonal close packed structure to bodycentred cubic (28) satisfies the observed orientation relationships. This process involves shear on the {112} planes of the body-centred cubic. In the retained $oldsymbol{eta}$ structures examined in this investigation the martensite reaction which produces \prec' occurs very readily with slower quenching rates, due to the 'inverse' nature of $oldsymbol{eta}$ stabilization in Ti-Ni alloys. Consequently, faulting on $\{112\}$ planes might be possible in specimens in which the martensite transformation has not been detected by X-ray methods but which may, nevertheless, have been initiated.

ORIENTATION RELATIONSHIPS

Introduction

The crystallographic relationship between martensitic \prec and retained β has been studied in alloys of titanium with Mn, Mo, Cr and Fe

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(29, 30, 31). In these studies the habit planes of the martensitic phase were determined as well as the planes parallel to each other in the two phases. The following habit planes were found:

'	TA	BLE	Ι
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SYSTEM	HABTT PLANE	REFERENCE
Ti - Mo	{334} ₆ {344} ₆	Liu (29)
Ti - Cr	{334 }	Liu (29)
Ti - Fe	{334} _{\$}	Liu (29)
Ti - Mn	{334} _{\$\$} {344} _{\$}	Liu and Margolin (28)

Liu has also found that orientation relations listed in Table II exist for the $\{334\}_{\beta}$ and $\{344\}_{\beta}$ habit planes.

TABLE II - ORIENTATION RELATIONSHIPS

HABIT PLANE	ORIENTATION
{334} _A	(110) B 11 (0001) X'
• •	$[111]_{\beta}$: $[11\overline{2}0]_{a'}$ 0 - 1/2.
{344} SPEC.	A $(1\bar{1}0)_{\beta}$: $(0001)_{\alpha'}$ approx. 14*
. 1	[110] ; [10] d' approx. 1.
SPEC.	B (110) β (0001) α'
	$[111]\beta$: $(11\overline{2}0)\alpha'$ approx. 1°

Liu has found that, in an alloy exhibiting two martensite habit planes, it is the temperature of martensite formation and not the nature of any externally applied stresses or quenching stresses (i.e. compression or tension) which determine the particular habit plane.

Orientations in Ti-Ni Alloys

In the present research program orientation relationships in a Ti-Ni alloy have been determined from spotty X-ray films (32). This method enables the use of polycrystalline specimens so long as their grain size is large enough to avoid continuous diffraction lines on the films. In this method use is made of the fact that parallel diffraction spots from the two phases indicate parallel planes in these phases. Parallel spots must necessarily occur in adjacent lines on account of the similar \mathcal{A} values necessary for parallelism of planes. Film exposures were made in a Unicam single crystal camera with specimen oscillations of 5°, 10° and 15°.

The following parallelisms were detected on diffraction films of an 8% Ni alloy:

B	d
{011 }	{0002}
{200}	{ 1012 }
{ 111 }	{21 30}
{ 211 }	{1013}

In order to check the relationships and also to determine fairly complete orientation relationships the (Oll) stereographic projection of a body centred cube (Figure 17) was superimposed on a standard (OOOI) projection of a hexagonal structure with $\frac{c}{a}$ of 1.58 (Figure 18). The crystallographic angles for titanium and zirconium (hexagonal close packed) have been reported by McHargue (33). The projections revealed that the observed parallelisms were possible. The following pole projections were coincident and hence indicative of parallel planes in the two phases:



Figure 17. - Stereographic projection of a cubic cell on (Oll)

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STANDARD (0001) PROJECTION FOR HEXAGONAL TITANIUM $\frac{C}{a} = 1.587$

Figure 18. - Stereographic projection of a hexagonal cell on (0001) for c/a = 1.587

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B	<u> </u>		•
(2 11)	(1010)	-	
(211)	(1010)		
(121)	(1013)	approx.	2•
(112)	(1013)	approx.	2 •
(111)	(2130)		
(111)	(1210)		
(111)	(2130)		
(111)	(1210)		•
(2 12)	(1102)		-
(001)	(0112)	approx.	4 •

Mechanism

A shear mechanism that produces the observed orientation relationships between β and α' has been proposed by Burgers (28) for zirconium. In this mechanism transformation is proposed to occur by heterogeneous shear on the $\{112\}\beta$ planes in the $[11\overline{1}]\beta$ direction. Burgers arrived at this mechanism since the atomic configuration in the (112) plane of the bodycentred cubic is exactly the same as that in the (10\overline{10}) of a close-packed hexagonal of the same atomic radius. The pattern on both these planes is a rectangle $\frac{d \times 2 \sqrt{2} d}{\sqrt{3}}$. The hexagonal structure is formed by displacement of (112) planes relative to each other. Since the spacings of the (112) planes and the (10\overline{10}) planes to which they transform are not equal an exact hexagonal array cannot be formed by pure shear. The observed orientation relationships are approximately attained by the proposed Burgers mechanism.

Other transformation mechanisms involving multiple shear processes have been considered for the $\beta \rightarrow \prec'$ reaction but these are not considered satisfactory or logical since a transition structure is involved. One such mechanism suggested by Burgers (28) does not satisfy all the orientation relations. It is therefore believed that the single shear on $\{112\}\beta$ applies in the $\beta \rightarrow \alpha'$ transformation in Ti-Ni alloys.

EFFECT OF QUENCHING RATE

The generally accepted theories of diffusionless transformations do not satisfactorily explain the fact that a more rapid quenching rate tends to retain the high temperature phase in some systems, while a slower quench produces a martensitic structure. In Ti-Ni alloys this effect is most marked in the 6% alloy, which may produce a structure consisting entirely of retained eta or of lpha' . The retention of a high temperature phase by rapid quenching (while slower quenching produces martensite) has also been observed in some iron alloys by Kurdjumov and Maksimova (34). They showed that shear processes could be suppressed and that martensite tended to form isothermally on holding below the Ms temperature. Kurdjumov and Maksimova's results were subsequently confirmed by Cech and Hollomon (35). Of even greater interest are some recent studies of Philibert and Crussard (36) on martensite transformation in hypereutectoid steels. They have shown that less martensite forms with more rapid cooling rates and referred to the phenomenon as 'inverse stabilization'. In their work they suggest that 'martensite nucleation is not athermal but due to thermal fluctuations so that all the martensite can be considered as forming in isothermal increments'. In view of these very important results it is evident that the reaction path theory (37) and theories due to Fisher, Hollomon, and Turnbull (38) cannot be applied to all systems. The observation of 'inverse stabilization' is sufficient in itself to indicate the need for a unified theory since it refutes the idea of athermal nucleation and, further, has modified our concepts of

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isothermal nucleation of martensite. Although Philibert and Crussard studied steel specimens their observations are certainly of no less general applicability than the existing theories.

The question may legitimately arise as to whether the \swarrow' formed by argon quenching is, in fact, martensite. This pertinent query has been raised by Margolin (39) and Jaffee (40). The following observations support the proposal of a martensitic reaction:

(a) The strained appearance of the structure and its broad X-ray reflections are consistent with a structure formed by a shear process.

(b) If the phase were \prec rather than \checkmark' a second phase Ti₂Ni would conceivably precipitate simultaneously. This might not be detectable by X-ray or microscopic techniques, but on subsequent tempering there would be no induction period prior to the growth of Ti₂Ni platelets. Reference to Figure 20 shows that an induction period is actually experienced.

(c) If a diffusion reaction occurred the hypereutectoid 6% Ni alloy would probably precipitate Ti₂Ni rather than \checkmark . No Ti₂Ni was detected in quenched specimens of this alloy.

(d) If on the other hand, proeutectoid \propto formed out of equilibrium, then β remaining at early stages of the quench would be of higher than average solute content and should be retained. No β is retained in the 6% alloy unless faster quenching speeds are used.

ISOTHERMAL DECOMPOSITION STUDIES

Introduction

It is necessary to know the mechanism and rate of decomposition of metastable phases before alloys can be sensibly heat treated or subjected to elevated temperatures in service. The tempering kinetics of some important

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ferrous alloys have been studied in detail (41-45) by applying theories of diffusion and precipitation developed by Johnson and Mehl (46) and Zener (47). This work included decomposition studies of retained and martensitically transformed austenite as well as graphitization in cast irons. Most of this previous research has been concerned with interstitial alloying elements (C,N) in materials of complex commercial compositions. In the present work, since it was possible to retain 100% β or produce 100% transformed β in the same alloy by simply varying the cooling rate, it was decided to compare the decomposition mechanism of these phases without the usually inherent complication of different composition. Hence, in this work, the composition of α' is believed to be identical to that of retained β but the atomic configurations are quite different (close-packed hexagonal and body-centred cubic respectively).

In studying decomposition processes it is necessary to emphasize that non-equilibrium conditions exist until the reaction is completed. Deviation from equilibrium is essential to provide a driving force for the reaction and the only place where equilibrium can be assumed to exist is at a reaction interface where for the Ti-Ni system, the following relationship holds for the nickel content in phases I and II:

 $(\mathcal{M}_{Ni})_{I} = (\mathcal{M}_{Ni})_{II}$ $(\mathcal{M}_{Ni} = \text{chemical potential of Ni}$ or $\left(\frac{\partial F}{\partial C_{Ni}}\right)_{I} = \left(\frac{\partial F}{\partial C_{Ni}}\right)_{II}$ $\frac{\partial F}{\partial C_{Ni}} = \text{partial molar free energy of Ni.}$

In the structure away from the reaction interface there are such metastable conditions as concentration gradients or structural imperfections which must be removed before equilibrium is achieved. In precipitation processes in alloys the diffusion reactions involve concentration gradients which are levelled by transport of solute atoms to the matrix - precipitate interface. This results in growth of the precipitate by the advance of the interface. The diffusion equations for reactions of this type have been studied theoretically by Wagner (48). However, quantitative solution of a diffusion equation is almost hopeless in practice due to the irregularities in concentration gradients and complications introduced by structural imperfections. The directional solidification of a melt offers an interesting analogy to the reaction between two solid phases. In this simpler case quantitative study is possible in some cases because a single interface can be observed and moved under carefully controlled conditions. The solute distribution about a solid-liquid interface during solidification has been studied by Chalmers et al (49).

It is possible in many cases to describe the intermediate stages of a solid phase reaction by a general rate equation from which an energy of activation can be determined. Precipitation reactions proceed by nucleation and growth mechanisms which are independent of each other and either may control the overall rate of a reaction. Consequently if an activation energy calculated for a particular reaction is to be compared with values obtained for other systems the processes must be similar. In many nucleation and growth reactions either of the steps may make a negligible contribution to the activation energy in comparison to the other. This is notable in such reactions as some isothermal martensite processes where nucleation is the dominating factor in the transformation. Also, in some precipitation and recrystallization processes the extent of transformation is determined by the growth rate of existing centres or nucleii which may be formed during the incubation period. Some reasonable assumptions and simplifications are necessary if useful information about the kinetic mechanisms is to be obtained.

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As previously indicated, it was possible to produce 100% transformed β (called \propto') in Ti-Ni alloy powders (-200 mesh) containing up to 6% Ni by quenching them from 1000°C with a blast of purified argon. Specimens of higher Ni content showed some retained β after quenching. Metallographic examination of completely transformed β specimens revealed pronounced strain patterns (Figure 19) which are typical of martensitic structures

Decomposition of K

observed in other Ti alloys (13, 14, 18). No other phase was detected by X-ray diffraction studies.

The 6% Ni alloy was particularly useful for the present study for the following reasons:

(1) It was possible to retain 100% β or produce 100% \prec' by varying the cooling rate from the β range for the alloy.

(2) Phase ratios could be assessed more accurately than in alloys of lower nickel content.

The phase diagram of the Ti-Ni system (Fig. 11) shows that the approach towards equilibrium during tempering yields the phase Ti₂Ni. During the formation of Ti₂Ni the \checkmark' phase is depleted in nickel until its composition conforms to that of equilibrium \backsim at the tempering temperature (probably less than 0.1% Ni at 500°C).

. Experimental Results for \checkmark' Decomposition.

A sufficient quantity of argon quenched 6% Ni alloy powder was prepared for subsequent isothermal heat treatments. X-ray diffraction checks ensured that the structure of this material was completely \sim' . The extent of the tempering reaction after heat treatment was determined by computing the amount of Ti₂Ni formed from X-ray diffraction line intensities (see Appendix VI).



Figure 19. - Photomicrograph of 100% \prec' in a quenched 6% Ni alloy powder - Mag. 2000X

Etchant: Etched in 5% HF in Glycerin with $\rm HNO_3$ rinse.

The tempering reaction in the 6% Ni alloy was followed at 450°, 500°, 525°, and 550°C. The weight % of Ti₂Ni is plotted as a function of log time in Figure 20. The curves exhibit the familiar S-shape (although the early stages are difficult to measure) and may be reasonably superimposed by translation along the log time axis. Once the reaction is initiated the amount of Ti₂Ni formed is approximately proportional to log time up to the concluding stages of the reaction (> than 14% Ti₂Ni) when the rate decreases quite markedly.

Specimens were examined metallographically after various amounts of tempering at each temperature in order to detect any microstructural changes due to diffusion and precipitation. The original strained structure appeared to be transformed to a Widmanstätten precipitation type. Figure 21 shows a typical microstructure for 90% transformation at 500°C. The structure appears extremely fine and needle-like. Since Ti₂Ni is not resolvable at 2000X it is presumably very finely dispersed. At 550°C the structure is a little coarser. (Figure 22) but no definite precipitation of Ti₂Ni can be seen. Microscopic examination of a specimen heated at 750°C for 15 minutes revealed a spheroidal precipitate of Ti₂Ni in a matrix of \propto .(Figure 23).

Hardness measurements of \prec' at various stages of isothermal decomposition at four temperatures are shown in Figure 24. With the depletion of nickel in the close-packed hexagonal structure and the corresponding formation of Ti₂Ni there is a gradual decrease in hardness values. No initial hardness increase was observed during the earliest stages of the process.

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Figure 21. - Photomicrograph of 6% Ni alloy powder showing Widmanstätten structure after 90% decomposition of \checkmark at 500°C - Mag. 2000X

Figure 22. - Photomicrograph of 6% Ni alloy powder after 90% decomposition at 550°C -Mag. 2000X



Figure 23. - Photomicrograph showing spheroidal precipitate of Ti₂Ni in an \propto matrix after 100% decomposition of \propto' at 750°C - Mag. 2000X

Etchant: Etched in 5% HF in Glycerin with HNO3 rinse





Discussion of Tempering Results.

The general shape of the curves in Figure 20 suggests a type of nucleation and growth reaction which was quantitatively analysed by Johnson and Mehl (46). They proposed an equation of the following form for a rate of nucleation N and rate of growth G which are both assumed constant for a given process:

(1)
$$f(t) = 1 - \exp(-\frac{\pi}{3} \cdot NG^{3}t^{4})$$

where f(t) represents the fraction transformed in time 't'

A more general form of equation (1) is

(2) $f(t) = 1 - \exp(-kt^n)$ which yields (3) $\frac{df(t)}{dt} = knt^{n-1}e^{-kt^n} = knt^{n-1}(1 - f(t))$

The coefficients 'k' and 'n' are constants for a particular process. If logarithms are taken in equation (2):

- (4) $\log_e (1 f(t)) = -kt^n$
- (5) $\log_{10} \log_{10} \frac{1}{1-f(t)} = \log_{10} \frac{k}{2.3} + n \log t$

Cohen et al (41, 42) have proposed the following equation which serves to relate the constant k in the above to the specific rate constant K for the process:

(6) $\frac{df(t)}{dt} = K (1 - f(t))t^m$ where m = n - 1

Equation (6) is merely another form of equation (2).

Comparison of (3) and (6) reveals

(7) nk = K

and

Substituting equation (7) in (5)

(8) $\log_{10}\log_{10} \frac{1}{1-f(t)} = \log_{10} \frac{K}{2.3n} + n \log t$

It can be seen that if the tempering reaction is to obey equation (8) then a plot of $\log_{10}\log_{10}\frac{1}{1-f(t)}$ versus $\log_{10}t$ will yield a straight line. The experimental values for the current investigation are plotted in Figure 25 and produce reasonably straight lines, up to the late stages of the reaction. The curves for different temperatures deviate from linearity at approximately the same ordinate values, suggesting the possibility of impingement which inhibits the growth process.

Reference to equation (8) shows that the slopes of the curves $\log \log \frac{1}{1-f(t)}$ versus log time gives 'n' for each temperature. The values for different temperatures are listed in Table III where it is seen that, except for the figure of 0.7 at 550°C, n is fairly constant at 0.52.

TABLE III	-	KINETIC	RESULTS -	\ م	DECOMPOSITION
TEMP °C.			n		$\log \frac{K}{2.3n}$
450			•53		- 2.40
500			. 51		- 1.45
525			•52		- 1.02
550			0.7		- 0.8

Table III also shows the value of $\log \frac{K}{2.3n}$ for each temperature. These were obtained from the log time = 0 intercepts of Figure 25.

From basic rate theory it is known that:

(9) $K_t = Ae^{-Qt/RT}$ where K_t is the activation energy and A is a frequency factor if the reaction is first order. If log K_t is plotted against the reciprocal of the absolute temperature then a straight line should result and it will have a slope equal to $\frac{Qt}{2.3R}$. (This is the standard Arrhenius method of obtaining activation energy).

From equation (7) the rate constant for a precipitation reaction



as defined by equations (6) and (8) is:

 $(10) \quad k = \frac{K}{n}$

Consequently, the values of $\log \frac{K}{2.3n}$ have been plotted against $\frac{1}{T}$ as shown in Figure 26. An excellent linear relationship yields an activation energy $Q_{\rm K} = 43,500$ cal/mole. From equation (8) it can be seen that the rate constant K is expressed in units time⁻ⁿ but, according to Zener (50), the corresponding activation energy $Q_{\rm K}$ must be evaluated in terms of K in units time⁻¹ before any comparisons can be drawn with other rate processes. The conversion can be made automatically by plotting $\frac{1}{n} \log \frac{K}{2.3n}$ versus $\frac{1}{T}$ or more simply by using the relationship $Q_{\rm t} = \frac{Q_{\rm K}}{n}$ where $Q_{\rm t}$ is the activation energy for the process. For this investigation $Q_{\rm t} = \frac{43500}{n} = 84000$ cal/mole.

Alternatively the activation energy, Q_t , for the tempering process can be obtained from the slope of a graph of log time against $\frac{1}{T}$ for a specific fraction of decomposition (e.g. 50%) (45) as shown in Figure 27. This method produces the same value for Q_t .

The similarity between the two methods of obtaining Qt has not been clearly indicated in the literature. This relationship is discussed in Appendix VII together with a modification of the rate equation as proposed by Burke and Owen (45).

Diffusion Model.

The following experimental results and conclusions have been considered in proposing a model for the tempering of transformed β in Ti-Ni alloys:

(1) The reaction is a growth process which can be adequately described



by the equation:

 $f(t) = 1 - \exp - kt^n$

where $n = 0.5 \text{ at } 450^{\circ}, 500^{\circ}, 525^{\circ}$

and $n = 0.7 \text{ at } 550^{\circ}$

(2) In the tempering treatments carried out at 450° , 500° , 525° , 550° the phase Ti₂Ni is not microscopically resolvable; however at 750° the precipitate appears clearly spheroidal. It is therefore concluded that at the lower heat treating temperatures growth of many more dispersed nucleii occurs than at higher temperatures.

(3) At the three lower tempering temperatures the coefficient n is approximately 0.5. Zener (47, 50) has indicated in his theoretical treatment of growth processes that the value of n corresponds to the advancement of planar interfaces of precipitate. Cohen (41, 42) has indicated a similar process in his treatment of first stage tempering in steels. The relationship between the coefficient n and the geometrical form of precipitates is discussed in Appendix VII.

(4) The later stages of the reaction do not comply with equation (2). This is perhaps due to the impingement of adjacent Ti₂Ni precipitates. Further, it is possible that there is a marked decrease in concentration gradient during the later stages and Ti₂Ni particles may compete in withdrawing solute from the depleted \prec' .

(5) Diffusion in this system is by substitution. Growth of a Ti₂Ni precipitate requires that Ni atoms be transported through the \checkmark' lattice to the interface. There is a great difference in nickel concentration between \checkmark and Ti₂Ni at the interface and consequently it is to be expected that the rate of interface movement will be extremely slow. In addition, a countercurrent diffusion of Ti atoms away from the interface in the same
direction as the TiNi growth must occur in order to create vacancies for nickel atoms to form Ti₂Ni. Actually, this situation should create a high density of vacancies in the \sim' at the interface so that incoming nickel atoms can assume the configuration of Ti₂Ni and thus enable the interface to advance.

(6) The activation energy for the overall process has been determined as 84,000 cal/mole; this value is based on the intermediate stage of the process only. The low n value of 0.5 has been attributed to a process in which nucleation has already occurred (42) and the reaction proceeds by growth only. This seems feasible in the present case since the incubation period has not been considered. It is therefore reasonable to assume that nucleation contributes insignificantly to the activation energy during the intermediate stage and the process is controlled by diffusion or growth. Hence the activation energy represents the rate-controlling diffusion process.

On the basis of these observations it is proposed that at 450-550°C (and probably below this range) growth of Ti₂Ni proceeds in platelike form as shown in Figure 28. Ti₂Ni is envisaged as advancing into the \checkmark' with a depletion of nickel ahead of the interface. The gradient of nickel concentration in \checkmark' will be determined by the diffusion coefficient of the reaction and by the maximum and minimum nickel concentrations C₀ and C₁ respectively. The line 'aa' represents the centre-line between the midpoints of two growing Ti₂Ni plates. Towards the end of the decomposition process the concentration C₀ at line 'aa' will start to diminish, resulting in a subsequent decrease in concentration gradient. In this model the product should consist of \checkmark regions surrounded by fine, well dispersed plates of Ti₂Ni. At low tempering temperatures (less than 550°C) it is probable that the growth of many nucleii will proceed with eventual impingement

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Figure 28. - Proposed Model for growth of Ti₂Ni from transformed β (α').

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which results in the non-linearity of the upper part of the curves log log $\frac{1}{1-f(t)}$ versus log time. Thus the Widmanstätten type of \propto precipitate seems reasonable on the basis of this model, and under such circumstances Ti₂Ni formation will be manifested as an apparent thickening of \ll boundaries. Calculations based on cylindrical \propto needles and uniform distribution of Ti₂Ni as interface layers around \ll have shown that the thickness of the Ti₂Ni layer will be in the order of 0.05 microns which would not be resolvable under the microscope. At 500°C the increased value of $n_1(0.7)$ implies that precipitates are expected. Although no measurements have been made at temperatures higher than 550°C the photomicrograph of a specimen treated at 750° (Figure 23) supports this view.

The diffusion coefficient for the controlling process, as calculated from:

(11) $\sqrt{D} = \frac{1}{6} a^2 \gamma \exp - \sqrt[6]{RT}$

where a is the interatomic spacing

 γ is the thermal oscillation frequency is in the order of 10^{-25} cm²/sec in the temperature range 450-550°C. Such a small value implies a slow diffusion rate which will favour the formation of a very fine and well-dispersed precipitate network.

Since the proposed model requires countercurrent diffusion of Ti and Ni, the self diffusion of Ti to create vacancies for the Ni may well be the rate controlling factor. Although no figure exists for the activation energy of self-diffusion in Ti (Qs) an analysis of self diffusion data for several metals indicates that Qs is roughly proportional to the melting point T_f . This is a reasonable relationship since melting involves the breaking of atomic bonds or release of an atom from its regular array which is actually what happens in substitutional diffusion. In Figure 29 the available values of Qs are plotted against T_f and a reasonably straight line is obtained. From Figure 29 the activation energy for self-diffusion of Ti is estimated to be 77000 cal/mole. This value corresponds remarkably well with the activation energy for the rate controlling step of the tempering reaction in the Ti-Ni alloy.

Decomposition of Retained $oldsymbol{eta}$

Experimental.

It has already been mentioned that it is possible to retain $100\% \beta$ in the 6% Ni alloy by gas quenching unsintered particles from $1000^{\circ}C$. The variation of constitution with quenching rate has already been considered.

A sufficient quantity of quenched powder consisting of 100% retained β was prepared for subsequent isothermal heat treatments. These neat treatments were performed as described in Appendix II and phase ratios were determined from relative X-ray line intensities of β_{110} and \prec_{101} as outlined in Appendix VI.

Results.

The isothermal decomposition of retained β was found to follow a step-wise reaction:

In the above reaction \checkmark'' is used to designate an intermediate phase which is formed before the presence of Ti₂Ni is detected. At temperatures up to 550°C an isothermally heat treated powder may consist of

 $\beta_{(b.c.c.)} \rightarrow \alpha''_{(c.p.h.)} \rightarrow \alpha_{(c.p.h.)} + Ti_{2Ni}$





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Figure 30(b). - Graph showing the fraction of β transformed, hardness, and line breadth as a function of time during tempering at 425°.

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Figure 30 (c). - Graph showing the fraction of β transformed, hardness, and line breadth as a function of time during tempering at 450°C.

•₽ •₽ 100% \checkmark'' . The reaction curves are shown in Figure 30 (a, b, c) with the corresponding hardness values for isothermal treatments at 400°C, 425°C and 450°C. At higher temperatures the reaction is extremely rapid; at lower temperatures it is extremely slow. There is no 'C-curve' behaviour.

The microstructure of retained β was shown in Figure 14 for the 6% alloy. During the $\beta \rightarrow {}^{\prime\prime}$ transformation there is no microscopic evidence of the reaction except that the substructure (previously noted) disappears with the formation of ${}^{\prime\prime}$ (Figure 31). Black marks on the structure are due to an etching effect. The metallographic appearance of the ${}^{\prime\prime}$ structure is most misleading and adds to the argument that X-ray evidence is needed to substantiate any conclusions made from the microscopic appearance of structures.

The positions of the diffraction peaks of the \checkmark'' phase correspond to those of \checkmark' formed on quenching, indicating that the $\frac{c}{a}$ ratio is similar in both phases. During the early stages of the reaction there is a broadening of the originally sharp β diffraction lines. The \checkmark'' reflections appearing as a result of the reaction show an initial broadening and then become progressively sharper. Figure 30 illustrates this fact and also shows that hardness values during the reaction follow the same initial increase and subsequent decline. These effects are attributed to coherency strains produced in the mixed structures during the early stages of \checkmark'' formation. As the reaction proceeds the \checkmark'' structure becomes incoherent with respect to the β phase and stresses set up due to coherency are at least partially relieved. Attempts were made to detect any transitional omega phase (3) which might form during the early stages of β decomposition. Although the transitional structure has been observed during the isothermal decomposition of β in several other systems (13) none was detected in alloys of Ti-Ni.



Figure 31. - Photomicrograph of 100% «" structure showing original β grain boundaries - Mag. 800X

Etchant: Etched in 10% HF in Glycerin with HNO3 rinse.

The second stage of the reaction (i.e. $\checkmark'' \rightarrow \checkmark' + \text{Ti}_2\text{Ni}$) yields very similar reaction curves (Figure 32) to the decomposition of \checkmark' . However the amount of Ti_2Ni detected at any time is slightly greater in \checkmark'' decomposition than in \checkmark' decomposition; and the incubation period is shorter. Figure 33 shows the plot of $\log_{10}\log_{10}\frac{1}{1-f(t)}$ versus log t for the decomposition of \checkmark'' . The values of n and $\log \frac{1}{2.3n}$ obtained from the graph in a similar way as for the decomposition of \checkmark' are listed in Table IV.

TABLE IV	- KINETIC RESULTS -	DECOMPOSITIO
TEMP.	<u>n</u>	log 2.3n
450	•5	- 1,9
500	•56	- 1.4
525	• 55	- 0.88
550	•55	- 0.66

The plot of log $\frac{K}{2.3n}$ versus $\frac{1}{T}$ is shown in Figure 34. The activation energy for the reaction in terms of time⁻¹ has been determined to be 71000 cal/mole from the slope of the curve. Microscopic examination of specimens during stages of the \checkmark'' decomposition revealed similar structures to those observed during the \checkmark' breakdown.

Discussion - $\beta \rightarrow \propto''$.

Kurdjomov and Maksimova (34) showed that the retained high temperature phase in their alloys decomposed to martensite on tempering at temperatures below Ms. No Ms temperatures have yet been determined for the Ti-Ni system but it is possible that the tempering temperatures in this work are above Ms. Consequently, at the present time it is impossible to be certain whether the $\beta \rightarrow \prec''$ transformation is a martensitic or diffusion

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Figure 32. - Isothermal reaction curves for the reaction $\alpha'' \rightarrow \alpha' + \text{Ti}_2\text{Ni}$.

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Figure 33. - Plot of $\log_{10}\log_{10} \frac{1}{1-f(t)}$ versus log time for the decomposition of $\ll^{\prime\prime}$.

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Figure 34. - Plot of log $\frac{K}{2.3n}$ versus $\frac{1}{T}$ for the decomposition of \propto ".

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type. The shape of the growth curves is similar to that of reaction curves reported by several other investigators (51, 52, 53) for isothermal martensite formation. In their analysis of isothermal martensite curves Cohen et al (53) have concluded that, during the early stages, the transformation proceeds primarily by nucleation of new plates rather than by growth of existing ones. Further, they found that the rate of reaction increased considerably once the transformation had started; i.e. the reaction is autocatalytic in the early stages. No reports of 100% martensite transformation by purely isothermal means has been found in the literature; but the $\beta \rightarrow \propto$ " reaction does proceed to completion isothermally. C-Curve behaviour has been noted in the isothermal martensite reactions but, as previously mentioned, no C-Curve behaviour was observed in the present work on Ti-Ni.

There is strong evidence to support the thesis that the $\beta \to \alpha''$ reaction involves diffusion. The formation of Ti₂Ni from α'' in the subsequent tempering operation proceeds much more rapidly than the decomposition of α' as indicated by the briefer induction period. This implies that nucleii of Ti₂Ni have formed during the $\beta \to \alpha''$ reaction, or that their formation during the early stages of α''' breakdown is facilitated by composition fluctuations set up during the $\beta \to \alpha''$ reaction. The reaction $\alpha'' \to \alpha'' + \text{Ti}_2\text{Ni}$ appears to occur more readily than

 $\measuredangle' \rightarrow \measuredangle' + \text{Ti}_2\text{Ni}$; and this behaviour is consistent with the lower activation energy calculated for the growth stage of $\swarrow'' \rightarrow \checkmark + \text{Ti}_2\text{Ni}$. X-ray diffraction and microscopic observations of specimens in which the β phase was just completely decomposed revealed 100% \backsim'' with no evidence of a second phase. The microstructure (Figure 31) is very misleading since it shows the original β grain boundaries but no indication that the β has transformed except that the previously noted sub-structures have disappeared. It is possible that crystals of \prec'' are extremely small and consequently not resolvable by optical methods. The X-ray diffraction lines of \prec'' (c.p.h.) were continuous and slightly broader than the corresponding reflections of \prec' (c.p.h.) which suggests a small crystal size of \prec'' . In addition the previously noted polygonization boundaries result in sufficient discontinuity in the β phase to obstruct growth reactions and promote nucleation sites. Consequently, the formation of a fine transformation product is strongly favoured.

Therefore it does not seem unreasonable that composition fluctuations, might arise during the $\beta \rightarrow \alpha''$ reaction, and create some regions which are richer in nickel. This situation would be similar to the formation of 'Guinier-Preston' Zones observed in the aging of Al-Cu alloys. The establishment of such nickel-rich regions in α'' would facilitate subsequent decomposition because the required induction period for nucleation of Ti₂Ni would be shortened. Further, because of the structural irregularities due to a high concentration of nickel atoms in certain regions there would probably be associated vacant lattice sites. On the basis of the decomposition mechanism proposed for the hexagonal close-packed structure this would explain the more rapid decomposition and correspondingly lower activation energy involved in the decomposition of α'' than in α' .

It was observed that the θ value of the broadened β_{110} peak decreased 0.1° - 0.2° during the early stages of β decomposition. This cannot be attributed to composition changes due to normal diffusion since such a process would imply that the nickel content of the β phase decreases and the β peak positions would increase in angle. Moreover it is difficult to believe that Ti₂Ni would not be detected by X-ray methods in such a case. This shift in line position is accompanied by line broadening, which in turn has been attributed to strain. Previous observations in strained metal aggregates (54) indicate that stacking faults induced by strain can cause a shift in X-ray line positions. The view that the line shift of β_{110} is due to stacking faults and strain is acceptable since considerable structure strain is involved during the first half of the $\beta \rightarrow \propto$ reaction as indicated by microhardness results (Figure 30).

It is concluded that nucleation rather than growth by diffusion is the controlling factor during the early stages of the $\beta \rightarrow \alpha''$ reaction (up to 50% transformation). During this stage the X-ray line breadths and hardness values increase to a maximum. These observations can be attributed to strain, which is probably of two types:

(1) Internal strain which will result from the formation of many widely distributed nucleii due to the specific volume difference between \sim and β (approx. 3%).

(2) Coherency strains which are set up between the \checkmark " and retained β since in this type of reaction, there is a tendency for lattice conformity along atomic planes having similar spacings. As transformation proceeds the strain increases to a maximum after which there is a gradual loss of coherency and corresponding relief of strain and decrease of hardness. The condition during the initial loss of coherency is generally designated as the 'semi-coherent state' in which some lattice registry is maintained by arrays of dislocations at the interfaces between the two phases.

Coherency generally contributes much more significantly than specific volume difference to the overall strain in a nucleation and growth reaction. The decrease of hardness observed during later stages

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(> than 50% transformation) of the $\beta \rightarrow \alpha''$ reaction may be attributed to the loss of coherency between β and α'' or possibly to strain relief by shear.

The shape of reaction curves for $\beta \to \alpha^*$, when compared to other rate curves, suggest that nucleation and growth both contribute significantly to the transformed fraction during the latter half of the process. The temperatures and holding times are such that a significant amount of diffusion is inevitable. On the other hand, the reaction is not retarded even at above 90% transformation. This implies that new nucleii must be forming at all times in the unreacted β since growth control would probably result in impingement effects, which in turn suppress the reaction in the late stages.

Decomposition of \checkmark'' .

The decomposition of the transition phase \checkmark appears to be a similar process to the breakdown of \checkmark . Microstructural observations and hardness measurements together with X-ray diffraction studies indicate that a similar mechanism operates in both processes.

An explanation of the more rapid nucleation and growth process has been given on page 72.

SUMMARY OF CONCLUSIONS

(1) The constitution of quenched Ti-Ni alloy powders is dependent on both composition and cooling rate from the β range. An 'inverse stabilization' of the β phase has been observed. The \prec' structure (martensite) becomes progressively finer with increasing nickel content.

(2) The 100% retained β phase in quenched powder specimens has exhibited two types of sub-structures:

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 (a) Sub-boundaries believed due to polygonization resulting from transformation stresses

(b) stacking faults created by quenching stresses.

(3) Hardness of the as-quenched alloys increases with nickel content and is higher in alloys containing mixed structures of \sim' and β . This is believed to be due to coherency strains at the \prec' and β interfaces.

(4) Orientation relationships between the \prec' and β phases after quenching have been studied in an 8% alloy. The relationship (0001) α' // (011) β' (observed from parallel adjacent diffraction spots) was used as the basis for stereograms from which other observed parallelisms were confirmed. The Burgers shear mechanism for Zr has been proposed as the likely crystallographic process for the $\beta \rightarrow \alpha'$ martensite reaction in Ti-Ni alloys.

(5) Decomposition studies of the \checkmark' phase have shown that \checkmark' decomposes by a growth-controlled process similar to that described by Johnson and Mehl. An activation energy of 84000 cal. per mole has been determined and a growth model has been proposed which involves plane interfaces of Ti₂Ni advancing into \checkmark' regions to produce a Widmanstätten-type microstructure. The self-diffusion of titanium is believed to be the growthcontrolling factor.

(6) Retained β decomposes on tempering by a two-stage process: $\beta \rightarrow \propto'' \rightarrow \propto + \text{Ti}_2\text{Ni}$

X-ray diffraction data indicate that \propto'' has the same crystal structure as \propto' . The $\beta \rightarrow \propto''$ reaction curves are similar to those observed for isothermal martensitic formation. However, the \propto'' formation appears to involve diffusion since:

(a) Formation of Ti₂Ni during subsequent tempering is facilitated,

as indicated by the brief induction period, suggesting that regions relatively rich in nickel are set up during $\beta \rightarrow \alpha''$ reaction.

(b) The tempering temperatures and times were such that diffusion processes are inevitable.

The reaction $\ll'' \rightarrow \ll + \text{Ti}_2\text{Ni}$ proceeds in a similar way to the decomposition of \ll' ; however, there is a shorter induction period for Ti₂Ni formation in the \ll'' decomposition, as already mentioned. Further, the activation energy for the $\ll'' \rightarrow \propto + \text{Ti}_2\text{Ni}$ growth process (71000 cal/mole) is lower than that for \ll' decomposition suggesting that regions which are rich in nickel exist in the \ll'' phase.

(7) During the tempering of \prec' the hardness of quenched powders decreases with heating time - the rate of hardness decrease being greater for higher tempering temperatures. This is in contrast to observations in the Ti-Fe system where the hardness increased with the formation of FeTi during tempering. The difference in behaviour is probably due to the stoichiometric and crystallographic differences of the intermetallic phases in the two cases. However, the Ti-Ni observations show a similar trend to results in the Ti-Cu system (23) where Ti₂Cu is precipitated during tempering.

(8) During the reaction $\beta \to \sigma''$ the hardness initially shows a sharp increase probably due to lattice coherency strains between σ'' and β ; as decomposition exceeds 50% the hardness decreases. The magnitude of X-ray line breadth follows the hardness curves.

(11) (11) .

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APPENDICES

APPENDIX I

LEVITATION MELTING

Titanium is a highly reactive metal which is particularly susceptible to interstitial contamination by O_2 , N_2 and H_2 at elevated temperatures. The effect of oxygen contamination on the hardness of pure titanium is illustrated in Appendix V. As a result it is necessary to prepare titanium alloys in either a vacuum or a purified inert gas atmosphere. This extreme reactivity of titanium at temperatures over 700°C forbids contact with nearly all refractory materials both during heat treatment and melting.

The customary method of preparing titanium alloys for research purposes is arc-melting in a water-cooler copper hearth. This process is carried out by using either a tungsten-tipped or titanium-tipped electrode in an inert gas atmosphere (argon or helium). Arc furnaces are commonly used for producing commercial alloys since they are readily adaptable to large scale operations. In arc-melting, the entire charge cannot be completely molten because of the chilling effect of the mold. Therefore it is necessary to remelt the alloy to ensure homogeneity. Margolin (1) has reported that even after several re-meltings significant heterogeneity exists in an alloy button. An additional disadvantage of arc-melting is the rather large cost of equipment, auxiliary installation, and operation.

Levitation melting is a possible alternative to arc melting for producing small quantities of alloys. This method was first suggested for metals by Muck (2). It was more recently considered by Comenetz and associates (3,4), who reported that they had 'almost completely melted a lump of titanium by levitation in a high frequency field'. However, it was believed that if complete fusion were achieved the metal would be unstable in the field and would tend to drip.

Subsequent experiments were performed in the U. B. C. laboratories (5), to develop a levitation process by which titanium and its alloys might be melted and cast. After experimenting with induction coils of many shapes a final design comprising a conical-shaped coil of seven parallel turns with an additional upper reversed turn proved successful. The upper reversed turn was necessary to stabilize the field in the coil. Without it metal levitated higher but moved around the periphery of the coil. It was necessary to have a large enough opening in the bottom of the coil to allow the molten metal to drop through into a cold copper mold.

The melting operation was performed under a positive pressure of purified argon and the system was enclosed by a lucite cylinder and brass end plates. In order to ensure that any traces of oxygen and nitrogen were completely removed the system was evacuated and flushed several times with purified argon before each specimen was melted. Positive argon pressure of 5 lbs./in² were necessary to prevent arcing between the coil and specimen. The levitation unit is illustrated in Figure 1 and shown in operation in Figure 2. The power source was a Lepel spark-gap oscillator with a rated output of 3.75 kw. and a frequency of 200 to 500 kc/sec. With this equipment up to six grams of titanium can be successfully levitated, melted and cast. The specimens melted within 30 seconds, remained stably supported without dripping after melting and were cast by cutting the power. Solidification and subsequent cooling were very rapid. There was no alloying between the metal and the mold; and a bright, clean ingot was produced.

Titanium alloys were successfully prepared from iodide titanium

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bar stock by inserting the alloying element (lump form) in a hole drilled in the titanium. Subsequent checks revealed that homogeneous ingots were consistently produced by the technique.

CONTAMINATION

Hardness measurements are accepted as a parameter for oxygen and nitrogen contamination in pure titanium. Values obtained after repeated melting and re-melting of pure titanium showed that no appreciable contamination occurred in levitation melting. Hardness figures are listed in Appendix V.

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Figure 1. - Levitation Melting Unit



Figure 2. - Levitation Melting Unit in Operation

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APPENDIX II

HEAT TREATMENT AND QUENCHING

Quenching Treatments

Precautions against contamination were particularly important in the present work because most heat treatments were performed on powder specimens which, due to their large surface area, are more reactive than lump samples. Even minute traces of oxygen and nitrogen in an 'inert' atmosphere will cause sufficient contamination to affect the properties of titanium alloys. Therefore the argon that was used for inert atmospheres was purified by passing it through two calcium trains at 500°C (to remove nitrogen and oxygen), copper mesh at 500°C (to remove oxygen) and a P_2O_5 trap (to remove water vapour).

Developing a technique for quenching powder specimens from 1000°C created some initial difficulties. In preliminary work specimens were heated in 1 1/2 inch diameter vitreosil tube furnaces followed by water quenching under a pressure head. Fears that the specimens would be severely oxidized by the water at 1000°C were immediately substantiated. Additionally, the long heating times involved in bringing the furnace and specimens to temperature gave further opportunity for contamination to occur. Subsequent work was done in smaller tube furnaces of 3/8 inch diameter which were wound with chromel ribbon and could be heated to 1000°C in one to three minutes. In addition, a gas quenching method was devised. The following requirements dictated heat treatment technique: (1) Furnace must be gas tight and vacuum tight.

(2)	A protective atmosphere is needed during heat treatment.	
(3)	Furnace must be capable of rapid heating to soaking temperature.	
(4)	Ti-alloy specimens must not be in direct contact with refractory mater-	
	ials, including SiO ₂ , at temperatures above 600-700°C.	

(5) Some non-contaminating quenching medium must be used. Since specimens are very small, inert gas quenching is the best available method.

The experimental arrangement for heating and quenching is shown in Figure 1. The specimen is contained in a small-molybdenum boat in an atmosphere of purified argon for the required soaking time. Then the system is evacuated, and immediately argon is passed into the furnace tube. The specimen is propelled from the furnace to the end of the tube where it is cooled by combined radiation and forced convection. This arrangement complied with the above requirements and produced consistently clean heat treated powders. As a check against contamination standard runs were made on pure titanium and hardness values indicated less than .03% oxygen + nitrogen pick-up during heating and quenching (see Appendix V).

Holding times at 1000°C prior to quenching were standardized at one and two minutes. Longer soaking times produced no difference in structure in Ti-Fe and Ti-Ni alloys.

Titanium powders finer than 65 mesh sinter quite readily during heat treatment at temperatures above 800-900°C. In some cases it was desirable to prevent sintering and the powders were continuously agitated during heating. This was done by using an arrangement shown in Figure 2. When unsintered powders are quenched the maximum possible cooling rate is expected since particles are individually exposed to the cooling medium.

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Figure 2. - Arrangement for preventing sintering of powders during heat treatment by rotation of specimen.

Both argon and helium were used for quenching, particularly in the Ti-Ni system where quenching rate affected the constitution of the product. In order to make an approximate determination of the relative quenching rates argon and helium cooling curves were observed on a cathode ray oscilloscope screen. The set-up involved connecting a thermocouple through an amplifier to a cathode ray oscilloscope. Measurements were made by observing the thermocouple potential change on the scope screen and showed that helium quenching from 1000°C is about five times faster than argon quenching. The measurements could not be made directly on alloy specimens since a thermocouple could not be maintained in contact with powders during quenching. It was possible to obtain the following quenching rates by using both argon and helium:

(1)	helium quench	unsintered	(fastest)
(2)	helium quench	sintered	(intermediate)
(3)	argon quench	sintered	(slowest)

The absolute quenching rates could not be determined with the apparatus available.

Isothermal Heat Treatments

Isothermal heat treatments were performed on specimens sealed in evacuated vitreosil tubing. For heat-treatments above 700°C the tubing was lined with molybdenum so that the titanium powder would not react with the silica. All silica capsules were pumped for one half to one hour before being sealed. Temperature control during isothermal heat treatment at $400^{\circ} - 600^{\circ}$ C was $\pm 3^{\circ}$ C. Wherever heat treatments were of less than 15 minutes duration a thermocouple was attached to the specimen tube and time was measured from the instant that the thermocouple reached temperature.

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APPENDIX III

MICRO-HARDNESS TESTING

Metallographic specimens of alloy powders were mounted and polished in transoptic mounting compound in the customary way but with low mounting pressures. After specimens were suitably etched (HF solutions) hardness measurements were made on +65 to -200 mesh powders by means of a Bergsman micro-hardness tester. Loads of 10 grams and 25 grams were commonly used. At least 10 hardness tests were made on each specimen and after rejecting the highest and lowest value the variation was not more than 10%.

Additional specimens were mounted in cold setting resin to see if mounting under pressure at 150°C affected the micro-hardness. No differences in micro-hardness were detected, implying that in the case of retained β structures precipitation did not occur to any extent during customary mounting procedures.

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APPENDIX IV

HIGH TEMPERATURE X-RAY GONIOMETRY

The constitution of alloys at elevated temperature is frequently studied by examining specimens which have been quenched to room temperature. In such studies it is possible that transformations may occur by shear or diffusion during cooling. Consequently in order to determine the true phase constitution of alloys at a high temperature (say up to 1000°C) it is necessary to actually make observations or measurements at the temperature. Recent progress has been made in developing hot-stage microscopy and high-temperature X-ray techniques.

A high temperature X-ray camera was used in conjunction with a Phillips X-ray goniometer to study phase transformations in titanium alloys. This camera has been described in detail elsewhere (1) and is shown in Figures 1 and 2. It is not proposed to elaborately describe the camera construction here but the following essentials are mentioned for clarity.

The alloy powder specimen is placed on a molybdenum sheet which, in turn, rests on a fused quartz plate. The specimen and holder are enclosed by a water-cooled brass case into which a platinum wound heating element is semi-permanently fitted. The winding of the heating element is parallel to the axis of the quartz plate specimen holder in order to minimize the temperature gradients in the specimen. The entire assembly, including bress can and specimen-holder, is fitted to a head which is attached to the goniometer axis by a shaft. During operation of the goniometer the specimen rotates at one half the angular velocity of the-geiger tube. The specimen temperature is measured by means of a thermocouple which is touching the specimen. The brass can has a slit or window of sufficient length about its circumference to allow the X-ray beam to enter and leave over a reasonable scanning range. This window is covered by aluminum foil. The entire heating chamber is vacuum tight if the window seals, O-ring connection between the can and head and other minor connections are carefully made.

When the camera_was.used to study the structure of titanium alloys up to 1000°C extreme caution_was_observed.in order to minimize contamination by oxygen and nitrogen. A continuous flow of helium was passed through the camera prior to heating in_order to ensure that any residual oxygen and nitrogen remaining after pumping_would be diluted. Further, the helium gas was purified by passing it through activated silica gel at liquid oxygen temperature to remove 0 and N. Zirconium powder was mixed with the titanium in some runs at 1000°C to act as a 'getter' for any traces of 0 and N which might be present. However, this was merely an additional precaution which produced no difference in results in most cases.

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APPENDIX IV



Figure 1. - High temperature attachment for the X-ray spectrometer (Furnace winding and water-cooling are not shown)



Figure 2. - Photograph of the High Temperature Attachment in position in the spectrometer.

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APPENDIX V

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CONTAMINATION OF ALLOYS

The magnitude of the effects of interstitial contamination on the properties of titanium is described in almost every introductory paper on titanium. Hardness measurements are generally used to estimate the degree of contamination due to oxygen and nitrogen in pure titanium. Accordingly, periodic heat treatments identical to those given to the alloys used in this work were performed on pure iodide titanium. The degree of contamination incurred in heat treatment could then be estimated. The heat treating techniques used in the present research were effective in restricting contamination to a very safe level. Typical results of hardness checks are summarized in the following, with estimated oxygen pick-up in parenthesis: 1. Iodide Titanium Bar Stock - 75 VPN (Rp 72)

2. Iodide Titanium Bar Stock Micro-Hardness 110 VPN

- 3. Ti after levitation melting R_F 80 to 90. No increase with successive remelting.
- 4. Ti Filings heat treated at 1000° in evacuated silica capsules,
 held 1 hour VPN 120 (.03% 0)

3 hrs. - VPN 130 (.04% 0)

- 5. Ti Lump -heat treated 3 hours at 1000° VPN 130 (.04% 0)
- 6. Ti Filings in Argon Atmosphere in heat treat furnace 1 hour at
 1000° 120 VPN (.03% 0)
- 7. Ti Filings heated to 1000° in high temperature camera, 1 1/2 hours -VPN - 150 (.20% 0)

The difference between hardness and micro-hardness values for iodide bar stock is not surprising since micro-hardness values tend to be higher. Effects of the polished surface together with the very light loads (10 gm., 25 gm.) used in microhardness testing appear to account for this difference.

The hardness of titanium after melting and chill casting is expected to increase slightly because of internal stresses due to rapid solidification and cooling, and also due to the extremely fine grain structure produced. Accordingly, there is a slight increase of hardness (5 to 10 points VPN).

APPENDIX VI

PHASE RATIO DETERMINATIONS

Throughout the work on titanium alloys phase ratios were determined from the relative intensities of X-ray diffraction spectra measured on a Phillips Geiger counter spectrometer. Introductory calibration studies showed that relative intensity measurements determined by pulse counting produced similar values to those obtained by measuring areas underneath the peaks on the recorder plots.

It is well known that the intensity of the diffraction lines of a particular phase depends on the number of reflecting planes and, therefore, on the quantity of phase present. The diffraction intensities for a series of lines of one phase should bear constant ratios to one another. By calculating the structure factor and applying several corrections as outlined by Barrett (1) and illustrated by Parr (2) the relative intensities of lines in two phases can be calculated from a knowledge of the structure cells and then used to assess phase ratios.

The relative intensity of diffraction for a particular family of planes in a phase is calculated from the following equation if the structure cell is known:

 $\left[\left|\mathbf{F}\right|^{2}\right] = \left[\sum_{i} f_{i} \cos 2\pi (h u_{i} + kv_{i} + lw_{i})\right]^{2} + \left[\sum_{i} f_{i} \sin 2\pi (hu_{i} + kv_{i} + lw_{i})\right]^{2}$ $I \propto \left[|F|^{2} \right]$ $I = \left[\frac{1 + \cos^{2} 2\Theta}{\sin^{2} \Theta} \right] \cdot \left[|F|^{2} \right] \cdot \left[A' \Theta \right] \cdot \left[f(\lambda) \right] \cdot \left[P \right]$

where

$$\frac{1 + \cos^2 2\theta}{\sin^2 \theta}$$
 = Lorentz - Polarization factor

 $|F|^2$ = Structure Factor $A'(\theta)$ = Absorption Factor

 $f(\lambda) = \text{Variation of photographic effect with wave length}$ The quantity I represents the relative intensity per atom for 100% of one phase and when this calculated intensity is compared with that estimated for a particular set of planes in another phase then the ratio of the two values is the amount expected when equal amounts of the two phases are present. It is then possible to determine the phase ratios corresponding to any other measured ratio of intensities, as for example:

For a 6 Atomic % Ni alloy containing $\alpha' + \beta$ Calculated relative scattering intensity/atom $\alpha_{101} = 62100$ $\beta_{110} = 89300$

Therefore ratio of intensities $\frac{\beta}{\alpha'}$ for equal amounts of α' and $\beta' = \frac{89300}{62100} = 1.435$

For a measured ratio $\frac{\beta}{\alpha'} = x$

$$\frac{x}{1.435} = \frac{\beta}{\alpha'} = \frac{1-\alpha'}{\alpha'}$$

Therefore $\[mathcal{p} \alpha' = \frac{100}{\frac{x}{1.435}} \[mathcal{p} \beta = 100 - \[mathcal{p} \alpha']$

The percentages of \swarrow' and β in specimens of both Ti-Fe and Ti-Ni were determined by calculating the expected relative intensities of \swarrow'_{i01} and β_{110} for equal quantities of the two structures. In this determination it was_necessary_to_assume_a random solute distribution and to calculate a mean_atomic scattering factor. In the Ti-Fe system the intensity of the 110 diffraction line of FeTi (body-centred cubic) was calculated on the basis that each structure cell consists of one atom of Ti and one of Fe. The % FeTi was then determined from the measured intensity ratio of <u>FeTi(110)</u>.

Several complications arise in determining phase ratios on the basis of theoretical intensity calculations:

(1) Absorption effects are difficult to compensate and hence it is necessary to use neighbouring diffraction lines since their absorption characteristics are similar and may be ignored. This is no serious problem in Ti-alloys because the 110 β , 002 \propto , 101 \propto , TiFe₁₁₀ and Ti₂Ni₃₃₃ occur over a range 19° to 22°0 with Cu K \propto radiation.

(2) Some difficulty arises since the 101 \propto and 110 β lines overlap. However the 002 \propto line at 19°9 can be accurately measured and from the calculated and measured infensity ratio $\frac{101 \ \alpha}{002 \ \alpha}$ it is possible to determine the 101 line intensity. The intensity of 110 β can then be estimated by difference.

(3) At low Θ values the X-ray diffraction lines of the \prec' (martensitic) and \prec structures are coincident (both are close-packed hexagonal structures). Consequently, determination of the hexagonal phase includes both \prec and \prec' . For the low alloys there is no marked difference between the mean atomic scattering factors of \prec and \prec' .

PHASE RATIOS FROM STANDARD CURVES

In the Ti-Ni work it was necessary to determine the percentage Ti₂Ni formed during heat treatment. The structure of this phase is complex

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face-centred cubic with 96 atoms per structure cell (3). The positions of the atoms are not yet known and hence, it is impossible to calculate the intensity of reflections from this phase. The alternate method adopted and described is, in any case, probably more accurate than the method involving calculation of intensity.

A series of Ti-Ni alloy powders were heat treated slightly below the eutectoid temperature to produce equilibrium phase ratios. The ratios of intensities $\text{Ti}_2\text{Ni}_{333}$: \swarrow 101 were measured from spectrometer plots and the corresponding phase ratio for each alloy was calculated from the phase diagram by using the lever law. A plot was made of percentage Ti₂Ni versus the ratio $\frac{511}{\text{Ti}_2\text{Ni}_{333}}$ for the range of compositions (Figure 1) and this \approx 101

was used as a standard in subsequent work to convert observed intensity ratios to percentage Ti₂Ni.

The effect of the isothermal heat treatments on the microstructure of the 6% Ni alloy is shown in Figures 2 and 3. Note that holding for prolonged periods causes agglomeration of Ti₂Ni.

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Figure 2. - Microstructure of 6% Ni alloy powder which was slowly cooled from the β temperature range. Note pro-eutectoid Ti₂Ni formation and eutectoid of \propto and Ti₂Ni - Mag. 800X



Figure 3. - Photomicrograph of 6% alloy heated 17 hours at 750°C to agglomerate Ti₂Ni in \propto matrix - Mag. 800X Etchant: Etched in 5% HF in H₂O - HNO₃ rinse

APPENDIX VII

RELATIONSHIP BETWEEN ALTERNATIVE METHODS OF DETERMINING ACTIVATION ENERGY - SIGNIFICANCE OF THE COEFFICIENT 'n'.

(1) The Cohen equation is $\frac{df}{dt} = K(1-f)t^m$

where m = n - 1

After integration and taking logarithms

(2) $\log \log \frac{1}{1-f} = (m+1) \log t + \log \frac{K}{2.3(m+1)}$

METHODS OF DETERMINING ACTIVATION ENERGY

Arrhenius Plot

A plot of $\log_e K$ versus <u>1</u> yields <u>Qt</u> equal to the slope of \overline{T} 2.3R

the line. However if the value Q_t is to be compared with other rate processes K must be expressed in units of time⁻¹. From equation (2) it is seen that K will have units time^{-(m+1)}. As a result, obtaining Q directly from a plot of $\log \frac{K}{2.3(m+1)}$ versus 1 will actually yield:

(3) $Q_{K} = (m+1) Q_{t}$ where Q_{t} is the true energy of activation.

For this reason it is necessary to plot $\frac{1}{m+1} \log \frac{K}{2.3(m+1)}$ versus $\frac{1}{T}$ and obtain Q_t directly or to apply equation (3) after plotting $\log \frac{K}{2.3(m+1)}$ versus $\frac{1}{T}$.

The value of Q_t can also be obtained by considering the relationship between log time and $\frac{1}{T}$ for a specific amount transformed (e.g. 50%).

It is known that

(4) $K = A e^{-Q_K/RT}$

Integrated form of equation (1) can be expressed as

(5)
$$K = \frac{-2.3(m+1)\log(1-f)}{t^{m+1}}$$

Consequently by substituting (5) in (4) for K (6) $\frac{-2.3(m+1)\log(1-f)}{+m+1} = Ae^{-QK/RT}$

Taking logs, numerator is a constant if m is assumed constant for a particular reaction.¹ Therefore:

(7) B - 2.3(m+1)log t = A' -
$$\frac{Q_K}{RT}$$

A is assumed constant and is a frequency factor for a first order reaction where $K = time^{-1}$

Rearranging equation (7), gather constants:

(8)
$$\log t = \neq + \frac{\Theta_{\mathbf{K}}}{2.3(m+1)RT}$$

Consequently, a plot of log t versus $\frac{1}{T_{L}^{2}}$ should yield a straight

line of slope $\frac{Q_K}{(2.3)(m+1)R}$

÷.

 Q_{K} bears no actual significance for comparison purposes unless it is converted to Q_{K} since it corresponds to a specific rate constant in $\frac{m+1}{m+1}$ units time^{-(m+1)} or time⁻ⁿ.

Zener (1,2) has shown that precipitation reactions which are growth controlled obey the following equation in the absence of impingement.

x m is constant until a late stage in reaction as indicated by similar slopes of loglog $\frac{1}{1-f}$ curves. $f(t) = const X t^n$

f(t) =fraction transformed

t = time

The coefficient n corresponds to m+1 of Cohen's equation as before. Zener has related the values of n to precipitate shapes as follows:

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n = 5/2 discs

n = 2 rods

n = 3/2 spheres

n = 1 pearlitic type of growth.

It is interesting to follow Zener's argument by which he relates the growth coefficient to precipitate shape.

(a) In his theory of spherical precipitate growth, Zener has shown that the radius of a growing sphere increases with time as follows:

 $\Delta r = (t - t_0)^{1/2} x \text{ const.}$

Therefore the volume increases as $(4/7)^3$ or $(t-t_0)^{3/2}$

(b) For a long thin rod the length increases uniformly with time $\Delta V = const \times \left[(t - t_0)^{\frac{1}{2}} \right]^2 \times (t - t_0) = const \times (t - t_0)^2$

(c) For a thin flat disc:

thickness increases as $(t - t_0)^{1/2}$

radius increases as (t - t_o)

Consequently Δ vol = const. x (t - t₀)^{1/2} (t - t₀)² = (t - t₀)^{5/2} x constant

(d) For a plane interface growth proceeds in one direction and hence 1/2

$$vol = const. x (t - t_0)^{-1}$$

ALTERNATIVE EQUATION

It should be pointed out that an alternative equation proposed

by Burke and Owen (3) for first stage graphitization in Fe-C-Si alloys can be applied equally well to the experimental results of this investigation.

(9)
$$f(t) = 1 - exp. - \left(\frac{t}{K_i}\right)^n$$

(10)
$$\frac{df(t)}{dt} = \frac{n}{K_{i}} t^{n-1} (1-f(t))$$

This equation differs from Cohen's equation only in the definition of the rate constant K. In the Burke and Owen equation K_1 is initially defined in terms of units of time and hence subsequent determination of Q_{K_1} yields the value Q_t obtained from the previous treatment. Comparison of equations (1) and (10) reveals the following relationship between K_1 and K:

$$K = \frac{n}{K_1^{n}}$$
$$K_1 = \left(\frac{n}{\kappa}\right)^{\frac{1}{n}}$$

Therefore:

Since Q_t is obtained from the earlier method by plotting $\frac{1}{n} \log \frac{K}{2.3n}$ versus $\frac{1}{T}$ it is seen that the same value will be obtained by plotting - $\log \frac{K_1}{2.3}$ versus $\frac{1}{T}$ by the Burke and Owen method.

1. C. Zener, Journ. of Applied Physics (1949), 20, p. 950.

 C. Wert, <u>Thermodynamics in Physical Metallurgy</u>, A. S. M. (1950), p. 178, Cleveland.

 J. Burke and W. S. Owen, Journ. of Iron and Steel Institute, Feb. 1954, <u>176</u>, p. 147.

APPENDIX VIII

SUMMARY OF SIGNIFICANT EXPERIMENTAL DATA

Ti-Fe SYSTEM and Ti-Ni SYSTEM

AS-QUENCHED SPECIMENS (SINTERED)								Q1000 AND TEMPERED 10 HRS. AT 570°C						
Spec÷ imen	<u>% Fe</u> Atomic	<u>002 «</u>	<u>101 ø</u>	<u>110 B</u>	<u>110</u> FeTi	专义.	\$B	% FeTi	<u>002</u> ¢	<u>101 a</u>	<u>110 ß</u>	the com	# B	% FeTi
F 3 4 5 6 7 8 8 8 9 10 11A 12	.20 .71 1.26 2.21 3.25 4.66 6.12 8.14 11.97 14.23 15.31	34 38 40 39	124 135 128 135 152 71 62 20 tr. tr.	tr. 21 42 55 83 95 106 127 100% 100%	;	100 89 80 76 65 49 40 17 tr.	tr. 11 20 24 35 51 60 83 100% 100%		37 24 30- 34 23 16 17 10 9 11	130 112 100 108 122 75 58 58 58 32 32 39	18 28 42 52 79 97 102 94 81 60	100 90 83 77 66 55 44 39 31 28 34	10 17 23 34 45 61 61 53 42	tr. 8 19 24
		<u>c</u>	21000 AM	ND. TEMPE	RED: 100	HRS. A	<u>T 570</u> •	sak .	<u> 91000</u>	AND TEN	PERED 1	000 HR	3. AT 5	070 •
F 3 5 6 7 8 8 8 9 10 11A	.20 .71 1.26 2.21 3.25 4.66 6.12 8.14 11.97 14.23	31 25 22 30 27 24 14 14 14 10 11	115 110 9976 50 36 393	tr. 5(est) 14 32 34 43 43 43 54 336	tr. 6 13 11 17 29 40	100 100 95 89 76 71 56 49 41 40	tr. 5 11 19 21 37 40 30	tr. 5 8 9 11 23 30	74 17 16 21 18 18 16 10 13 12 14	240 60 59 65 65 58 65 58 44 58 44	5 7 12 19 25 25 17 18 13 8	100 100 96 757 63 55 57 56 557 56	tr. 2 10 16 20 21 26 17 13	tr. 2 4 9 13 16 19 26 33 34

Ti-Fe ALLOY CONSTITUTIONS

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CONSTITUTION AND HARDNESS OF

QUENCHED TI-Fe ALLOY POWDERS AND LUMP SPECIMENS

		. 1	POWDERS	LUMPS			
ALLOY	1 IRON	<u>% ∝'</u>	HARDNESS	\$ \$ d'	HARDNESS		
F3	0.20	100	237		170		
4	0.71	90		*	195		
5	1.26	80	257	Line of	254		
6	2.21	75		P Versus	454		
7	3.25	65		estd.	600		
8	4.66	50		from	493		
8 A .	6.12	4 Q	2 8 0	lines.	366		
9	8.14	18	280		311		
10	11.97	Q	307		446		
11A	14.23				503		
12	15.31		411 4				
13	19.62		458				
1 ¹ 4	25.32		580				

TI-NI ALLOY (6% NI) - DATA FOR DECOMPOSITION OF 2

at 450°C - 550°C for Figures 20, 25, 26 and 27

<u>TEMP</u> . <u>TIMÉ</u> <u>min</u> .	LOGio Time	AREA RATIO Ti2NI ∝ 101	<u>from</u> <u>Standard</u> <u>Plot</u>	formed al	$\frac{1-f(t)}{x+100}$	<u>1-\$(t)</u>	$\frac{\underline{IOG_{10}}}{1}$ $\frac{1}{1-f(t)}$	$\frac{10\dot{G}_{10}^{\dagger}LOG_{10}}{1}$	LOG LOG
450° 300 1440 3000 4320 6000 30000 50000	2.478 3.158 3.478 3.636 3.778 4.478 4.478 4.700	.0512 .0814 .11 .1475 .169 .198 .240	4 % 6.3 9.2 10.9- 12.0 14.7 16.3	21.2 33.3 48.6 57.9 65.0 77.7 86.4	78.8 66.7 51.4 42.1 35.0 22.3 13.6	1.285 1.5 1.95 2.37 2.85 4.48 7.35	.0.109 .176 .290 .375 .455 .652 .866	1.037 1.246 1.462 1.574 1.658 1.814 1.938	963 754 538 426 342 186 062
500° 5 15 20 30 47 60 120 180 300 600 3000	0.7 1.176 1.303 1.478 1.671 1.778 2.08 2.255 2.478 2.778 3.478	.0379 .0435 .08 .1024 .123 .126 .157 .176 .196 .211 .222	3.0 3.4 6.1 7.8 9.25 9.5 11.6 12.75 14.25 15.4 16.3	15.9 18.0 32.3 41.3 49.0 50.2 60.4 67.5 75.4 81.5 86.0	84.1 82.0 67.7 59.7 51 49.8 39.6 32.5 24.6 18.5 14.0	1.19 1.22 1.47 1.67 1.96 2.01 2.52 3.08 4.06 5.4 7.15	-0.075 0.086 .167 .222 .292 .303 .402 .498 .609 .732 .854	2.875 2.934 1.222 1.346 1.465 1.465 1.604 1.604 1.697 1.784 1.865 1.931	- 1.125 - 1.066 - 0.778 - 0.656 - 0.535 - 0.519 - 0.303 - 0.303 - 0.216 - 0.135 - 0.069
525°,75 1.0 1.25 1.5 3.0 5.0 8.0 15 30 85 130	1.87 0 0.095 0.178 0.478 0.70 0.904 1.178 1.478 1.930 2.114	.0148 .0231 .060 .077 .093 .119 .139 .184 .207 .247	1.2 2.0 4.5 6.0 7.5 9.0 10.5 13.4 15.1 16.7	6.35 10.6 24.8 31.8 39.6 47.5 55.7 70.9 80.1 84.7	93.65 89.4 75.2 68.2 60.4 52.5 44.3 29.1 19.9 16.3	1.07 1.12 1.33 1.47 1.66 1.90 2.25 3.44 5.02 6.14	0.029 0.049 0.124 0.167 0.220 0.278 0.352 0.536 0.701 0.788	2.462 2.690 1.094 1.222 1.343 1.444 1.546 1.730 1.846 1.896	- 1.538 - 1.310 - 0.906 - 0.778 - 0.657 - 0.556 - 0.454 - 0.270 - 0.156 0.104

(continued next page....)

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TEMP.	TIME min.	LOG ₁₀ Time	AREA RATIO <u>Ti2N1</u> × 101	<u>from</u> Standard Plot	file frac ion tra formed	$\frac{1-f(t)}{\frac{1}{X100}}$	$\frac{1}{1-f(t)}$	<u>LOG₁₀ 1 1-F(t)</u>	$\frac{100_{10}L00_{10}}{1}$	<u>LOG LOG</u> 	
550°	.25 .75 1.0 1.5 2.0 3.0 4.0 6.0 9.0 15.0 30.0 60.0	1.398 1.7 1.875 0 0.178 0.303 0.478 0.6 0.778 0.955 1.178 1.478 1.778	.019 ¹⁴ .0594 .062 .071 .095 .109 .129 .171 .19 .195 .203 .201 .23	1.7 4.2 4.8 5.5 7.4 8.3 9.75 12.2 13.9 14.25 14.8 15.8 16.8	9.0 22.2 25.4 29.1 39.1 43.7 51.6 64.5 75.7 75.7 78.3 83.6 88.8	91 77.8 74.6 70.9 -56.3 48.4 35.5 26.5 24.3 21.7 16.4 11.2	1.1 1.28 1.34 1.41 1.64 1.77 2.11 2.82 3.77 4.11 4.6 6.1 8.91	-041 -107 -127 -149 -215 -248 -325 -45 -576 -614 -663 -785 -950	$\overline{2}.613$ $\overline{1}.029$ $\overline{1}.104$ $\overline{1}.173$ $\overline{1}.332$ $\overline{1}.394$ $\overline{1}.512$ $\overline{1}.653$ $\overline{1}.761$ $\overline{1}.788$ $\overline{1}.822$ $\overline{1}.895$ $\overline{1}.978$	- 1.387 - 0.971 - 0.896 - 0.827 - 0.668 - 0.666 - 0.488 - 0.347 - 0.239 - 0.212 - 0.178 - 0.105 - 0.022	ţ.
				· · · · · · · · · · · · · · · · · · ·							L10-

DATA FOR FIRST STAGE DECOMPOSITION OF RETAINED

FOR FIGURE 30 (a, b and c)

Temp.	Time min.	$\frac{\text{Ratio of}}{\text{Intensities}}$ $\frac{\beta_{110}}{\alpha_{101}} =$	x <u>*</u> ~"	\$B	<u>10 Gm. load</u> <u>V.P.N.</u> Hardness
- 400°C	30 60 120 240 360 480 900 1380 1680 2400	3.95 2.04 1.49 1.24 1.14 1.03 .58 .48 .29 .07	26.6 41.3 49.2 54.0 56.0 58.4 71.5 75.2 83.0 95.0	73.4 58.7 50.8 46.0 44.0 41.6 28.5 24.8 17.0 5.0	580 570 624 560 465 450 •425
425 °	2000 4 15 30 60 90 120 150 240	4.96 3.31 2.0 1.53 .73 .77 .33	22.4 30.2 41.7 48.4 39.9 65.4 81.2 100	77.6 69.8 58.3 51.6 60.1 34.6 18.8	600 577 570 482 444 420
4 50 •	1 2 5 10 15 20	3.50 2.11 1.35 .69 .31	29.0 40.4 51.5 67.6 82.2 100	71.0 59.6 49.5 32.4 17.8	570 520 500 472 425 420

NOTE: Each hardness listed represents the average of at least 10 values.

DATA FOR ISOTHERMAL DECOMPOSITION OF ~"

IN 6% NI - ALLOY FOR FIGURES 32, 33 AND 34

<u>TEMP</u> . <u>TIME</u> <u>min</u> .	LOG ₁₀ Time	AREA RATIO Ti2Ni X 101	<u>from</u> <u>Standard</u> <u>Plot</u>	$\frac{f(t)}{\text{fraction}}$ $\frac{f(t)}{\text{transfor}}$ $\frac{f(t)}{\text{med } X = 100}$	$\frac{1-f(t)}{x\ 100}$	$\frac{1}{1-f(t)}$	$\frac{\underline{LOG_{10}}}{\underline{1-f(t)}}$	$\frac{\frac{\text{LOG}_{10}\text{LOG}_{10}}{1}}{\frac{1}{1-f(t)}}$	LOG LOG
450° 50 100 400 1000 3150 7280	1.7 2.0 2.6 3.0 3.5 3.9	.043 .060 .106 .150 .20 .215	3.4 4.5 8.0 11.2 14.6 15.7	•180 •238 •422 •593 •772 •832	.820 .762 .578 .407 .228 .168	1.22 1.31 1.73 2.45 4.38 5.95	0.086 0.118 0.238 	2.934 1.072 1.376 1.590 1.808 1.889	- 1.066 - 0.928 - 0.624 - 0.410 - 0.192 - 0.111
500° 4 10 25 50 100 600	0.6 1.0 1.4 1.7 2.0 2.8	.04 .065 .095 .14 .20 .23	3.2 5.0 7.3 10.5 14.7 16.7	.170 .265 .386 .556 .778 .884	.830 .735 .614 .444 .222 .116	1.20 1.36 1.63 2.25 4.50 8.60	0.080 0.133 0.212 0.352 0.653 0.934	2.90 1.124 1.326 1.546 1.815 1.970	- 1.1 - 0.876 - 0.674 - 0.454 - 0.185 - 0.03
525°0.5 1.0 4.0 10 50 100	1.7 0.6 1.0 1.7 2.0	.04 .05 .117 .175 .217 .230	3.0 4.0 8.8 12.9 15.8 16.8	.159 .211 .471 .682 .836 .890	.841 .789 .529 .318 .164 .110	1.19 1.26 1.89 3.14 6.09 9.10	0.075 0.100 0.276 0.497 0.784 0.960	2.875 1.000 1.441 1.696 1.894 1.982	- 1.125 - 1.000 - 0.559 - 0.304 - 0.106 - 0.018
550°•3 •5 1 3 6 10 35	1.48 1.7 0.48 0.78 1.0 1.54	.045 .065 .090 .153 .200 .220 .245	3.7 5.0 7.0 11.3 14.7 16.0 18.0	.195 .265 .370 .598 .778 .846 .953	.805 .735 .630 .402 .222 .154 .047	1.24 1.36 1.59 2.48 4.50 6.50 21.3	0.093 0.133 0.201 0.395 0.653 0.813 1.329	2.968 1.124 1.304 1.596 1.814 1.910 0.124	- 1.032 - 0.876 - 0.696 - 0.404 - 0.186 - 0.090 0.124

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Ci-Ni	ALLOYS	-	CONSTITUTIO)N 🗄	AND	HARDNESS	OF	6	UENCHED	POWDERS

Alloy	Atomic	<u>10 gm.</u>	V.P.N. Hardness	<u>% Retained</u>
	76 Ni	Argon Q	<u>He Q</u>	HeQ
N 1 2 3 4 5 6	0.25 0.5 1.0 2.0 4.0 6.0	143 197 225 254 345 440	159 207 229 297 429 475	12 20

<u>N 6 - 6% Ni - Micro-Hardness of</u>

Tempered Structures (10 gm. Load)

Temp.	Time	Hardness	Temp.	Time	Hardness
450°	60 1440 4320 30120	387 365 320 309	525°	1 1/2 6 1/2 15 180	369 330 320 318
500°	5 45 120 600	400 357 329 313	550°	15 45 4 9	362 320 310 290 275

APPENDIX IX

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PUBLICATIONS RELATED TO THE PRESENT THESIS

 Levitation Melting Titanium and Titanium Alloys, Research (1954), vii, 2, S 12.

 Some Techniques for Melting Reactive Metals, Research (1954), VII, p. 272

Three basic melting methods are reviewed that may be applied to metals which, on account of their reactivity, cannot be melted in 'refractory crucibles. Levitation melting is considered in most detail, as the technique is felt to warrant more attention than it has received in the past.

3. Phase Transformations in Titanium-Rich Alloys of Iron and Titanium, Journal of Metals, Oct. 1954; Trans. A. I. M. E. (1954), <u>200</u>, p.1148.

High purity alloys of titanium and iron, made by a technique of levitation melting have been investigated with particular reference to martensite formation and decomposition in the hypoeutectoid range. A preliminary study has been made of the phase corresponding to the structure Ti₂Fe.

- 4. Martensite Formation in Powders and Lump Specimens of Ti-Fe Alloys, Journal of Metals, January, 1955.
- 5. Non-Equilibrium Structures in Ti-Alloys, Letter to the Editor, Journal of the Institute of Metals, Oct., 1954.
- Isothermal Decomposition Kinetics of Transformed-β Phase in a Ti-Ni Alloy, Acta Metallurgica, in press.