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I hereby recommend that the thesis prepared under my supervision by WILLIAM PFEIFFER KOSTER

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OF

TITANIUM - IRON - VANADIUM ALLOYS

be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY

Approved by:

John F. Kahles

Roy O. McDuffie

Fred Westermann

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THE ISOTHERMAL TRANSFORMATION CHARACTERISTICS

OF

TITANIUM - IRON - VANADIUM ALLOYS

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WILLIAM PFEIFFER KOSTER

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W.P.K.

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TITANIUM - A MODERN METAL

I

TITANIUM - A MODERN METAL

Since its introduction to the engineering world a few years ago, titanium has been the cause of a great deal of interest and speculation. The rather remarkable set of intrinsic properties of the metal are the chief cause for this excitement. While not as spectacular as once promoted to be, the facts indicate that titanium does possess definite potentialities as a useful engineering material.

Pure titanium is silvery gray in color, strong, ductile, and has a density of about 4.5, midway between that of aluminum and iron. It has excellent corrosion resistance in many applications; its resistance to salt water and marine atmospheres is not equalled by any other structural metal. To add to the enhancement, titanium is readily available, or at least its ores are readily available. In fact, titanium is the fourth most abundant structural metal in the earth's crust. Only aluminum, iron, and magnesium are present in greater percentages. The abundance of titanium far exceeds that of other common metals such as nickel, copper, zinc, lead, chromium, etc.

All of these factors weighed together give some insight into the reasoning behind the rather rosy outlook which is envisioned for titanium and titanium alloys.

EVALUATION OF TITANIUM FOR MILITARY AND CIVILIAN USE

AIR FORCE:

Titanium is vital to the Air Force. By virtue of its attractive physical and mechanical properties it is primarily an aircraft material and is urgently needed for this application. It is believed that the nation which adapts titanium successfully to its military equipment will achieve an important advantage over its enemies. This advantage must be obtained for the United States.

There is every indication that many metals and materials used today will, because of their inherent limiting characteristics, be inadequate for the supersonic aircraft of tomorrow. Progress in aircraft design and development beyond 1956 has been said to be strongly dependent upon the development of new materials which will exhibit better combinations of properties than those currently available. (1) Titanium appears very promising in this respect. Supported by a research program of adequate calibre, this metal should aid materially in meeting the new engineering requirements of tomorrow. Through utilization of titanium, it will be possible to design and produce aircraft to operate at speeds which involve skin temperatures considerably in excess of those that can be tolerated by today's materials, specifically aluminum and magnesium alloys. Furthermore, the effective use of the highly advantageous strength-weight ratio of future titanium alloys will enable the design of planes of greater maneuverability, range, and striking power operating at higher speeds than is possible with currently available materials.

But there is also another need. . . equally urgent. Titanium is needed in airplanes being produced at this very moment. Its incorporation into present designs would materially improve the operating characteristics of our current aircraft by virtue of the weight savings which it would afford. The development of titanium and titanium alloys and fabrication methods is at the threshold of where titanium can be dependably and continuously used in current production. This continuous use would accomplish, among other things, 1) the weight savings and improved performance of aircraft as mentioned above, 2) improved quality of available titanium by virtue of volume production, and 3) greatly expanded knowledge and experience in the fabrication of titanium alloys which will be so necessary for the future. In addition, many production economies would be introduced. Therefore, it seems imperative that full-scale use of titanium materials be effected at the earliest possible date.

Secretary of Defense Lovett has stated that "when one pound of weight (pay load) is added to a plane, ten pounds must be added to the structure at a cost of about $ 400. Hence the feasability of economically using titanium in aircraft is apparent. However, cost comparisons should be based not on the cost of a pound of titanium but on the "fabricated part cost," which takes into account the present high production costs and scrap losses involved. Nevertheless, in many situations the substitution of titanium for stainless steel and aluminum is feasable both economically and strategically.

Desirable alloys should be versatile and available as sheet, forging stock, and bar stock. Experimentally, jet engine designers are using titanium for spacers, rings, stator vanes, compressor blades, bearing housings, baffles, and tubing, plus other minor structural parts. In production, the present consumption is relatively small and, where used, the titanium is in the unalloyed or commercially pure form. Baffles, shields, tubing, and couplings are about the only titanium components now going into regular aircraft production. These parts are replacing annealed stainless steel in most cases at a weight saving of about 40 o/o. Greater savings will be made possible as soon as good sheet alloys of titanium are developed.

In airframe construction, titanium is currently being considered as a replacement for present alloys in firewalls, nacelles, fuselage structure, shrouding, and other stress-bearing members. Titanium nuts, bolts, rivets, and special mechanical fittings to replace rivets have also received attention. Based on present designs, these substitutions will result in substantial weight savings, hence increased pay load or performance of aircraft. For example, (2) substituting unalloyed titanium for present materials in firewalls, cowling, ducts, and fairings will result in weight savings up to 1,100 lbs., depending upon the plane. Substituting for armament can save up to 300 lbs. in one case; replacing all annealed stainless steel in one plane with a total of 1,100 lbs. of titanium will result in a weight saving of 800 lbs. Replacing presently used bolts, screws, nuts, and rivets with 2,400 lbs. of a titanium alloy having an ultimate strength of 150,000 psi will result in a weight saving of up to 1,500 lbs. Unalloyed titanium is presently being used in limited quantities in airframe construction, principally in non load-bearing members. In the very near future, more widespread use of both commercially pure and alloy grades of titanium is almost a certainty.

It can thus be seen that the importance of this material to the aircraft industry in general and the Air Force in particular is great. In order to improve our aircraft of today and to make possible more advanced designs for tomorrow, the successful development and utilization of titanium-based materials is absolutely essential.

ARMY:

The Department of the Army is interested in the successful employment of titanium and titanium alloys primarily because of the weight savings which would be made possible. These savings are considered to be of advantage in three principle ways: 1) improving the maneuverability of equipment, 2) increasing the facility of transporting this equipment by air, and 3) increasing the potential of the equipment load a foot-soldier is able to bear. Each of these factors is important in materially increasing the effectiveness of a fighting army.

The Ordnance Corps, U.S. Army, has conducted extensive research into the potentialities of titanium in order to determine its value in connection with the goals mentioned above. (3) On September 1, 1952, production was authorized for the 81 m/m Mortar Base Plate, their first firm application of titanium. This plate was formerly made as a welded steel structure in two sections, weighing a total of 48 lbs. Two men were required to transport this assembly. Because of its lightness and strength, titanium allowed redesign to a one-piece welded construction, weighing only 24 lbs. This releases one man for other duties. A host of other applications from wheels to guns are under consideration. Tests were recently initiated on titanium armor plate for tanks and vehicles, flash suppressors, and structural components such as outriggers. Present indications are that titanium-based alloys can be produced which will be satisfactory for these purposes.

In addition to the items mentioned, a program has been initiated to review all types of standard Army equipment pertaining to the individual soldier with a view toward using titanium wherever it will lighten the load or reduce physical effort. (3) In all cases where the resulting lightened item is at least equal in properties and performance to present equipment, serious consideration will be given to the adoption of the titanium version as standard.

Since most Ordnance applications would require titanium in comparatively high tonnages, a considerable reduction in the price of the material will be necessary before its use becomes widespread. Even at present high prices it is feasable for some purposes, but it is hoped that the price reduction necessary to make further uses practicable is very near at hand.

NAVY:

The Navy, like the other military arms of the Government, has a large titanium development program. For use in naval aircraft, the Navy's interests in titanium parallel to those of the Air Force and this phase of their research is carried out in co-ordination with that service. Since the application of titanium in aircraft has been previously covered at length, it will not be dealt with again in this section.

The advantageous strength-weight ratio of titanium is somewhat attractive in naval applications since it would permit weight reductions in fighting ships of all types, hence providing greater speed and cruising range. However, the very large tonnages that would be required in this application make it seem rather impractical. In addition, the imminence of nuclear power for naval craft, power almost unlimited, would still further discourage the use of titanium on naval vessels solely as a weight saver.

But the Navy still needs titanium. By far, the most attractive property of the material, so far as the sea-going Navy is concerned, is its excellent corrosion resistance in salt water and marine atmospheres. In this regard, it is surpassed only by electrolytic platinum. (4) It is one of the few known high strength structural materials that has a corrosion fatigue limit in salt water closely approaching that in air. Titanium is also the most corrosion resistant structural material known in many other corrosive situations. In naval service, the excellent corrosion resistance and corrosion fatigue properties of titanium will mean less repairing and maintenance of equipment. In turn, this implies less time out of service for a given unit, consequently greater fighting efficiency and lower operating cost.

There are a number of straightforward applications for titanium in naval equipment that have been tested and which now appear ready for service. (5) Development work on more complex components is also advancing. Such items include: submarine snorkel tubes, superstructure, andfair-weather construction; shipboard condenser and heat exchanger tubes and globe valves; low temperature steam turbine blades; salt water pump and valve bodies and parts. Because of the involved structural nature or because of fabrication problems, this work is quite tedious. Nevertheless, many of the above components are being tested under actual ship-board conditions although at the present time there are none being put into general service.

In addition to the above, the Bureau of Ships is considering, for test purposes, fabrication from titanium and installation of the following: gas turbine compressor blades, propeller shafts, salt water pump impellers, fire hose nozzles, radar wave guides and antennas, miscellaneous machinery parts, etc. The Navy is also giving titanium some consideration in their gun, guided missile, and armor plate programs. (5)

Except in aircraft, the Navy's use of titanium is still very limited. The Bureau of Ships has no current production uses for titanium. Neither has it any contemplated production uses. However, the satisfactory conclusion of several test programs will undoubtedly be followed by the regular use of titanium on an increasing scale, once the metal becomes more generally available at a reduced cost.

CIVILIAN:

Titanium will undoubtedly establish itself firmly in civilian economy - in commercial industry and possibly in consumer production. If this is to be done, however, the material will have to pay its own way, so to speak. In military applications, which have thus far been discussed, cost is secondary in many situations and of practically no account at all in certain critical applications. Quite the contrary is true when considering titanium for civilian uses. In a competitive peacetime economy, the extent to which titanium will be developed and used, and the relative degree of importance which it will attain in the engineering world, are directly dependent upon the extent to which prices can be reduced.

Civilian applications will employ both the excellent corrosion resistance and the desirable strength-weight ratio of titanium. It is probable that utilization of titanium as a corrosion resistant material will generally precede its use for structural purposes. Even at today's high prices, the chemical, food processing, and petroleum industries have found it successful as well as economical to use titanium. Many corrosion, contamination, and working temperature problems in these fields can be greatly alleviated in this way. Since such applications can be justified economically at present, it seems reasonable to assume that even a slight drop in price would bring in many more possibilities.

Commercial aircraft will of course utilize titanium as it becomes available, in much the same way as military aircraft are planning to use it at present. But since peak maneuverability and maximum cruising range are not primary considerations in planes of this type, the demand for the use of titanium in civilian aircraft is not nearly so pressing. Douglas Aircraft is currently using about 1,000 lbs. of titanium sheet for engine nacelles in each DC-7 transport they produce. (6) This application, however, is not economically justifiable at present titanium prices, but is being done since the company is anxious to get experience in design, fabrication, and use of the metal. Even when titanium becomes generally available, the aircraft industry operating on a peacetime basis would probably not be a large consumer.

Other fields may show promise for rather high titanium consumption. One in particular is that of diesel truck engines. In many cases the weight limitations are serious not only to pay load and engine size but to the many other restrictions placed on large highway vehicles. Concievably the metal could be used in either structural or reciprocating parts. Stainless steel trailers are now standard in the motor carrier field, and titanium might find good use here. Merchant marine craft will find titanium valuable particularly because of its corrosion resistance. Likewise, power generation stations and other industrial units using large volumes of salt water for cooling purposes will find this new material to be very helpful in solving their corrosion problems.

During the next few years, titanium is certain to be put into general use in industry wherever its physical or mechanical properties can be economically used to advantage. More widespread use will directly accompany the forthcoming decreases in titanium cost. However, titanium is inherently an expensive structural material. It is probable that its cost will always be above that of aluminum and magnesium, and certainly above that of iron and structural steel. Therefore, the general use of titanium for structural purposes in consumer goods such as automobiles, appliances, farm machinery, etc., is not anticipated. However, where certain critical corrosion problems exist, it is certain to be employed. In a civilian economy, it is expected that titanium and titanium alloys may soon become competitive with many classes of stainless steels.

PRODUCTION OF TITANIUM

OCCURRENCE AND AVAILABILITY:

Titanium ranks ninth in abundance among the elements in the earth's crust and fourth among the commonly used structural materials. In this latter group, aluminum, iron, and magnesium are more plentiful than titanium. The present high price of titanium ($5.00 per pound in sponge form) and titanium alloys is caused by several factors the most significant of which being the difficulty of economically getting it from the ore to the metallic form. Mining of the ore is relatively inexpensive. Suction dredges or power shovels are practical for most deposits. It seems certain that melting and fabricating costs, now high, will come down as production goes up.

Titanium is obtained chiefly from ilmenite, an iron titanate having the theoretical formula $FeO \cdot TiO_2$ (52.7 o/o TiO_2). Actually, the TiO_2 content of ilmenite varies considerably from this theoretical value, the exact composition depending mainly upon the section of the world in which the ore was mined. In North America, the beach sands of Florida are an important source of ilmenite. These deposits have been concentrated substantially by wave action through the years. Other important deposits now being worked are located in eastern Quebec, northern New York, and the highlands of Virginia. Deposits are known to exist in Arkansas, Oregon, Idaho, and Washington. Considerable ilmenite and zircon have also been found at the mouth of the Rio Grande River in Texas.

EXTRACTION PROCESSES:

The first step in the treatment of titanium ores is concentration, preceded by crushing and grinding if necessary. In general, the first aim is to obtain a rather pure oxide of titanium. Magnetic concentration is common for removing magnetite and gravity methods are suitable for separating titanium minerals from silica and silicates. In difficult cases, flotation and electrostatic separation have been used successfully.

Ilmenite concentrates are then treated with sulfuric acid so as to dissolve the iron and titanium. Ferric iron is reduced to the ferrous state usually by the addition of scrap iron, hence making the iron more soluble. The pH of the solution is adjusted properly and then the hydrolyzation of titanium is carried out. The precipitate is washed free of iron and other contaminants and calcined to produce titanium dioxide (TiO_2).

Titanium has been produced from its dioxide by several methods including the direct reduction of TiO_2 with hydrogen. The Kroll process, the most satisfactory method reported to date, involves first converting the dioxide to the tetrachloride: titanium dioxide + chlorine → titanium tetrachloride + oxygen ($TiO_2 + 4Cl \rightarrow TiCl_4 + O_2$). Titanium carbide, produced by heating titanium concentrates with carbon in an electric furnace, will also combine with chlorine to yield $TiCl_4$. The titanium tetrachloride is then reacted exothermally with molten magnesium under an inert atmosphere usually of helium, the result being magnesium chloride and titanium sponge: titanium tetrachloride + magnesium → magnesium chloride + free titanium ($TiCl_4 + 2\ Mg \rightarrow 2\ MgCl_2 + Ti$). The chloride is then separated and recycled: chlorine converting the titanium dioxide or carbide, magnesium reacting with the resulting tetrachloride. Minor variations in this process can be found, but at the time of writing most commercial titanium is produced basically in this way. This process results in a fairly pure product containing from about 99.0 o/o to 99.5 o/o titanium.

High-purity titanium can best be produced by the thermal decomposition of a volatilized titanium iodide. This method results in a compact form of titanium which can be processed directly, without melting, pressing, or sintering.

In operation, crude titanium is reacted with iodine in the absence of any other reactive gas. Below 250°C., titanium tetraiodide is formed: titanium + iodine → titanium tetraiodide ($Ti + 2\ I_2 \rightarrow TiI_4$). At higher temperatures, the tetraiodide reacts with more crude metal to form iodides of lower valence. These lower-valence iodides have a much lower vapor pressure than the tetraiodide and therefore the crude metal temperature must exceed 425°C. for satisfactory cycle operation whenever lower-valence iodides are formed. The titanium iodide(s) is then passed over a hot filament of ductile titanium where it is decomposed: titanium tetraiodide → titanium + iodine ($TiI_4 \rightarrow Ti + 2\ I_2$). The iodine is then recirculated and reacted with more crude metal. Over a period of several hours, a hot "hairpin" filament, maintained at between 1090 and 1480° C., can be enlarged to an ingot of 5/8" or more in diameter. The final product is a very ductile titanium of high purity containing at least 99.9 o/o titanium.

CONSOLIDATION OF REFINED TITANIUM:

On a commercial basis, further consolidation of titanium is necessary in order that the metal may be gotten into a usable form since the product of the commercially used Kroll or chloride reduction process is titanium in the sponge form. As stated previously, iodide titanium is produced directly as an ingot but this process has been found suitable only for laboratory purposes. There are several methods for converting the titanium sponge to the ingot form. Basically, these involve crushing and grinding the sponge into powder followed by some compacting and sintering technique or direct melting of the sponge necessarily in an inert atmosphere. Both powder and direct melting processes are adaptable for making titanium alloys.

Considerable attention has been directed toward the compacting and sintering of titanium and titanium alloys by conventional powder metallurgy methods. While satisfactory on a laboratory scale, it is doubtful that such a process could be made commercially feasable, except in specific applications. One innovation of this, the sheath rolling of titanium powder, is quite interesting. This process involves placing powdered titanium in a metal sheath and completely sealing it in by welding; plain carbon steel is usually used for the sheath material. The sheath and powder are then rolled as a single sheet while heated to an elevated temperature, about 900^{o}C. Similar or better results were obtained in this way than by standard powder metallurgy techniques. A thorough weld of the titanium powder is obtained resulting in a dense, uniform structure. Pressed but unsintered compacts have been consolidated in this way. Each compact was completely welded during rolling and no evidence of the original interface between the compacts could be found on microscopic examination. Furthermore, the sheath could be easily stripped from the finished metal probably due to the formation of a very thin layer of a brittle Fe-Ti alloy. The contamination of the titanium surface was found to be slight and can easily be removed by pickling.

There are several advantages of sheath rolling as opposed to conventional powder techniques: it does away with the necessity of compacting the powder under high pressure, it eliminates the need for vacuum sintering, it permits the preparation of almost unlimited masses of titanium in a single piece, and the metal prepared in this way is dense and smooth, as contrasted to the porous structure usually found in pressed and sintered parts. The sheath-rolled material is most like conventionally sintered titanium that has also been worked and annealed and is therefore quite ductile and in general satisfactory. However, sheath rolling is a complex operation compared to simple melting and rolling. Furthermore, it is not suited to alloy production. These drawbacks would rule it out as a possibility for a commercial production process.

The melting and casting of titanium presents many difficult problems. The metal has a very high melting point (about 1750°C.) and, when molten or even at elevated temperatures below the meling point, it reacts with nearly everything it contacts. All known oxide refractories are reduced by titanium to some extent, and the titanium in turn is contaminated and embrittled by both the oxygen and the metallic elements from the decomposed refractory. Needless to say, the atmosphere must be excluded in any practical melting process.

One satisfactory method has been developed which employs induction heating. The titanium is contained in a dense graphite crucible which is sealed and flushed with an inert gas under positive pressure. Either helium or argon can be used, but argon is preferable because of its greater density. The crucible is so designed that the melt can be dropped into a graphite mold immediately below when the proper casting temperature us reached. This mold is also purged with the same gas as the melting crucible, in most cases. This same type of furnace can be adapted for vacuum melting but this procedure is not generally satisfactory with units of large capacity.

Titanium sponge properly melted in graphite will contain between 0.2 and 0.7 o/o carbon, the carbon pickup being reduced by using shorter melting cycles. Other impurities found in the finished product were, for the most part, present in the sponge used in the charge. There has been considerable controversy regarding the desirability of the carbon content of graphite-melted titanium and titanium alloys. Carbon in excess of 0.8 o/o is definitely undesirable since it causes excessive embrittlement of titanium; present in lower amounts, it increases the yield and tensile strengths of the material but does so at the expense of ductility. Carbon has been shown to affect the machinability of titanium quite adversely, even when present in rather small amounts.

On the other hand, the natural stirring action - a feature of induction melting - renders this melting technique very suitable for making titanium alloys. Additions can be made in almost any form, and since this is a batch process, control of the additions is quite simple. The resulting ingots are chemically homogeneous and generally exhibit good surface quality.

In spite of the advantages of this process, the embrittling effect of carbon which has not thus far been overcome is causing it to be superceded by an arc melting process, using a crucible of water-cooled copper.

Furnaces for the arc melting of titanium are characterized by three main features: a water-cooled copper crucible, a provision for an inert gas atmosphere of high purity, and an electrode either of water-cooled tungsten or titanium, of the consumable type made of titanium, or of carbon. Water-cooled copper is used in crucible construction since it is not wetted by molten titanium. The thermal efficiency of melting is obviously low. Argon and helium can both be used as inert atmospheres. Because of its greater density, however, agron apparently sweeps the system more thoroughly and gives rise to a purer product.

In one manner of operation, the charge of a controlled mixture of ground titanium sponge and alloying elements is fed into the upper portion of the furnace from where it can drop into the melt area. The water-cooled metal or carbon electrode is rotated over the surface of the melt, striking an arc with the melt and thereby introducing the necessary heat. As the level of the melt in the crucible rises, the electrode is automatically withdrawn from the furnace, so that the current flowing, hence the energy input, is kept constant. In this way, the ingot is successively built up until the capacity of the furnace is reached. This method is very successful in eliminating external contamination. However, some tungsten contamination has been noted when a tungsten electrode is used, which is particularly undesirable because tungsten is not totally miscible with molten titanium and separates out in an almost pure form. Furthermore, making alloy additions successfully and ending up with a homogeneous product has been difficult. This is principally due to the layer effect noted in melting.

In an attempt to minimize these difficulties, consideration has been given to the consumable electrode type of furnace. In this system, the titanium sponge is compacted into a suitable electrode shape and fed into the furnace directly, being melted into an ingot by its own arc. It is also possible to make alloy additions directly in the compacted electrode, but the uniformity obtained by this method may be no better than that possible by making controlled alloy additions to the furnace during the melting cycle. Double melting is one possibility for improving uniformity but this leads to increased production costs. Nevertheless, consumable-electrode arc melting seems at present to be the best solution to the problem of titanium sponge consolidation. Of course, a method for producing the basic metal in other than sponge form may drastically revise the whole production process for titanium.

TITANIUM ALLOYS

METALLURGICAL CHARACTERISTICS:

Titanium offers very attractive possibilities for alloy development. This becomes more and more evident as research in the field progresses. The atomic diameter of titanium is favorable for alloying with most common metals. Furthermore, pure titanium can exist in two different crystallographic forms: body-centered cubic (beta) above 885°C. and hexagonal close packed (alpha) below this temperature. It is this same sort of transformation occurring in pure iron that makes possible the wide variety of steels as we know them today. Unfortunately, there are certain differences between iron and the titanium systems which tend to minimize the influence of this transformation in titanium alloys. A range of properties as varied as that possible with iron and steel cannot therefore be anticipated. Nevertheless, titanium is inherently a useful material and a proper development and understanding of its alloy systems will be most worthwhile.

The basic result of adding alloying elements to titanium is the marked influence exerted on the crystallographic transformation, resulting in either a raising or lowering of the temperature at which it occurs. By the addition of certain elements, the high-temperature beta phase can be stabilized down to and below room temperature. Such elements are called beta stabilizers and include molybdenum, columbium, vanadium, and tantalum. (7) The typical phase equilibrium diagram for these alloy systems is shown in Fig. 1. This diagram is of the beta-isomorphous type and is characterized by a continuous range of beta solid solution with the formation of an alpha plus beta field which grows wider with decreasing temperature.

Other elements such as manganese, chromium, iron, and nickel cause a stabilization of the beta phase similar to that just described, except that a eutectoid reaction takes place somewhere above room temperature. (7) A typical eutectoid phase diagram for this type of reaction is shown in Fig. 2. Although it would be the equilibrium condition, these systems frequently do not exhibit a eutectoid decomposition in the alloy ranges considered useful. Their general characteristics are therefore about like those of the beta-isomorphous type. Should a eutectoid reaction take place, however, the usual effect is a rather severe embrittlement caused by the formation of the third phase, shown in Fig. 2 as gamma (γ).

A few elements, notably aluminum, carbon, oxygen, and nitrogen, have the affect of stabalizing alpha rather

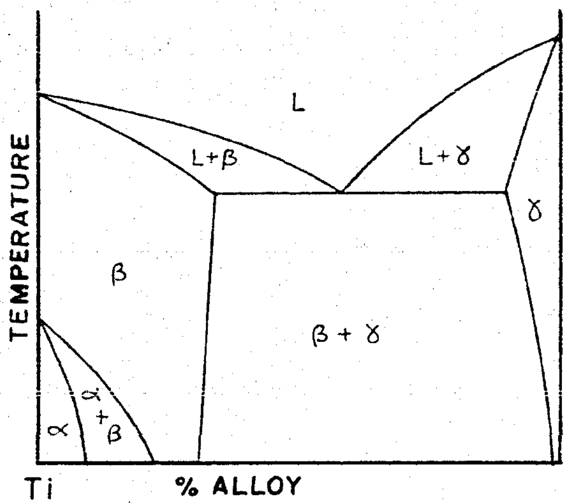


Figure 1
BETA ISOMORPHOUS

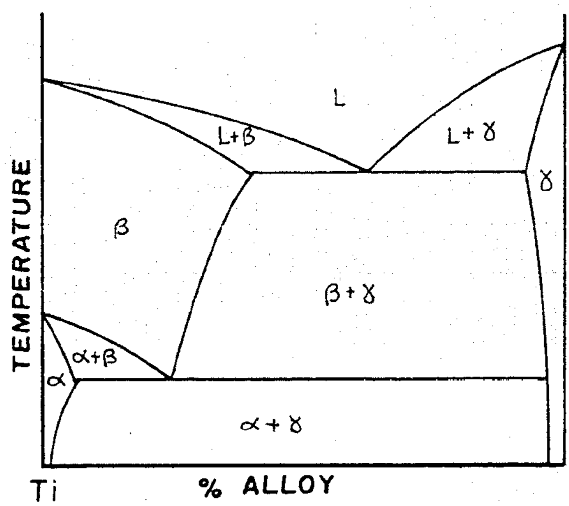


Figure 2
EUTECTOID

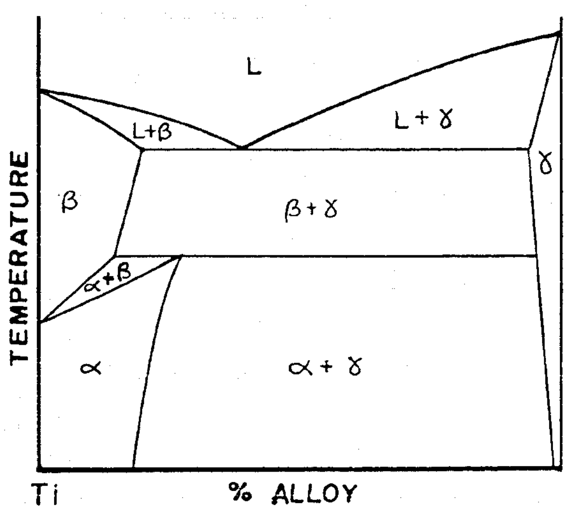


Figure 3
PERITECTOID

THE THREE PRINCIPLE TITANIUM BINARY SYSTEMS

than beta (7). Hence alpha can be found in such alloys above the transition temperature of pure titanium, 880°C. A typical phase diagram for this system is found in Fig. 3. It has been designated as the peritectoid type. It is significant to note in this case that alpha can be stabilized from well above the transition point down to room temperature and below. Upon the possibility of this single continuous phase is based most hope for useful high temperature titanium alloys.

The mechanism of phase stabilization, in other words the reasoning behind whether a particular addition element will stabilize alpha or beta, depends on which phase it is most soluble in. All beta stabilizers are more soluble in beta than in alpha. Conversely, all alpha stabilizers are more soluble in alpha than in beta. Under proper conditions, segregation in keeping with these solubilities will take place. For example, in an annealed titanium alloy containing 7 o/o manganese (a beta stabilizer), the alpha may contain less than 1 o/o manganese whereas the beta may contain as much as 12 o/o manganese. An similarly, an alpha-stabilizing element would partition itself predominantly in the alpha phase present. It should be added that the general effect of alpha stabilizers is to strengthen the alpha phase, and for beta stabilizers to strengthen the beta phase. "Strengthen" in this case is referred to in the normal mechanical sense.

It is of course possible to design an alloy based on any one of these systems: the beta-isomorphous, the eutectoid, or the peritectoid. Generally speaking, beta has excellent bend ductility, good hot and cold strength, and is comparatively easy to forge and roll. Alloyed alpha has better hot strength than beta but also has considerably lower ductility. But for a compromise it is entirely possible and actually common practice to make additions of both alpha and beta stabilizers to titanium, the result being that both phases are stabilized, hence a two-phase alloy. In this case, the alpha stabilizers will partition themselves in the alpha and the beta stabilizers in the beta. This strengthens each phase separately, making it theoretically possible to tailor alloys directly to meet a particular need. Such a practice enables the advantages of both alpha and beta to be realized to a large extent in a single alloy.

Alpha titanium has generally good mechanical characteristics and fabrication properties except for its ductility which is notably poor in bending. Nevertheless, its performance under plastic deformation is better than that displayed by other metals which crystallize in a hexagonal lattice, such as magnesium, cadmium, and zinc. Alpha can be stabilized from room temperature to well above 885°C., as mentioned before. Aluminum does this job very efficiently and provides promising possibilities for the development of high-temperature alloys. Aluminum also provides some oxidation resistance to the material which further enhances the outlook for its use at elevated temperatures. Even when used in an alpha-beta alloy, the aluminum content of the alpha seems to improve the elevated temperature properties. Aluminum does, however, further strengthen alpha alloys and antagonize their already low ductility.

The body-centered cubic structure of beta titanium is, as previously noted, more versatile than that of alpha. This is because a cubic structure has inherently more planes on which slip can take place and thus can undergo plastic deformation more readily. Therefore, while alloys in which alpha is strengthened are good for elevated temperature applications, they are rather difficult to form. Alloys containing some or all beta are forged and rolled rather easily and are ideally suited for lower temperature applications. Materials containing large amounts of beta should be ideal as sheet alloys.

Very large additions of beta-stabilizing elements to titanium result in a completely stable beta alloy. Such alloys will remain all beta regardless of thermal and mechanical treatment. They require very large additions of beta stabilizers: 20 o/o or greater. Between this very stable range and that characterized by alpha-beta alloys containing only small amounts of beta stabilizers, is a region in which alloys will retain beta in an unstable form on water quenching or even on air cooling. However, several hours to several days at temperatures between 150 and 450°C. permit some of this beta to transform. This characteristic generally appears to cause embrittlement but there are some indications that if carefully controlled it can aid materially in providing a useful set of properties to alloys in this category. Materials in this class have been termed unstable beta.

Industrial interests to date have been centered almost exclusively on commercially pure titanium and the alpha-beta alloys, both of which have established themselves firmly in the field of structural titanium materials. They have thus far been used only in the annealed, as-forged, or as-rolled condition. No specially heat treated materials have actually been used in production. The alpha-beta alloys generally have a medium alloy content of 3 to 9 o/o. It is actually not necessary to add alpha stabilizers to titanium in all alpha-beta alloys. Merely adding only small quantities of beta stabilizer will cause only partial beta stabilization, the balance being soft, relatively ductile alpha. This can be seen from Figs. 1 and 2. A comparison of the strength-weight ratio vs. temperatures of several titanium alloy types and other common structural materials is found in Fig. 4 (8). The titanium curves are representative of those alloys in the as-forged condition. It can readily be seen that titanium is most useful on a strength-weight basis in filling the gap between aluminum and stainless steel for elevated temperature service between 100 and 550°C.

It is typical of metals and alloys that any treatment which raises the strength level lowers the ductility accordingly. Titanium, in this regard, is no exception. This has been a major problem in titanium alloy development but present indications are that high strength alloys can be made useable although combinations of very high strength and high ductility are certainly not probable. Some alloys have also exhibited low impact strength, notch sensitivity, and relatively low fatigue strength, the latter being equal to about half of the ultimate strength of a given material. While not outstanding, some progress has been made in correcting these deficiencies.

The modulus of elasticity of titanium and titanium alloys is only about half that of steels. This means that titanium stretches twice as much under a given load when compared to a piece of steel of similar size. Such a

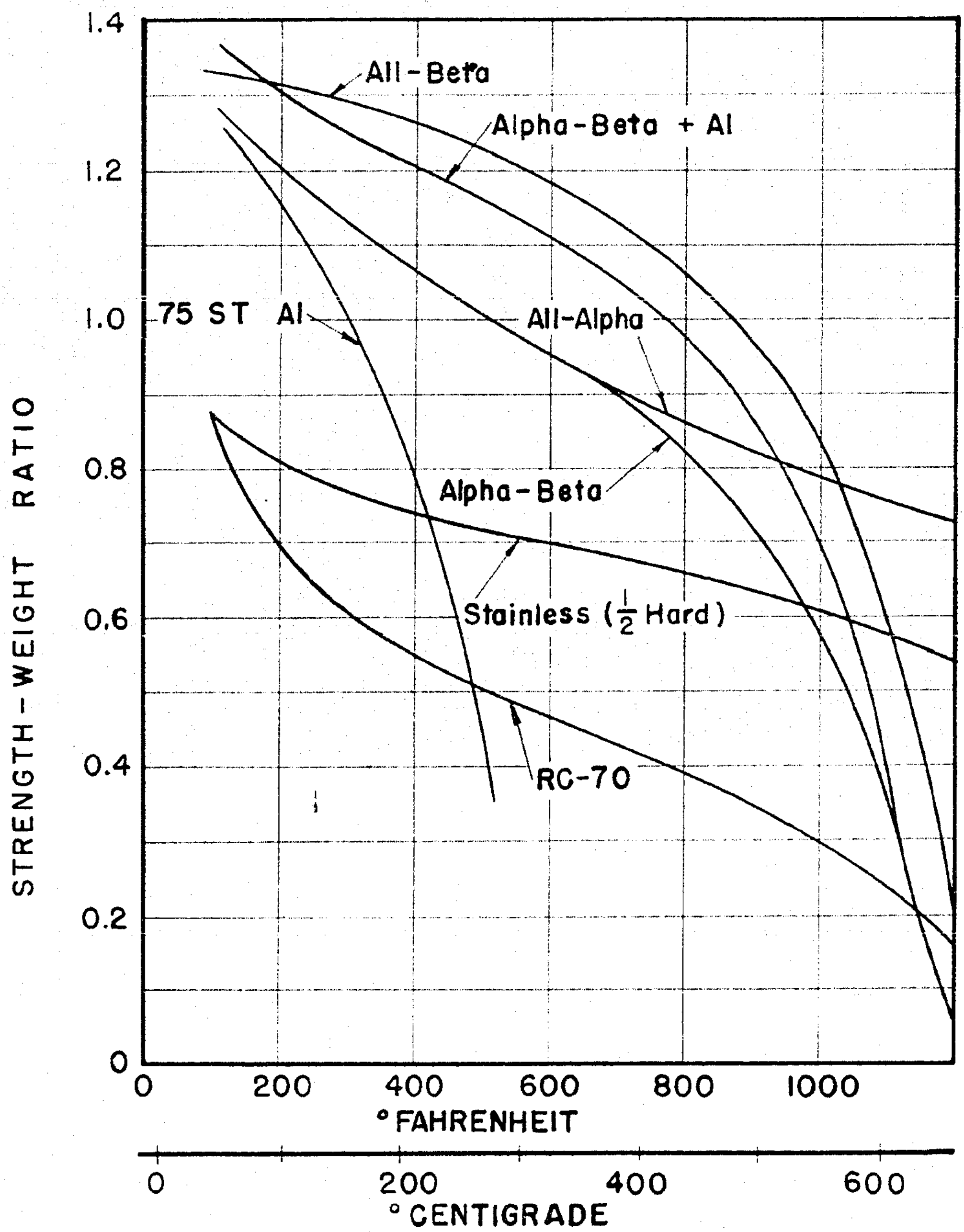


Figure 4

COMPARISON OF SEVERAL TITANIUM-BASE ALLOYS WITH 75 ST ALUMINUM AND STAINLESS STEEL

difference will probable not be serious in small shapes and most continuous sections but would definitely require attention if titanium were considered for lengthy structural members. This problem is one that can be easily corrected by redesign but in some cases the use of titanium would not be practical from a stiffness or rigidity standpoint eventhough strength requirements were easily met. It is not likely that new alloys or heat treatments will bring about a significant change in the elastic modulus of titanium.

Many of the titanium alloys can show a wide variety of microstructures as a result of heat treatment. This is particularly true of those materials containing all or some unstable beta, the microstructural changes observed being primarily the result of different modes of beta decomposition. If beta is decomposed slowly as in an anneal, a coarse structure of the decomposition product (alpha) and the residual beta will result. The alloy content in this situation will determine the final proportions of alpha and beta. Faster and faster rates of cooling will result in finer and finer alpha formation and in some cases, nearly complete retention of the beta phase is possible by rapid cooling. The cooling rate necessary to retain all beta is again dependent on the alloy composition. Under certain conditions, a martensitic shear reaction takes place in titanium alloys. Unfortunately, titanium martensite is not hard as is the similar product in steel, and a great variation in physical properties of titanium alloys based on this reaction is therefore not believed possible.

A second heat treatment response is manifest in retained beta. This material will undergo an ageing or decomposition to alpha upon holding at elevated temperatures. This process takes place generally on a submicroscopic basis and results only in a gradual darkening of the microstructure.

There is a reasonable change in physical properties with both of the types of heat treatment just mentioned. Slow cooling from forging temperature ranges and isothermal holding with prior quenching generally result in alloys softer and more ductile than the as-forged materials. Ageing retained beta following a quench to room temperature generally results in substantial strength improvement coupled with great loss of ductility. The approximate range of possible heat treatment response in alpha- and beta-stabilized alloys is shown in Figs. 5 and 6 (9). Information is too scattered at present, but it seems reasonable that more complete data on these classes of reactions will enable useful, high-strength alloys and concomitant heat treating cycles to be developed.

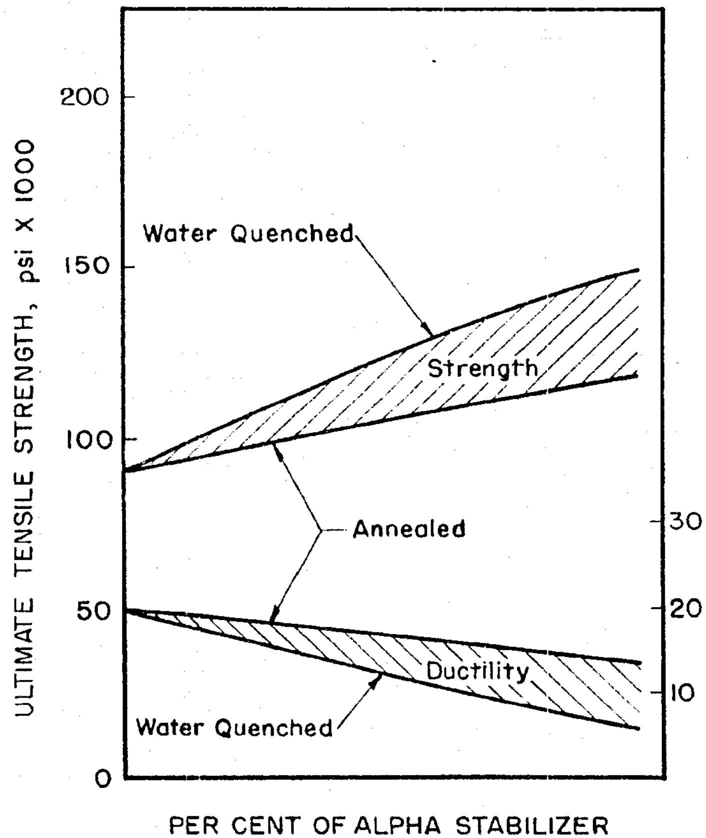


Figure 5

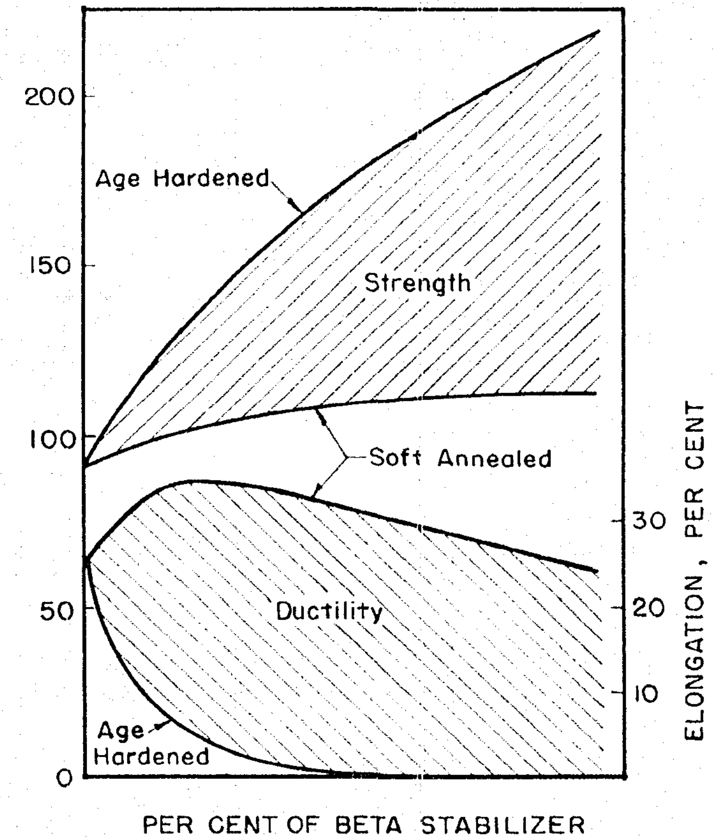


Figure 6

INFLUENCE OF ALPHA AND BETA STABILIZERS ON TITANIUM ALLOYS

FABRICATION CHARACTERISTICS:

The development of suitable fabrication procedures for titanium and titanium alloys has been difficult. Although there are differences of opinion on the ease of fabrication, available information indicates that the normal troubles to be expected in working with a new material are gradually being overcome. On e of the major difficulties has been a lack of uniformity of the material being produced. This situation can be remedied only by true volume production accompanied by possible improved melting and casting practices. As a result of a trend in this direction, a considerable improvement particularly in sheet quality has been recently noted.

Commercially pure titanium can be fabricated by bending, spinning, drawing, and similar operations. Annealed sheet can be bent on diameters of 1T to 1.5T;* half hard material requires about 5T. Blanking, edge rolling, etc. are also possible on the commercial grades. More difficult working operations can in many instances be performed in the temperature range from 250 to 400°C.

Commercial titanium can be readily welded by resistance inert-gas-shielded arc methods. Various resistance welding techniques produce a ductile and generally satisfactory union, with strength approaching

* T refers to the thickness of the sheet.

that of the parent metal. Fusion welding must be performed in an inert gas atmosphere because of the reactivity of titanium with air at high temperatures. Both top and bottom surfaces must be protected. However, strong, ductile welds can be regularly obtained with unalloyed titanium, providing that this necessary precaution is taken. In general, welding of the available alloy grades has not been found satisfactory. Of course, these materials can always be joined by other methods that do not involve a fusion of the metal. Welding procedures for joining titanium to dissimilar metals are still in the development stage.; there are reports that successful unions with aluminum can be made. Titanium can be brazed using titanium-copper or manganese-nickel alloys as brazing materials. Soldering can be accomplished by first plating the titanium with copper and then proceeding in the normal fashion. Although the metal does not generally handle with great ease, there are probably no deficiencies in this area of titanium metallurgy that cannot be overcome or at least by-passed by judicious engineering.

FUTURE OUTLOOK FOR TITANIUM

At present there are many difficulties with titanium production and consistency of the final product. Limited quantity output, in turn caused by the high cost of the raw material, is basic to all of these difficulties. The solution of this problem of cost in itself is quite complex. The Kroll process, currently used for all commercial titanium production, is inherently expensive. Large, efficient plants designed to operate on the Kroll reduction cycle have not been built since it seems entirely possible that this process will be superceded at any moment. As a result, titanium is now produced in over-sized pilot plants, a factor which magnifies the inherent expense of the Kroll process. If full attention were presently devoted to making the Kroll process as efficient as possible on a large plant scale, a goal of cutting the cost of titanium sponge to at least one fourth of its present value would be ultimately reached. However, from the long-range point of view, it has been felt that a wiser investment involves research for an entirely new process inherently less expensive to operate. At the present time, the outlook for a new titanium production process is not bright. A continuous electrowinning process offers as many or more engineering problems than the magnesium reduction (Kroll) process. The recent re-examination of the old iodide method by one large organization emphasizes the fact that no new process is likely to appear in the near future.

The ultimate place of titanium in the engineering world is of course difficult to predict. There is no doubt that very useful titanium and titanium alloy products will be developed. It is certain that their relative importance among engineering materials will depend greatly upon the economies of production which can be realized. Inherently, because of its high reactivity and melting point, titanium will probably remain more expensive than the other common structural metals. It is expected that its tonnage production will certainly remain far behind that of iron and aluminum, and probably behind magnesium, for many, many years to come. Based on presently familiar applications, it is visualized that titanium will be mainly used in corrosion situations where less expensive materials are not satisfactory, and as a structural material in transportation equipment, particularly aircraft.

THE THESIS

II

THE THESIS

The purpose of this investigation was to study the isothermal transformation characteristics of a commercially-produced titanium forging alloy nominally containing 2.5 o/o iron, 2.5 o/o vanadium, the balance, titanium. This alloy is one of several manufactured by the Mallory-Sharon Titanium Corporation, under whose sponsorship this program was carried out.

First supplied to the author were samples of this alloy which had been induction melted in a graphite crucible. The induction melted material, Heat IM 31, contained about 0.50 o/o carbon. Toward the end of this program, perfection of melting techniques at the Mallory plant made available the same nominal alloy which had been consolidated in a water-cooled copper crucible by consumable-electrode melting (a form of arc melting). Samples of this consumable-electrode melted alloy were obtained for comparison to the induction melted material. These samples, from Heat CE 14, contained about 0.11 o/o carbon.

The data obtained as a result of this investigation are presented here chiefly in the form of isothermal transformation diagrams, frequently referred to as time, temperature, transformation (T-T-T) diagrams. This method of presentation has become classic in the field of ferrous metallurgy and is believed to be equally applicable in this situation. Supplementary information is also included in this section as well as in the later section entitled "Experimentation."

SIGNIFICANCE OF THIS WORK

The mechanics and manifestations of many solid state reactions may be conveniently and systematically investigated by isothermal transformation studies. This technique has been well developed in recent years and has become practically invaluable in the understanding of many complexities of ferrous metallurgy, where it has been chiefly applied. Furthermore, proper application of T-T-T data has made possible far reaching advances in this same field. Martempering and Austempering are examples of two such developments. The importance of phase equilibrium diagrams is well known. While these diagrams represent static or equilibrium conditions, as their name implies, isothermal transformation diagrams represent dynamic conditions within solids. The significance of these two types of diagrams may be closely paralleled.

In the most general sense, isothermal transformation studies are usually applied to eutectoid reactions. A eutectoid may be defined as that condition where one solid solution, stable at high temperatures, decomposes into two different solid phases on cooling. It is characterized by an equilibrium, temperature-concentration diagram as shown in Fig. 7, t_2 being the eutectoid reaction

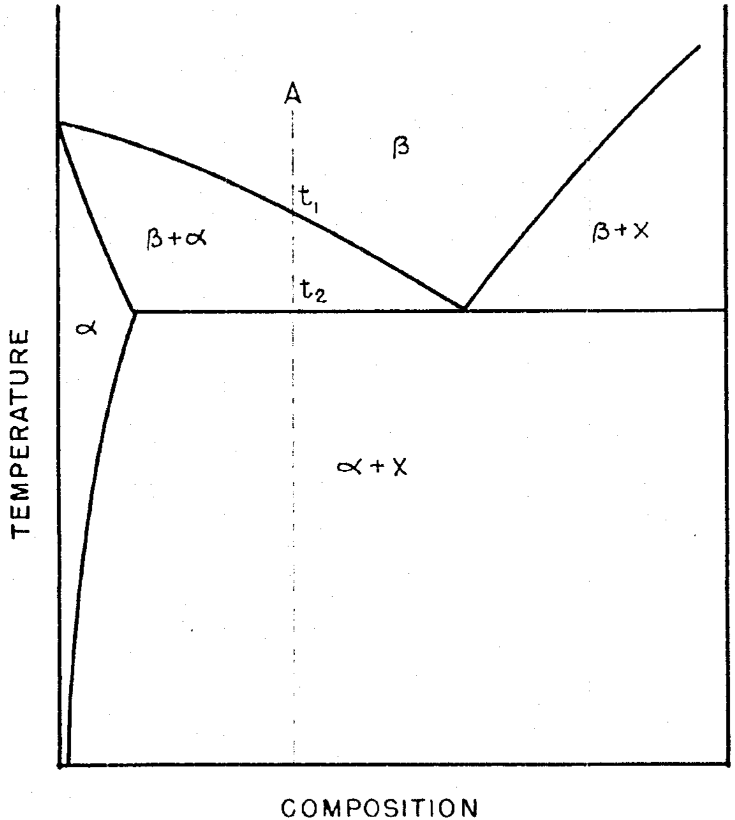


Figure 7

EQUILIBRIUM DIAGRAM FOR A EUTECTOID REACTION

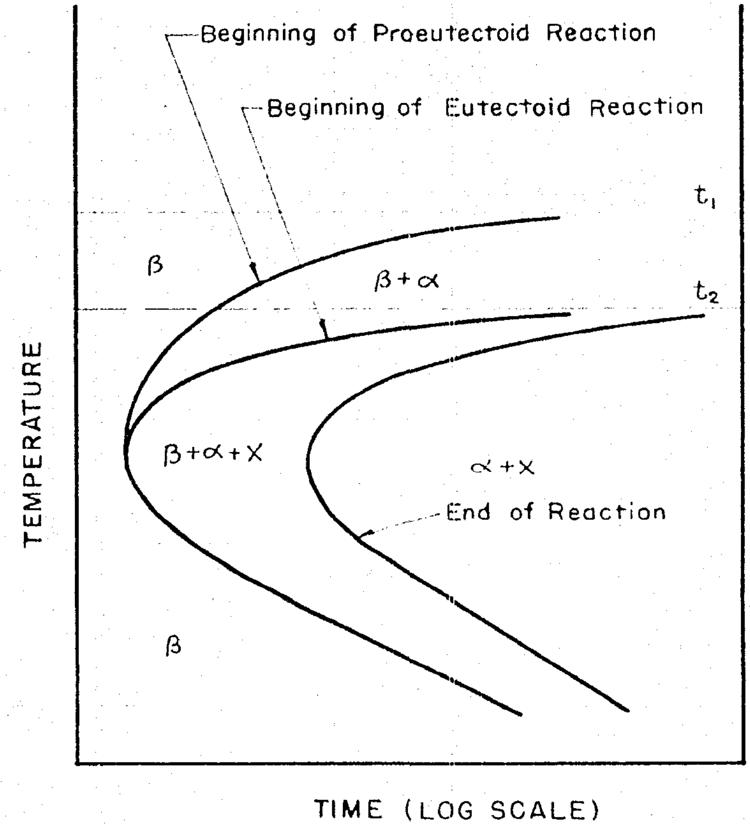


Figure 8

POSSIBLE T-T-T DIAGRAM FOR ALLOY "A" SHOWN IN FIG. 7

temperature.

Considering an alloy of composition "A" in Fig. 7, we find on cooling that beta first becomes supersaturated with respect to alpha at temperatures below t_1 and above t_2. If homogeneous beta were held at a constant temperature within this range, separation of alpha would take place. This reaction would begin and also progress more rapidly as the temperature of holding is set more closely to t_2. This is primarily because of the increasing degree of supersaturation of beta under these conditions. The change in reaction timing is shown graphically in Fig. 8. A separation of this type is known as a proeutectoid reaction and is normally considered as a part of a eutectoid reaction study. If alloy "A" is held at temperatures below the eutectoid temperature (t_2), the eutectoid decomposition will also take place at varying rates, depending upon temperature. The progress of this reaction from beginning to end is also shown in Fig. 8.

It is significant to note the wide variation in time required for a reaction to start. Of particular interest is the fact that beta may remain untransformed for long periods (sometimes indefinitely) at very low temperatures. This is quite in contrast to the equilibrium conditions depicted in Fig. 7 but is nevertheless a definite reality.

A great deal of this transformation characteristic depends upon the relative rates of nucleation and growth in a given system. Referring to Fig. 8, it is seen that a high rate of nucleation is obtained in the temperature range of the "nose" of the curve where the reaction starts most rapidly. This nucleation rate decreases with either an increase or decrease in temperature. As illustrated in Fig. 8, the growth rate is relatively low at high temperatures since a reaction takes a long time to go to completion. As the temperature is lowered, the growth rate increases steadily as evidenced by shorter and shorter total reaction times.

Another way to illustrate this would be with a series of typical isothermal reaction curves, shown in Fig. 9 (15). Curve "A" has a high nucleation and high growth rate; curve "B" has the same nucleation but a lower growth rate. Curve "C" has both a low nucleation and a low growth rate. Isothermal reaction curves typified by Fig. 9 can be used directly in the construction of the more commonly used T-T-T curves. It can easily be seen that materials with inherently different nucleation and growth properties will exhibit widely varying transformation

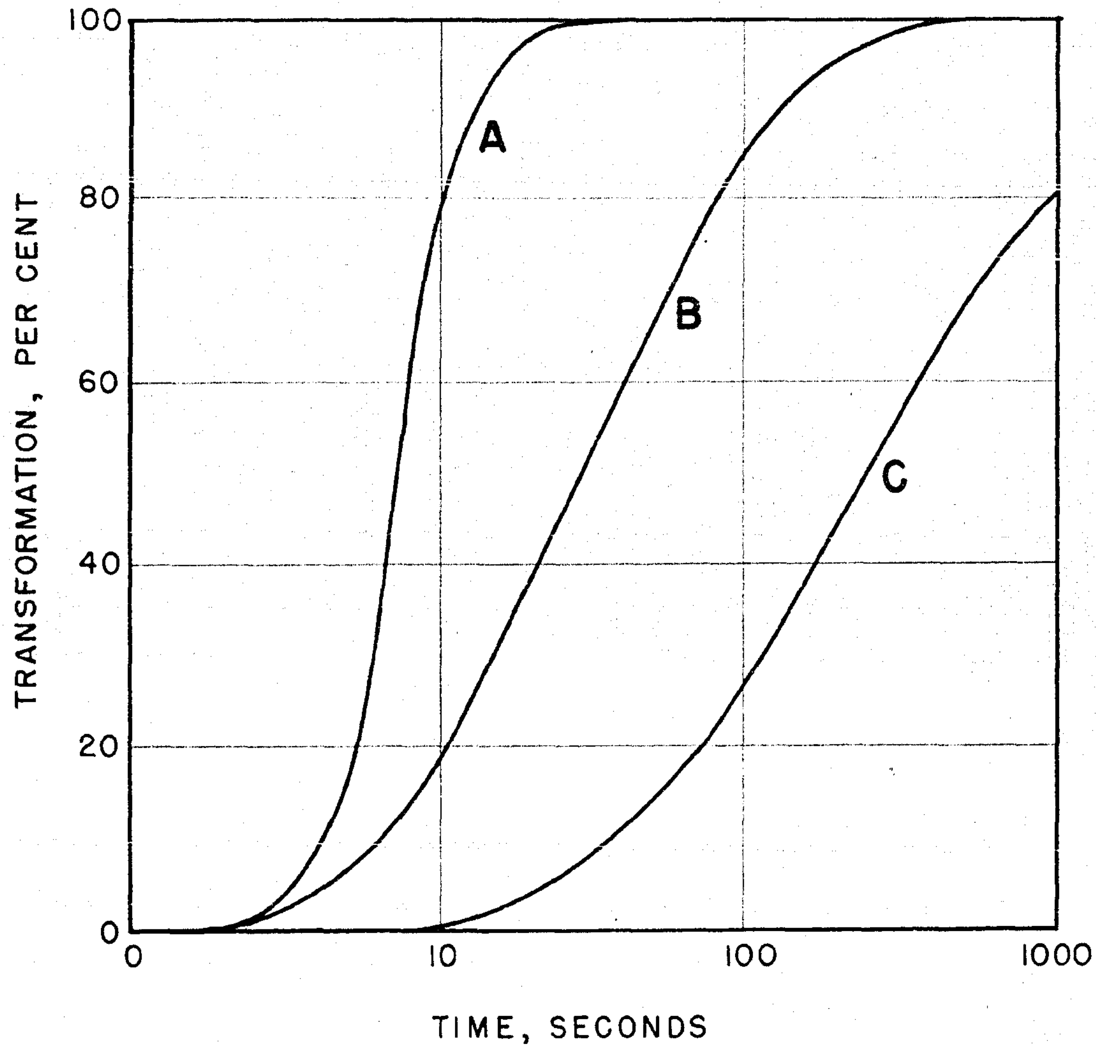


Figure 9

TYPICAL ISOTHERMAL REACTION CURVES

characteristics.

The addition of alloying elements is known to have a marked influence on the phase equilibrium diagram of a given system. The effect of such additions on T-T-T characteristics is usually even more pronounced since nucleation and growth rates as well as equilibrium phases are influenced. By a systematic study of the influence of a particular alloying addition on nucleation and growth, almost any desired T-T-T characteristic can theoretically be produced. It is exactly this sort of study, which has been so successfully executed in the field of ferrous metallurgy, that makes possible the intelligent use of the wide varieties of steel as we know them today.

But it should be emphasized that isothermal transformation studies are not limited to ferrous materials; nor are they limited to eutectoid reactions. Actually, almost all solid state reactions could be studied in this way, though many types of systems would not be best approached from this point of view. Isothermal studies are of particular value, however, in following the decomposition of the high temperature phase in those materials which exhibit an allotropic modification. Iron is one such metal; others include titanium, zirconium, cobalt, and uranium.

When one considers the similarity between iron and titanium, particularly with a view toward the allotropic modification occurring in each and the great value this modification has proved to have in the case of iron, the application of isothermal studies to titanium alloys seems most logical. There are many reasons to believe that a wide variety of useful titanium alloys can be developed if all of the possibilities presented by the metal's change in crystal structure are fully exploited.

THE TITANIUM-IRON-VANADIUM SYSTEM

This research is centered on the isothermal study of a ternary titanium-iron-vanadium alloy. The separate Ti-Fe and Ti-V binary equilibrium phase diagrams are shown in Figs. 10 and 11 (7). The similarity between the Fe-Ti system and Fig. 7 will be seen immediately. The Ti-V system is also like Fig. 7 if we consider that a eutectoid reaction may take place below 600°C., the lowest temperature shown. (Equilibrium conditions may well call for such a eutectoid decomposition in the Ti-V system, but this reaction, if existent, is so sluggish as to have thus far evaded observation.) The ternary system Ti-Fe-V has not been studied as such, but the influence of vanadium probably does not greatly alter the Ti-Fe system shown in Fig. 10, except to enlarge the beta field and reduce the eutectoid temperature. Therefore, the ternary alloy being studied in this research project can be expected to react very much like a binary alloy of the eutectoid type. The conclusions set forth previously for eutectoid reactions should in general apply equally well in this case.

To facilitate comparison with subsequently presented work, microstructures of IM 31 and CE 14 in the as-forged condition are shown in Figs. 12 and 13.

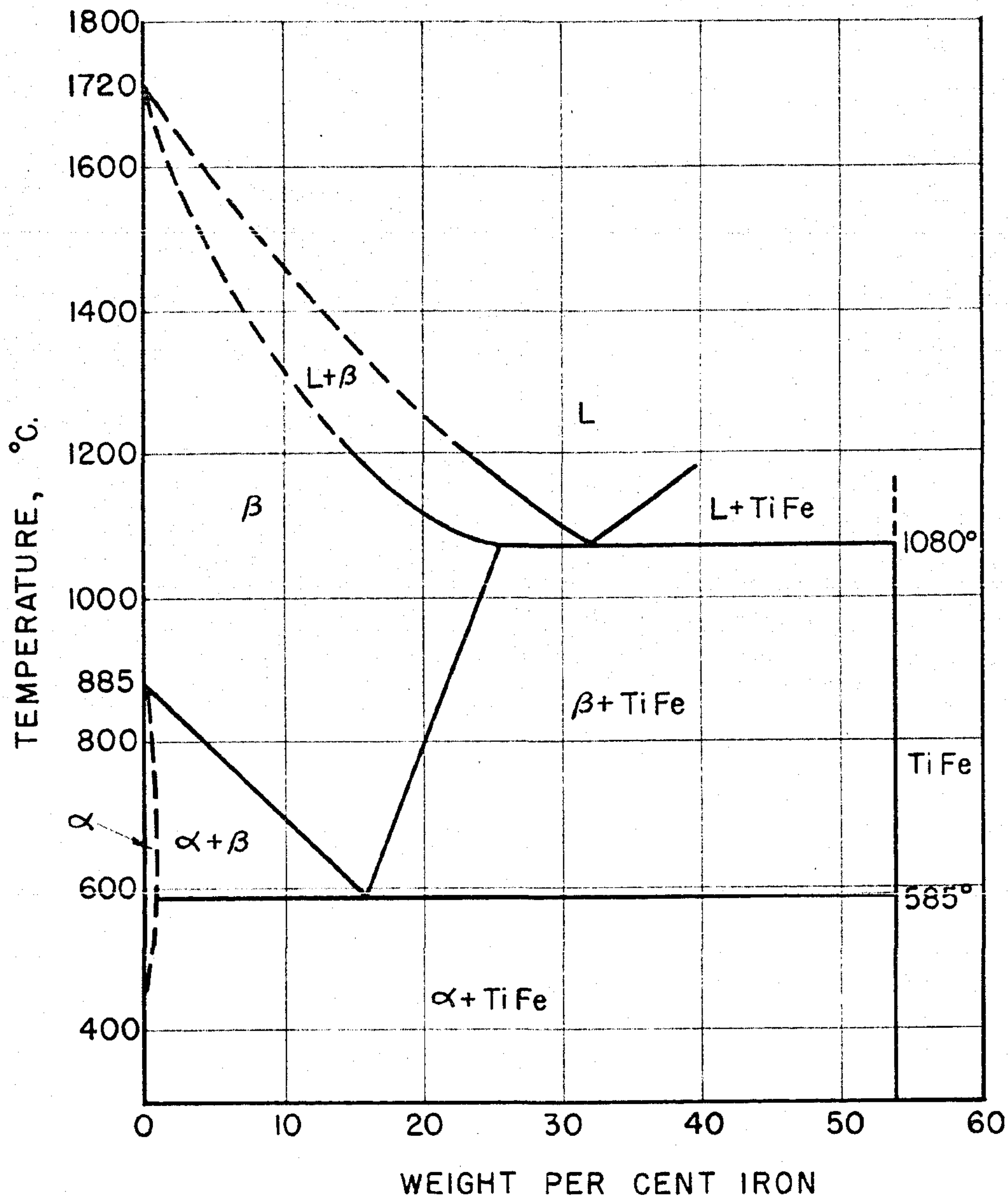


Figure 10

PHASE DIAGRAM
TITANIUM-IRON SYSTEM

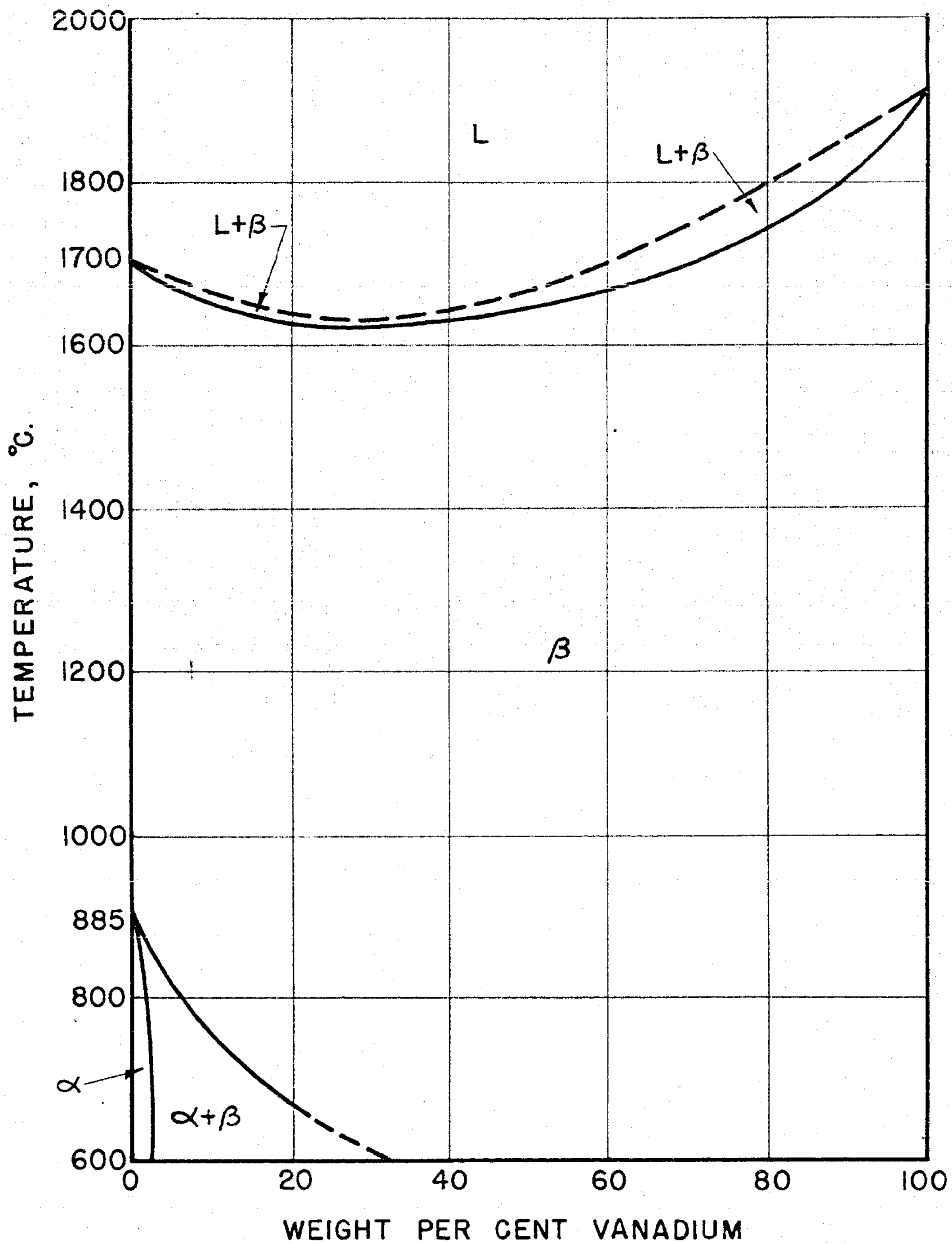


Figure II

PHASE DIAGRAM
TITANIUM-VANADIUM SYSTEM

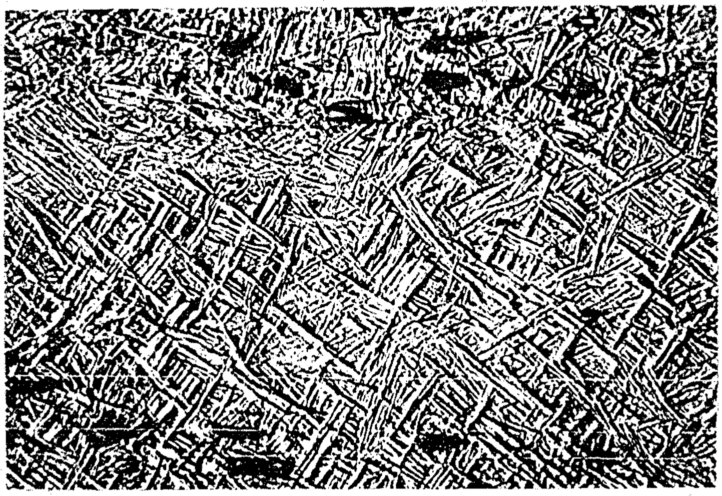


Figure 12.

Induction Melted MST-2.5Fe-2.5V,
Heat IM 31 (as forged).
X 500

Showing basketweave alpha, a duplex structure of grain-boundary alpha and Widmanstatten alpha, plus carbides. Some beta (not visible) is retained.

Figure 13.

Consumable-electrode Melted MST-2.5Fe-2.5V, Heat CE 14 (as forged).

X 500

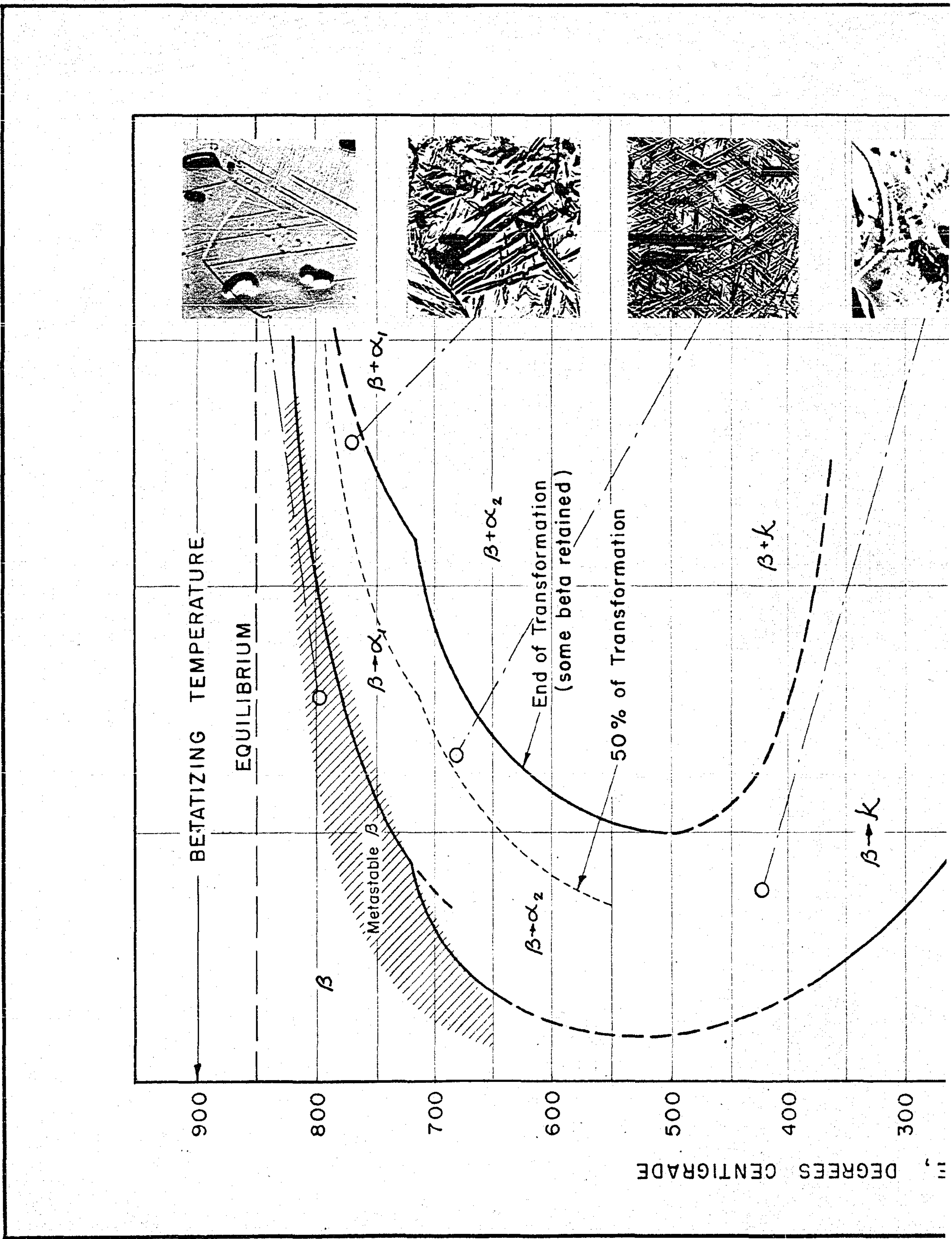
Showing basketweave alpha, a duplex structure of grain-boundary alpha and Widmanstatten alpha, plus carbides. A very small amount of beta (not visible) is retained.

ANALYSIS OF THE T-T-T DIAGRAMS

INDUCTION MELTED MATERIAL:

The time-temperature-transformation diagram for MST-2.5Fe-2.5V (induction melted, Heat IM 31) is shown in Fig. 14. Photomicrographs of typical structures are included. This diagram was composed from an integration of metallographic, X-ray, hardness, dilatometric, and thermal analysis data obtained as a part of this research. The interpretation of the results of each of these techniques is discussed elsewhere in this thesis.

Evaluating Fig. 14 in detail, consideration will first be given to the zone designated as "metastable beta." Beta quenched from this region will contain substantial quantities of alpha prime, also known as acicular alpha. Betatized specimens quenched directly into water or held at an elevated temperature for a shorter time than this zone includes will retain practically all of the beta on quenching. Likewise, once the isothermal transformation begins, the remaining beta matrix is again stabilized. In other words, beta will quench out (at 25°C.) with the formation of considerable alpha prime only when subjected to a combination of time and temperature falling within the metastable beta zone illustrated. This reaction is,


BETATIZING TEMPERATURE
EQUILIBRIUM
β
Metastable β
$\beta \rightarrow \alpha_1$
$\beta + \alpha_1$
$\beta + \alpha_2$
$\beta \rightarrow \alpha_2$
End of Transformation (some beta retained)
50% of Transformation
$\beta + \kappa$
$\beta \rightarrow \kappa$
900
800
700
600
500
400
300
DEGREES CENTIGRADE

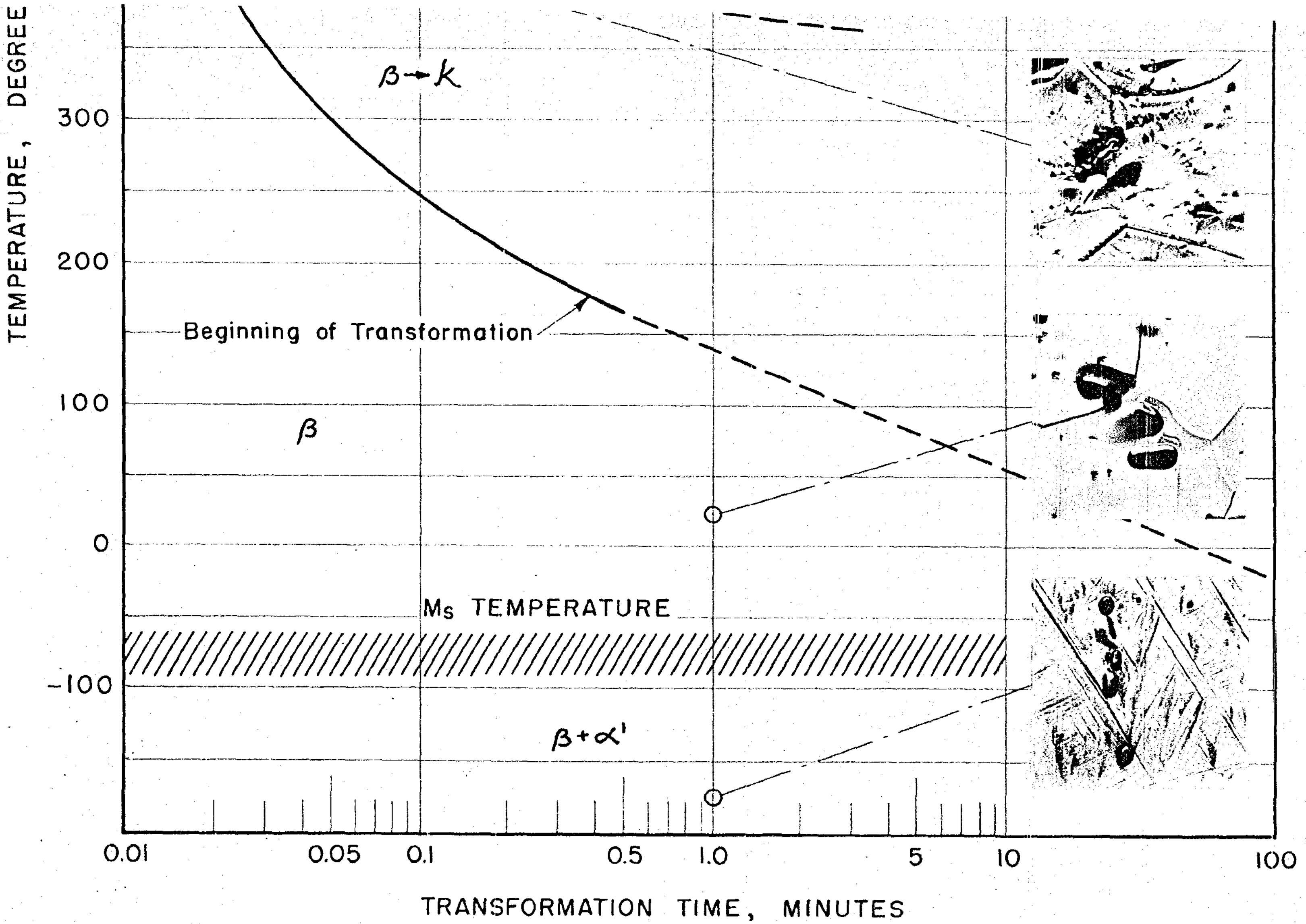


Figure 14

TIME-TEMPERATURE-TRANSFORMATION DIAGRAM FOR IM 31

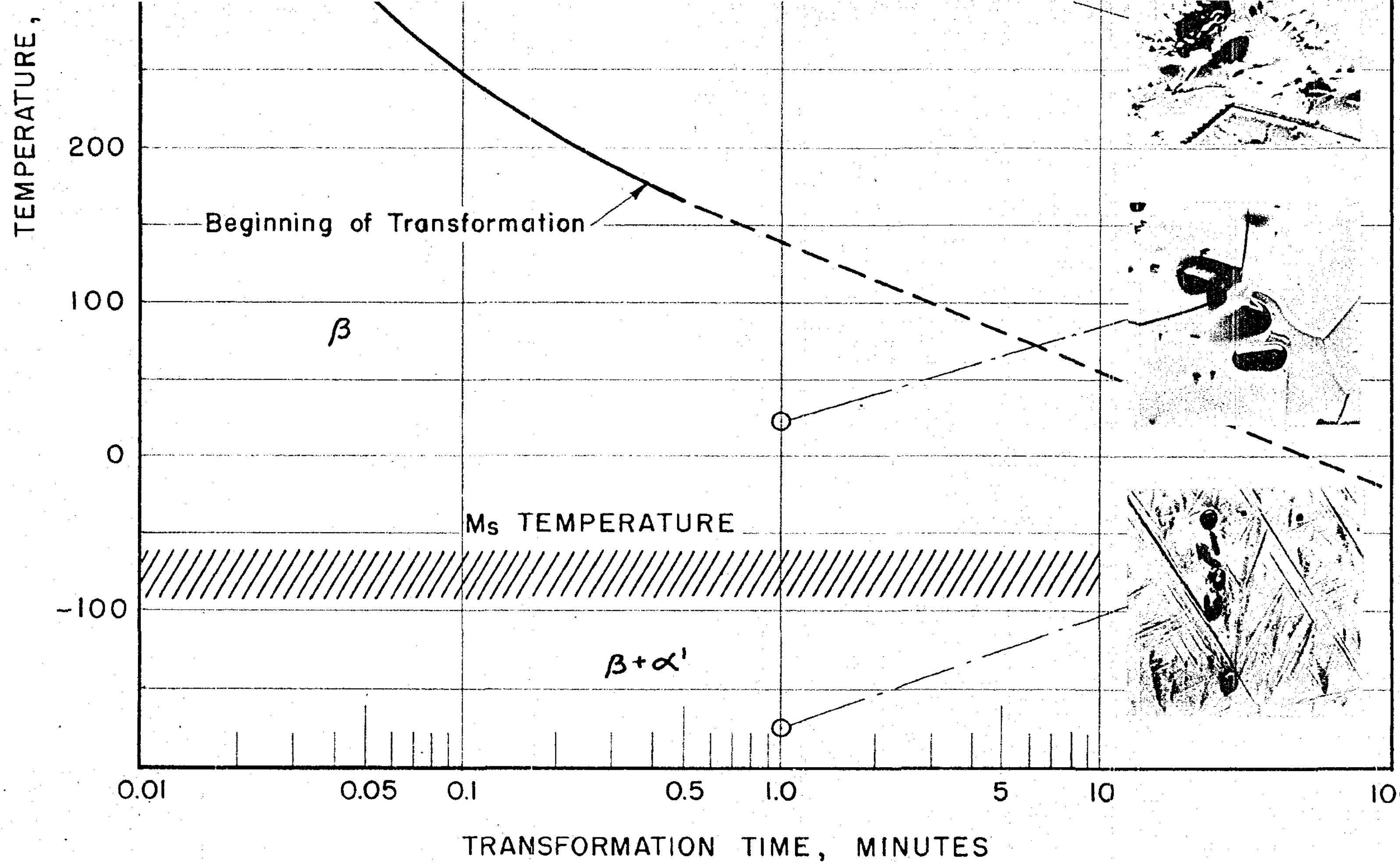


Figure 14

TIME-TEMPERATURE-TRANSFORMATION DIAGRAM FOR IM 31

of course, not one taking place at the temperature of isothermal holding but rather is occurring during the quench. It is probably prompted by alpha nuclei forming on a pre-precipitation basis at the elevated temperature.

Grain-boundary alpha, referred to in Fig. 14 as $alpha_1$ and sometimes referred to in the literature as lamellar alpha, is formed in this alloy upon isothermal holding above about 715°C. This type of alpha is nucleated at grain boundaries and carbide particles at the beginning of the reaction. As alpha separation progresses, previously formed alpha lamellae will serve as nuclei for other lamellae. The appearance of the microstructures of $alpha_1$ is quite dependent upon the temperature of formation. Slightly above 715°C., the lamellae formed are quite needle-like, growing out from the grain boundaries as colonies of parallel needles. At higher temperatures of transformation, the lamellae become coarser and shorter tending to lo se their orientation with respect to each other. Growth in the direction of length is retarded; that in the direction of width is increased. This trend continues until the alpha $_1$ formed above 800°C. has lost most of its lamellar appearance and takes the form of spherical particles of alpha located at the grain boundaries. At elevated temperatures this reaction becomes more and more sluggish, making the "End of Transformation" difficult to locate.

This accounts for the open end shown on the T-T-T diagram in this region.

Widmanstatten alpha, referred to in Fig. 14 as $alpha_2$, results from the isothermal transformation of beta at temperatures below 715°C. This decomposition product is formed by nucleation within the grains of beta and has been observed to suppress the $alpha_1$ reaction. The formation of Widmanstatten alpha is definitely distinct from that of grain-boundary alpha. This has been shown metallographically (compare Figs. 25 and 26) and also by thermal analysis. This microstructure is not particularly dependent upon temperature except that it becomes somewhat finer as the formation temperature is lowered. The nucleation rate of $alpha_2$ is much higher than that of $alpha_1$ although the growth rates are probably about the same. Because of this very high nucleation rate, the microstructure appears complete in a very short period of time. Nevertheless, it is to be realized that more subtle reactions not discernable with a microscope may well take place.

There have been reports in the literature that beta decomposition resulting in a similar Widmanstatten microstructure was martensitic in nature. This was attributed to the extremely rapid formation of this product at an apparent constant temperature and to its microstructural resemblance to some kinds of non-ferrous martensite. However, Widmanstatten alpha ($alpha_2$) occurring in this alloy has been proven conclusively to be non-martensitic in nature. This is predicted on thermal analysis data which indicates that the temperature of reaction is not constant and on the fact that the reaction can be suppressed by rapid cooling. Both of these factors are contrary to those defining a martensitic reaction.

The kappa phase indicated in Fig. 14 implies the formation of a metastable beta decomposition product. While not definitely isolated, there are several factors pointing to its existence. For one thing, the X-ray patterns of several specimens treated isothermally between 250 and 400°C. show evidence of a new phase as indicated by a diffraction line at a forward reflection angle of about 16°. This line did not appear in any patterns other than those of specimens transformed in this temperature range. Secondly, the microstructure characteristic of these temperatures contains large amounts of material something like $alpha_2$, although X-ray patterns show absolutely no alpha whatever to be present.

Furthermore, specimens treated between 250 and 400°C. show an increase in hardness over the water-quenched material (retained beta), while treatment in all other temperature ranges resulted in a hardness reduction. See Fig. 18. There is no sharp change in microstructure observed between the $alpha_2$ and kappa regions and when both transformation products are present in large quantities, it is difficult to detect a difference. However, when isolated at early stages of transformation, the $alpha_2$ takes the form of a series of overlapping triangles while the kappa is manifest by groups of very fine short needles each resembling a six-pointed star.

All of these items seem to contribute positive proof of the existence of this new phase. It occurs slightly below the temperature where a eutectoid reaction in the Ti-Fe system is indicated and is in all probability connected with this eutectoid reaction. In this event, however, the reason for the absence of any alpha as detected by X-ray analysis is not clear. It is felt that more research in this area is definitely indicated.

As the temperature of isothermal transformation is lowered still further, more and more beta is retained. Specimens water-quenched, which in reality are transformed indefinitely at 25°C., retain most if not all of the beta. However, dilatometric tests indicate a slight transformation occurring at 25°C. over a period of several hours. Although not substantiated by X-ray analysis, it is suspected that this is due to the slight formation of kappa, taking place very sluggishly at this temperature.

If beta is quenched rapidly enough to miss the "nose" of the transformation curve, thus avoiding the formation of $alpha_2$ or kappa, samples of IM 31 were found to form a martensitic structure at -75°C. and below. This is presumed to represent the formation of alpha prime. This structure is the same as that obtained by quenching from the metastable beta zone into water. A continuous quench of a modified type was necessary, as explained in detail in the section of experimentation. If the alloy was held for any length of time at room temperature before the sub-zero quenching, no martensitic reaction was observed. From the behavior of several samples given treatments in an attempt to induce this alpha prime reaction, it is concluded that its formation is extremely dependent upon the prior treatment to which the beta was subjected.

In the isothermal work with the induction melted material, it was found impossible to completely decompose all the beta originally present. Consequently, the "End of Transformation" curve illustrated in Fig. 14 does not represent the completion of the decomposition reaction, but rather, the condition at which it stops, presumably being close to an equilibrium state. Therefore, to illustrate more clearly the ultimate effect of isothermal

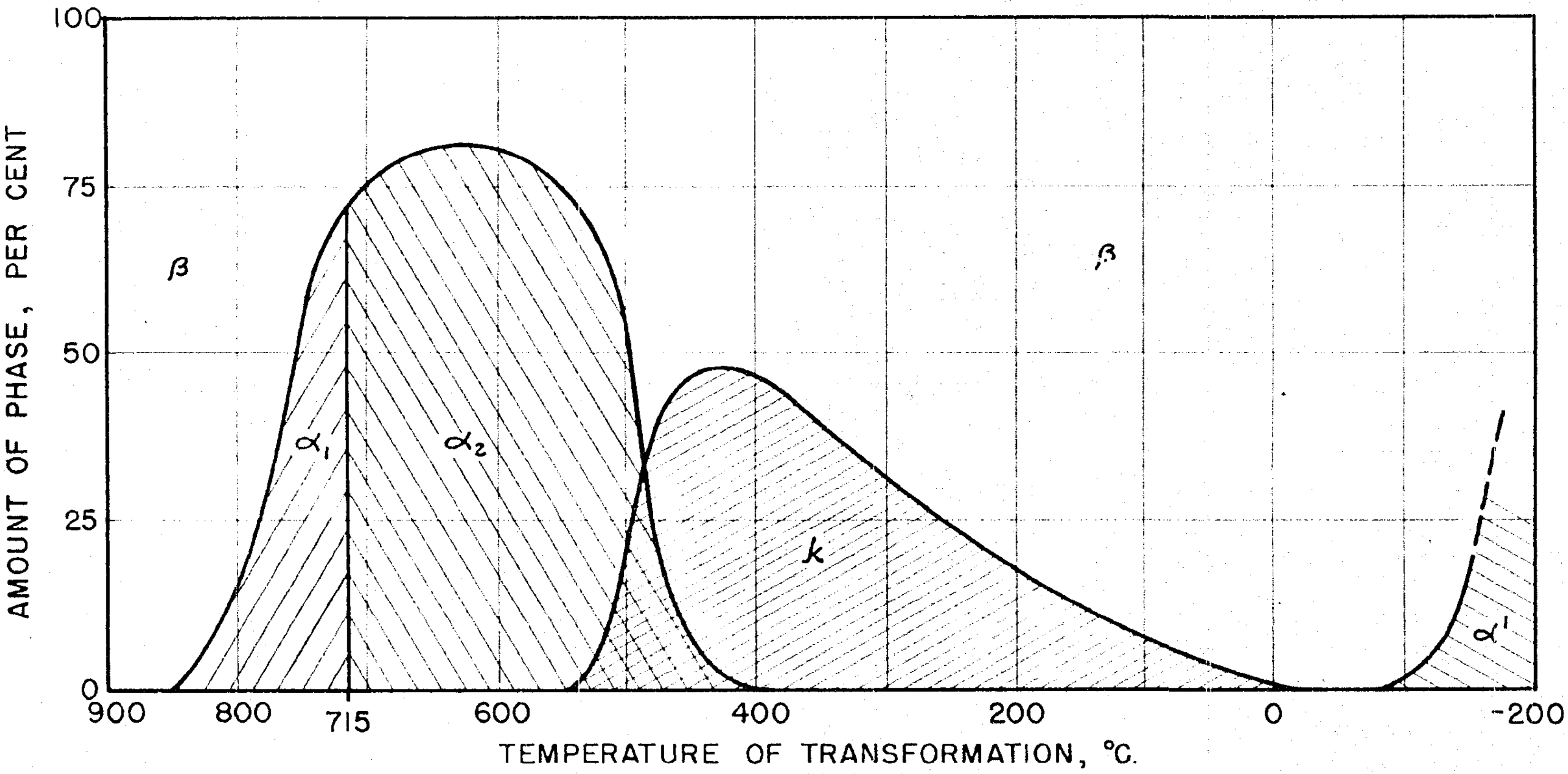


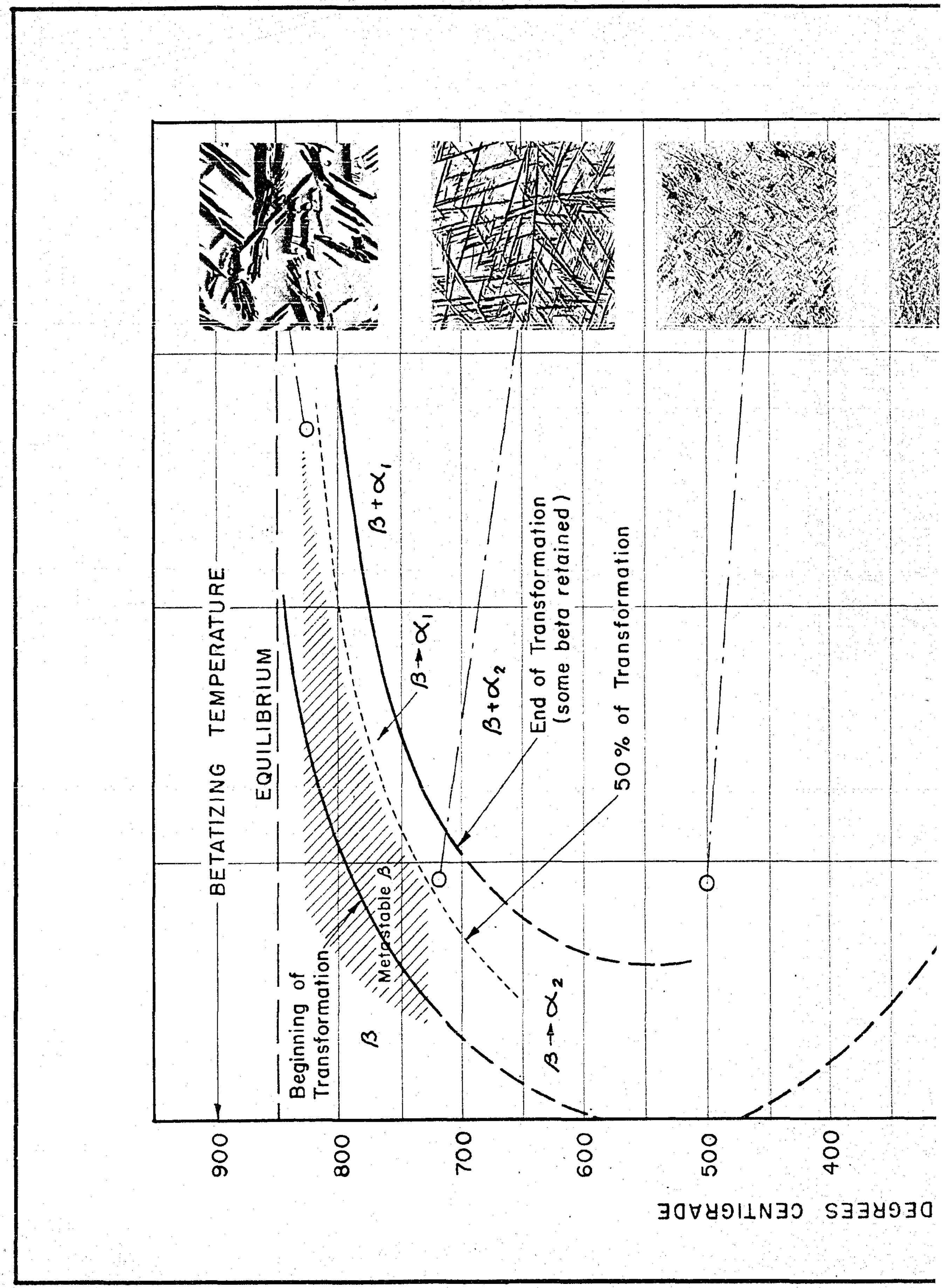
Figure 15

EQUILIBRIUM PHASE DISTRIBUTION OF ISOTHERMALLY TRANSFORMED IM 31 transformation, a chart showing the equilibrium phase distribution of transformed IM 31 is included as Fig. 15. This chart indicates approximately the amounts of phases obtained as a result of transforming beta to the end of the isothermal reaction at various temperatures.

CONSUMABLE-ELECTRODE MELTED MATERIAL:

The time-temperature-transformation diagram for MST-2.5Fe-2.5V (consumable-electrode melted, Heat CE 14) is shown in Fig. 16. Many of the comments stated above for the induction melted alloy and the T-T-T diagram obtained for that material apply equally well in this case.

There are, however, rather surprising differences between these two alloys, believed to center mainly around the greater tendency for alpha formation in the consumable-electrode melted material. The induction melted alloy contains about five times as much carbon as the other type, but the amount of carbon in solution in each alloy is probably about the same. However, nitrogen, a strong alpha former, is present in much greater quantities in the consumable-electrode melted alloy: 0.053 o/o compared to 0.014 o/o nitrogen in the induction melted material. It is believed that this difference in nitrogen content is sufficient to influence the alpha


BETATIZING TEMPERATURE
EQUILIBRIUM
Beginning of Transformation
β
Metastable β
$\beta + \alpha_1$
$\beta \rightarrow \alpha_1$
$\beta + \alpha_2$
$\beta \rightarrow \alpha_2$
End of Transformation (some beta retained)
50% of Transformation
900
800
700
600
500
400
DEGREES CENTIGRADE

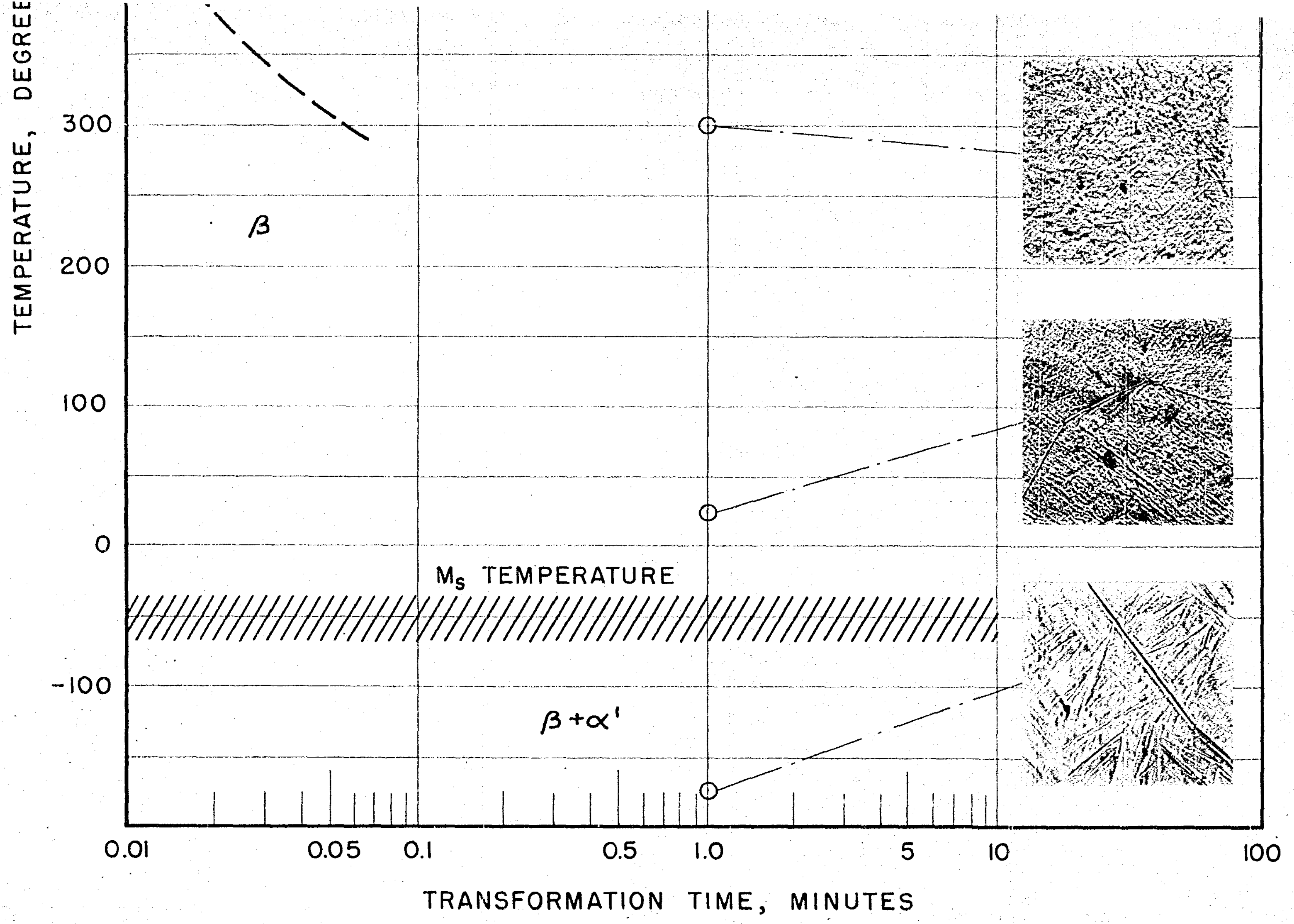


Figure 16

TIME-TEMPERATURE-TRANSFORMATION DIAGRAM FOR CE 14

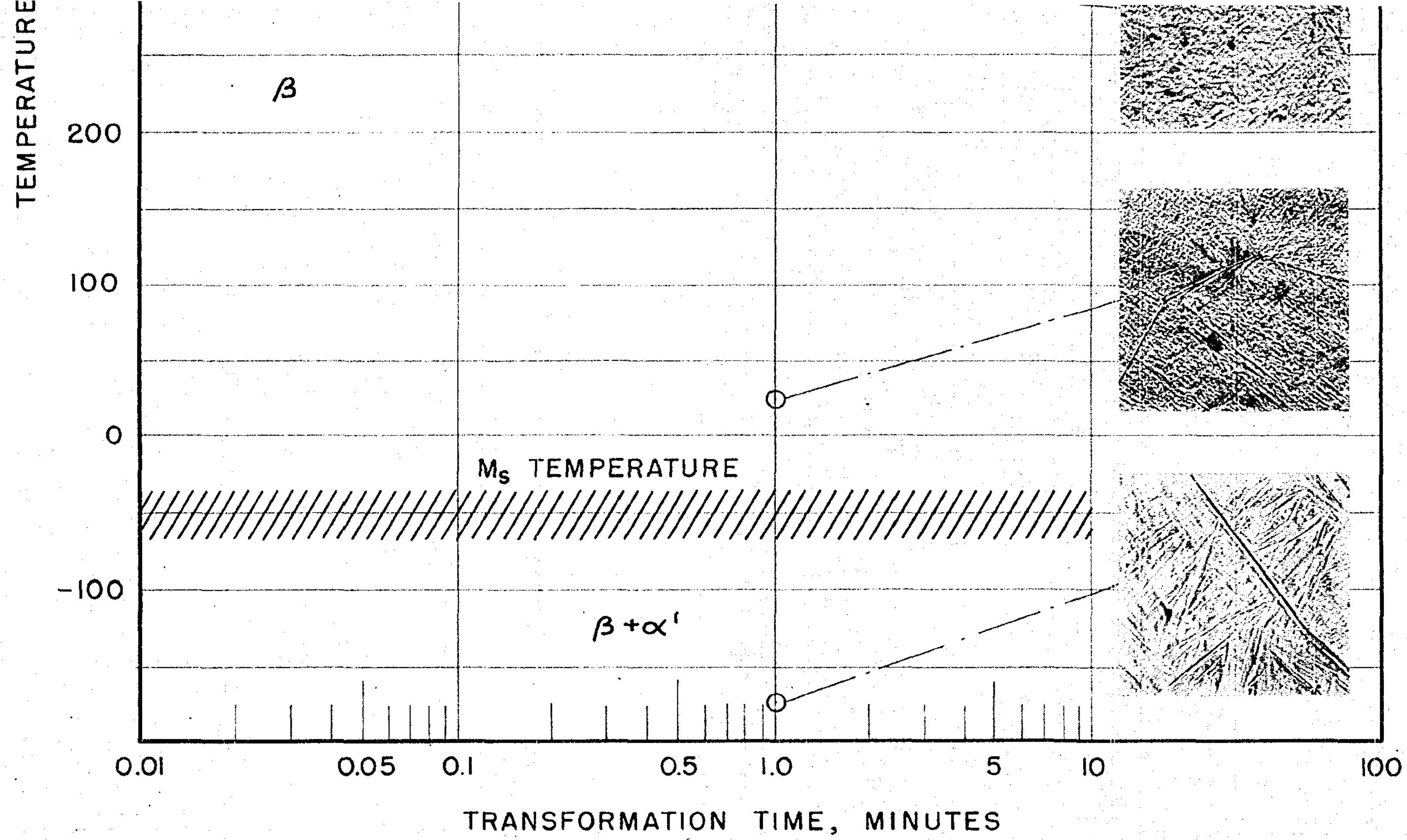


Figure 16

TIME – TEMPERATURE – TRANSFORMATION DIAGRAM FOR CE 14

formation and therefore may be responsible for the differences noted in these two alloy types.

Metastable beta was also found in the consumable-electrode melted alloy, giving rise to alpha prime on quenching. The alpha prime tended to form later during the isothermal reaction in this case, indicative of the greater alpha-forming tendency of CE 14. It was also observed that a greater number of alpha prime needles were formed in this alloy than in IM 31 following a quench from the metastable beta zone.

The $alpha_1$ and $alpha_2$ formed in CE 14 were like their counterparts in IM 31, except that the temperature ranges in which they formed were different. Generally speaking, the diagrams can be compared by saying that the consumable-electrode melted alloy undergoes transformation equivalent to the induction melted material at a temperature of about 50°C. higher. The real comparison, however, is in starting times. Inspite of temperature differences, a series of microstructures for a given isothermal transformation in one alloy will compare very closely to that series in the other alloy which exhibits the same starting time. This is significant since it shows that the difference in characteristics of the microstructures is dependent mainly upon the rate of nucleation.

There is no sharp transition between $alpha_1$ and

$alpha_2$ formation in CE 14. It does take place gradually, as seen metallographically and verified by thermal analysis. Likewise, the exact nature of the alpha reaction below the nose of the T-T-T curve is not clear, since it is difficult to observe a decrease in alpha formation under this nose. Furthermore, much alpha forms on a water quench, whereas the IM material will retain all beta under these conditions. These phenomena are also due to the greater alpha stability in CE 14. The nose of the transformation curve is so far to the left that the $alpha_2$ reaction cannot be suppressed completely by rapid quenching.

But this is not to be construed as martensite, for it has been found that CE 14 when quenched in sub-zero baths will also form true martensitic needles, as does IM 31. In this case, however, more martensitic product is formed. For this reason and also because of the greater alpha forming tendency of CE 14, it has been concluded that the M_s temperature in the consumable-electrode melted alloy is somewhat higher than in IM 31, but is still below 25°C.

The X-ray patterns of CE 14 are much more difficult to interpret than are those of IM 31. This is attributed to the large amount of alpha formed at all temperatures. If any kappa is formed in this alloy, it is certainly not possible to detect it by the X-ray method used in connection with this research. Likewise, no hardness or microstructure changes were noted. However, it must be realized that all such tendencies could easily he obscured by the large amount of alpha which is ever present. Inspite of the strong tendency to form alpha, beta is still retained following a "complete" isothermal transformation. An indication of the approximate equilibrium phase distribution is shown in Fig. 17.

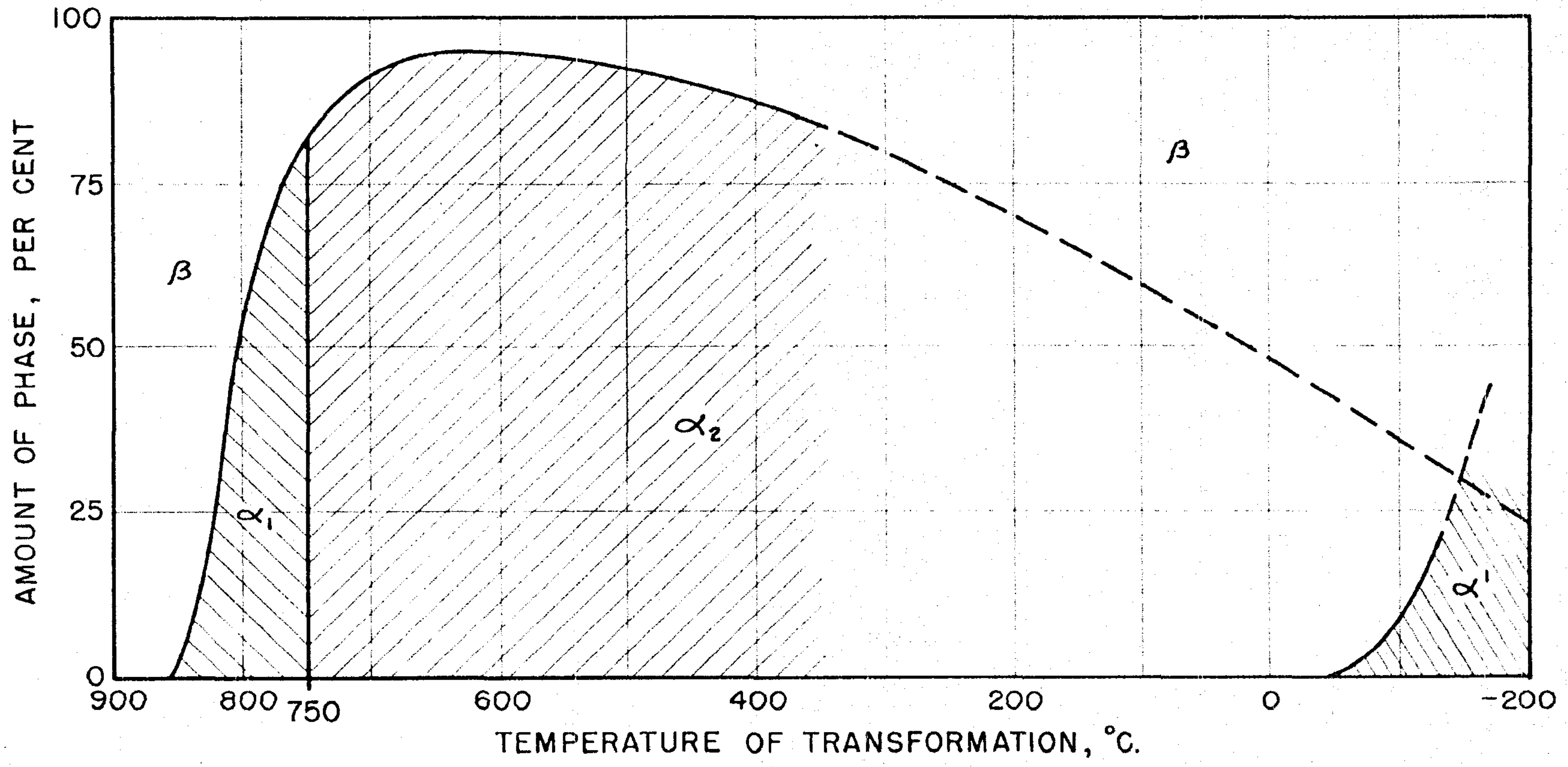


Figure 17

EQUILIBRIUM PHASE DISTRIBUTION OF ISOTHERMALLY TRANSFORMED CE 14

EVALUATION OF INDUCTION AND CONSUMABLE-ELECTRODE MELTED MST-2.5Fe-2.5V

Using the T-T-T diagrams as a guide, a few heat treatments were selected which would isolate the several distinctly different microstructures obtainable in these alloys. Tensile bars of as-forged material were subjected to these heat treatments and then tested for physical properties. The results of these tests are shown in Table 1. Hardness variations of several typical microstructures are shown in Figs. 18 and 19.

Upon examining the physical properties closely, it can be seen that no worthwhile trend is evidenced. Any increase in strength is accompanied by a decrease in ductility. In fact, the tendency toward embrittlement is disproportionately great. Nevertheless, these isothermal treatments have revealed, at least from an academic viewpoint, some interesting trends. The characteristics of IM 31 should aid in the more detailed study of many titanium alloy systems.

TABLE I

PHYSICAL PROPERTIES OF ISOTHERMALLY TRANSFORMED MST-2.5Fe-2.5V

ISOTHERMAL TREATMENT	INDUCTION MELTED ALLOY (Heat IM 31)			CONSUMABLE-ELECTRODE MELTED ALLOY (Heat CE 13)[a]		
	UTS	YS, 0.2%	% Elong, 2"	UTS	YS, 0.2%	% Elong, 2"
As forged	139,000	124,900	12.1	137,500	128,000	15.6
	147,800	136,200	9.8	--	--	--
Water quenched	162,220	*	*	178,600	*	*
	161,100	*	*	161,600	*	*
30 mins. at 355°C.	107,500	*	*	144,600	*	*
	117,300	*	*	165,200	*	*
30 mins. at 660°C.	139,200	127,100	8.5	138,600	132,100	10.9
	141,300	130,400	7.0	140,700	133,900	6.3
30 mins. at 750°C.	171,900	157,400	7.0	162,300	148,700	3.9
	173,500	159,400	7.8	163,600	152,100	7.8
15 mins. at 825°C.	169,900	*	*	154,800	*	*
	161,100	*	*	159,000	*	*

[a] Heat CE 13 is very similar chemically to Heat CE 14 which was used in the balance of this research.

* Indicates a brittle fracture.

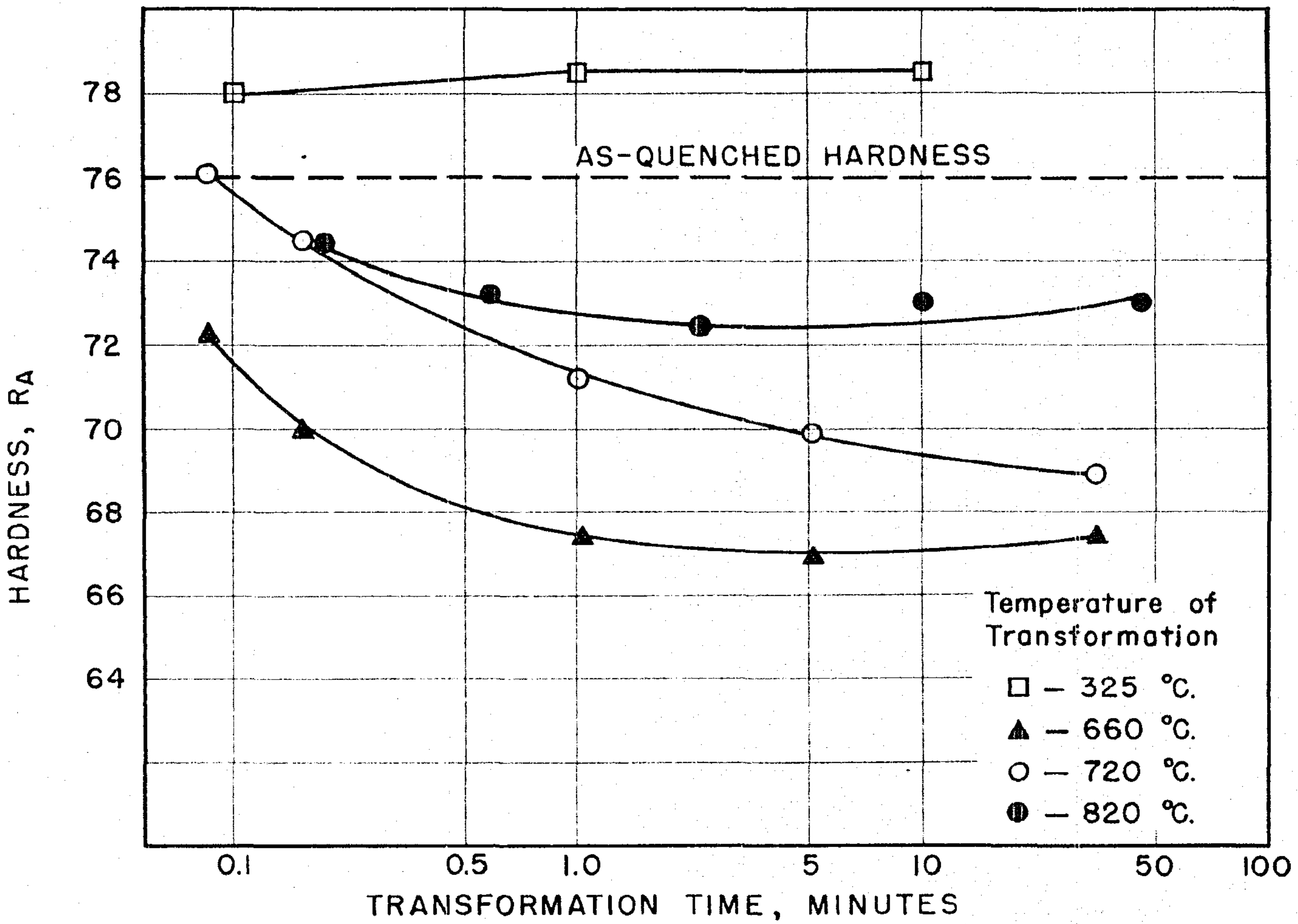


Figure 18

HARDNESS OF CHARACTERISTIC MICROSTRUCTURES OF IM 31

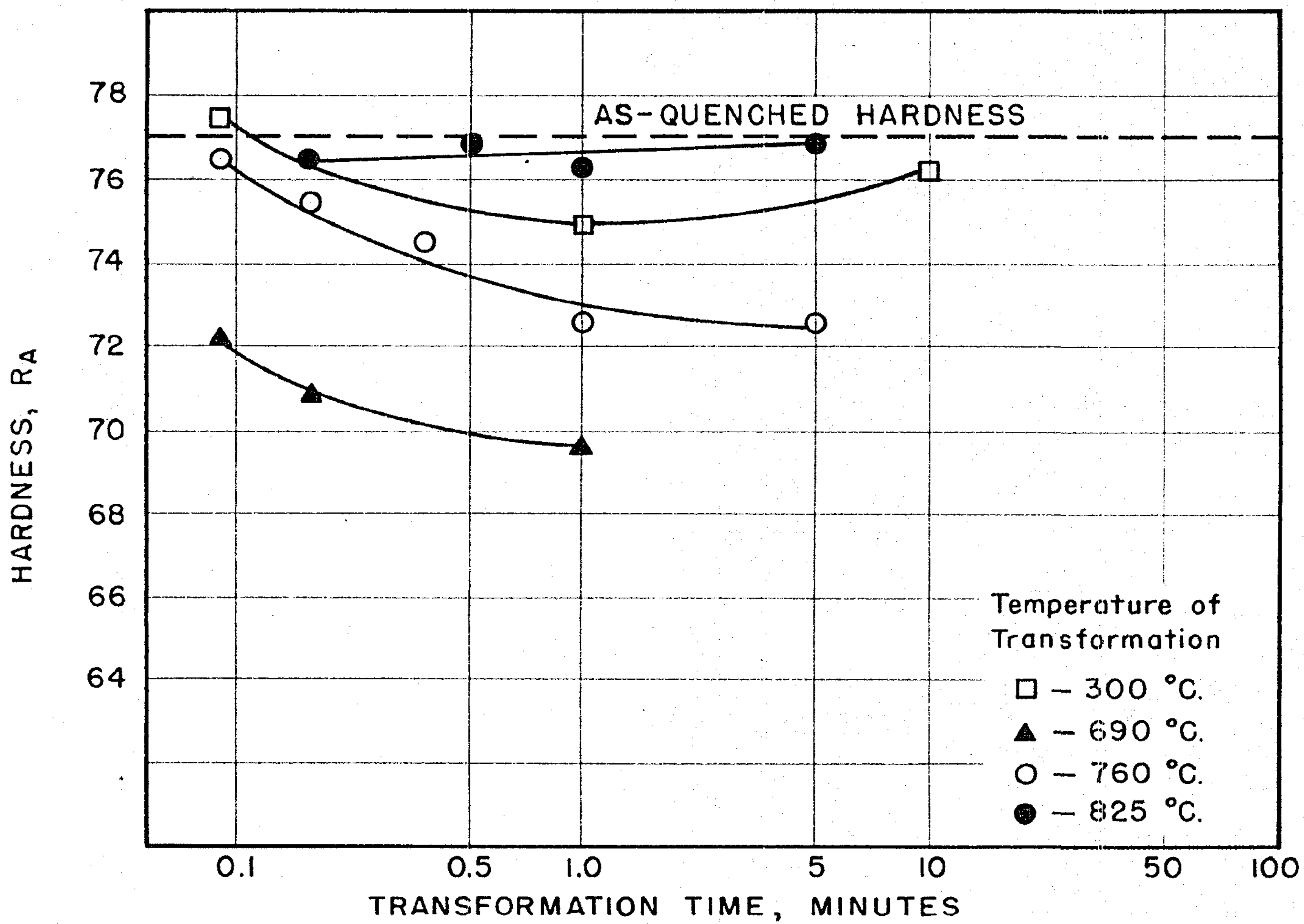


Figure 19

HARDNESS OF CHARACTERISTIC MICROSTRUCTURES OF CE 14

EXPERIMENTATION

III

EXPERIMENTATION

As indicated previously, the primary purpose of this investigation was to study the isothermal transformation characteristics of MST-2.5Fe-2.5V, both induction and consumable-electrode melted. Fundamentally, such a study is performed by solution treating the material to form a homogeneous elevated temperature phase (in the case of titanium, betatizing to form the single phase, beta) followed by quenching into a bath at the desired temperature of transformation. After holding isothermally for various lengths of time the alloy is quenched in water, presumably to arrest the transformation taking place at the elevated temperature. The microstructure is then examined making it possible to observe the type of transformation product formed as well as the progress of the transformation.

Because of a complete lack of background information on this alloy it was first necessary to investigate suitable betatizing conditions. Once the optimum condition was established, the isothermal transformation and metallographic work connected with this study was begun. A rough, overall plot of the desired T-T-T diargram was obtained first, followed by a more detailed study of the critical points. Thermal analysis, X-ray diffraction, and dilatometry were subsequently used to clarify, substantiate, and supplement metallographic observations. An integration of the information supplied by these several sources resulted in the T-T-T curves presented.

SPECIMENS

The alloy around which this work is centered, MST-2.5Fe-2.5V, is intended by the manufacturer to be used as a forging alloy. It is commonly supplied either as ingot suitable for forging or as forged bar stock. It was therefore thought desirable to have the material for this research in the as-forged condition.

To provide this material, a 30-pound melt of typical chemical analysis was selected. The as-cast ingot was forged in one operation to a 4 1/2-inch diameter bar and in a second operation to 5/8-inch diameter bar stock. The specimens were machined from this 5/8-inch diameter bar to form small flat discs 0.500" dia. x 0.125" thick. A No. 36 drill hole was placed near the edge of each specimen parallel to the circular axis. A mild steel wire was inserted in this hole to facilitate handling. A flat subtending an arc of about 60° was milled on the periphery opposite the hole to facilitate metallographic preparation of the specimen following the heat treatment.

It should be noted that all surfaces were machined. This practice eliminated the possibility of distorting the structure due to cut-off wheels and other common sectioning devices. All specimens were prepared by

P.R. Mallory and Co. and supplied to the author in this finished form, minus the steel wires. A considerable amount of 5/8-inch bar stock from the same heat as the specimens was set aside for subsequent physical testing.

BETATIZING

A complete betatization study was carried out only for the induction melted material. It was desired in this case to convert the as-forged structure to homogeneous beta at some elevated temperature, thus conditioning it properly for isothermal transformation studies. The titanium carbide particles shown in all microstructures of this alloy (IM 31) cannot be taken into solution by any reasonable treatment. They, although really a second phase, are considered more or less inert as far as beta decomposition is concerned; however, the carbides do have some slight nucleative effect during the early stages of alpha separation.

A preliminary estimate of a suitable betatizing temperature was gained from an inspection of the equilibrium phase diagrams for the Ti-Fe and Ti-V systems. It was found that in both cases beta is stabilized by these elements to lower and lower temperatures by increasing the alloy content. But considering also that the betatizing temperature must be far enough above the equilibrium point to facilitate rather rapid solution, it was decided that a temperature somewhere near the alpha-beta transition in pure titanium, 885°C., would probably be suitable.

The selection of atmospheric conditions for betatizing titanium is, of course, a compromise. Titanium is a very reactive metal and absorbs oxygen, nitrogen, and hydrogen quite readily at a rate increasing with temperature. One choice would be the use of an inert atmosphere furnace, purged with helium or argon, the latter being preferable because of its greater density. However, operating consistently under these conditions would have been quite tedious with the equipment available. A second choice would be to betatize in air in an electric muffle furnace. Undoubtedly some atmospheric gases would be absorbed under these conditions, but the seriousness of this contamination was questioned. Several specimens were soaked for up to five hours in air at 885°C. and examined. It was found that the contamination was principally limited to the surface areas as evidenced by alpha stabilization in that region. An example of this phenomenon is illustrated by Fig. 20. Furthermore, it was recognized that this alloy has been previously forged in air at 950°C. and possibly higher, where the tendency toward atmospheric absorption is considerably greater than at the probable betatizing temperature. In consideration of these facts and also with a view toward ease of duplication of procedure, air was selected as the standard betatizing medium for this work.

In later work where the effects of betatizing in

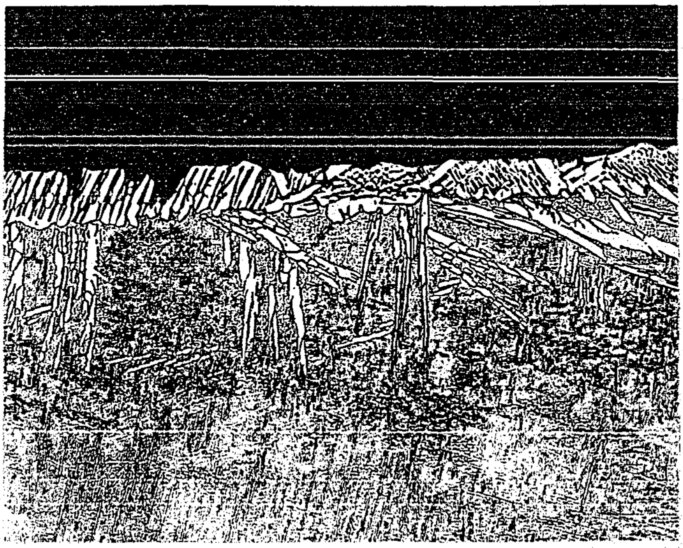


Figure 20.

Titanium Alloy Betatized in Air for One Hour at 900°C. (Notice the alpha stabilized at the surface due to atmospheric contamination.)
X 250

air vs. betatizing in an inert atmosphere because of interest in relation to the T-T-T characteristics of these titanium alloys, an attempt was made to set up an inert atmosphere train, employsing argon. The argon was dried in sulfuric acid and drierite, then passed through dull red copper to remove any oxygen present, and through hot magnesium turnings (maintained just below the melting point) to remove nitrogen. The atmosphere next passed through a tube furnace containing the titanium samples being betatized, and out to the atmosphere through a pressure trap displacing about 15 inches of sulfuric acid. It was not found possible to remove all of the nitrogen from the argon, however, and this plan was abandoned.

In order to determine the optimum time and temperature for betatizing, a series of specimens were solution treated in a closed electric muffle furnace from five minutes to three hours at temperatures ranging between 800 and 1000°C., followed by a water quench. The results of this study are shown in Fig. 21. Beta was considered homogeneous at the solution treating temperature when the quenched structure was uniform, showing no traces of the prior basketweave alpha structure. A few inconsistencies attributed to chemical segregation were noted although the trend illustrated was quite definite.

It was concluded from this study that one hour at 900°C. would be a suitable betatizing treatment.

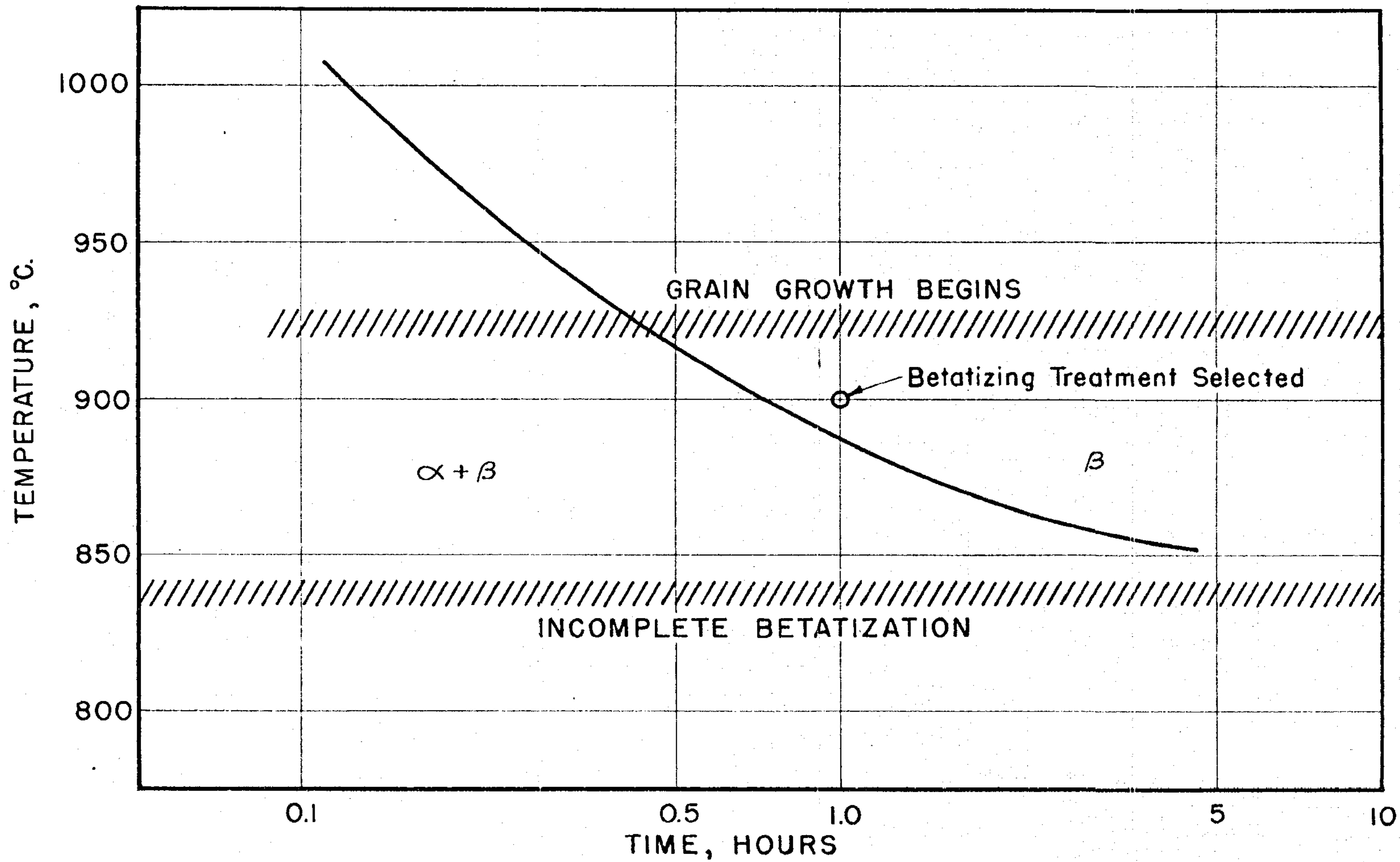


Figure 21

BETATIZATION RESPONSE OF IM 31

Generally speaking, this temperature would avoid grain growth and yet be high enough to limit the total betatizing time, hence limit atmospheric contamination. Subsequent work proved this to be an entirely satisfactory choice of betatizing conditions for the induction melted material.

At a later date, when it became desirable to compare the new consumable-electrode melted alloy (low carbon) with the induction melted alloy, the same betatizing procedure was used (one hour at 900°C.). While possibly not the ideal treatment for this new alloy type, it was thought better not to vary betatizing conditions in a comparison of this kind since the specific influence of this variable on the isothermal transformation characteristics of titanium alloys is unknown.

ISOTHERMAL TRANSFORMATION

There are many ways of determining the progress of an isothermal transformation or decomposition. These include optical metallography, dilatometry, X-ray diffraction, thermal analysis, and measurement of changes in hardness and electrical resistence. The optical method is the most basic and direct and therefore was selected for the groundwork in this research.

TECHNIQUE:

It was known that isothermal transformation was to be carried out at temperatures ranging from slightly below the equilibrium point (about 850°C.) down to and below room temperature. The selection of suitable media was necessary. Lead and tin baths were considered for the elevated temperature region since these metals were readily available and are molten over much of the desired range. Neither metal attacks titanium nor is absorbed by it to any great extent (10). Since tin is molten over a broader range than lead and since there is no danger of poisoning from tin vapors, tin was finally selected as the medium for the greater part of the transformation work. Water, a mixture of dry ice and acetone, and liquid air were used for transformation at temperatures not possible with molten tin.

Specimens were treated isothermally by betatizing for one hour at 900°C. as previously described, withdrawing them from the betatizing furnace and quickly immersing them in a bath consisting of about ten pounds of tin contained in a well-insulated electric pot furnace. Specimens were agitated vigorously for the first ten seconds in the tin bath and then allowed to "soak" undistrubed for whatever balance of the transformation time remained. The specimens were then withdrawn and quenched into water at about 25°C. The interval vetween each of these quenching steps did not exceed one second. Furnaces were maintained at ± 2°C. of the desired temperature, based on chromel-alumel thermocouples calibrated at the melting point of pure aluminum, 660.2°C.

Specimens quenched into sub-zero baths (acetone-dry ice and liquid air) were at first quenched directly, but it was found that the cooling rate in this case was lower than a quench in water (by observing the resulting microstructure). This was due to excessive gassing of these media when the hot titanium was immersed. However, a modified procedure of quenching for four seconds in water followed by a quench into the sub-zero bath enabled a more or less continuous cool from the beta region to be effected, the intermediate water quench being necessary to suppress the slight transformation which took place at about 500°C. during the slower cool directly in the sub-zero media.

Following the final quench, the specimens were wet-belt-ground very lightly on one flat face and marked for identification with a marking tool. Grinding was next begun on the flat cut in the specimen during preparation and approximately 1/10-inch of metal was removed. The geometric center of these small test specimens was now exposed and prepared for metallographic examination. See the Appendix for details of this operation.

METALLOGRAPHIC ANALYSIS:

As a beginning, specimens of induction-melted material (Heat IM 31) were transformed isothermally at 660, 690, 720, and 750°C. for approximately equal increments of log time ranging from two seconds to 30 minutes. Log time was chosen since the rate of these decomposition reactions is exponential in nature and in turn T-T-T curves are generally plotted using log time as abcissa. Photographs of the resulting structures were taken at 500X using offset illumination and 2-inch square prints were mounted at their proper positions on a large plot of log time vs. temperature which had been drawn. At the completion of this early work, the direction which subsequent research should take was clearly indicated.

Time and temperature were varied over a much wider range than originally mentioned, using the full useful range of molten tin plus water and sub-zero baths. Times up to two hours and temperatures from -175 to 840°C. were covered. Actually, value might well have been derived from holding times up to several hundred hours, although the chief manifestation of such tests would be in physical properties and possibly X-rays, but not in microstructure. Furthermore, equipment limitations made such long holding times impracticable.

A total of 94 samples of IM 31 were subjected to isothermal treatment. Four or five rather critical points were run twice as a check on reproducibility. These results were quite satisfactory indicating that reliable metallographic data could be obtained without a large number of duplication runs. After all of this metallographic information was assembled, a good idea of the transformation curves could be obtained at a glance. However, optical methods were found completely suitable only in the elevated temperature region. There were several points not clarified by optical means at transformation temperatures of about 700°C. and lower; other techniques were necessarily resorted to.

In later work comparing the consumable-electrode melted material (Heat CE 14) to the induction melted type

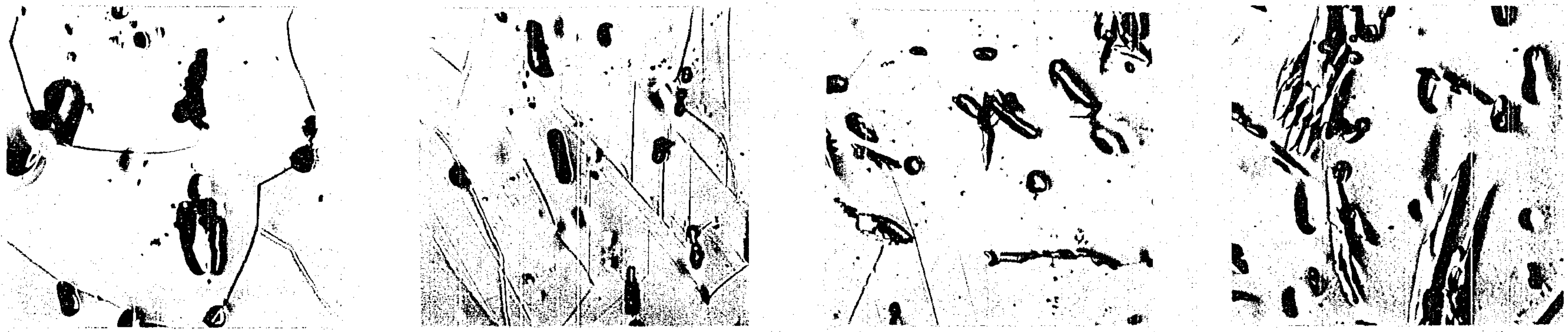
45 specimens of the low-carbon alloy were treated isothermally at certain selected temperatures. The resulting microstructures were all compared together in a way similar to that described for the induction melted material. In addition, a cross-comparison between CE and IM materials was made. The procedure enabled a detailed set of T-T-T curves to be drawn for the CE material also, although about half as many samples were actually heattreated.

Once assembled, a certain amount of interpretation of the space photomicrographs is necessary. A reaction has been assumed to begin when there is a general scattering of the new phase evenly distributed over the microstructure. Hence, the so-called "Beginning of Transformation" generally refers to somewhere between 2 and 4 o/o of transformation, if strictly evaluated. Other percentages of transformation product have been estimated visually. The "End of Transformation" is somewhat more difficult to define. While reactions may appear complete on the basis of microstructure after a minute or even less time at temperature has elapsed, X-ray studies have shown slight changes taking place in such materials even after 500 hours(14). Some of these changes, however, may be due to a secondary reaction. For the purposes of this work, the "End of Transformation" has been defined as approximately that condition where further isothermal soaking does not result in further change in microstructure or marked change in X-ray patterns. It does not imply complete beta decomposition nor the attainment of complete equilibrium. In reality, it probably represents the attainment of about 95 o/o of the true equilibrium condition at the particular temperature considered.

Several examples of the type of metallographic data obtained are shown in Figs. 22 through 31. It should be mentioned that the dark globular particles and occasional uneven spots in some of the microstructures are titanium carbide or complex carbides on or just under the surface. These may be ignored for the purpose of this study, except to note that they serve as nucleating points for certain types of transformation products.

THERMAL ANALYSIS:

The significance of several points remained somewhat obscure after completion of the metallographic portion of this research. Of prime importance was the marked difference in alpha formation observed between specimens of IM 31 quenched at 690°C. and lower and specimens of IM 31 quenched at 700°C. and above. See Figs. 25 and 26 for a comparison of these microstructures. The lower temperature phase, appearing as Widmanstatten alpha, has on several



a b c d

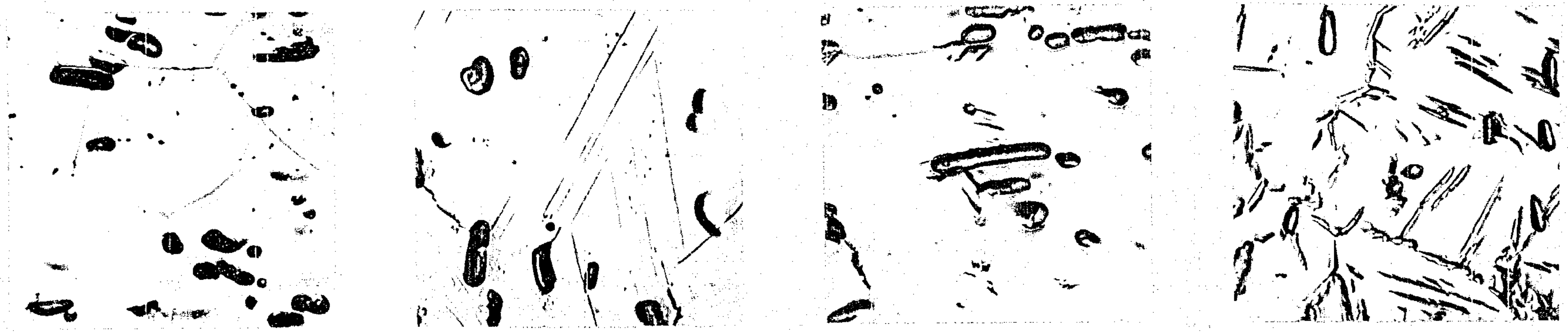
Figure 22. IM 31 Transformed at 820°C. for the Times Indicated. X 500

(a) 30 seconds - no transformation; showing retained beta plus carbides.

(b) 2 minutes - quenched from metastable beta zone; showing alpha prime needles, retained beta, and carbides.

(c) 10 minutes - transformation begins; showing some $alpha_1$, a few alpha prime needles, plus retained beta and carbides.

(d) 40 minutes - transformation progressing; showing $alpha_1$ and carbides in a matrix of retained beta.



a b c d

Figure 23. IM 31 Transformed at 795°C. for the Times Indicated. X 500

(a) 10 seconds - no transformation; showing retained beta plus carbides.

(b) 20 seconds - quenched from the metastable beta zone; showing strong alpha prime formation plus carbides and some retained beta.

(c) 1 minute - transformation begins; showing some $alpha_1$ in addition to retained beta and carbides.

(d) 5 minutes - transformation progressing; showing $alpha_1$ lamellae and carbides in a matrix of retained beta.

Figure 24. IM 31 Transformed at 720°C. for the Times Indicated. X 500

(a) 5 seconds - still in metastable beta zone, transformation almost beginning; showing alpha prime needles and some alpha_1 plus retained beta and carbides.

(b) 10 seconds - transformation progressing; showing alpha_1 at grain boundaries plus retained beta and carbides.

(c) 20 seconds - like b but more complete.

(d) 1 minute - like b and c but still more complete. (Note the thickening of the alpha_1 lamellae.)

(e) 5 minutes - apparently complete formation of alpha_1 plus carbides which are inherently present. (Though not visible, X-ray analysis indicates some retained beta in this structure.)

a b c d

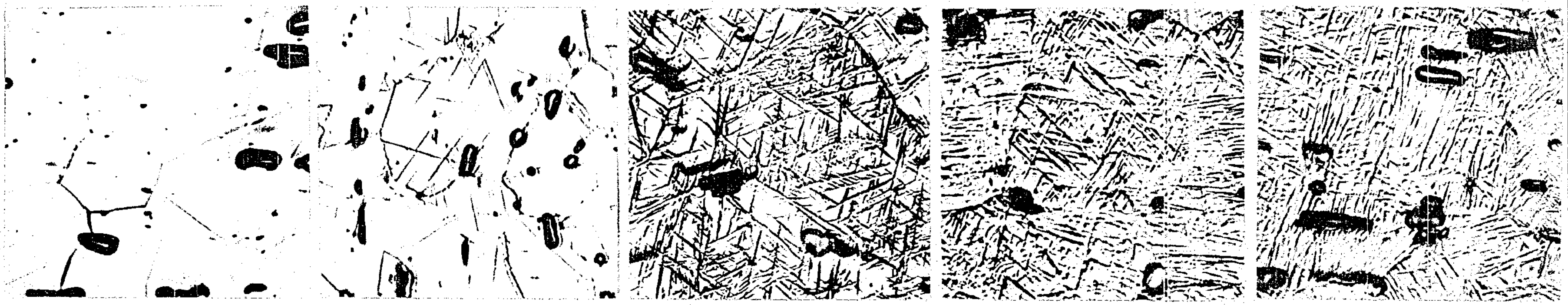
Figure 25. IM 31 Transformed at 700°C. for the Times Indicated. X 500

(a) 5 seconds - transformation begins; showing $alpha_1$ plus retained beta and carbides.

(b) 10 seconds - transformation progressing; showing $alpha_1$ plus retained beta and carbides.

(c) 20 seconds - like b but more complete.

(d) 1 minute - transformation nearly complete; showing network of $alpha_1$ needles plus carbides and small areas of untransformed beta.



a b c d e

Figure 26. IM 31 Transformed at 690°C. for the Times Indicated. X 500

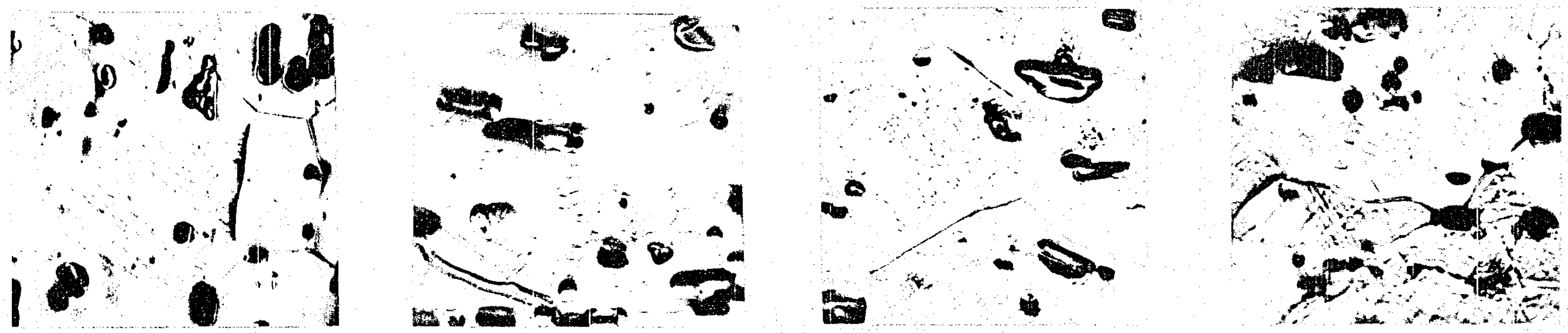
(a) 2 seconds - quenched from metastable beta zone; showing alpha prime needles and carbides in a matrix of retained beta.

(b) 5 seconds - transformation about 10% complete; showing $alpha_2$ needles plus carbides in retained beta. (Compare with Fig. 25a.)

(c) 10 seconds - transformation about half complete; showing needles of $alpha_2$ plus retained beta and carbides.

(d) 20 seconds - like c but nearly complete.

(e) 1 minute - apparently complete transformation; showing $alpha_2$ and carbides. Though not visible, some beta is retained.



a b c d

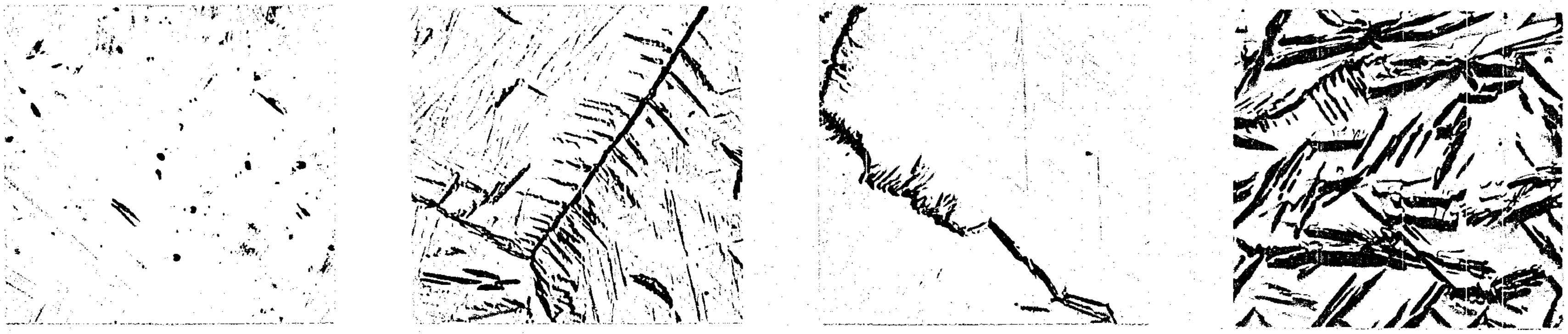
Figure 27. IM 31 Transformed at 375°C. for the Times Indicated. X 500

(a) 5 seconds - transformation progressing; showing typical kappa formation plus carbides in a matrix of retained beta.

(b) 15 seconds - like <u>a</u>.

(c) 1 minute - like <u>a</u> and <u>b</u> but more complete.

(d) 5 minutes - like <u>c</u> but still more complete.



a b c d

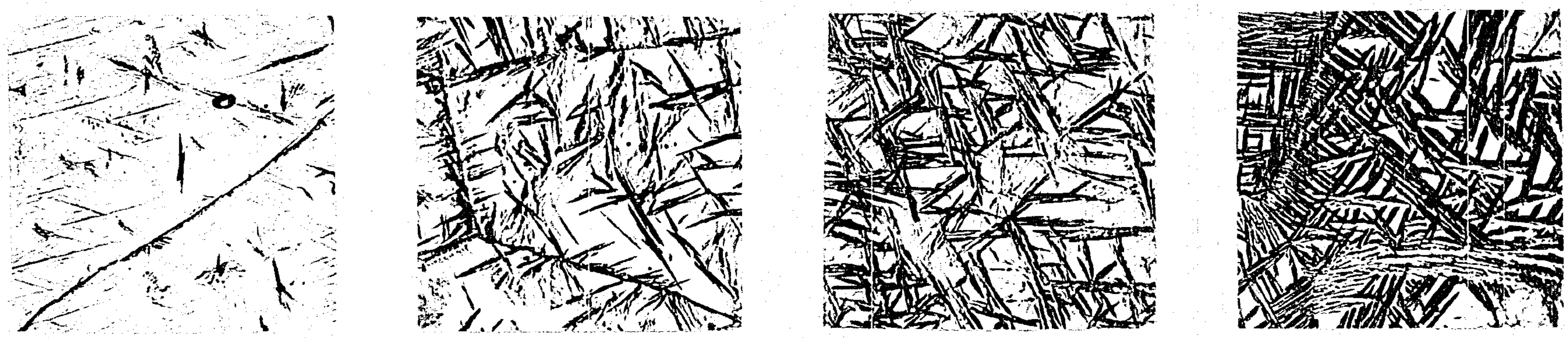
Figure 28. CE 14 Transformed at 825°C. for the Times Indicated. X 500

(a) 10 seconds - quenched from metastable beta zone; showing alpha prime needles. Some beta is retained though not distinguishable.

(b) 30 seconds - transformation progressing; showing alpha$_1$ at grain boundaries and alpha prime.

(c) 1 minute - like b; note suppression of alpha prime reaction due to quenching from fringe area of the metastable beta zone.

(d) 5 minutes - transformation progressing; showing alpha$_1$ lamellae in a matrix of retained beta.



a b c d

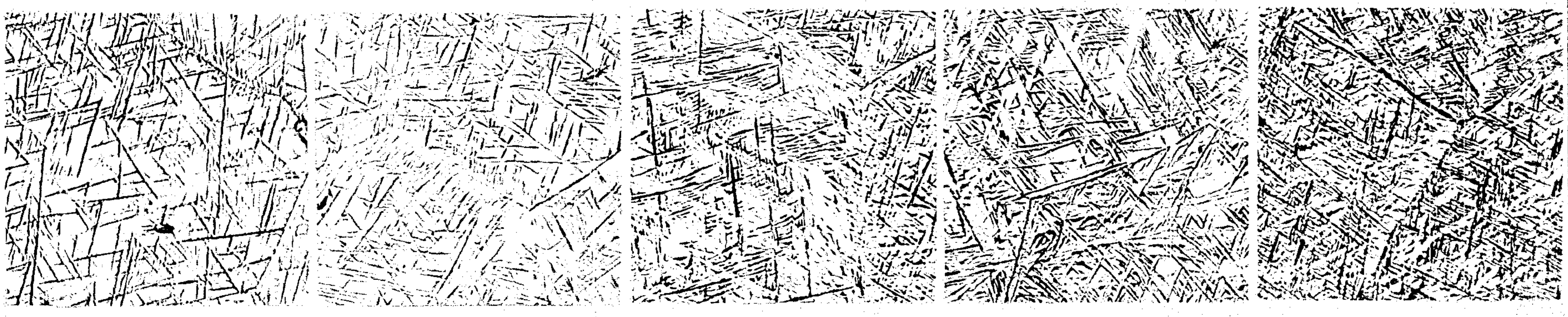
Figure 29. CE 14 Transformed at 760°C. for the Times Indicated. X 500

(a) 5 seconds - transformation begins; showing $alpha_1$ and alpha prime.

(b) 10 seconds - transformation progressing; showing $alpha_1$ lamellae and retained beta.

(c) 20 seconds - like b but more complete.

(d) 1 minute - like b and c but still more complete.



a b c d e

Figure 30. CE 14 Transformed at 720°C. for the Times Indicated. X 500

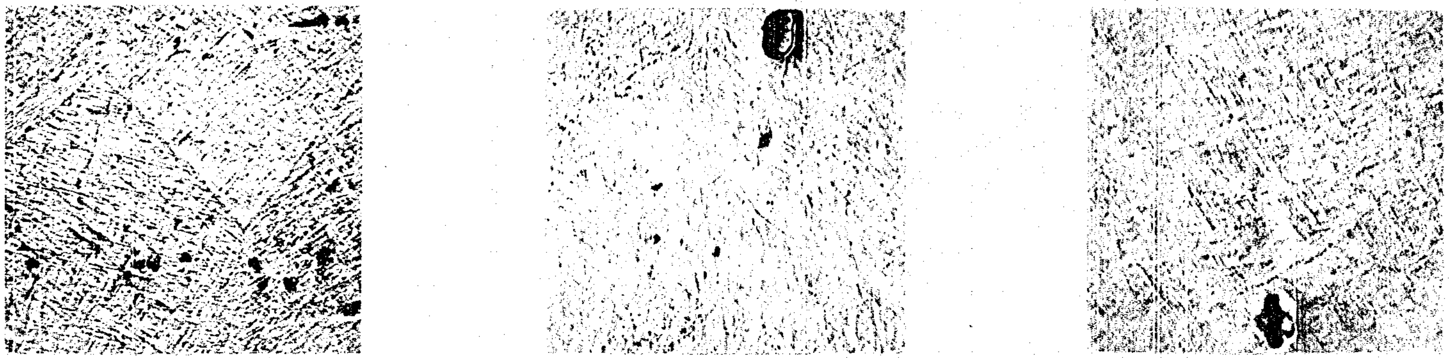
(a) 5 seconds - transformation about half complete; showing $alpha_2$ and retained beta.

(b) 10 seconds - like <u>a</u> but more complete.

(c) 20 seconds - like above but more complete.

(d) 1 minute - like above but more complete.

(e). 30 minutes - like above but still more complete. Note some coalesence of the $alpha_2$ needles.



a b c

Figure 31. CE 14 Transformed at 300°C. for the Times Indicated. X 500

(a) 5 seconds)
(b) 1 minute)
(c) 10 minutes)

All exhibit a fine $alpha_2$ structure plus some retained beta, the latter being detectable only by X-ray analysis.

occasions been referred to in the literature as martensitic in nature. This has probably been because of its general resemblance to some types of non-ferrous martensite and also because of its extremely rapid formation. It was noted, however, that water-quenching would suppress this reaction, which indicates the strong possibility of its not being martensitic.

Another characteristic of martensite is the concept that the temperature of the start of the martensitic reaction cannot be depressed by quenching, no matter how rapid (11). It was decided to investigate this latter point in the titanium alloys being studied to determine with more centainty whether or not the observed sudden change in microstructure was in reality due to a martensitic reaction. It had previously been shown that the martensite start temperature (M_s) can be detected by dilatometry, metallography (in the case of ferrous alloys) and by cooling curves response due to the heat of formation of the martensitic product (12, 13). The last mentioned procedure seemed most suitable for titanium alloys. Therefore, a setup to do thermal analysis work was initiated.

After considerable development, a technique was perfected which involved the insertion of the welded junction of a 28-gage chromel-alumel thermocouple in the geometric center of each of several titanium samples - 5/8-inch in diameter by 1/4-inch thick. (The smaller samples used in the metallographic work were tried but were found too small to give a suitable thermal response.) The thermocouple wires were insulated by 5/64-inch diameter 2-hole alundum tubes, countersunk into the peripheral surface of the specimen. A Speedomax Type G recorder was used in conjunction with this work. It was altered to provide greatly increased chart speed and a full scale range of 15 mv., reading 25 mv. at the low end and 40 mv. at the high end of the scale. These modifications enabled the full range of the Speedomax to be used, thus affording increased chart accuracy.

In operation, specimens with thermocouples inserted were betatized in the usual way. Toward the end of the betatizing cycle, the thermocouple was connected to the recorder and the temperature checked. In most cases, the temperature indicated by these specimens was within 5^{o}C. of that indicated by the master thermocouple in the betatizing furnace. At the end of the betatizing cycle and with the recorder running, the temperature of the tin bath was checked and recorded; the specimen was then withdrawn from the betatizing furnace and put into the tin bath. After equilibrium was reached, the actual tin bath temperature as well as that indicated by the specimen were recorded. Any error noted here was applied as a correction to the cooling curve drawn by the recorder.

Specimens of induction melted material were quenched into tin baths at temperatures ranging from 730 down to 550°C. At 720°C. and above, the normal logarithmic cooling curve was indicated, except that the last drop of 3 or 4°C. was very slow. Three minutes were required to reach equilibrium at 730°C.; 2.5 minutes at 720°C. This is believed to indicate the progression of the grain-boundary alpha formation found at these temperatures. Many specimens quenched at 710°C. and below exhibit a sharp isothermal hold or even a slight upsurge of temperature typical of that occuring in water when undercooled during rapid freezing. This isothermal arrest does not occur at a constant temperature but rather at from 5 to 15° C. above the bath temperature. Several typical curves are shown in Fig. 32. Data obtained from reading the complete set of cooling curves is contained in the following table:

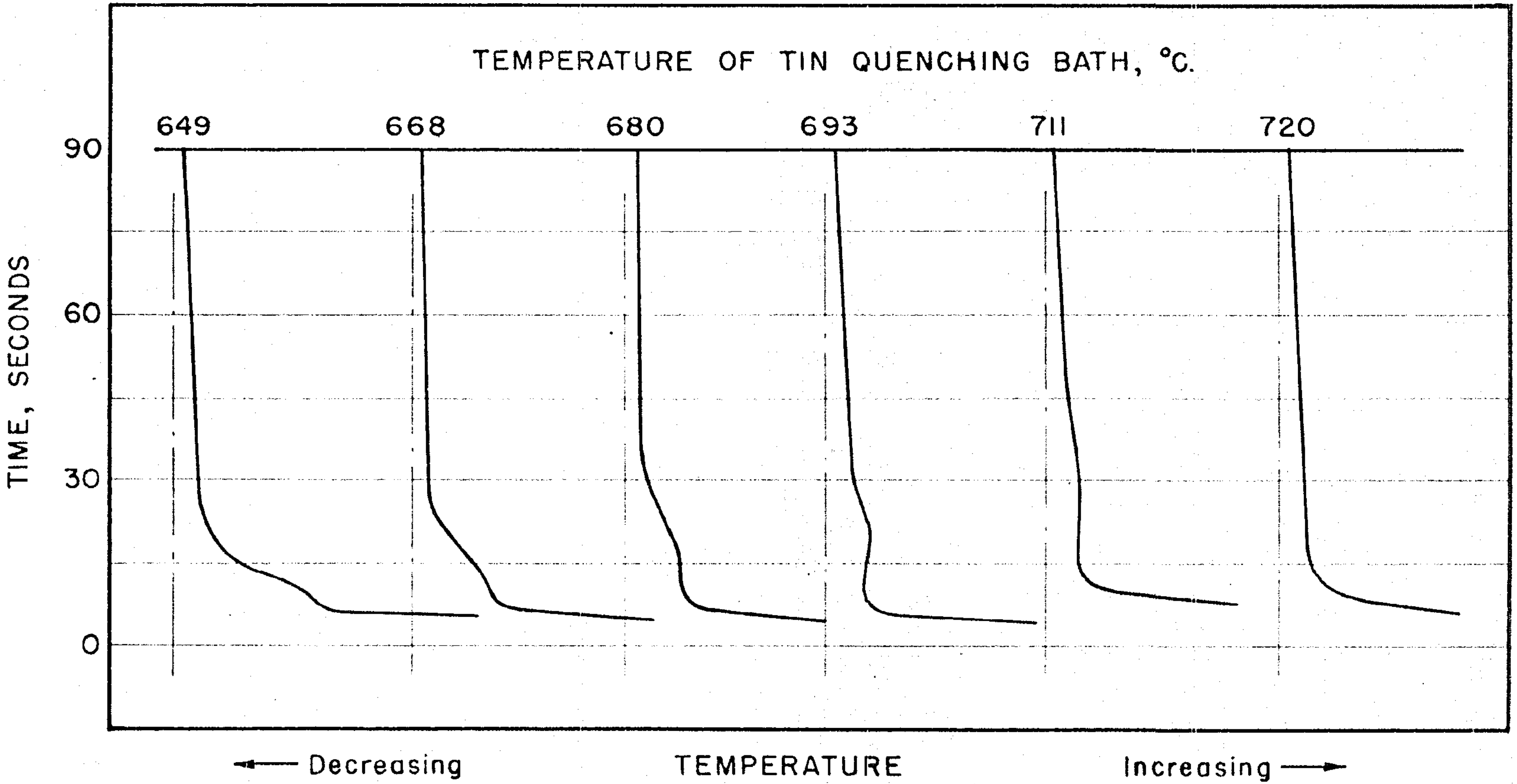


Figure 32

TYPICAL COOLING CURVES OF IM 31

Cooling Curve Data for IM 31

Quenching Bath Temp. °C.	Temp. of Isothermal Arrest °C.	Duration of Isothermal Arrest Sec.
730	none	---
720	none	---
711	716	15.6
710	713	6.7
693	698	9.5
680	690	3
680	687	instant.
668	685	instant
660	680	instant
649	679	instant
638	684	jog in curve
619	665	jog in curve
590	661	jog in curve
550	645	jog in curve
500	none	---

The isothermal arrest indicated above coincides with the formation of Widmanstatten alpha and is presumed to be due to that reaction. Widmanstatten alpha is observed here (by thermal analysis) in specimens quenched at 711°C. and lower, while appearing in the regular specimens (smaller, without thermocouples) only following a quench at 690°C. or lower. The presence of this product in the larger thermal analysis specimens following slightly higher quenching temperatures was verified metallographically. It is concluded that the lower cooling rate obtained in the larger specimens may well be responsible for this, predicted on the assumption that Widmanstatten alpha is a nucleation and growth product.

Reverting now to the original problem, it is seen that the formation of Widmanstatten alpha does not take place at constant temperature. This fact coupled with others previously mentioned seems to prove conclusively that this product is formed by nucleation and growth and is not martensitic (nucleation and shear) in nature. The type of cooling curve obtained, however, indicates that Widmanstatten alpha forms very rapidly and that the nose of the T-T-T curve in this region is very close to the zero time axis.

It was evident from an examination of the microstructures obtained for the consumable-electrode melted alloy (CE 13) that this same sort of Widmanstatten reaction was occurring in that material also. It was observed at somewhat higher temperatures, however, and was less distinctly separated from the grain-boundary alpha formation which also takes place. Thermal analysis of this material followed the same pattern as the analysis of IM 31. In this case, however, it is interesting to note that the manifestation by thermal analysis of this Widmanstatten reaction is less pronounced in CE 14 than in IM 31, paralleling the less distinct demarcation of microstructure. Several typical cooling curves are shown in Fig. 33. Data obtained from reading the complete set of cooling curves is contained in the following table:

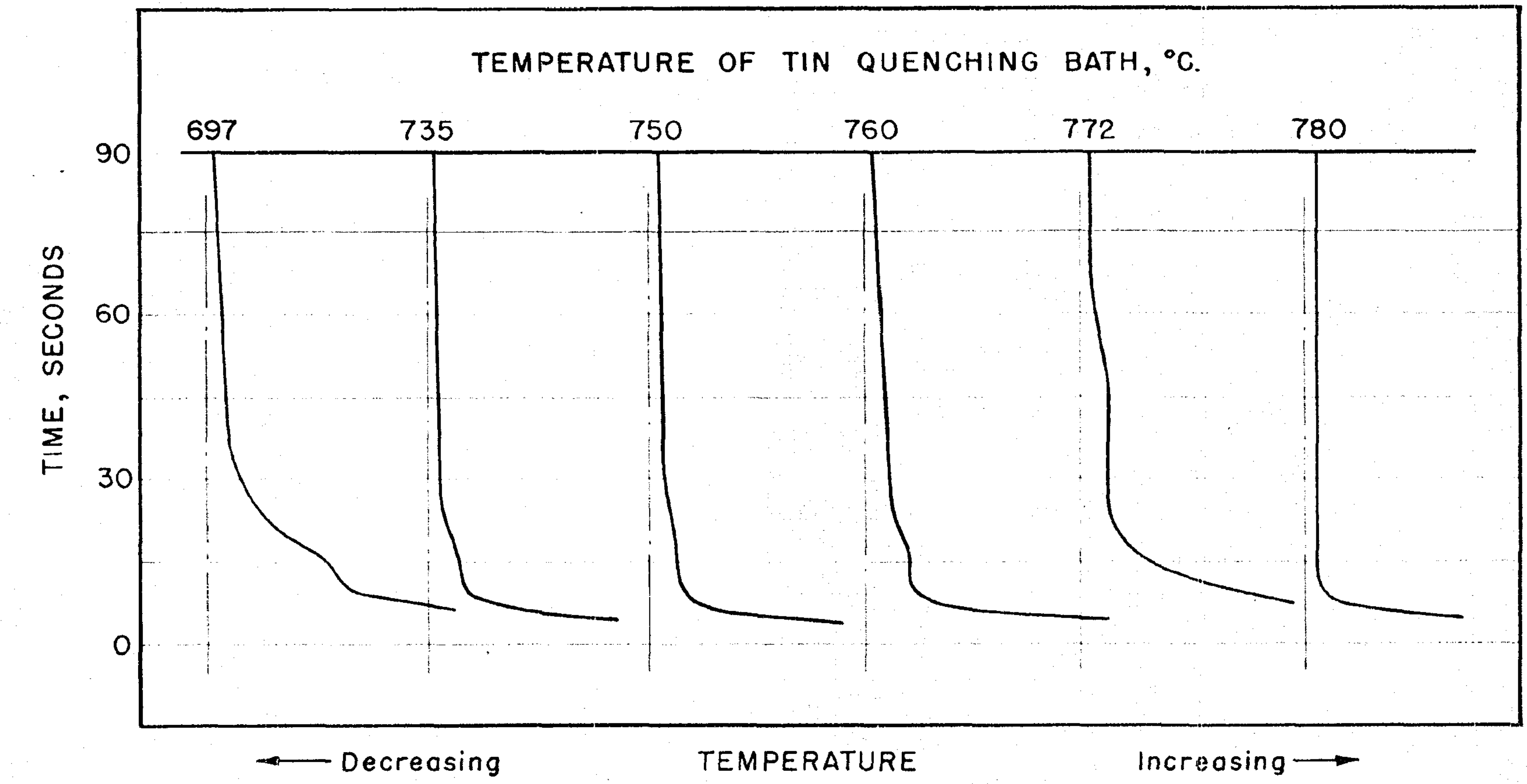


Figure 33

TYPICAL COOLING CURVES OF CE 14

Cooling Curve Data for CE 14

Quenching Bath Temp. °C.	Temp. of Isothermal Arrest °C.	Duration of Isothermal Arrest Sec.
780	none	---
772	777	17
760	763	5
750	758	instant
735	744	instant
697	720	jog in curve
649	none	---

In general, the conclusions drawn above regarding the validity of thermal analysis in the case of IM 31 apply equally well to the consumable-electrode melted alloy.

One additional detail considered most worthwhile evolved from this work on thermal analysis. It was obvious from the beginning that a true isothermal transformation was not possible, particularly where the total time in the tin bath was of the order of five or ten seconds. A finite time lag existed before the transformation temperature was reached, the problem being how to evaluate it. By thermal analysis applied to the small standard specimens used in the metallographic portion of the project, it was found that five seconds were required for the specimen to come to within 3 or 4°C. of the bath temperature and about five more seconds to actually reach equilibrium. Taking this into account, an approximate compensation to T-T-T data was made by considering that structures transformed for five seconds in tin were actually typical of 15°C. higher than the bath temperature; specimens transformed for ten seconds were considered typical of 5°C. higher than the bath temperature. No compensation was made for longer holding times. This of course is only a very rough approximation but is believed to be closer to the true situation than would be the case without any correction whatever. (This compensation was applied in the drawing of the final T-T-T curves only. It was not used in composing Figs. 22 through 31.)

In a still further attempt to isolate the isothermal beta decomposition reactions, a scheme for differential thermal analysis was set up. One sample of the alloy being observed and one sample of an alpha-stable alloy containing aluminum were each fitted with thermocouples, so connected that the net EMF would be indicated. When the specimens were at the same temperature, this EMF would be zero. As the specimens were simultaneously withdrawn from the betatizing furnace and quenched into tin at the desired temperature of isothermal transformation, this EMF would presumably remain zero until transformation began in the material under test. (There would be no transformation in the alpha-stable material and this would cool normally.) As tran sformation began in one specimen, a temperature would supposedly be set up causing a recorder deviation. At the completion of transformation, the temperature differential should then remain constant or decrease slightly, ultimately reaching zero. This procedure would result directly in a plot of transformation vs. time and the duration of transformation could be more easily evaluated. In practice, however, the influence of the transformation was obscured by the difference in heat transfer characteristics of the two alloys[1] and the plan was necessarily abandoned due to lack of other, more suitable materials.

X-RAY ANALYSIS:

It was decided that X-ray studies would be very useful in this research to substantiate the conclusions drawn from metallographic observations and also to clarify certain points left obscure by other methods of analysis.

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[1] The titanium alloy containing aluminum is inherently more resistant to oxidation than the alloy without aluminum. The difference in surface films formed during betatizing is hence believed responsible for the difficulty encountered.

From a metallographic point of view, this research was somewhat easier than similar work done with other titanium alloys. This is because microstructural changes turned out for the most part to be clear cut and well defined. While this facilitates optical work, a suitable check was of course desirable. Not only can the conclusions drawn from optical data be verified by X-ray studies, but the continuation of a reaction following apparent completion as observed by optical methods can be detected. Likewise, distinction between two or more phases alike in appearance or the identification of a new phase previously unknown can be accomplished.

The first X-ray work was done to determine whether the induction melted alloy (IM 31) would retain beta on a quench in water at 25°C. It had been anticipated by the manufacturer that not a great deal of beta would be retained. However, the microstructure of samples treated in this manner showed no evidence whatever of any alpha or other transformation product. The structure appeared to be all retained beta plus carbides. In an attempt to determine the true nature of the structure, powder was very carefully prepared (by filing) from two water-quenched samples of IM 31 and X-ray powder diffraction patterns were taken. These patterns showed almost equally strong alpha and beta lines, by comparison to diffraction patterns of other metals known to be all alpha and all beta (16). This meant definitely that at least some beta was retained on water quenching. However, alpha was also indicated which could not be detected optically. While a very fine alpha dispersion is most probably possible, it did not seem too logical that an amount of alpha sufficient to give a strong diffraction pattern could completely escape metallographic observation. Consequently, there remianed some doubt as to the suitability of this method.

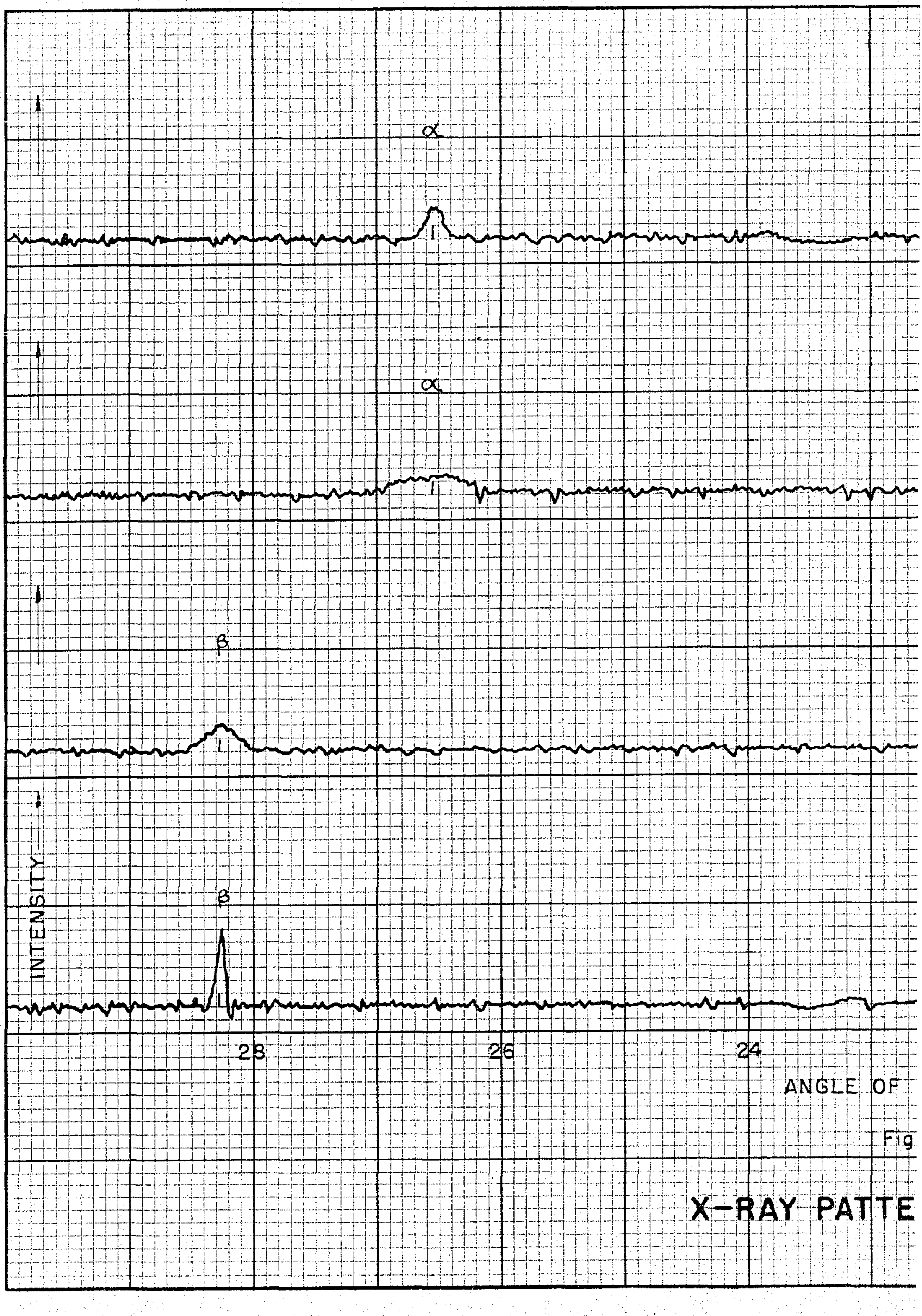
It was recognized that beta titanium is quite strain sensitive under certain conditions. Therefore, it seemed very possible that the alpha detected by powder analysis methods wwas not present in the alloy originally, but that it really resulted from a strain-induced beta to alpha transformation during the preparation of the powder from the heat-treated specimens. Later work confirmed this.

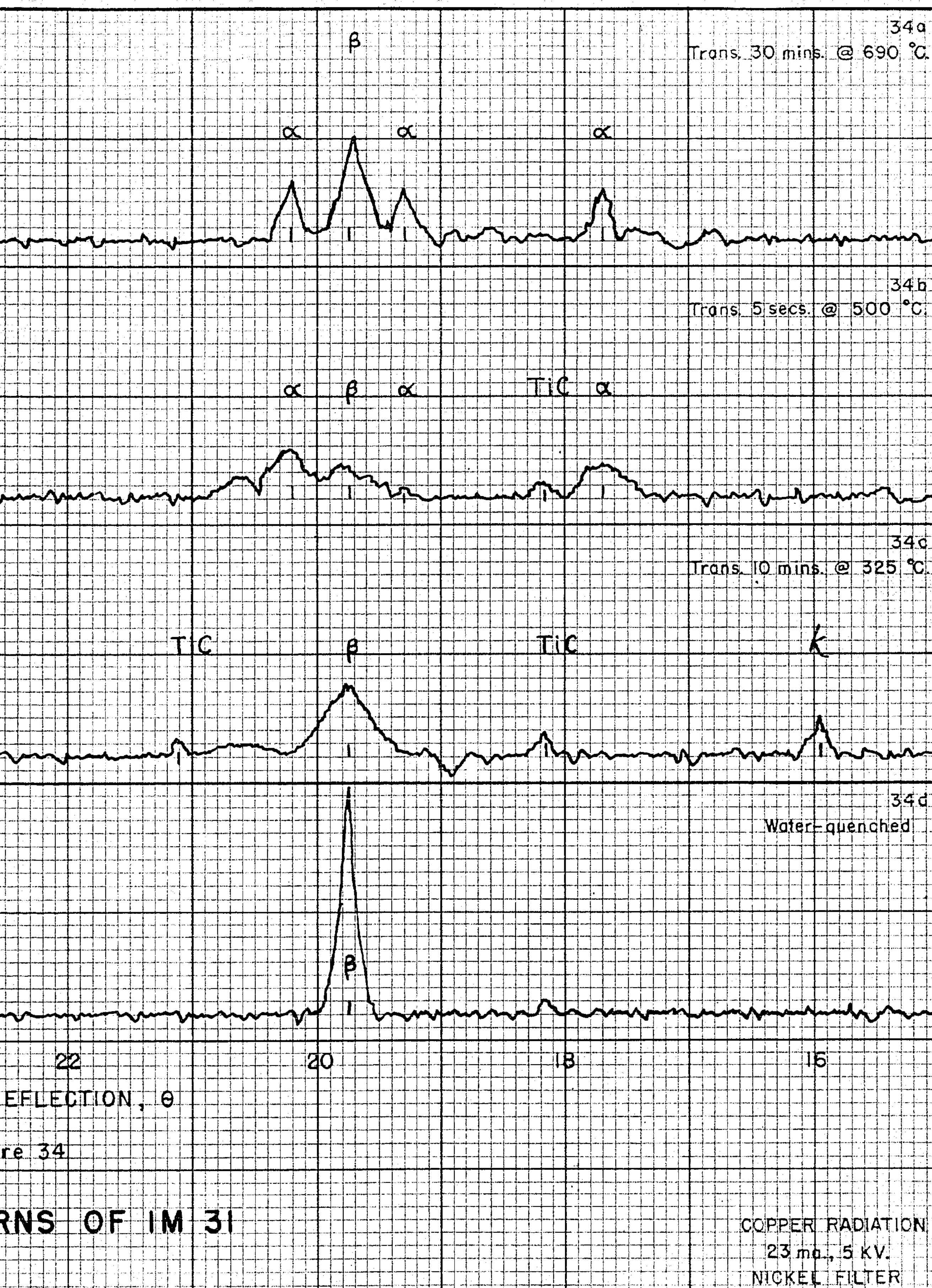
In order to gain precision in this as well as different aspects of titanium metallurgy, other methods for obtaining X-ray data not involving powdering of the sample were considered. Arrangements were finally made to have X-ray analyses run by P. R. Mallory and Company of Indianapolis. Their laboratories are equipped with a Geiger Counter Spectrometer manufactured by the Ohio X-ray Company coupled to a General Electric X-ray unit, model XRD-1. Forward-reflection patterns could be conveniently made with this unit, hence eliminating the problem of powdering the sample.

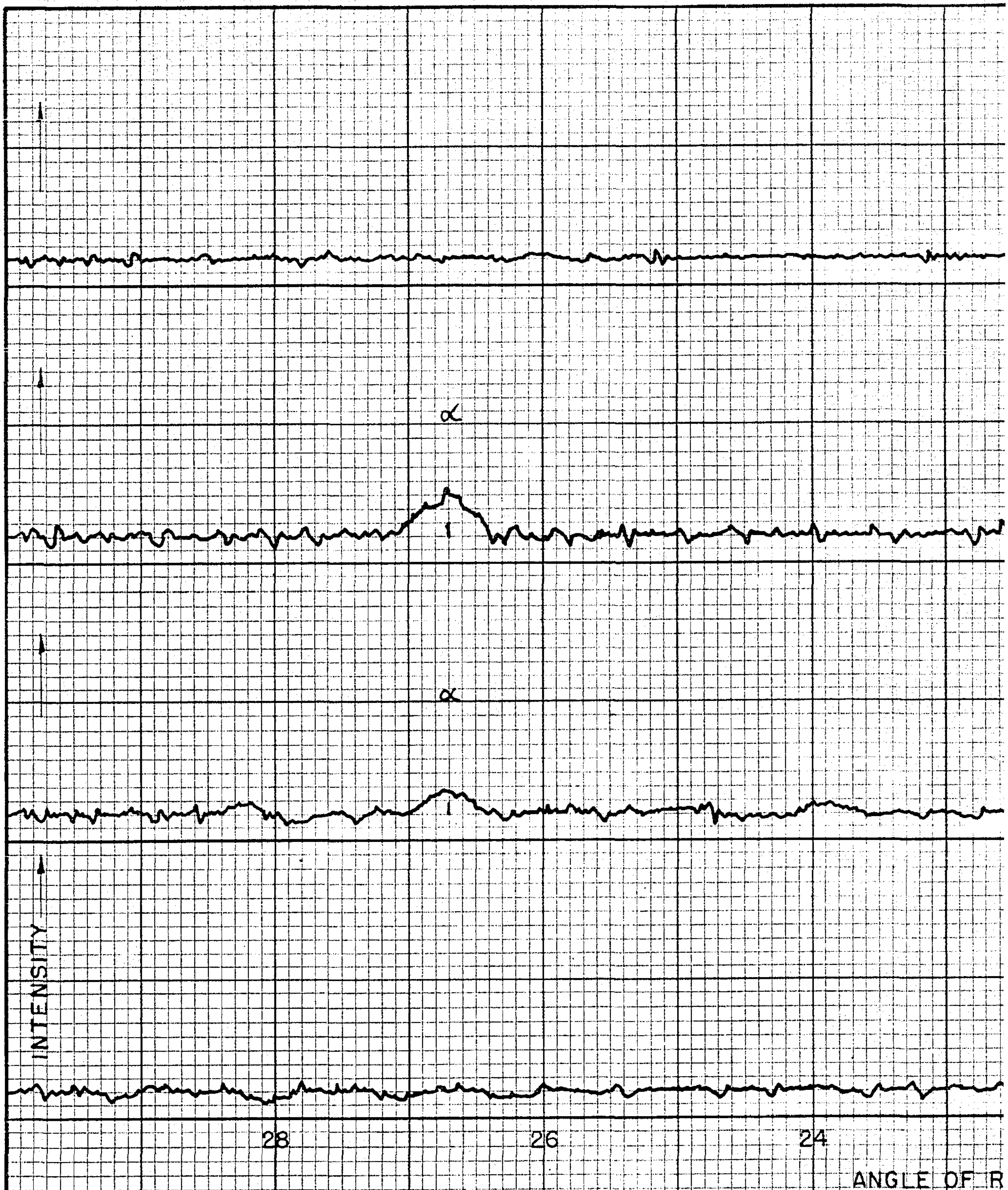
By trial and error, it was decided to use the same face of each specimen which had been previously used for metallographic work. This was found to be the surface most free of strain and distortion, by virtue of its yielding the sharpest diffraction pattern. A copper target X-ray tube operating on 23 milliamperes at 5,000 volts was used. Runs were made with radiation both unfiltered and filtered with nickel. Identification of phases was accomplished by comparison of the charts produced with charts of known alpha, beta, and titanium carbide.

Figs. 34 and 35 illustrate several typical X-ray diffraction patterns taken of variously treated samples of MST-2.5Fe-2.5V. Each pattern has been selected on the basis of its being typical of several specimens in the same microstructure group. Their patterns have been reduced in vertical height so as to facilitate presentation.

It should be noted here that the reproducibility obtained in this diffraction work was not outstanding. While the X-ray data was sufficiently consistent to enable an explanation of the patterns to be made on the basis of metallographic data, conclusions could not generally be drawn from the X-ray data alone. There were a few exceptions as will be discussed. Much of the trouble with

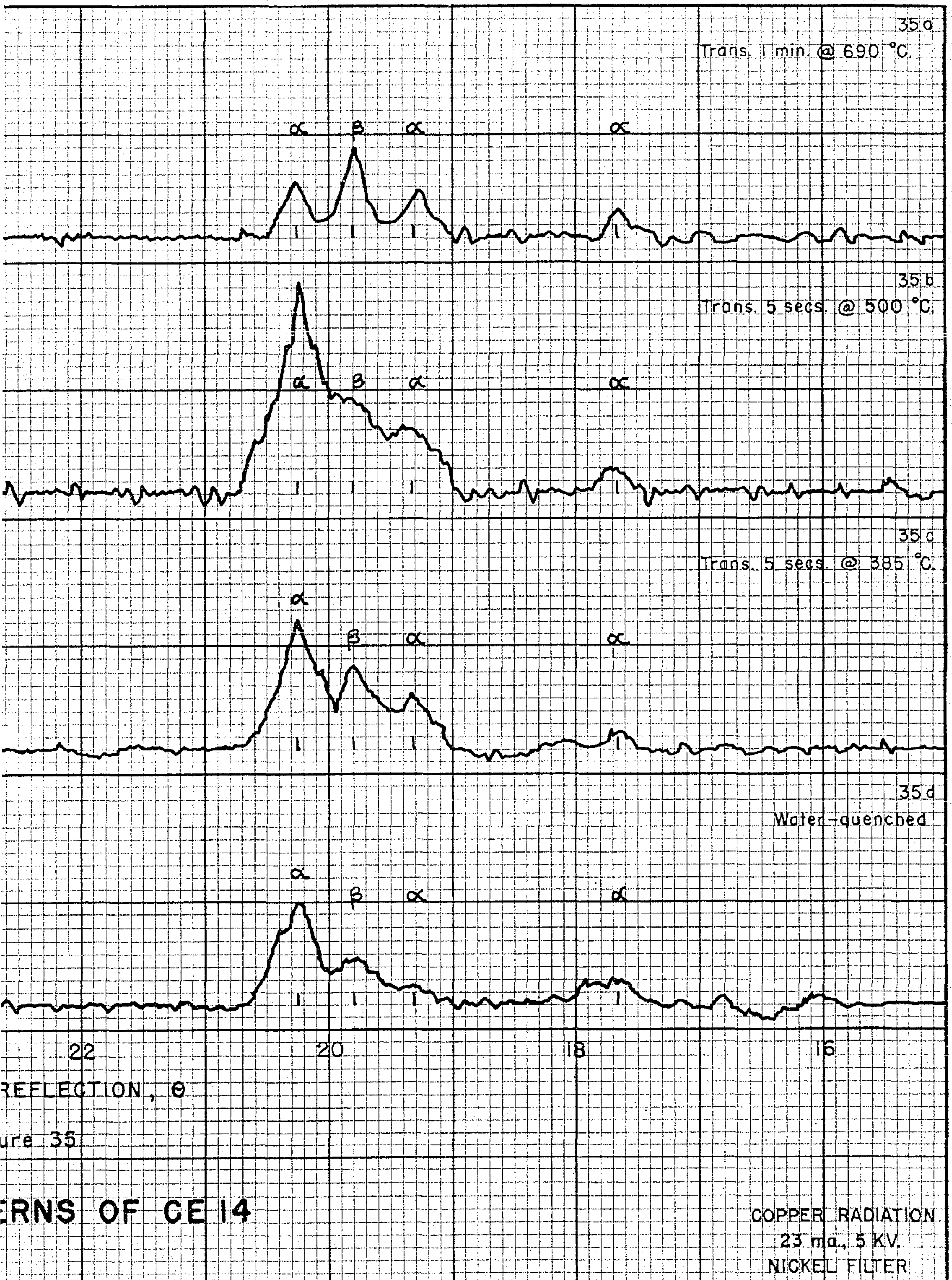

α
α
β
β
INTENSITY
28
26
24
ANGLE OF
Fig
X-RAY PATTE


34a
Trans. 30 mins. @ 690 °C.
β
α
α
α
34b
Trans. 5 secs. @ 500 °C.
α
β
α
TiC
α
34c
Trans. 10 mins. @ 325 °C.
TiC
β
TiC
K
34d
Water-quenched
β
22
20
18
16
EFLECTION, θ
re 34
RNS OF IM 31
COPPER RADIATION
23 ma., 5 KV.
NICKEL FILTER



Figu

X-RAY PATTE



ure 35

ERNS OF CE 14

obtaining consistent data probably rests on problems of grain orientation within the specimen coupled with the fact that too few grains are covered during the Geiger Counter pass. This difficulty might be eliminated by rapidly rotating the specimens being X-rayed. However, the equipment was not available for this modification in technique to be tried.

After carefully evaluating the many spectrometer charts, a few definite conclusions can be reached. Fig. 34a, typical of IM 31 transformed isothermally at relatively high temperatures, shows a clearcut distinction between alpha and beta. In this temperature range, patterns consistently show increasing amounts of alpha and decreasing amounts of beta as isothermal holding time increases, thus being in keeping with observations and theoretical considerations. Generally, however, X-ray diffraction reveals more retained beta in the structure than would be expected from optical examination. This one feature was found true in all photomicrographs of the induction melted alloy. Fig. 34b is quite typical of the Widmanstatten microstructure formed between 500 and 650°C. It will be noted that this pattern is rather broad and diffuse indicating a strained or distorted lattice. As the isothermal reaction temperature is lowered, the amount of alpha decreases steadily and the titanium carbide (TiC) lines become more pronounced; compare

Figs. 34b and 34c. The time of isothermal holding in this region appears to have little effect on the crystal structure. Fig. 34c also reveals a definite line at about 16°. This trend was found in several specimens transformed between 250 and 425°C. It matches no known lines of alpha, beta, or titanium carbide and is therefore presumed indicative of a new phase. This phase has been labeled kappa.

Water-quenched specimens (Fig. 34d) are found, by X-ray examination, to contain virtually all retained beta. A second strong beta line appears as about 28.3°. This is reflection from the 200 plane of beta titanium and is moderately intense. Its appearance was found to be somewhat erratic, however. It was never observed in specimens quenched from high temperatures even though the amounts of beta present were high. This behavior is not understood but may be due to orientation differences. Notice that traces of the carbide lines and the kappa line have disappeared in the pattern of the water-quenched specimen, indicating that the kappa reaction as well as the alpha reaction has been suppressed. It can be seen that this test now substantiates the metallographic observation that all beta is retained on a water quench of the induction melted alloy. This is in sharp disagreement with the result described above as obtained with powder methods, leading to the conclusion that powder techniques are not suitable for X-ray studies of at least some classes of titanium alloys.

The reason for the appearance and later disappearance of the TiC lines is unknown. All of these induction melted specimens contain about the same distribution of carbides and hence the carbide manifestation should be the same in all cases. One possible explanation might be that the thermal treatment in the region where these lines appear causes some reaction in the carbide itself giving rise to a more intense X-ray diffraction. On the other hand, these lines might be associated with the formation of the kappa phase, just happening to be coincident with the known TiC lines. There is no further evidence available at the moment to indicate which of these possibilities is more feasable.

Induction melted specimens quenched in sub-zero baths all indicate completely retained beta in spite of some differences in microstructure. Therefore, they have about the same X-ray pattern as the water-quenched alloy, Fig. 34d.

Fig. 35 illustrates typical X-ray diffraction patterns obtained with the consumable-electrode melted alloy, Heat CE 14. As indicated by Fig. 35a, good separation of alpha and beta is obtained at the elevated temperatures. Below 600°C. however, a marked broadening of all lines is noted, resulting in considerable uncertainty in interpreting the diagrams.

Comparing Figs 34 and 35, it is evident that much more alpha is obtained in the consumable-electrode melted material. This substantiates metallographic observations. The amount of beta retained decreases steadily with temperature and even following a water quench, little beta is retained.

This is seen to be the principle difference between induction melted and consumable-electrode melted materials. Because of the broad, diffuse diffraction patterns obtained, there is no positive indication of a new phase appearing in the consumable-electrode material.

While these X-ray data have been of interest and to some degree useful, a considerable refinement in technique is clearly desirable. In any event, the potential usefulness of X-ray methods in clarifying many of the problems in titanium metallurgy is indicated.

DILATOMETRY:

In order to investigate the possibility of transformation in retained beta occurring at room temperature over a period of several hundred hours, a dilatometer was set up. This consisted of a heavy cast iron jig in which a sensitive extensometer could be held in line with a mechanical slug of titanium in such a way that any expansion or contraction taking place in the titanium could be observed.

From a piece of 5/8-inch diameter bar stock of induction melted titanium was cut a sample 0.600" in diameter by 1.25" long. A slight projection was formed on each end of the specimen so that point contact could be obtained between the titanium sample and the jig, thus assuring better accuracy of the test. This specimen was then betatized for the usual time (one hour at 900°C.) and quenched in rapidly agitated water at 25°C. Within three minutes of quenching, the specimen was mounted in the dilatometer and the entire unit placed on a secure, vibration-free shelf for observation.

Within the first ten hours, a slight contraction amounting to 0.02 o/o was observed. A second contraction was observed after about 200 hours and was thought somewhat anomalous. In a second run of this experiment, the first contraction was verified, the second was not. A similar test was run with consumable-electrode material, but no dimension changes were observed.

In the case of induction melted MST-2.5Fe-2.5V, all or almost all beta is retained on water quenching, as we have seen metallographically and by X-ray analysis. It is quite apparent from dilatometric observations that this beta undergoes some type of sub-microscopic decomposition during the first few hours of transformation at room temperature. The consumable-electrode melted alloy does not retain much beta on a water quench, as has also been shown. The lack of dimensional change in this alloy can therefore be attributed directly to the lack of sufficient beta present in the microstructure to cause a noticable change or to a condition of the beta which would not favor its decomposition.

APPENDIX AND BIBLIOGRAPHY

CHEMICAL ANALYSES OF ALLOYS

NOMINAL DESIGNATION: MST-2.5Fe-2.5V (Specifications call for 5 o/o Ferrovanadium, the latter being 44 o/o Fe, 56 o/o V. This results in the following true nominal composition Ti-2.2Fe-2.7V.)

INDUCTION MELTED ALLOY: (Heat IM 31, as cast and scalped)

Spectrographic analysis on the ends of the ingot, each value being an average of five shots:

Fe, o/o	2.63	2.53
V, o/o	3.15	3.25

Wet analysis: (A is specimen from original ingot end; B is specimen from cut end.):

	A	B
Fe, o/o	2.13	2.24
V, o/o	2.97	2.96
C, o/o	0.49	0.50
N, o/o	0.0135	0.0153

CONSUMABLE-ELECTRODE MELTED ALLOY: (Heat CE 14, as cast and scalped)

Wet analysis: (A is specimen from top of ingot; B is specimen from the bottom.)

	A		B
Fe, o/o	2.01		2.10
V, o/o	2.80		2.95
C, o/o		0.11	
N, o/o		0.053	

METALLOGRAPHIC PREPARATION OF TITANIUM AND TITANIUM ALLOYS:

All of the metallographic preparation in connection with this project was done by electrolytic means. Samples were wet-belt-ground in order to remove the surface layer which had been contaminated mainly during betatizing. They were next ground by hand on either emery or silicon carbide papers, from No. 1 down through 3/0. Electrolytic polishing was done on a Disa Electropol unit in the conventional manner using the following electrolyte recommended by P.R. Mallory and Company:

390 cc.	Methyl Alcohol
350 cc.	Ethylene Glycol
36 cc.	70-72 o/o Perchloric Acid
24 cc.	Water

The electrolyte temperature was maintained below 15°C. for best results, since it was observed that operating at higher temperatures sometimes resulted in a mildly pitted structure. Usually, a potential of 25 to 30 volts applied for 10 to 15 seconds was most satisfactory, although in some certain instances, a slightly higher voltage was found desirable.

Since the alloys worked with contained moderate amounts of beta stabilizers, the following etch was employed, usually for about 15 seconds:

10 cc.	Hydrofluoric Acid
10 cc.	Nitric Acid
20 cc.	Glycerine

Specimens were stored in a dessicator when not being examined and could be kept satisfactorally for several weeks in this manner.

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