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The Bainite and Massive Transformations in Ti-X Eutectoid Systems

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Department of Metallurgical Engineering
Michigan Technological University

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on

The Bainite and Massive Transformations in Ti-X Eutectoid Systems

by

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The survey of eutectoid decomposition mechanisms in hypoeutectoid Ti-X alloys has been virtually completed. At temperatures from the eutectoid to the M_s in the Ti-Bi, Ti-Co, Ti-Cu, Ti-Ni, Ti-Pb and Ti-Pd systems, the bainite reaction is the only one operative. Bainite was also the only eutectoid decomposition product found in a hypoeutectoid Ti-Fe alloy reacted at a single temperature. Among the eutectoid alloys studied, Ti-Co, Ti-Cr and Ti-Cu exhibit eutectoid decomposition essentially only by the pearlite reaction and

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Ti-Ni, Ti-Pd and Ti-Pt transform predominantly or only by the bainite reaction; eutectoid decomposition by either mechanism has yet to be observed (because of its exceedingly slow kinetics) in the Ti-Fe, Ti-Ir and Ti-Mn eutectoid alloys. Whereas the TTT-curve for the initiation of eutectoid decomposition is displaced smoothly to longer times the lower the eutectoid temperature of the alloy system in the eutectoid alloys so far investigated, in hypoeutectoid alloys this generalization is often violated, evidently as a consequence of the widely varying, system parameter-sensitive nucleation kinetics of intermetallic compounds at $\alpha:\beta$ boundaries, for the formation of pearlite and of bainite. A theoretical discussion is presented of the nucleation and growth kinetics of intermetallic compound crystals at fixed and at moving $\alpha:\beta$ boundaries.

In studies of the massive transformation, $\beta \rightarrow \alpha_m$, in Ti-Ag, Ti-Au, Ti-Si and Ti-In alloys, the composition region in which this transformation occurs in each alloy system was defined. Both metallographic and electron probe confirmation was secured of the existence of this mode of transformation. By means of continuous cooling experiments, the enthalpy of transformation and the average rate of growth as a function of temperature were determined in a number of alloys in the four systems. A major deficiency appears to have been uncovered in the published configuration of the Ti-rich region of the Ti-In system.

The Bainite and Massive Transformations in Ti-X Eutectoid Systems

H. I. Aaronson, G. W. Franti and M. R. Plichta

Abstract

The survey of eutectoid decomposition mechanisms in hypoeutectoid Ti-X alloys has been virtually completed. At temperatures from the eutectoid to the M_s in the Ti-Bi, Ti-Co, Ti-Cu, Ti-Ni, Ti-Pb and Ti-Pd systems, the bainite reaction is the only one operative. Bainite was also the only eutectoid decomposition product found in a hypoeutectoid Ti-Fe alloy reacted at a single temperature. Among the eutectoid alloys studied, Ti-Co, Ti-Cr and Ti-Cu exhibit eutectoid decomposition essentially only by the pearlite reaction and Ti-Ni, Ti-Pd and Ti-Pt transform predominantly or only by the bainite reaction; eutectoid decomposition by either mechanism has yet to be observed (because of its exceedingly slow kinetics) in the Ti-Fe, Ti-Ir and Ti-Mn eutectoid alloys. Whereas the TTT-curve for the initiation of eutectoid decomposition is displaced smoothly to longer times the lower the eutectoid temperature of the alloy system in the eutectoid alloys so far investigated, in hypoeutectoid alloys this generalization is often violated, evidently as a consequence of the widely varying, system parameter-sensitive nucleation kinetics of intermetallic compounds at $\alpha{:}\beta$ boundaries, for the formation of pearlite and of bainite. A theoretical discussion is presented of the nucleation and growth kinetics of intermetallic compound crystals at fixed and at moving $\alpha{:}\beta$ boundaries.

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I. Introduction

The program consists of fundamental studies of the mechanisms of the massive and the bainite reactions in Ti-X eutectoid systems. The massive transformation is defined as the conversion of a matrix to a product phase without a change in composition by means of a diffusional nucleation and growth mechanism. Diffusional jumps across the matrix:massive phase boundary is the basic atomic process involved in this transformation. The massive transformation is being studied in the Ti-Ag, Au, In and Si systems. On the view (1) used here, the bainite reaction is a eutectoid reaction yielding a non-lamellar arrangement of the two co-precipitating product phases; both phases differ in composition from the matrix throughout the transformation process and both form by diffusional nucleation and growth. The bainite reaction is being studied in the Ti-Bi, Co, Cr, Cu, Fe, Ir, Mn, Ni, Pb, Pd and Pt systems.

The basic experimental procedure is the encapsulation of specimens, wrapped in Ta foil, in Vycor capsules. The capsules are repeatedly evacuated and flushed in dried and purified helium and then lightly torched to drive off absorbed gases prior to heat treatment. Specimens being used to study the bainite reaction are solution annealed at 1000°C for 30 min. in a tube furnace and then isothermally transformed in a stirred lead bath. Many specimens employed in the massive transformation studies are quenched directly from the

same solution annealing treatment into iced 10% brine. Only in the Ti-In system have isothermal transformation studies proved feasible. For studies of the thermodynamics and growth kinetics of the massive transformation in the Ti-Ag, Au and Si systems, the continuous cooling transformation apparatus of Professor John H. Perepezko of the University of Wisconsin-Madison has been extensively utilized with Professor Perepezko's collaboration; this apparatus was described in the previous interim technical report on this grant.

II. The Bainite Reaction (Dr. G. W. Franti, Postdoctoral Research Associate)

A. Hypoeutectoid Alloys

The planned survey of eutectoid decomposition mechanisms in these alloys is now nearly complete. All such studies have been performed on the hypoeutectoid Ti-Bi, Ti-Co, Ti-Cu, Ti-Ni, Ti-Pb and Ti-Pd alloys, at 50°C intervals between the transus temperature and the M_s. In all cases, the only mechanism of eutectoid decomposition operative is the bainite reaction. No trace of the pearlite reaction was observed. Eutectoid decomposition kinetics are exceedingly slow in hypoeutectoid alloys of the Ti-Fe and Ti-Mn systems. In the Ti-Fe case, transformation for 28 days at 550°C (ca. 50°C below the eutectoid temperature) has finally shown that the only mechanism of eutectoid decomposition operative is again the bainite reaction (Figure 1). The initiation of either form of eutectoid decomposition has yet to be observed in hypoeutectoid Ti-Mn (if necessary, specimens will be reacted for months at temperatures near that of the eutectoid). Observation of eutectoid decomposition in Ti-Pt, the only remaining system in which hypoeutectoid alloy studies are to be conducted, is still being prevented by the resistance of this alloy to chemical etching.

The bainitic microstructures generated in hypoeutectoid alloys are essentially identical to those of upper bainite in steel. Compound nucleation occurs largely, if not entirely, at α:β boundaries. The scale of the microstructure diminishes rapidly with decreasing temperature, but not at the same rate in the various systems. For example, the microstructures in Ti-Cu are particularly fine. Figure 2 is a scanning electron micrograph of a Ti-4.6 A/O Cu alloy reacted for 20 min. at 725°C, ca. 75°C below the eutectoid temperature. The spacing between adjacent α plates is ca. 0.4μ; the compound particles average 0.36μ long and 0.1μ wide. Bainite is optically unresolvable ca. 50°C below the eutectoid temperature. In the Ti-Bi and Ti-Pb systems, on the other hand, compound precipitation at the α:β interfaces occurs after the α plates have thickened and coarsened extensively, and hence the scale of the bainite structures is coarse. Bainite is optically resolvable in these systems down to the M_s temperature.

An unexpected observation was made on the bainite reaction in the Ti-Fe system. As shown in Figure 1, compound precipitation occurs only at impinged α plates in the interiors of β grain, and not at its usual preferred location, the surfaces of grain boundary allotriomorphs. Evidently this is due to faceting of the allotriomorphs during the very long transformation times required to nucleate compound particles. The energy of the interphase boundaries of these crystals is accordingly reduced to too low a level to make them effective nucleation sites. On the other hand, intersections between α plates parallel to different habit planes of the same crystallographic form necessary retain their high energies and remain good nucleation sites.
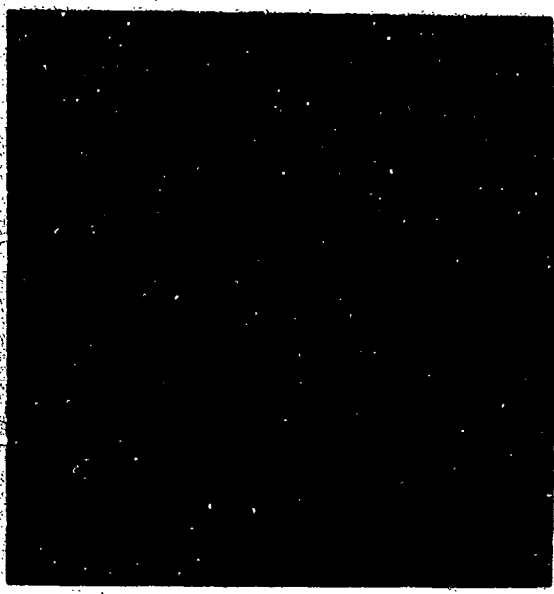
Figure 1. Ti-4.5 A/O Fe reacted for 28 days at 550°C. (1500X)

Figure 2. Ti-4.6 A/O Cu reacted for 20 min. at 725°C (10,000X)

Figure 4. Ti-14 A/O Cr reacted for 24 hrs. at 650°C. (500X)

Figure 5. Ti-5 A/O Ni reacted for 2 hrs. at 750°C. (500X)

Figure 3 shows the TTT-curves for the initiation of the bainite reaction
in the seven hypoeutectoid alloys in which this data has so far been obtained.
Overall, a tendency is observed for the TTT-curve to be displaced to longer
times the lower the eutectoid temperature. When examined in more detail,
however, several anomalies become apparent. The bainite reaction begins more
rapidly in Ti-Bi ($T_{eutectoid}$ = 725°C) than in Ti-Ni (770°C), more rapidly in
Ti-Co (685°C) than in Ti-Pb (725°C), and more rapidly in Ti-Bi (725°C) than
in Ti-Pb (725°C). Additionally, the bainite reaction begins orders of magni-
tude more rapidly in Ti-Pd (595°C) than in Ti-Fe (585°C), despite the small
difference in the eutectoid temperatures of these two systems. In the Bi vs.
Pb case, the composition difference (in A/O) between the $\beta/(\alpha+\beta)$ transus
and the $\beta/(\beta + compound)$ transus—both extrapolated to temperatures below that
of the eutectoid—which provides the driving force for both nucleation and
growth, is greater in Ti-Bi than in Ti-Pb. Similarly, the lattice of the
compound appears to match those of α and β better in the Bi than in the Pb
system. Hence both factors favor more rapid compound formation in Ti-Bi. In
the other cases, however, the direction of the driving force difference is the
reverse of that of the kinetics. It is not yet apparent whether interfacial
energies between the compound particles and the α and the β phases are likely
to be less in the more rapidly reacting eutectoid systems. The planned
orientation relationship studies among these phases, to be undertaken during
the coming report year, should assist considerably in answering this question.
An effort is also to be made to effect improved calculations of the transus
curves in order to provide better indications of the relative supersaturation
for bainitic compound precipitation in the various alloy systems. However,
the accuracy of the resulting driving force calculations will be limited by
the sparseness of activity measurements in the β phase of Ti-X alloy systems.
Understanding the fundamentals of the nucleation and growth kinetics of bainitic
compound precipitation (see section II-D) is clearly essential to the economical
design of Ti-base eutectoid alloys in which the compound is finely and more or
less uniformly dispersed throughout the material.

B. Eutectoid Alloys

Research on these alloys has gotten underway recently, following
the much appreciated receipt of nine alloys of approximately eutectoid
composition in as many different Ti-X systems from the Rockwell International
Science Center through the courtesy of Dr. Neal Paton. All alloys were homo-
genized at the Rockwell laboratories prior to shipment to MTU.

The results so far obtained on these alloys divide into three groups.
In the first group, comprising the Co, Cr and Cu alloys, the eutectoid
decomposition product is pearlite. Figure 4 shows pearlite nodules formed
at grain boundaries, apparently in association with grain boundary allotriomorphs
of proeutectoid $TiCr_2$, in a Ti-14 A/O Cr alloy reacted 24 hrs. at 650°C, about
20°C below the eutectoid temperature. Transformation kinetics in the eutectoid
Ti-Cu alloy are so rapid that it is difficult to discern the nucleation sites
of the pearlite nodules. In Ti-Co, where kinetics are slower, pearlite nodules
are observed at α allotriomorphs and also at α plates with irregular interfaces,
but not at smoothly shaped α plates.

The second group of eutectoid alloys, comprising the Ni, Pd and Pt systems,
exhibit bainite as either the primary or the only eutectoid decomposition
product. Figure 5 shows a primarily bainitic eutectoid structure in a Ti-5
A/O Ni alloy reacted for 2 hrs. at 750°C. In both the Ti-Pd and Ti-Pt alloys,
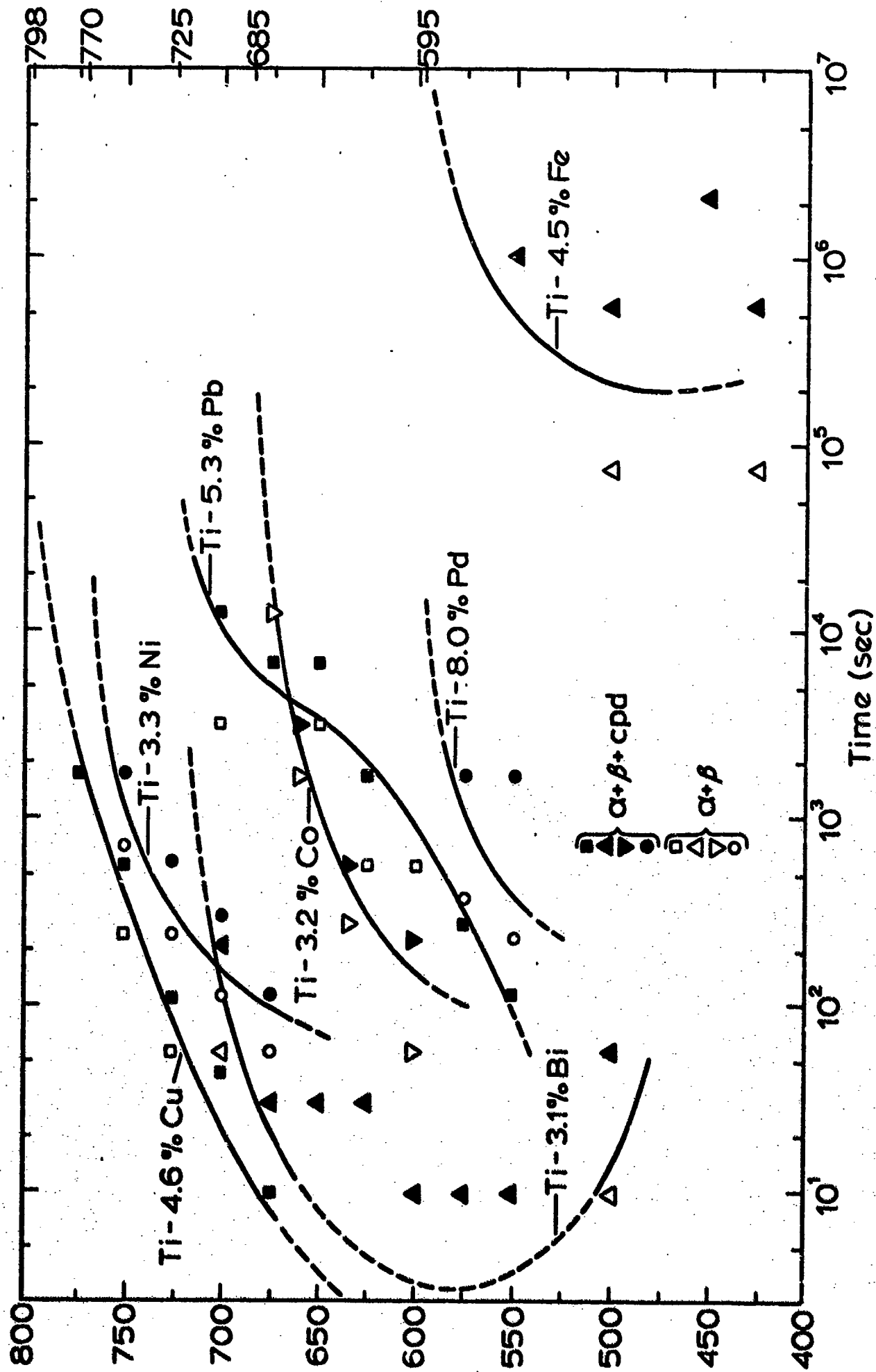etching problems have significantly interferred with our studies; results

Figure 3

achieved to date indicate, however, that bainite froms instead of pearlite in Ti-Pt and probably also in Ti-Pd. Grain boundary allotriomorphs of Ti_2Pd were present in the Pd eutectoid alloy and of α were formed in Pt alloy.

The third group of eutectoid alloys, including the Fe, Ir and Mn alloys, has yet to yield any sign of either the pearlite or the bainite reaction after reaction times as long as four weeks at temperatures near that of the eutectoid. A number of capsules of these alloys and of hypoeutectoid Fe and Mn alloys are undergoing simultaneous and continuing reaction, each at two temperatures not far below that of their respective eutectoids; capsules are removed and quenched periodically to ascertain the progress of eutectoid decomposition.

Figure 6 shows the TTT-curve for the initiation of the eutectoid reaction so far obtained for the eutectoid alloys. Note that, unlike the hypoeutectoid alloys, there are no anomalies; as the eutectoid temperature is decreased, the TTT-curves are displaced to longer times. No inst·nces of intersecting TTT-curves appear. Empirically, this simpler set of results is apparently due at least in part to the circumstance that three of the four TTT-curves are for alloys in which eutectoid decomposition occurs in the pearlitic mode. The implications of this observation are considered in the next sub-section.

C. Interpretation of the Results Obtained on Hypoeutectoid and Eutectoid Alloys

Our basic approach to interpretation, both of the present results and of the differences between the balance of bainite vs. pearlite in steel vs. that in Ti-X alloys is the following. Because of the short and constant growth path involved, the growth rates of pearlite are characteristically very high; and in substitutional alloys the pearlite:matrix boundary can serve as a high-diffusivity path (2). Hence once pearlite is nucleated it can grow at rates competitive with nearly all of those characteristic of the proeutectoid reactions. Further, the nucleation of pearlite preferentially at the interphase boundaries of proeutectoid crystals tends to cripple growth of these crystals by straightforward steric interference. The principal "barrier" to pearlite formation is evidently the "nucleation" process. As used here, "nucleation" means not only the formation of critical nuclei of the two co-precipitating phases but also the growth of these phases in the "cooperative" manner needed for the evolution of a pearlite colony (3). Observations (3,4) on the pearlite reaction in off-eutectoid steels indicate that appreciable areas of disordered interphase boundary between austenite and proeutectoid ferrite or austenite and proeutectoid cementite are required if the "cooperation" necessary for the development of pearlite is to evolve during the further growth of the proeutectoid phase and the nucleation and growth of the other precipitate phase. In relatively fine grained steels, especially, grain boundary allotriomorphs are a major or the predominant morphology over wide ranges of reaction temperature and carbon content (5). Not until relatively large undercoolings below the Ae_3 or Acm are achieved, or very large grain sizes are employed, which enable the amount of undercooling required to be reduced, do Widmanstatten plates form extensively. These plates have been shown to be very poor sites for the nucleation of pearlite in hypoeutectoid steels (4). At lower reaction temperatures, however, the broad faces of ferrite plates prove quite suitable as nucleation sites for bainitic carbides (6). Ledges on these faces, which are present in relatively large numbers (7), are likely candidates for such sites. In titanium alloys, much smaller undercoolings are required to make sideplates and intragranular plates the dominant proeutectoid morphology in

Temperature (°C) vs Time (sec)

Ti-5.5%Cu

Ti-5.0%Ni

Ti-8.0%Co

Ti-14.0%Cr

α+β+cpd

α+β
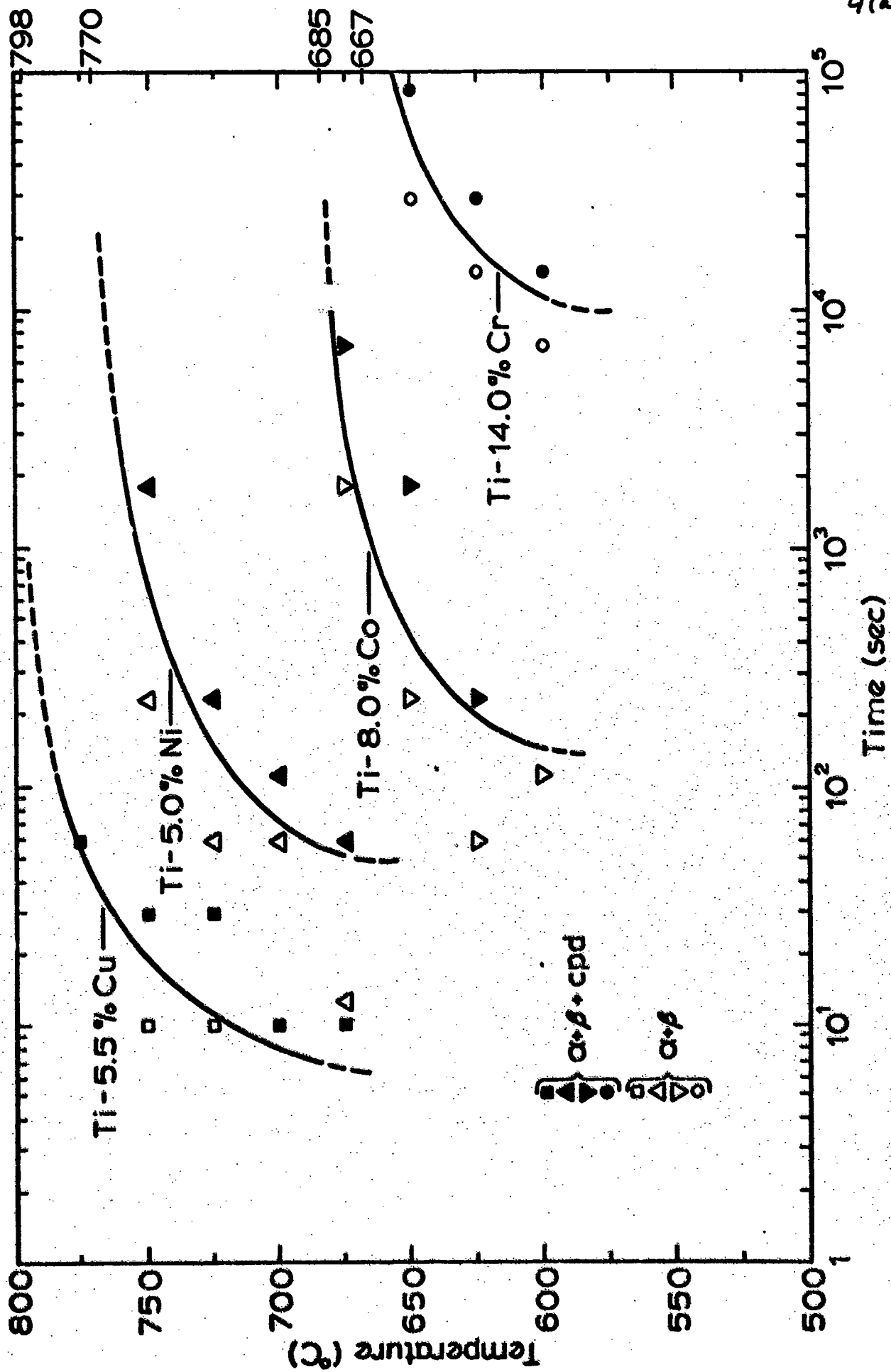
hypoeutectoid alloys (8,9); it is, in fact, quite difficult to create the conditions which make grain boundary α allotriomorphs the dominant morphology. And at reaction temperatures below that of the eutectoid, the undercooling below the transus is normally sufficient to make Widmanstatten α the dominant morphology in hypoeutectoid alloys by an overwhelming margin. Hence the formation of pearlite is crippled whereas the precipitation of compound particles at ledges and possibly at other defects on α plates can still occur at reasonable rates.

These considerations account for our finding that in all hypoeutectoid Ti-X alloys in which we have been able to observe eutectoid decomposition the bainite reaction has been the only mode in which it occurs. They also provide a basis for explaining the more complex pattern of results so far observed in eutectoid alloys. In such alloys, the driving forces for the precipitation of α and of compound are more nearly equal. Hence even if allotriomorphs of α precipitates first there is a significant probability, at reasonable undercoolings below the eutectoid temperature, that compound precipitation can begin at the interphase boundaries of the allotriomorphs before sideplates evolve from the allotriomorphs. Compound precipitation in such locations provides the optimum opportunity for initiation of the evolutionary process leading to pearlite formation and may simultaneously interfere with the development of α sideplates from the allotriomorphs. (Once the sideplates are formed in considerable numbers they will seriously inhibit the evolution of pearlite, again on steric grounds.) Alloys in which the bainite reaction is predominant even near the eutectoid composition are likely those in which the nucleation of compound crystals at α:β boundaries is relatively slow. Reference to Figure 3 indicates that the nucleation of compound particles is rapid in Ti-Cu and Ti-Co. Previously published TTT-diagrams for hypoeutectoid Ti-Cr alloys show that TiCr$_2$ precipitation is slow (8,9); but the "eutectoid" Ti-Cr alloy used in this investigation is actually slightly hypereutectoid; proeutectoid TiCr$_2$ allotriomorphs precipitated and thus evolution of proeutectoid α sideplates was automatically precluded. (Proeutectoid TiCr$_2$ sideplates are very rare (10).) Figure 3 also indicates that compound precipitation is slow in Ti-Pd; hence the formation of bainite in eutectoid Ti-Pd instead of pearlite to be expected. The only alloy in which this approach runs into some difficulty is eutectoid Ti-Ni; here the compound appears to precipitate rapidly (Figure 3), yet the microstructure of the eutectoid alloy (Figure 5) is not readily distinguishable from that of an alloy of hypoeutectoid composition. There are indications, however, that the eutectoid composition may not be accurately known in Ti-Ni (11), and must be checked experimentally before this anomaly can be considered further.

D. Theory of Compound Precipitation at α:β Boundaries

The considerations of this subsection are equally applicable to the very old problem of bainitic carbide nucleation in steel, where the question of whether such carbides nucleation in austenite or in ferrite as a function of reaction temperature has been inconclusively debated for more than 40 years (6). Mr. N. R. Plichta, graduate student, and Professor K. C. Russell of M. I. T. have also participated in developing the following material.
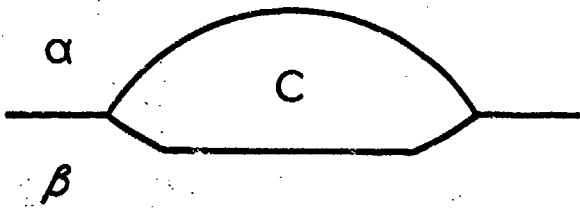
Consider first the question of whether compound particles nucleated at α:β boundaries form in α or in β. Figure 7 shows that the entire question is a non-sequitor. Initially ignoring the orientation-dependence of the energy of α:compound and β:compound boundaries, the critical nucleus shape
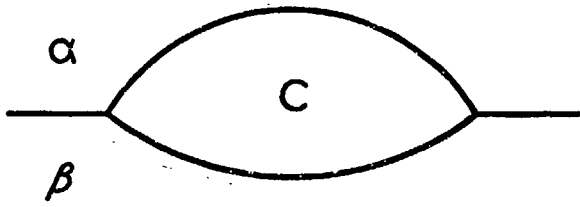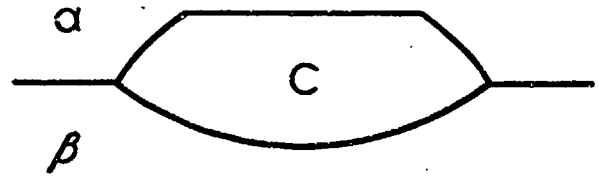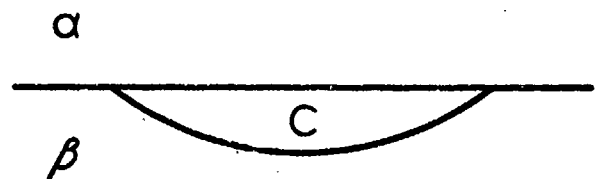
Figure 7

of Figure 7a applies. (Volume strain energy significantly affects such shapes only in the quite unusual situation in which it is a large fraction of the volume free energy change (12).) Clearly the nucleus penetrates both α and β. As long as the α:β boundary is disordered, the volume free energy change attending nucleation is the same in both phases. Hence such a nucleus must be said to have formed in both phases, not in either. In Figures 7b and 7c, a facet is introduced first on one side of the nucleus and then on the other. Physically, a facet means that a closely matched (probably fully coherent) pair of conjugate habit planes forms the interphase boundary at this particular boundary orientation. The presence of a facet has been shown to increase markedly the rate of nucleation, primarily by lowering the activation free energy for the formation of the critical nucleus (13). Whether a facet forms between the compound nucleus and α between the compound and β, or between both is strictly a function of which of these shapes yields the highest nucleation rate. (For the sake of completeness, and probably also better accuracy, we should note that facets may be present at more than one orientation, possibly on both sides of the nucleus, and that the curved or disordered portions of the nucleus surface will be non-spherical if interfacial energy is a continuously and smoothly varying function of composition at these orientations.) In none of these situation, however, does the nucleus fail to penetrate both phases. Only in the special situation of Figure 7d, where a facet lies precisely in the plane originally occupied by the α:β boundary, is entry into one phase prohibited. The classical method of deducing the disposition of the critical nucleus relative to the interphase boundary is to determine whether it has a specific and reproducible orientation relationship with respect to one or both of the two phases forming this boundary. The nucleus is taken to form in the phases with respect to which it has such a relationship. Application of this mode of deduction is seen to yield the wrong answer in the cases of Figures 7b, 7c and 7d. As long as the lattice of the compound is even modestly compatible with that of one of the crystals forming the interphase boundary the critical nucleus shape of Figure 7a is unlikely to be present; the shapes of Figures 7b-d all yield very much higher nucleation rates.

We next consider the question of compound nucleation at a moving interphase boundary. For the case of alloy steels Honeycombe (14) has recently provided an excellent review of current experimental evidence and thinking on this subject for the case of carbide nucleation at austenite:ferrite boundaries. It seems generally agreed that carbides nucleate primarily on the broad faces of ledges on these boundaries because such interfaces are immobile, and that nucleation on the more mobile risers connecting the ledges is much less frequent despite their larger contribution of interfacial energy to the nucleation process. These observations may be understood theoretically on the following simple basis. Unless the migration rate of an interphase boundary is much less than the average growth rate of the nucleus, a portion of the developing nucleus taking up a less than optimum shape—if it can even survive long enough to do so before being overrun by the advancing interphase boundary—and hence reducing its rate of nucleation by many orders of magnitude. One may thus formulate the problem simply by writing the following inequality governing the condition under which a nucleus can form at an advancing α:β boundary:

$$a_o / \tau > G^{\alpha:\beta}$$

where a_0 = a lattice parameter in the nucleus, τ = incubation time for nucleation (13,15) and $G^{\alpha:\beta}$ = growth rate of the $\alpha:\beta$ boundary = $\alpha/2t^{1/2}$, where α = parabolic rate constant for the migration of a planar, disordered boundary and t = growth time. Substituting an appropriate expression for τ (13) and using the (sufficiently accurate) Zener (16) linearized gradient approximation for α,

$$\frac{v_c^2 \, DxL \cdot \Delta G_v^2}{8kT\gamma a^3 K} > \frac{D_\beta^{1/2}(x_\beta^{\beta\alpha} - x_\beta)}{2t^{1/2}(x_\beta^{\beta\alpha} - x_\alpha^{\alpha\beta})^{1/2}(x_\beta - x_\alpha^{\alpha\beta})^{1/2}}$$

where in the left hand side of this inequality v_c = average volume of an atom in the compound phase, D = diffusivity and x = solute concentration (both defined below), L = ratio of the nucleus area in either α or β at which atomic attachment is feasible to the area of a sphere of the same radius (again see below), ΔG_v = free energy change per unit volume of the compound phase, kT has its usual meaning, γ = interfacial energy of the α:compound or β:compound boundary (see below), a = one lattice parameter in the nucleus and K = ratio of the volume of the nucleus to that of a sphere of the same radius (see below). Since the two spherical caps comprising these nuclei will have different radii, the set of parameters different in α and in β which yields the highest value of τ is appropriate. Hence, $\gamma K/DxL$ should be calculated, under given conditions, for the portions of the nucleus facing the α and the β phases and only that set of values yielding the highest value of this ratio should be retained. (In this ratio K and L apply to ratios of volumes and areas with the same radius as the spherical cap facing each matrix phase, Dx becomes $D_\alpha x_\alpha^{\alpha c}$ and $D_\beta x_\beta^{\beta c}$, where D_α and D_β = diffusivities in α and in β at compositions $x_\beta^{\beta c}$ = mole fractions of solute in β at the β/β + compound phase boundary.) In the right hand side of this equation, it remains necessary to define only x_β = mole fraction of solute in the alloy as a whole and t = isothermal growth time. Rearranging,

$$t > \frac{16 D_\beta a^6 (kT\gamma K)^2 (x_\beta^{\beta\alpha} - x_\beta)^2}{(DxL)^2 (v_c \cdot \Delta G_v)^4 (x_\beta^{\beta\alpha} - x_\alpha^{\alpha\beta})(x_\beta - x_\alpha^{\alpha\beta})}$$

This equation gives the growth time required for the migration of the $\alpha:\beta$ boundary (assumed disordered along its entire length) to slow down to the point where nucleation can occur at it. The values of the parameters involved are readily available in the case of Fe-C alloys; preliminary calculations indicate growth times within the order of magnitude experimentally observed for the nucleation of pearlite and of bainitic carbides at the interphase boundaries of ferrite allotriomorphs. The necessary values of certain of these parameters are presently being collected for representative binary Ti-X systems. The results of the calculations so far made for steel indicate, however, that the correct physical explanation for the difficulty of compound nucleation at disordered interphase boundaries is probably at hand.

The third problem attacked is that of the relative growth rates of a compound particle into the α and β phases. Assuming for simplicity that the α:compound and β:compound interfaces can be approximated as planar (an oblate ellipsoid is a better model for such a particle, but as long as the aspect ratio is not much greater than ca. 1/3 the effect of this assumption upon growth kinetics is usually quite small (17)) and again using the Zener (16) linearized gradient solution for growth rate,

$$\frac{G^\alpha}{G^\beta} = (\frac{D_\alpha}{D_\beta})^{1/2} \frac{(x_\alpha^{\alpha\beta} - x_\alpha^{\alpha c})}{(x_\beta^{\beta\alpha} - x_\beta^{\beta c})}$$

In writing this relationship, use has been made of the circumstance that the mole fraction of solute in the compound is usually much greater than that corresponding to any of the other composition terms to simplify considerably the the compositional portion of this relationship. In any system in which "α" represents a very dilute terminal solid solution, the numerator of the composition component of this equation will be appreciably smaller than the denominator. In the case of Fe-C alloys, however, D_α exceeds D_β (i.e., D in austenite) by a sufficient margin so that G^α/G^β at 700°C is 0.47. In Ti-Ni alloys, G^α/G^β varies from 0.14 to 0.05 as temperature is decreased from 750° to 300°C. This expectation is borne out by our present observations on Ti-bainite, wherein growth of the compound particles occurs predominantly into the β phase. Although the much smaller scale of bainitic carbide precipitation is steel and the usually quite poor definition of α:γ boundaries as the result of transformation of the austenite to martensite during quenching makes parallel observations on steel difficult, it appears that the expectation of roughly equal penetration of bainitic carbides into austenite and ferrite is borne out experimentally. In the case of steel, therefore, the metallographic observations, necessarily made when the growth stage of compound precipitation is far advanced, would appear to provide a reasonable representation of the "partition" of the nucleus between austenite and ferrite. In the case of Ti-X bainites, however, this calculation and the assumption that α:compound and β:compound interfacial energies are similar indicates that the observation made during growth on the "partition" of the compound particles between α and β is grossly misleading with respect to the partition which occurs during nucleation. In fact, early observations on the growth "partition" led us to the (conventional) conclusion that the compound nucleates in β at α:β boundaries (8).

These considerations are now being refined and written up for publication. The results obtained provide the theoretical framework which will be needed for the interpretation of the orientation relationship determinations among the α, β and compound phases scheduled to be undertaken as soon as the survey of eutectoid decomposition mechanism in hypoeutectoid and eutectoid alloys has been completed.

III. The Massive Transformation (Mr. M. R. Plichta, Graduate Student)

A. Introduction

This portion of the program consists of confirming the existence of the β→αm massive transformation in Ti-Ag, Ti-Au, Ti-In and Ti-Si, establishing its existence rages in these systems, determining its thermodynamics, kinetics and crystallography and on the basis of this information deducing its mechanism.

B. Metallographic Confirmation and Establishment of the Existence Range of the β→αm Transformation

1. Ti-Ag

The maximum solubility of Ag in equilibrium α is 14.5 W/O and the eutectoid composition lies at 22.6 W/O Ag. Evidence for the massive

transformation has been obtained at Ag contents as high as 26.0 W/O. (The maximum solubility of Ag in β Ti is about 28 W/O.) Hence the kinetics of α_m formation can exceed not only those of equilibrium proeutectoid α but also those of proeutectoid Ti₃Ag. The table of pct. α_m vs. composition presented in the annual report for the previous year has been revised; with the assistance of transmission electron microscopy, it has been found that a noticeable proportion of the phase identified in the microstructure as α_m is actually martensite. The revised table still shows, however, that substantial proportions of the microstructure can be transformed to α_m even in the most Ag-rich alloy investigated:

W/O Ag in Alloy	Pct. α_m
10.0	100
13.5	60-80
17.5	50-70
20.0	50-60
23.0	30-60
26.0	10-50

The scatter in the proportion of α_m exhibited at most compositions is due to the usual sensitivity of this rapidly occurring mode of transformation to the details of the quenching process.

Precipitation of intermetallic compound, presumably Ti₃Ag (this tentative identification is to be checked with selected area diffraction), from α_m in all Ti-Ag alloys investigated provides further proof that this phase is indeed supersaturated with respect to Ag and is thus α_m. Uniquely in the four massive transformations being studied, precipitation takes place by means of the cellular reaction.

2. Ti-Au

The maximum solubility of Au in equilibrium α is 11 W/O and the eutectoid composition occurs at 16 W/O. When capsules were broken under iced brine after solution annealing, α_m was found in alloys containing from 7 to 13 W/O Au. Cooling the evacuated capsules in air permitted about 40% α_m to form in the 16 W/O Au alloy. Massive α was not observed in the 20% Au alloy and hence may not appear very far into, if at all in the hyper-eutectoid region in this eutectoid system. Estimation of the pct. α_m as a function of the Au content has not proved feasible because it is sometimes difficult to distinguish between α_m and the packet martensite that consumes the remaining β. Such difficulties have been previously encountered in the $\gamma \rightarrow \alpha_m$ transformation in Fe-Ni alloys (18).

Precipitation of compound (possibly Ti₃Au) from α_m was observed in all alloys but the one containing 7 W/O Au. Precipitates formed largely at grain boundaries in α_m.

3. Ti-Si

In this system, the maximum solubility in equilibrium α and the eutectoid composition are 0.45 and 0.65 W/O Si, respectively. Iced brine quenches of 0.4 and 0.65 W/O Si alloys caused complete transformation to packet martensite. In an 0.9 W/O Si alloy proeutectoid intermetallic compound was also present in the otherwise packet martensite microstructure. Massive α was only formed during vacuum cooling, and also in the continuous

cooling experiments (see sub-section III-D), and then only in the 0.4 and 0.65 W/O Si alloys. Precipitation of intermetallic compound from α_m again supported the identification of the massive transformation and was again largely confined to the grain boundaries in α_m.

4. Ti-In

The maximum solubility in equilibrium α and the eutectoid composition in Ti-In are ca. 22 and 25 W/O In, respectively. The alloys available in this system contain from 23 to 28 W/O In. Upon iced brine quenching, these alloys transform almost entirely to martensite, with only a small amount of α_m forming at the β grain boundaries. In the continuous cooling experiments, only at the two slowest rates did significant amounts of α_m appear; at the higher cooling rates less than 5% α_m was formed. No compound could be precipitated from α_m in this system, despite extensive efforts, involving prolonged isothermal aging anneals, to do so. An alternate confirmation of the massive transformation in Ti-In is presented in the next subsection and an explanation for the failure to observe precipitation from α_m is offered in subsection III-E.

C. Electron Probe Analysis Confirmations of the Massive Transformation

Analyses of the α_m and the martensitic phases have been made in all four alloy systems with an electron probe. In each system, the compositions of the two phases were shown to be identical to within the limits of the counting errors. In principle, these results are decisive evidence in favor of our identification of α_m as the product of a massive transformation. However, the similarity of the compositions of equilibrium α and equilibrium β and the imprecise knowledge of the boundaries of the $\alpha + \beta$ region—see subsection III-E concerning re-determination of these boundaries—make these results somewhat less definitive at the present time. Not until the $\alpha + \beta$ regions have been more accurately defined, and the ability of the electron probe to distinguish between equilibrium and massive α has been established will these results constitute impeccable proof of the massive transformation in these Ti-X systems.

D. Thermodynamics and Kinetics of the Massive Transformation

This portion of the investigation is being conducted in collaboration with Professor John H. Perepezko of the University of Wisconsin at Madison. Professor Perepezko has constructed a sophisticated version of the now standard type of apparatus for investigating the massive transformation during continuous cooling. With this apparatus, the thermal arrest temperature is determined as a function of cooling rate. Except in a relatively slow massive transformation, such as that in Ti-In, the arrest appears because the transformation takes place with such rapidity that the heat of transformation released is readily detectable and is sufficient to make the transformation roughly isothermal when the cooling rate (in our alloy systems) is less than ca. 600°C/sec. From a relationship due to Ayres (19), the enthalpy of the transformation, $\Delta H^{\beta \to \alpha_m}$, can be obtained from the thermal arrest data:

$$\Delta H^{\beta \to \alpha_m} = \frac{\Delta T(C_\alpha - C_\beta)}{\ln(C_\alpha/C_\beta)}$$

where ΔT = temperature rise due to the transformation and C_α and C_β are the heat capacities of the α and β phases (data for pure Ti must be used, perhaps without much error, because such information is not available for our alloys). Growth rate can then be calculated as a function of temperature from a relationship due to Hillert (20):

$$G = \frac{dC\dot{T}}{\Delta H^{\beta \to \alpha_m}}$$

where G = rate of growth, d = average diameter of α_m grains, C = average heat capacity and $\dot{T}$ = cooling rate. Finally, the principal parameter characterizing the growth rate, ΔH_{D_b}, the enthalphy of activation for trans-interphase boundary diffusion, can be obtained from the data on G and $\Delta H^{\beta \to \alpha_m}$ through the standard relationship:

$$G = \frac{\delta kT}{h} \exp(\Delta S_{D_b}/R)(-\Delta F^{\beta \to \alpha_m}/RT)\exp(-\Delta H_{D_b}/RT)$$

where δ = interphase boundary thickness (ca. one lattice parameter), k = Boltzmann's constant, T = absolute temperature, h = Planck's constant, ΔS_{D_b} = entropy of activation for trans-interphase boundary diffusion, R = gas constant and $\Delta F^{\beta \to \alpha_m}$ = free energy change associated with the massive transformation. Evaluating $\Delta F^{\beta \to \alpha_m}$ from $\Delta H^{\beta \to \alpha_m}$ requires accurate knowledge of the T_0 temperature. We had originally expected to obtain this temperature from plots of the Bhattacharyya et al (21) type, i.e., linear relationships between the thermal arrest temperature and $T^{1/2}$. However, further consideration of their analysis led to the conclusion that the assumption underlying this relationship, namely, that the effects of the temperature dependence of the trans-interphase boundary diffusivity can be ignored, is insufficiently accurate for our purposes. Hence the T_0 temperature must be evaluated in another way. Since the $\alpha + \beta$ regions of the four Ti-X systems in which the massive transformation occurs are very narrow, assuming that the T_0-composition curves are the bisectors of these regions cannot introduce significant errors. These regions are not defined with sufficient accuracy by presently available phase diagrams. Hence these regions are being redetermined as part of the present investigation; when the T_0 temperatures are known evaluation of ΔH_{D_b} for the various alloys will be straightforward.

The results presently available on the thermodynamics and kinetics of the massive transformation in the systems under investigation thus consist of data on $\Delta H^{\beta \to \alpha_m}$ and G vs. temperature for most of our alloys. Thermodynamic data have been obtained for one Ti-In alloy; growth kinetics cannot be determined by the continuous cooling method because they are too slow; a conventional isothermal transformation technique is now being used to secure this data.

The enthalpy of transformation data are the following:

Alloy (W/O)	$\Delta H^{\beta \to \alpha} m$ (cal./mole)
10.0 Ag	−640 ± 40
13.5 Ag	−585 ± 45
17.5 Ag	−525 ± 40
7.0 Au	−585 ± 35
9.9 Au	−600 ± 30
13.0 Au	−520 ± 35
0.4 Si	−640 ± 90
0.65 Si	−400 ± 45
23.0 In	−465 ± 60

Typical growth rate data are shown in Figure 8. These data are of the indicate rates considered appropriate for the massive trnasformation.

E. Phase Diagram Studies

Conventional isothermal annealing technique is being used to re-determine the α + β regions of all four Ti-X systems which undergo a massive transformation.

In the Ti-Ag system, the finding of precipitated intermetallic compound in the Ti-10 W/O Ag alloy is inconsistent with the published phase diagram (22). Hence the solvus curve in this system is also being re-determined.

Precipitation behavior in Ti-Au is consistent with the available phase diagram and hence no further work on the solvus of this system appears to be required.

The observations made on intermetallic compound formation in Ti-Si indicate that the published solvus (23) lies at temperatures considerably below the correct ones; hence this solvus must also be redone.

In the Ti-In system, no evidence of precipitation has been found, indicating that the published phase diagram (24) is basically incorrect. It seems unlikely, in fact, that Ti-rich Ti-In alloys may not undergo a eutectoid reaction. Hence the available alloys are being used to redetermine this portion of the Ti-In phase diagram.

F. The β Phase Retention Problem

Mr. Plichta's Ph.D. thesis problem is to determine the interfacial structure, habit planes and lattice orientation relationships of planar facets on $\beta : \alpha_m$ interfaces. On the basis of our theoretical considerations of nucleation in the massive transformation, we have concluded that nucleation of a massive phase without a special orientation relationship (and hence without low-energy facets on the critical nucleus) is kinetically most improbable, given the relatively small driving forces for nucleation usually available (25). The proposed structural and crystallographic studies should provide a critical test of this theoretical deduction.
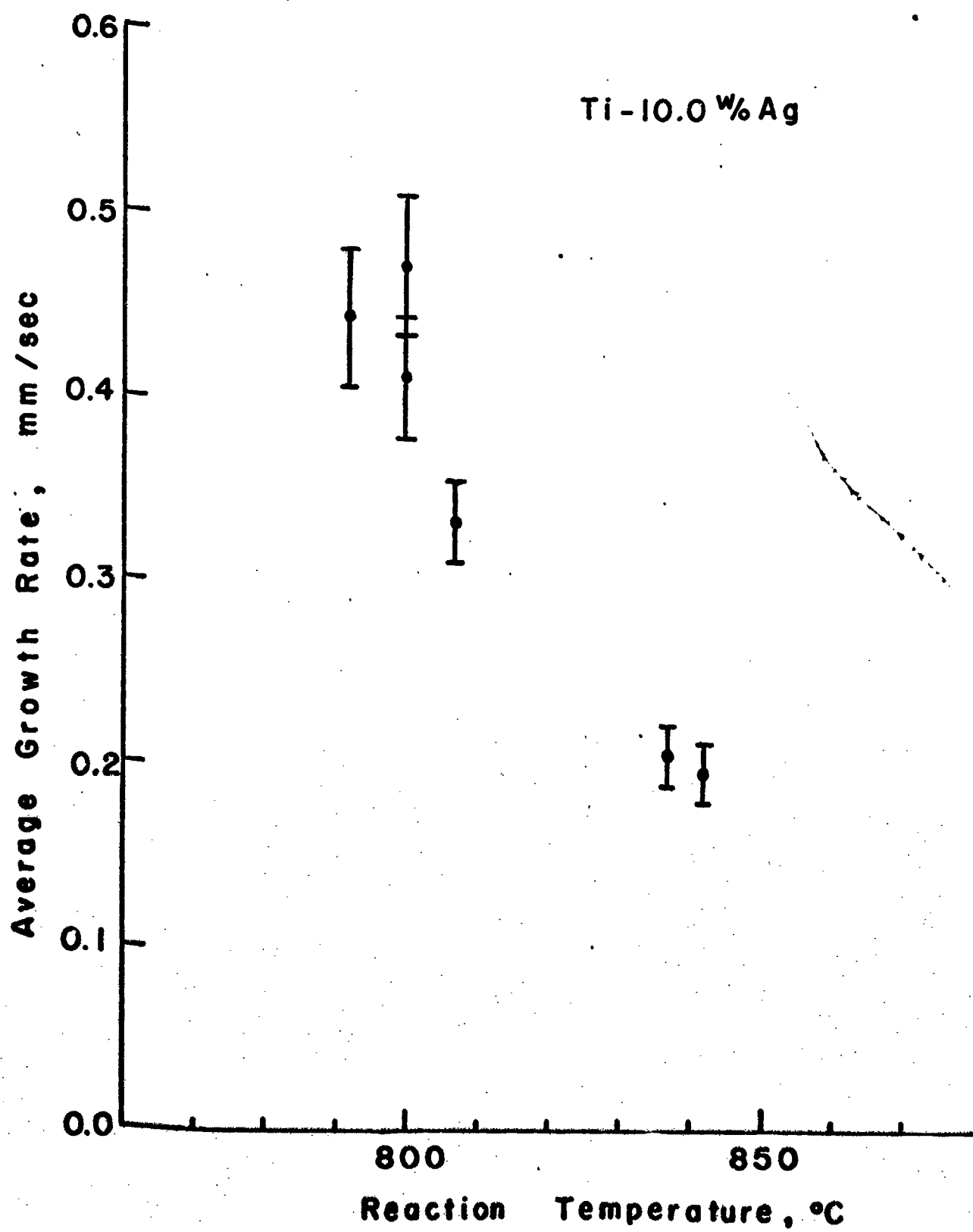
Figure 8. Average growth rate for the massive transformation in a Ti-10.0 W/O Ag alloy as a function of reaction temperature.

In order to execute these studies, however, it is necessary that a considerable proportion of the β phase which is not transformed to α_m be retained during quenching. Insofar as one can discern by means of optical microscopy, no β is retained in Ti-Si, Ti-Ag, Ti-Au or Ti-In. Sass (26) has shown, however, that oxygen-contaminated Zr-25 W/O Ti alloys contain appreciable amounts of retained β. This observation has been confirmed by Paton (27). Through the courtesy of Dr. Paton, the Rockwell Science Center has prepared and homogenized for us two alloys of this composition, one containing 2000 ppm and the other 4000 ppm oxygen. In the initial experiments on these alloys, samples of each were quenched directly into iced brine, and were found to consist entirely of martensite. Further experiments are shortly to be undertaken in which some specimens of these alloys will be cooled more slowly and others will be isothermally reacted. These procedures should give α_m more time to form, and also permit the development of the omega phase, whose presence is thought to be the factor inhibiting martensite formation. Additionally, some specimens will be encapsulated in a poor atmosphere, thereby enabling their oxygen (and nitrogen) contents to be increased further.

In order to be certain that we will have a bcc→hcp massive transformation available to study in which the bcc matrix phase can be retained, and also to investigate such a transformation in a completely different alloy system for comparative purposes, we are preparing to obtain an Ag-24.5 A/O Al alloy. Hawbolt and Massalski (28) have extensively investigated the massive transformation in this alloy quite well and have clearly demonstrated that the β matrix can be retained.

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V. Personnel

VI. Publications

1. K. F. Michaels, W. F. Lange, III, J. R. Bradley, and H. I. Aaronson, "Considerations on the Kaufman Approach to Binary Phase Diagram Calculation," Met. Trans., 6A, 1843 (1975).

2. M. R. Plichta, J. M. Rigsbee, M. G. Hall, K. C. Russell and H. I. Aaronson, "Nucleation Kinetics of the Massive Transformation in Cu-Zn in the Presence and Absence of Special Orientation Relationships," Scripta Met., submitted.

3. H. I. Aaronson, M. R. Plichta, G. W. Franti and K. C. Russell, "Precipitation at Interphase Boundaries," in preparation for submission to Met. Trans.

VII. Coupling

Mr. M. R. Plichta continued to work with Professor J. H. Perepezko, University of Wisconsin-Madison, making use of his apparatus to complete the planned studies of the thermodynamics and kinetics of the massive transformation in Ti-X alloys.

Discussions were held with Dr. Alan H. Rosenstein of AFOSR and Professor D. A. Koss of MTU on employing the knowledge being developed during the bainite component of this program to design high-strength, high-toughness Ti-base alloys with bainitic microstructures. The use of a second alloying elements, of special heat treatments and of thermomechanical processing to obtain suitable micro-structures were considered during these discussions, which are still continuing.

Several discussions were held with Professor J. C. Williams of Carnegie-Mellon and Dr. N. Paton of Rockwell Science Center of specific technical problems arising during this investigation. Access to the great resevoir of experience with Ti alloys acquired by the Rockwell Science Center has been invaluable to us both directly in developing answers to problems and indirectly in giving us confidence that specialized assistance can be readily obtained when unusual difficulties arise.