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May 29 1958

HOGUE

METALLOGRAPHY OF TITANIUM ALLOYS

TITANIUM METALLURGICAL LABORATORY
Battelle Memorial Institute
Columbus 1, Ohio

The Titanium Metallurgical Laboratory was established at Battelle Memorial Institute at the request of the Assistant Secretary of Defense (R & D) to provide the following services:

1. Under the general direction of the Steering Group on Titanium Research and Development, of the Office of Assistant Secretary of Defense (R & D), to conduct laboratory investigations directed toward solution of current metallurgical problems involved in the use of titanium.

2. As directed by OAS/D, to assist the Government agencies and their contractors in developing data required for preparation of specifications for titanium metal and titanium mill products.

3. To provide assistance and advice to OAS/D in its appraisal of the Department of Defense research and development program on titanium and make recommendations with respect to the program.

4. To collect and, as directed by OAS/D, disseminate to Government contractors or subcontractors having related Government contracts or subcontracts, available information on the current status of titanium research and development.

5. When directed by OAS/D, to provide technical consulting services to producers, melters and fabricators of titanium metal and designers and fabricators of military equipment containing titanium, on titanium utilization problems, including appropriate consideration of alternate materials.

6. To provide such other research and related services in connection with the titanium program as may be mutually agreed upon between Battelle and the Assistant Secretary of Defense (R & D) or his designee.

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METALLOGRAPHY OF TITANIUM ALLOYS

by

H. R. Ogden and F. C. Holden

to

OFFICE OF ASSISTANT SECRETARY OF DEFENSE
FOR RESEARCH AND ENGINEERING

Titanium Metallurgical Laboratory
Battelle Memorial Institute
Columbus 1, Ohio

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Many of the microstructures reproduced in this report were taken from research sponsored by the Air Force and Watertown Arsenal at Battelle and at other organizations. Since it would be impractical to record all of the contract numbers from which such microstructures were obtained, each structure is identified by organization only.

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METALLOGRAPHY OF TITANIUM ALLOYS

INTRODUCTION

Metallography is one of the most important tools available to metallurgists. It is used in basic studies for determining phase diagrams, solid-state reactions, and other fundamental processes as well as in many practical applications such as quality control in fabrication and heat-treatment processes. The usefulness of metallography is dependent on the ability of the metallographer or metallurgist who interprets the structure. This ability is, of course, dependent on the experience of the metallurgist and the information available on the material being studied.

Because of the importance of metallography to the technology of titanium and because of the current interest in titanium technology, it is essential that the metallurgists working with titanium understand its metallography. In this report emphasis is placed on the microstructures of titanium and its alloys. Other aspects of the physical metallurgy of titanium, heat treatment, and mechanical and physical properties have been covered in other TML reports.

This report contains both a general description of titanium metallography as it is affected by composition and thermal treatment and specific illustrations of microstructures of commercial alloys as they are affected by fabrication and thermal treatments. An index is provided for the various structures illustrated in the sections on commercial alloys. This is given in Appendix A. Appendix B contains a glossary of terms that are often used in describing titanium microstructures and Appendix C describes methods of preparing titanium samples for metallographic examination.

FACTORS THAT INFLUENCE THE STRUCTURE OF TITANIUM ALLOYS

Among the alloy systems of commercial interest, the alloys of titanium produce a very wide variety of structures. As the understanding of the relationship between properties and microstructure is increased, the proper interpretation of these microstructures becomes more important. As in

any alloy system, the presence and distribution of phases depend on the composition and history of the alloy. This section of the report will deal briefly with the types of titanium alloy systems and the principal structural features that result from various thermal cycles. Specific examples of titanium alloy microstructures are presented in later sections.

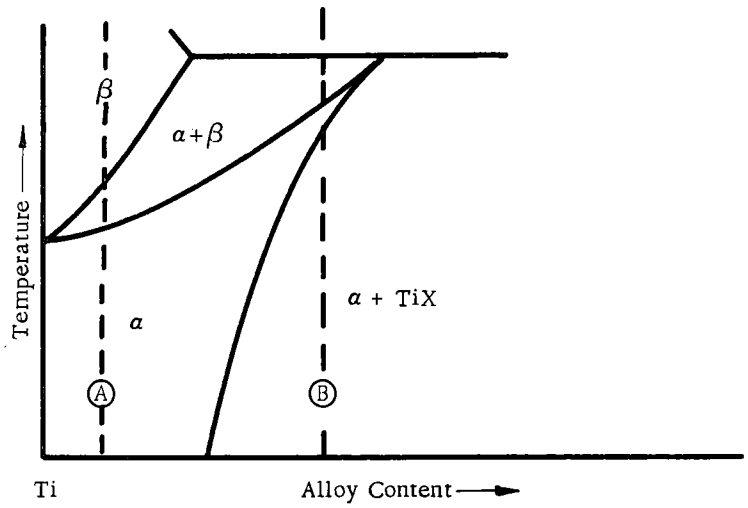
Phase Diagrams

The phase diagram is a map of the equilibrium structural features of a given alloy system; it is almost invariably given for constant (atmospheric) pressure, with temperature and composition as the variables. It is convenient to consider only binary systems for the purpose of describing microstructural changes, although it should be kept in mind that this may be only an approximation of the actual case.

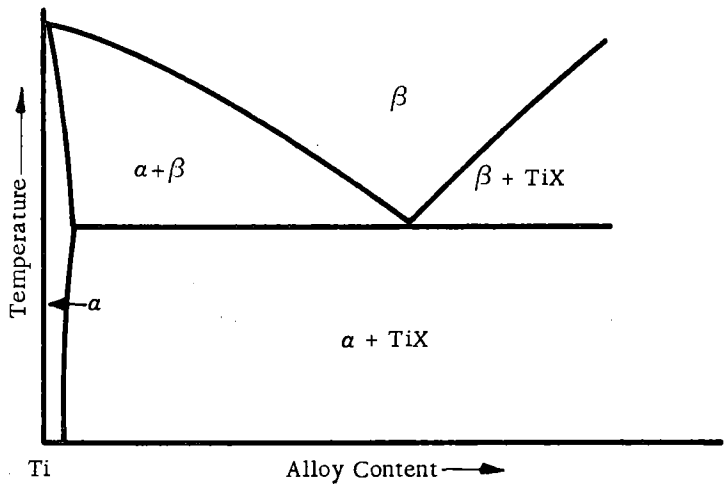
Figure 1 shows portions of the principal types of binary constitution diagrams encountered in titanium alloys. The alpha-peritectoid type is characteristic of titanium alloys with aluminum, carbon, oxygen, and nitrogen. For the range of compositions usually encountered with Ti-Al, Ti-O, and Ti-N alloys, the alpha solubility limit is not approached, as represented by the vertical line at A. Recent studies of the Ti-Al system, however, have indicated a probable phase modification in the regions from 6 to 10 per cent aluminum. The solubility of carbon in alpha titanium is within the range of carbon contents that may be encountered in practice, corresponding to the vertical line at B.

The beta-eutectoid type of alloy system is characteristic of many commercially important alloying additions. These include manganese, iron, chromium, nickel, copper, and silicon, in order of increasing eutectoid temperature. Binary alloys of titanium with these elements have limited alpha solubility, on the order of 0.5 per cent or less. The activity of the eutectoid transformation ranges from very sluggish, in Ti-Mn alloys, to very rapid, in Ti-Cu and Ti-Si alloys. In most cases, the transformation to eutectoid products is not a result of intentional heat treatment; it may occur, usually with detriment to mechanical properties, following service exposure at elevated temperatures. There are beta alloys of interest (B 120VCA) where the beta eutectoid reaction is important in heat treatment. Hydrogen is a somewhat special case of a beta-eutectoid element in which the phase relationships are strongly dependent on pressure. Hydrogen usually is considered separately from the other beta-eutectoid systems.

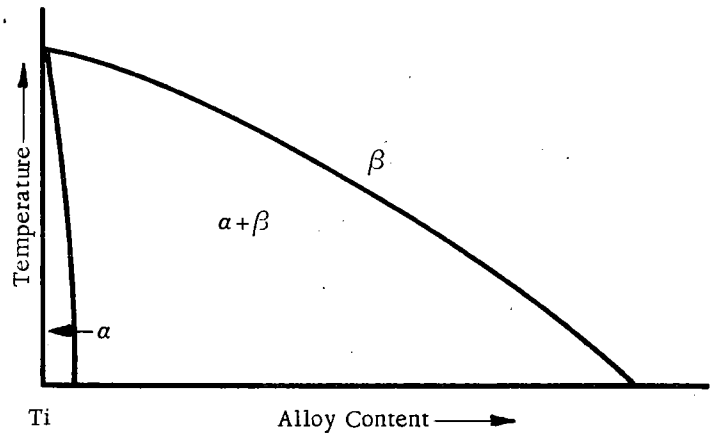
The beta-isomorphous alloys include binary titanium alloys with molybdenum, vanadium, tantalum, and columbium. Their general behavior, except



a. Alpha Peritectoid



b. Beta Eutectoid



c. Beta Isomorphous

FIGURE 1. PRINCIPAL TYPES OF TITANIUM ALLOY CONSTITUTION DIAGRAMS

for the absence of a eutectoid reaction, is similar to that for the beta-eutectoid alloys. They are generally less potent strengtheners than the beta-eutectoid elements, and have somewhat greater alpha solubilities.

The elements tin and zirconium have appreciable solubilities in both alpha and beta phases of titanium; these are sometimes called neutral elements. Zirconium is isomorphous in both allotropes, and lowers the beta transus slightly, while tin first lowers and then raises the beta transus somewhat.

In addition to the equilibrium phases indicated on the phase diagram, metastable phases also may exist. These include the alpha-prime, or martensite structure and omega phase. The martensite structure generally is easily recognized metallographically from its acicular appearance. Omega is not observed metallographically, although evidence of omega formation is apparent in electron micrographs.

Although isothermal sections of ternary phase diagrams have been established for a number of titanium alloy systems, many practical implications can be inferred by assuming that the vertical sections are similar to the binary diagram of the principal alloying elements. For example, in an alloy such as Ti-6Al-4V, the vertical section of the ternary diagram would appear similar to that of the beta-isomorphous type (Figure 1c). The addition of aluminum raises the beta transus temperature and may increase the alpha solubility limit, but the microstructures that are developed as a result of the transformations that occur are quite similar to those encountered in the analogous binary alloys.

Fabrication and Thermal History

The sequence of mechanical and thermal treatments determines the microstructure of the finished part, and, to a large degree, determines its performance in service. Thermal treatments usually are involved in both primary and secondary fabrication, and frequently a final anneal or strengthening heat treatment is used to impart the desired properties to the formed part. The specific response of a given alloy to the thermal and mechanical treatments is discussed more fully in later sections of this report. However, some general features of these effects are listed below.

Primary Fabrication

Primary fabrication is considered to include reduction of the ingot to a standard mill product. This may include forging, extrusion, or rolling.

The microstructural features that may result from these operations include the distribution of segregated or impurity phases, and the preferred oriented structures, such as may occur in rolled strip. The structures resulting from primary fabrication usually are uniform except for minor degrees of segregation.

Secondary Fabrication

Secondary fabrication includes a variety of hot and cold forming operations, ranging from heavy forgings to cold formed sheet. Overheating during die forging is a common source of abnormal microstructures; also, inadequate reduction in some parts of the forging may result in wide variations in structure from one part of the forging to another. Material heated into the beta field without enough subsequent working in the alpha-beta field will retain the coarse transformation structure.

Thermal Treatment

Final heat treatments may erase the prior structure, but, more commonly, the gross microstructure is established during fabrication. Stress relief anneals do not ordinarily cause a visible change in structure while annealing at higher temperatures can change the distribution of phases in a two-phase alloy, or cause recrystallization and grain growth. A final heat treatment above the beta transus will produce a transformed structure, which is generally regarded as detrimental to the ductility of alpha and alpha-beta alloys in common use.

ALPHA-STABILIZED ALLOYS

Included under the general heading of alpha alloys are unalloyed titanium and those titanium alloys for which the alpha phase is in equilibrium at room temperature. Of these, only the high-purity base materials usually appear as single-phase structures; the presence of impurities in commercial-base titanium and its alloys usually produces some particles of additional phases. In contrast with the beta-stabilized alloys, comparatively few microstructural variables are possible for the alpha alloys. These are discussed in the following sections, and include mainly variations in grain size and grain shape resulting from heat treatment.

High-Purity Titanium

The allotropic transformation in pure titanium between the low-temperature alpha phase (HCP) and the high-temperature beta phase (BCC) has been established at about 1625 F. The transformation cannot be suppressed even by cooling at extremely rapid rates, and it appears to occur through a nucleation-and-shear, or martensitic, process. Microstructures typical of high-purity titanium are shown in Figure 2; the schematic diagram indicates the annealing treatments that were used to produce the structures.

The transformation structures in Figure 2a and b show the result of quenching and slow cooling from the beta field. These specimens were etched rather heavily in order to develop substructures.* What appear to be irregularly shaped grains actually are colonies of similarly oriented plates formed during transformation. These plates, which are barely visible here, become more distinct when impurity phases are present to outline them. At the slower cooling rate (Figure 2b) the serrated outlines are more rounded, showing adjustment of the apparent grain boundaries with diffusion. The apparent grain size in these structures is approximately that of the prior beta phase. These transformed structures are commonly designated as "transformed beta" or "transformed alpha", although their structure is actually that of the alpha phase.

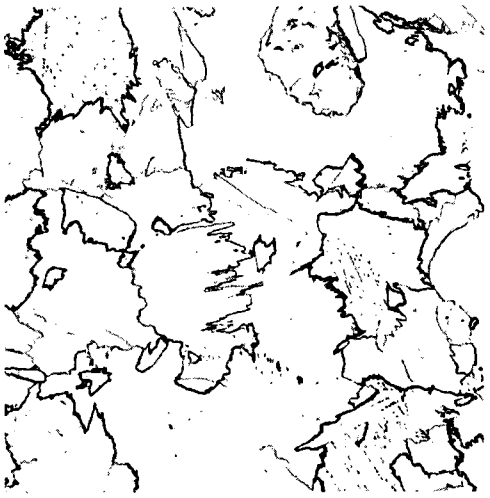
The equiaxed structures shown in Figure 2c and d were obtained by fabricating and annealing below the transformation temperature. To obtain large grains, a long annealing time was required (100 hours at 1600 F). For this material, which had been cold-reduced 75 per cent, a 1-hour anneal at 1110 F was sufficient to cause recrystallization.

High-Purity Alpha Alloys

Alloying additions that stabilize the alpha phase of titanium include both interstitial and substitutional elements. In addition, some of the beta-stabilizing elements have an appreciable alpha solubility limit.

Figure 3 shows typical microstructures for an alpha-stabilized alloy. Specimens annealed in the alpha field (Figure 3a and b) have equiaxed alpha structures, the grain size increasing with increased temperature and time. Structures resulting from a quench from the alpha-beta field (Figure 3c) consist of equiaxed alpha grains within a transformed matrix. It should be noted

*For details of metallographic preparation and etching for these and subsequent specimens, see Appendix C.



100X N2290

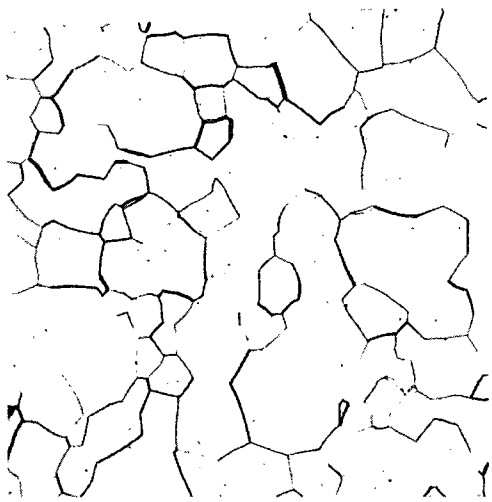
a. Annealed 1 hour at 1830 F and quenched (1-1/2HF-3-1/2HNO_3)

100X N2291

b. Annealed 1 hour at 1830 F and furnace cooled (1-1/2HF-3-1/2HNO_3)

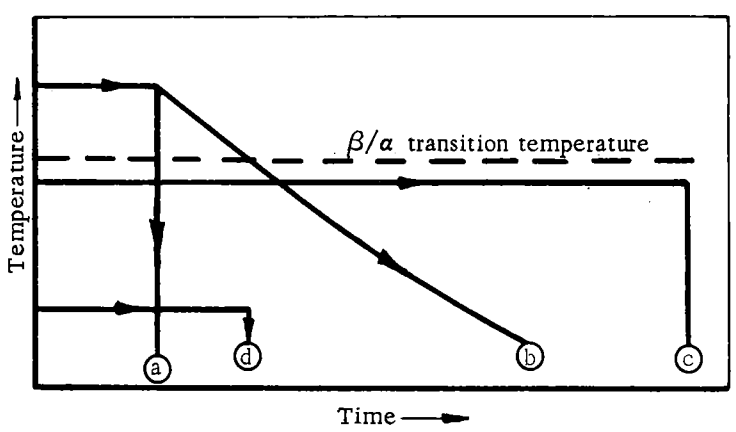
100X N2292

c. Annealed 100 hours at 1610 F and quenched (1-1/2HF-3-1/2HNO_3)



100X N2288

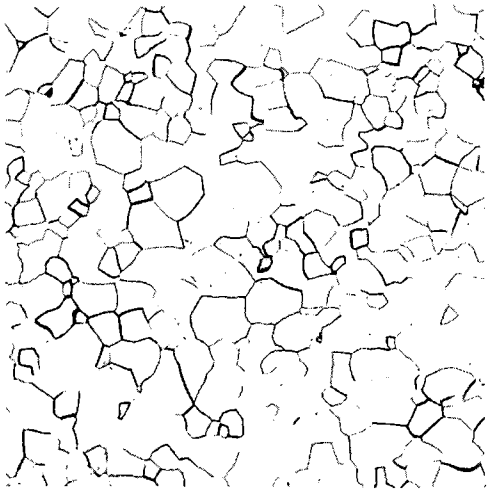
d. Annealed 1 hour at 1470 F and quenched (1-1/2HF-3-1/2HNO_3)



Schematic Diagram of Heat Treatments

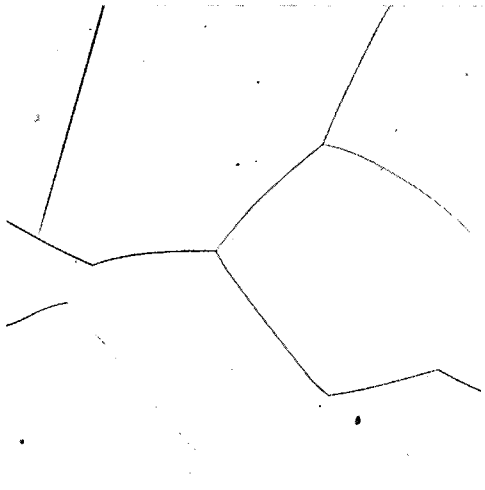
FIGURE 2. TYPICAL MICROSTRUCTURES FOR HIGH-PURITY (IODIDE-PROCESS) UNALLOYED TITANIUM

(Battelle Memorial Institute)



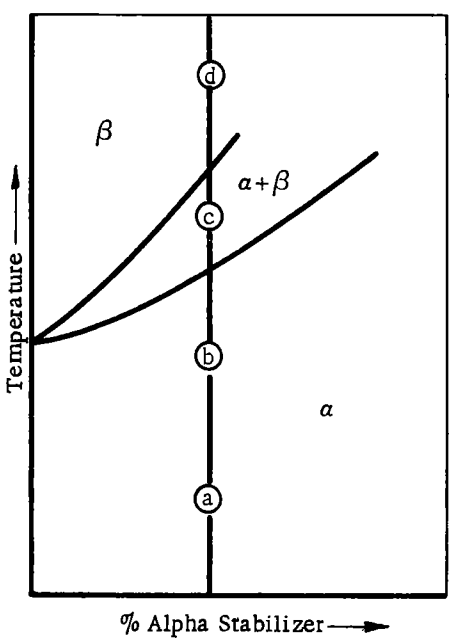
100X N15088

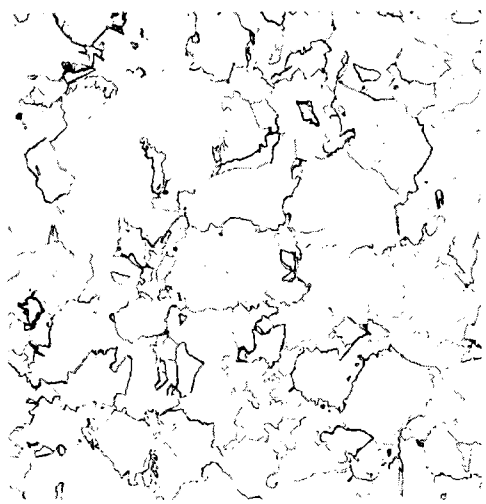
a. Annealed 1 hour at 1290 F and quenched (1-1/2HF-3-1/2HNO_3)



100X N15090

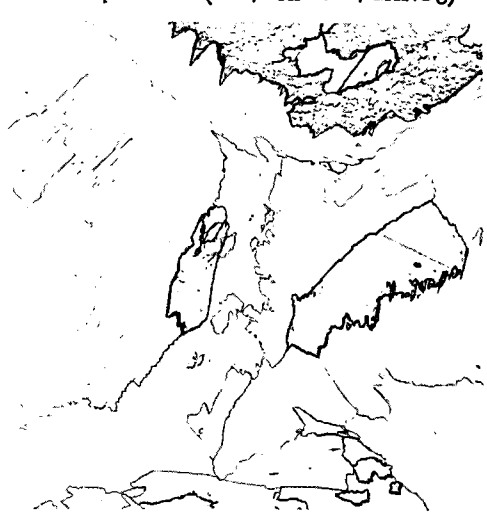
b. Annealed 16 hours at 1560 F and quenched (1-1/2HF-3-1/2HNO_3)





100X N15093

c. Annealed 1 hour at 1650 F and quenched (1-1/2HF-3-1/2HNO_3)



100X N15092

d. Annealed 1 hour at 1710 F and quenched (1-1/2HF-3-1/2HNO_3)

FIGURE 3. EFFECT OF ANNEALING TEMPERATURE ON THE MICRO-STRUCTURES OF A TYPICAL ALPHA-STABILIZED ALLOY (Ti-0.07 O)

(Battelle Memorial Institute)

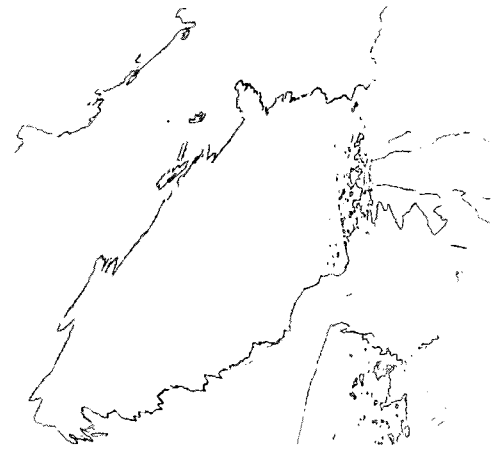
that, in accordance with the lever law, the alloy contents of these two alpha structures differ, the composition of the equiaxed grains being higher and that of the transformed alpha being lower than that of the alloy. Quenching from the beta field produces the same type of serrated structures that were found in unalloyed titanium. However, the platelets usually are more easily distinguished in the alloys (see Figure 3d) than in pure titanium. In fact, it is only in the transformation structures that there is any significant difference that can be attributed to alloy content. In high-purity titanium-aluminum alloys serrated alpha structures are obtained by quenching from the beta field, with little evidence of subgrain markings, Figure 4a. Beta-quenched alloys containing interstitial solutes and having low hydrogen contents have serrated alpha grains with subgrain markings, Figure 4b. Nitrogen-containing alloys appear to have more pronounced subgrain markings than do oxygen-containing alloys (compare Figure 4b to 3d or 5a). When hydrogen is present with other interstitial solutes, the acicular or basketweave transformation structure is obtained.

Cooling rate also has an effect on the subgrain structure and the serration of the alpha grains. Slow cooling from the beta field brings out more subgrain boundaries and smooths out the serrated grain boundaries as compared to quenching. This is illustrated for a Ti-0.13O alloy in Figure 5.

High-Purity Alpha-Compound Alloys

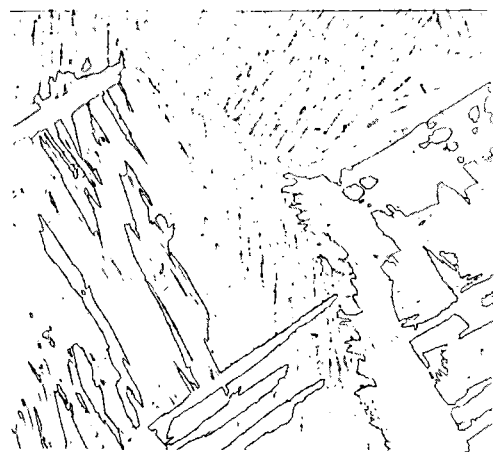
Titanium-Carbon Alloys

The solubility of carbon in alpha and beta titanium is relatively low, so that the presence of TiC particles may be expected with carbon contents as low as about 0.2 per cent. Figure 6 shows some typical structures for high-purity titanium-carbon alloys. The structure in Figure 6a contains 0.16 per cent carbon completely in solution; the structure is equiaxed alpha. The specimen in Figure 6b contains 0.47 per cent carbon, an amount exceeding the solubility limit, so that TiC particles are present in equilibrium with the alpha phase. A specimen quenched from the α-β field (Figure 6c) contains only alpha phase, which appears as equiaxed grains surrounded by a transformed matrix. Finally, Figure 6d and e show structures obtained by quenching from the β + TiC field. These contain TiC particles in a matrix of transformed beta. At the annealing temperature, the TiC particles probably were present mainly in the beta grain boundaries, thereby accounting for their somewhat elongated shapes.



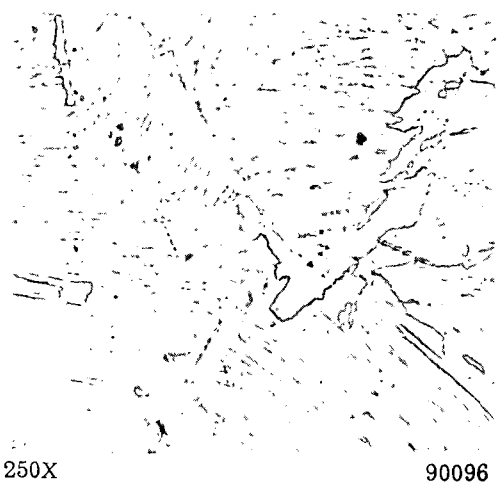
250X N10558

a. Ti-2.5Al



250X N11960

b. Ti-0.07N-0.0018H



250X 90096

c. Ti-0.064N-0.0133H

FIGURE 4. MICROSTRUCTURES ILLUSTRATING THE EFFECT OF COMPOSITION ON THE TRANSFORMATION STRUCTURE OF HIGH-PURITY TITANIUM-BASE ALLOYS QUENCHED FROM THE BETA FIELD

1-1/2HF-3HNO_3 etch

(Battelle Memorial Institute)

100X N15085

a. Quenched

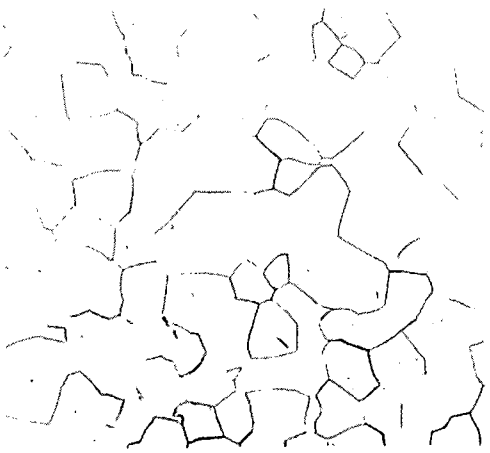
100X N15087

b. Furnace cooled

FIGURE 5. MICROSTRUCTURES ILLUSTRATING THE EFFECT OF COOLING RATE ON THE TRANSFORMATION STRUCTURE OF A HIGH-PURITY Ti-0.13 O ALPHA ALLOY COOLED FROM THE BETA FIELD

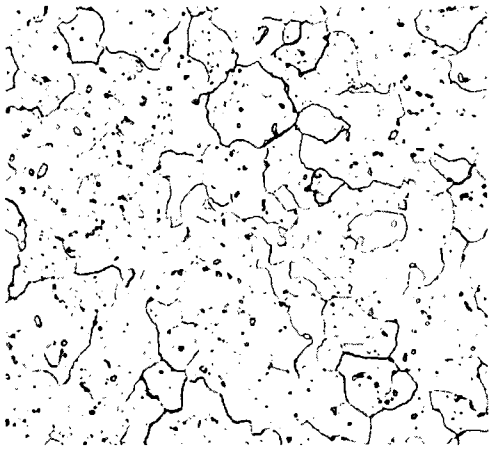
1-1/2HF-3HNO3 etch

(Battelle Memorial Institute)



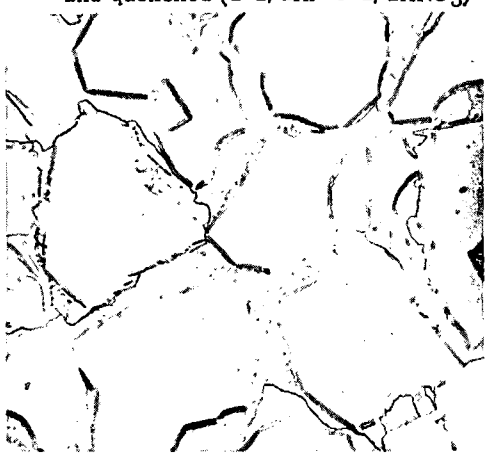
250X N4807

a. Ti-0.16C; annealed 4 hours at 1290 F and quenched (1-1/2HF-3-1/2HNO_3)



250X N4809

b. Ti-0.47C; annealed 4 hours at 1290 F and quenched (1-1/2HF-3-1/2HNO_3)

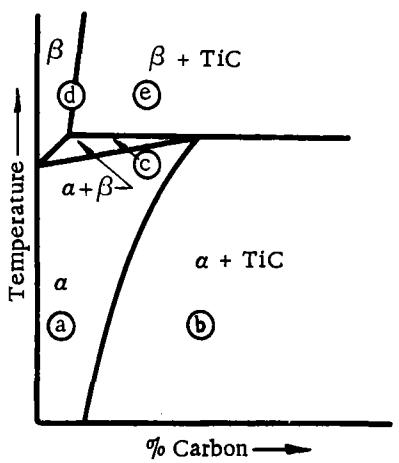


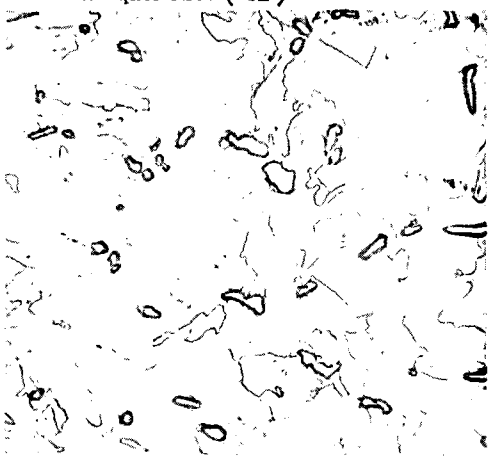
250X N3635

c. Ti-0.27C; annealed 1 hour at 1670 F and quenched (1-1/2HF-3-1/2HNO_3)

250X N4818

d. Ti-0.16C; annealed 1 hour at 1740 F and quenched (1HF)





250X N3627

e. Ti-0.27C; annealed 1 hour at 1740 F and quenched (1-1/2HF-3-1/2HNO_3)

FIGURE 6. MICROSTRUCTURES OF HIGH-PURITY TITANIUM-CARBON ALLOYS

(Battelle Memorial Institute)

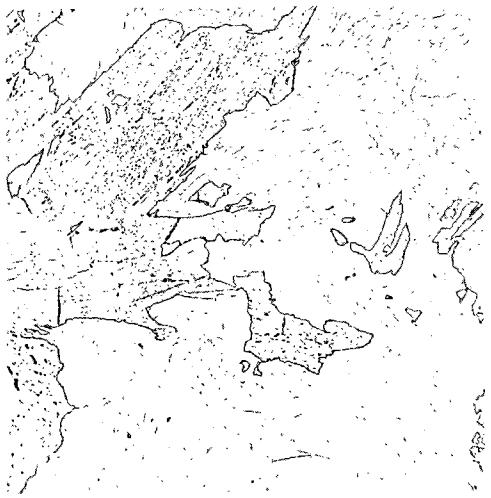
Titanium-Hydrogen Alloys

Hydrogen, an interstitial beta stabilizer, has been shown to have a pronounced effect both on microstructure and mechanical properties of titanium. Its solubility in alpha titanium at atmospheric pressure has been established at about 8 atomic per cent (1800 ppm) at the eutectoid temperature of 615 F. This solubility decreases with decreasing temperature to less than 0.14 atomic per cent (30 ppm) at 250 F. This low room-temperature solubility means that, unless the hydrogen level of unalloyed titanium is reduced to a very low level, there will be TiH particles present in the microstructure.

Figure 7 shows typical microstructures of high-purity titanium containing 91 ppm hydrogen (0.0091 weight per cent, or 0.44 atomic per cent). Both the primary structure and the appearance of the TiH particles are affected by the heat treatment used. The specimens quenched from the annealing temperature contain a fine uniform dispersion of TiH particles, as seen in Figure 7a and c. The basic structures are transformed or equiaxed, according to the annealing temperature. Specimens slowly cooled to room temperature precipitate the platelike "line markings" seen in Figure 7b and d. Comparison of these structures with those of vacuum-annealed (low hydrogen) unalloyed titanium shown in Figure 2 shows that the TiH precipitate is superimposed on the basic structures.

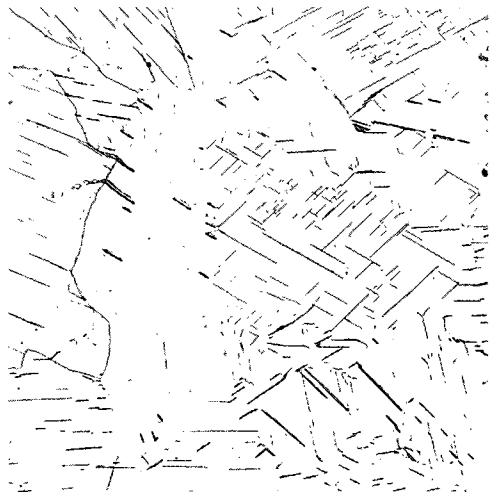
The presence of hydrogen in high-purity alpha alloys results in microstructures similar to those shown for high-purity titanium. The TiH structure is superimposed on the basic microstructure as shown in Figure 8. However, the hydrogen solubility limits are different for the alpha alloys than for unalloyed titanium.

The additional complication of TiH formation from metallographic preparation has been observed in some alpha titanium alloys, which may lead to incorrect conclusions concerning hydrogen concentration. This is illustrated by the series of photomicrographs shown in Figure 9. The alloy was made with high-purity titanium containing 0.8 per cent copper; after vacuum annealing, the hydrogen concentration was analyzed as 19 ppm. The specimens were annealed high in the alpha field and quenched to produce a coarse equiaxed alpha structure. The specimen then was polished and etched with the standard 1-1/2HF-3-1/2HNO_3-H_2O solution. The microstructure, as shown in Figure 9a, consisted of equiaxed alpha grains with no apparent trace of a second phase. After storage in a desiccator for 3 to 7 days, the specimen was re-examined and found to contain a heavy dispersion of a second phase, as shown in Figure 9b and c. This structure was developed more clearly by etching a second time, resulting in the structure shown in Figure 9d, which was identified visually as TiH. This clearly is a surface effect, since



250X 90322

a. Annealed 1 hour at 1830 F and quenched (1-1/2HF-3-1/2HNO_3)



250X 90323

b. Annealed 1 hour at 1830 F and furnace cooled (1-1/2HF-3-1/2HNO_3)

250X 90321

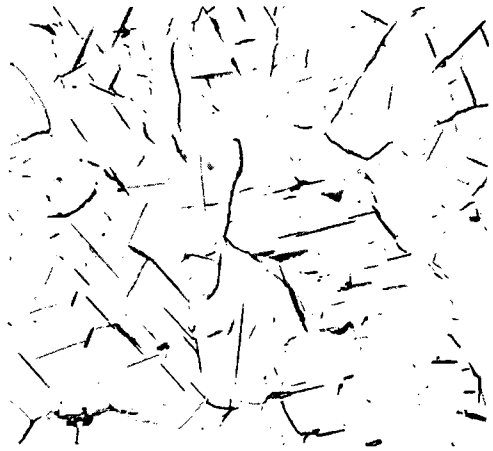
c. Annealed 1 hour at 1470 F and quenched (1-1/2HF-3-1/2HNO_3)

250X 90324

d. Annealed 1 hour at 1470 F and air cooled (1-1/2HF-3-1/2HNO_3)

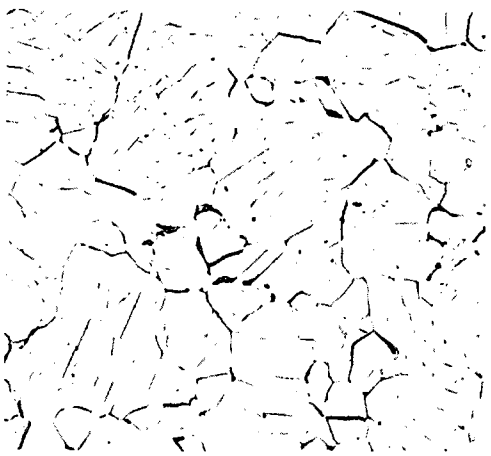
FIGURE 7. EFFECT OF ANNEALING TEMPERATURE AND COOLING RATE ON THE MICROSTRUCTURES OF HIGH-PURITY TITANIUM CONTAINING 91 PPM HYDROGEN

(Battelle Memorial Institute)



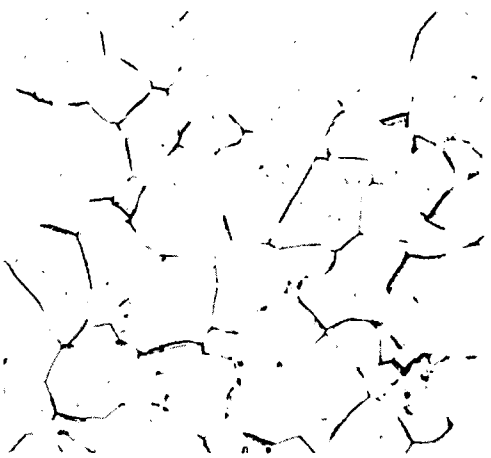
250X N35137

a. High-purity titanium containing 230 ppm hydrogen



250X N35140

b. Ti-2.5Al alloy containing 245 ppm hydrogen



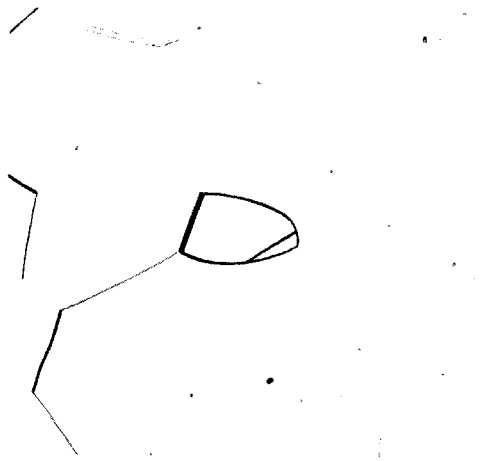
250X N35142

c. Ti-5Al alloy containing 315 ppm hydrogen

FIGURE 8. MICROSTRUCTURES OF HIGH-PURITY TITANIUM-ALUMINUM ALLOYS CONTAINING SUFFICIENT HYDROGEN TO FORM HYDRIDE PHASE

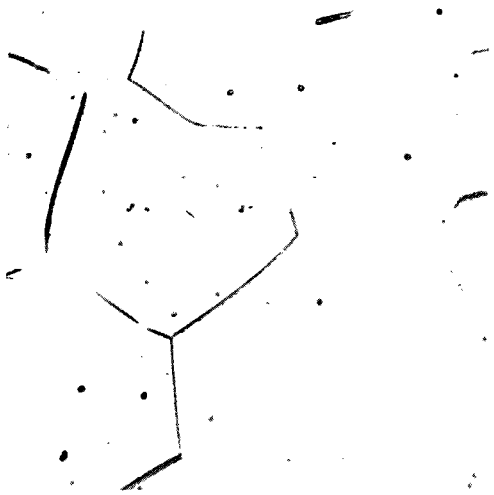
1-1/2HF-3-1/2HNO_3 etch

(Battelle Memorial Institute)



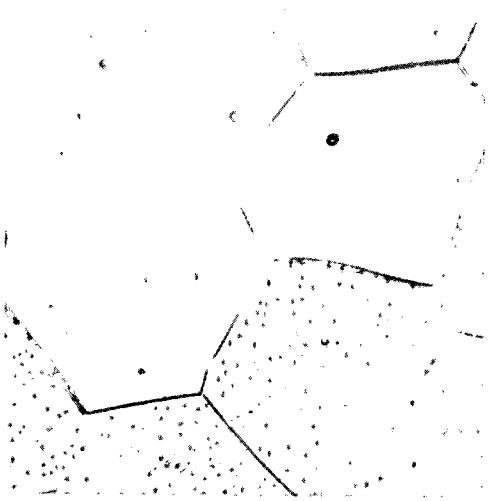
250X N6924

a. Specimen etched with 1-1/2HF-3-1/2HNO_3-95H_2O solution



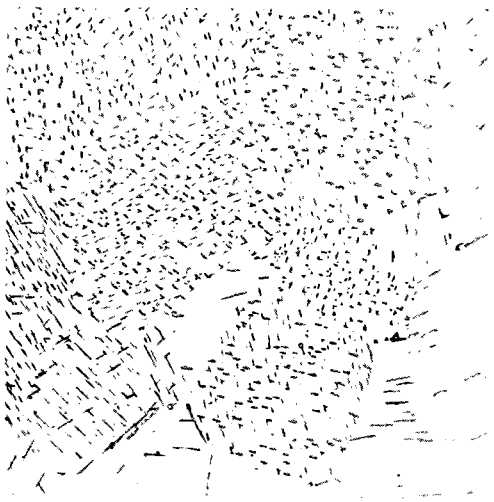
250X N7877

b. Same as (a), after storage in desiccator for 3 days



250X N7880

c. Same as (a), after storage in desiccator for 7 days



250X N7884

d. Same as (c), except re-etched with 1-1/2HF-3-1/2HNO_3-95H_2O solution

FIGURE 9. SURFACE AGING OF A HIGH-PURITY Ti-0.8Cu ALLOY ANNEALED 2 HOURS AT 1450 F AND QUENCHED

(Battelle Memorial Institute)

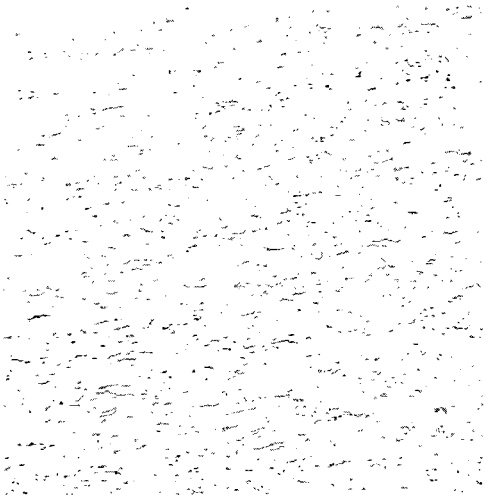
the original structure could be obtained by regrinding the specimen to remove the contaminated surface layer and repolishing and etching. The same surface aging effect has been observed in specimens of a Ti-0.2O alloy. This points up the difficulty of estimating hydrogen concentration from microstructural appearance alone, and the desirability of examining a microstructure as soon after preparation as possible.

Commercial-Purity Titanium

Unalloyed titanium of commercial purity contains small quantities of alpha- and beta-stabilizing elements as impurities. These impurities introduce variations into the structures obtained for high-purity titanium mainly due to the retention of small amounts of beta phase. Figure 10 shows the microstructures encountered in a typical lot of commercial-purity titanium. Figure 10a is a longitudinal section of cold-reduced strip, in which the directionality of the deformed alpha grains is evident. The remaining structures (Figure 10b through e) show the microstructural effects of annealing at increasing temperatures. At 1290 F, recrystallization is completed, with an average alpha grain size of about 0.01 mm. The small particles of second phases are a mixture of retained beta and TiH particles. At 1520 F (Figure 10c) the grain size has increased to about 0.02 mm, and the impurity phases have coalesced more into the alpha grain boundaries. An appreciable amount of transformed beta is apparent in the structure of the specimen annealed at 1650 F (Figure 10d). This indicates the presence of a two-phase field introduced by the interstitial impurities in place of the single transformation temperature for pure titanium. The specimen annealed at 1830 F (Figure 10e) clearly was heated into the all-beta field, and transformed to the serrated colonies of alpha plates during cooling. Impurities (TiH and retained beta particles) are apparent in this structure. They frequently form between the alpha plates, thus outlining them to make the platelike structure more evident.

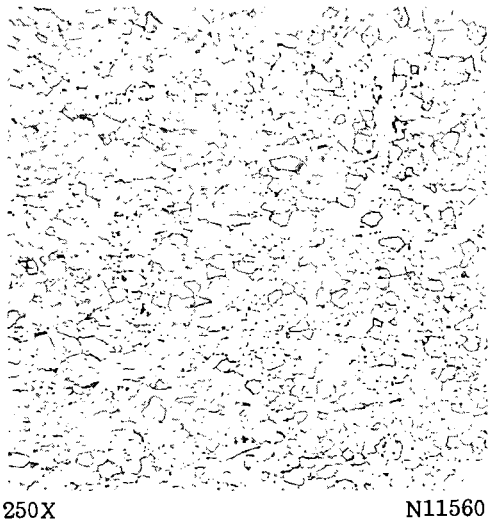
BETA-STABILIZED ALLOYS

In contrast with the alpha-stabilized titanium alloys, alloys containing the beta-stabilizing elements have a wide variety of microstructural variables. The beta-stabilizing elements usually are classified as beta isomorphous or beta eutectoid; the latter may be further divided according to the relative activity of the eutectoid reaction. In addition to the equilibrium structures indicated by the constitution diagram, two important metastable



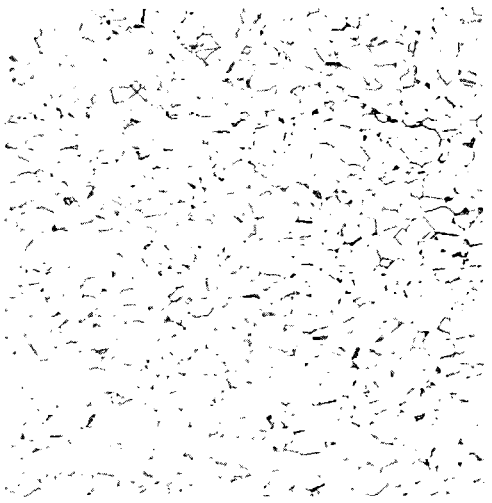
250X N11566

a. As fabricated at 1400 F (1-1/2HF-3-1/2HNO_3)



250X N11560

b. Annealed 2 hours at 1290 F and air cooled (1-1/2HF-3-1/2HNO_3)

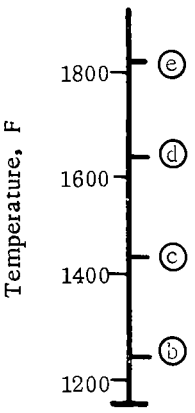


250X N11561

c. Annealed 4 hours at 1520 F and air cooled (1-1/2HF-3-1/2HNO_3)

250X N11563

d. Annealed 1 hour at 1650 F and air cooled (1-1/2HF-3-1/2HNO_3)



250X N11564

e. Annealed 2 hours at 1830 F and air cooled (1-1/2HF-3-1/2HNO_3)

FIGURE 10. EFFECT OF ANNEALING TEMPERATURE ON THE MICRO-STRUCTURES OF COMMERCIAL UNALLOYED TITANIUM

(Battelle Memorial Institute)

structures are possible. These are the alpha-prime, or martensite, and the omega structures. The alpha-prime structures are easily identified from their acicular appearance; omega is not visible in the optical microscope, although evidence of omega formation can be found in electron micrographs.

The various types of microstructures that occur in the beta-stabilized alloys are presented in the following sections, grouped according to the variables of composition and heat treatment.

Effects of Alloy Composition

The addition of a beta-stabilizing element to titanium lowers the beta transus temperature, forming a two-phase (alpha-plus-beta) field. The effect on microstructure of increasing alloy composition at a single annealing temperature is demonstrated in Figure 11. These specimens were fabricated at or slightly below the annealing temperature, and were quenched from within the two-phase region. They contain increasing amounts of beta phase as the alloy content is increased. The two terminal solid solutions, alpha and beta, appear as equiaxed single-phase structures. It should be noted that in this example the terminal beta phase is retained (see Figure 11e). If the specimens had been quenched from a higher temperature (i.e., T_2), the terminal beta phase would have transformed to alpha-prime during the quench.

Effects of Annealing Temperature

Considerable variations in microstructural appearance may occur when a given beta-stabilized alloy is annealed at different temperatures. The structures also are importantly affected by alloy content and cooling rate, as well as by the prior thermal history of the material. The structures shown in Figure 12 are typical for a low beta-stabilizer-content alloy. The specimens were fabricated at a temperature in the alpha-beta field, so that recrystallization in the alpha-beta field produces an equiaxed structure.

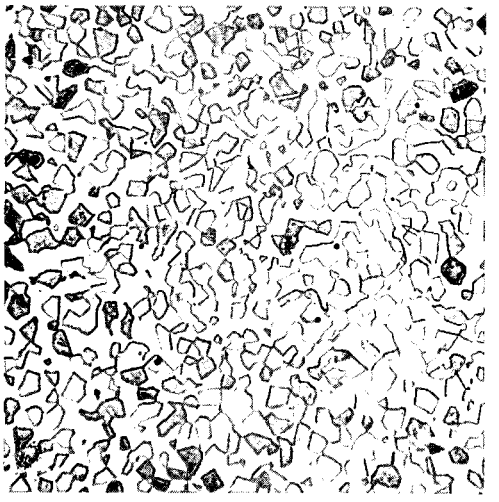
Specimens annealed at temperatures low in the alpha-beta field are shown in Figure 12a, b, and c. They consist of a very fine mixture of alpha and beta grains, for which it is difficult to measure an effective grain size or even to identify the individual phases. Fine-grained equiaxed structures of this type are generally desirable from the viewpoint of optimum mechanical properties. The specimen quenched from a temperature high in the alpha-beta field (Figure 12d) consists of equiaxed alpha grains in a matrix of

100X N2288

a. Unalloyed titanium (1-1/2HF-3-1/2HNO_3)

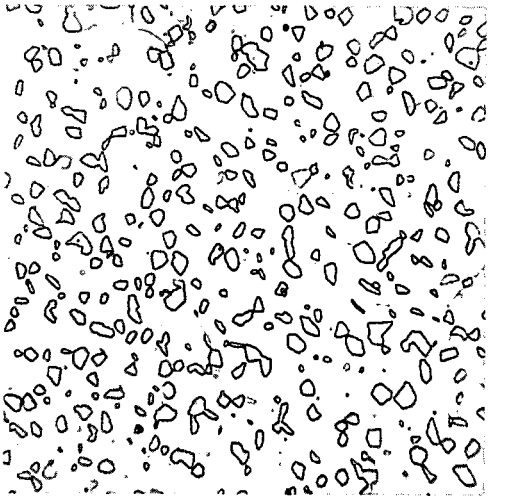
250X 95251

b. Ti-0.5Mn (1-1/2HF-3-1/2HNO_3)



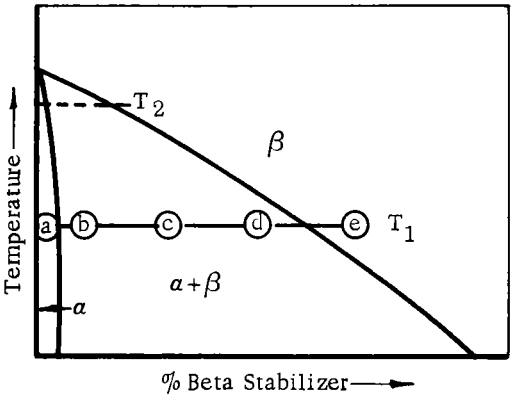
250X 95248

c. Ti-3.5Mn (1HF)



250X 98162

d. Ti-6.4Mn (1-1/2HF-3-1/2HNO_3)

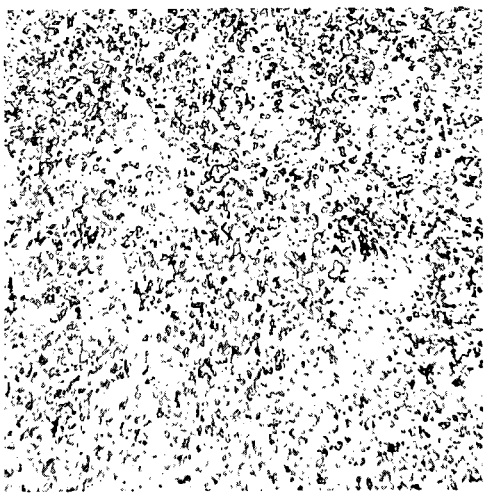


250X 92092

e. Ti-9.4Mn (1-1/2HF-3-1/2HNO_3)

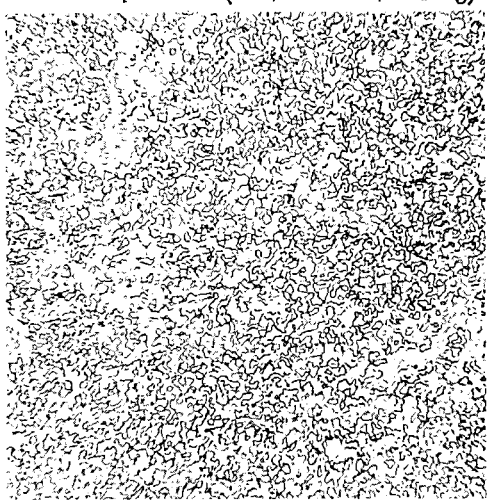
FIGURE 11. EFFECT OF ALLOY CONTENT ON THE MICROSTRUCTURES OF HIGH-PURITY TITANIUM-MANGANESE ALLOYS ANNEALED AT 1380 F AND QUENCHED

(Battelle Memorial Institute)



250X 95258

a. Ti-4.4Mn annealed 1 hour at 1200 F and water quenched (1-1/2HF-3-1/2HNO_3)



250X 95259

c. Ti-4.4Mn annealed 1 hour at 1380 F and water quenched (1-1/2HF-3-1/2HNO_3)

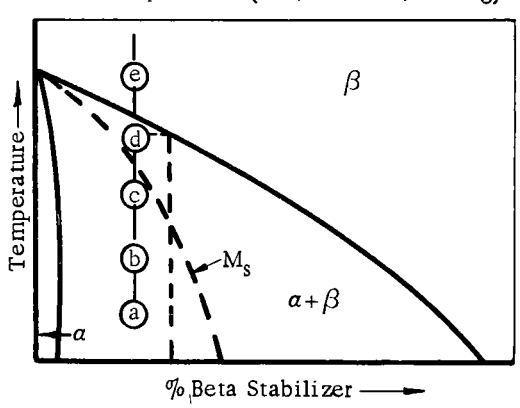
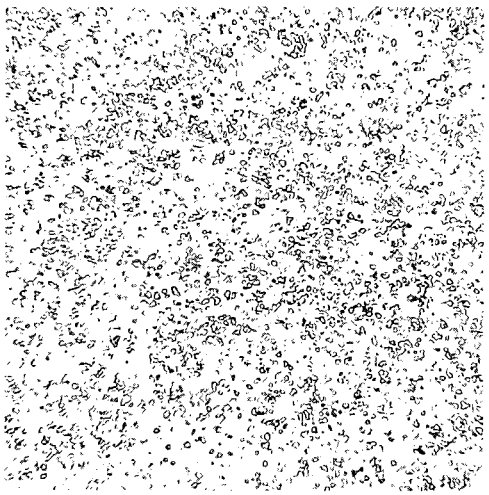


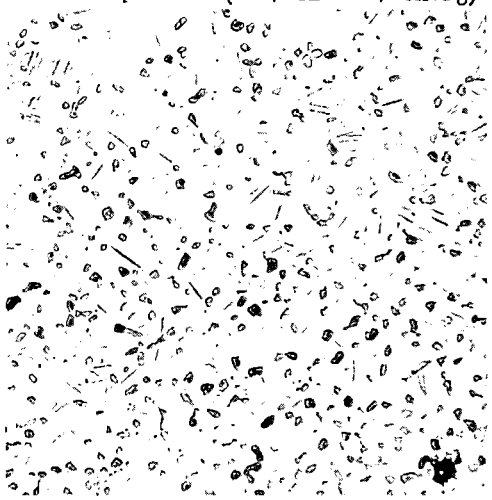
FIGURE 12. THE EFFECT OF SOLUTION-TREATMENT TEMPERATURE ON THE MICROSTRUCTURES OF A Ti-4.4Mn ALLOY

(Battelle Memorial Institute)



250X 95265

b. Ti-4.4Mn annealed 1 hour at 1290 F and water quenched (1-1/2HF-3-1/2HNO_3)



250X 95266

d. Ti-4.4Mn annealed 1 hour at 1490 F and water quenched (1-1/2HF-3-1/2HNO_3)

250X 95250

e. Ti-4.4Mn annealed 1 hour at 1530 F and water quenched (1-1/2HF-3-1/2HNO_3)

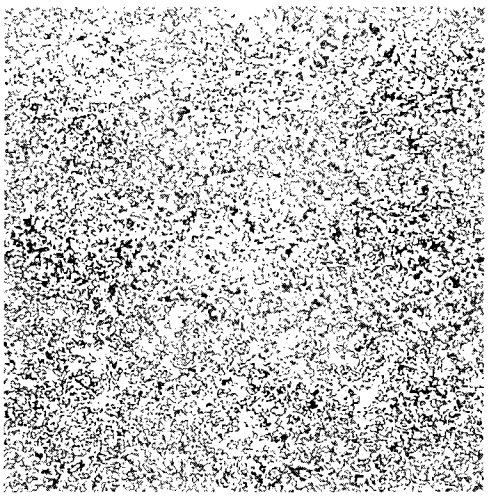
martensite. At the temperature (d), the equilibrium beta phase is low in alloy content, so that it transforms to martensite (alpha-prime) on quenching. This is indicated on the schematic diagram of Figure 12 where the alloy content of the equilibrium beta phase is shown to be below the room temperature M_s composition. Structures of this type frequently are encountered in the solution treatment of commercial alloys; for example, the Ti-6Al-4V alloy solution annealed at 1750 F. A specimen quenched from the beta field (Figure 12e) appears to be wholly martensitic; however, the position of the M_f curve is uncertain, so that the degree of completion of the transformation (presence of some retained beta phase) is not known precisely.

A similar series of photomicrographs for an alloy of higher beta stabilizer content is shown in Figure 13. The composition of this alloy is higher than the M_s at room temperature, so that alpha-prime does not form on cooling. Specimens annealed at temperatures in the alpha-beta field contain a mixture of alpha and beta phases, similar to those for the preceding example. The amount of alpha present decreases as the annealing temperature is increased. The specimen quenched from the beta field shows an equiaxed retained beta structure (Figure 13d). Actually, there is a second phase in this structure, the omega phase, which is not visible in the micrograph. Omega formation is discussed briefly in a later section of this report.

In the two preceding examples, the alloys were fabricated at a temperature in the alpha-beta field, so that subsequent annealing in the alpha-beta field resulted in equiaxed microstructures. At higher alloy contents, it usually is necessary to fabricate in the beta field. This results in an initially transformed structure that persists through subsequent annealing treatments. An example of this is shown in Figure 14. The specimens annealed in the alpha-beta field (Figure 14a and b) show clearly the outlines of the prior beta grains that were formed during fabrication. The alpha phase has formed in the prior beta grain boundaries and in thin platelets within the beta grains. Structures such as that shown in Figure 14a sometimes are described as "basketweave" alpha-beta structures. The general types of structures shown in Figure 14a and b usually are described as transformed, or acicular, alpha-beta to distinguish them from the equiaxed structures shown in the preceding examples. Acicular structures are encountered in commercial alloys that have been heated into the beta field at some stage of fabrication or heat treatment. The specimen quenched from the beta field (Figure 14c) is composed of equiaxed retained beta.

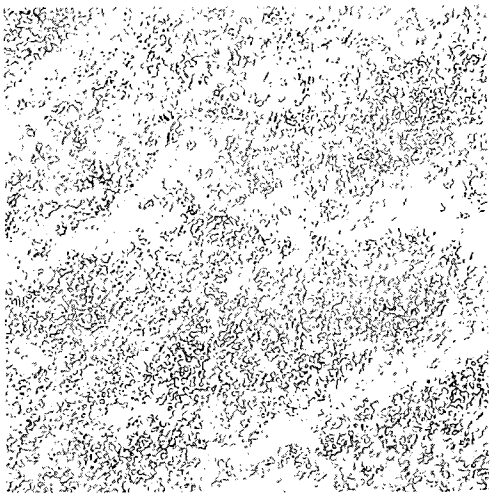
Effects of Cooling Rate

The transformation from beta to alpha that occurs on cooling from the beta field is a nucleation-and-growth process, and thus can be described



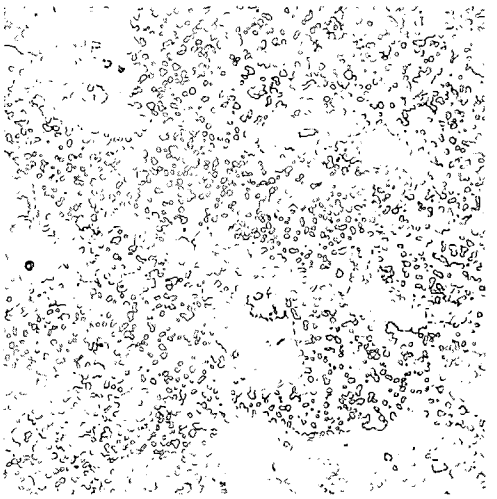
250X 92094

a. Ti-6.4Mn annealed 1 hour at 1200 F and quenched (1-1/2HF-3-1/2HNO_3)



250X 92097

b. Ti-6.4Mn annealed 1 hour at 1290 F and quenched (1-1/2HF-3-1/2HNO_3)



250X 92091

c. Ti-6.4Mn annealed 1 hour at 1380 F and quenched (1-1/2HF-3-1/2HNO_3)

250X 92102

d. Ti-6.4Mn annealed 1 hour at 1490 F and quenched (1-1/2HF-3-1/2HNO_3)

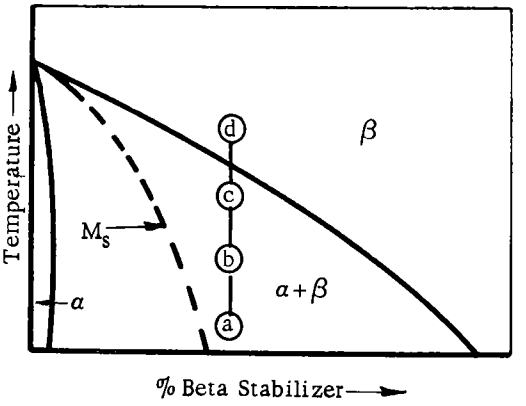
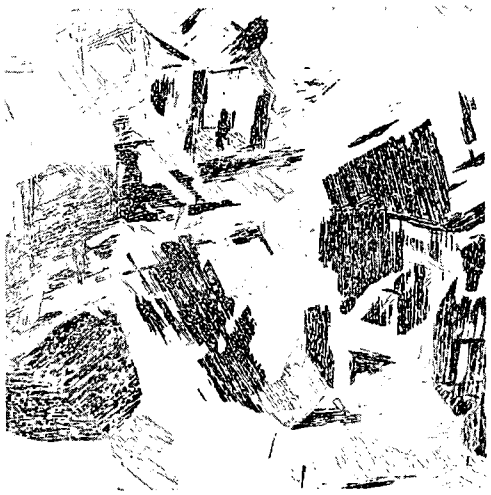


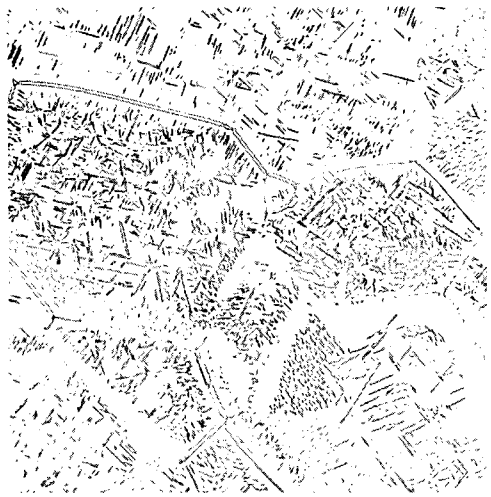
FIGURE 13. THE EFFECT OF SOLUTION-TREATMENT TEMPERATURE ON THE MICROSTRUCTURES OF A Ti-6.4Mn ALLOY

(Battelle Memorial Institute)



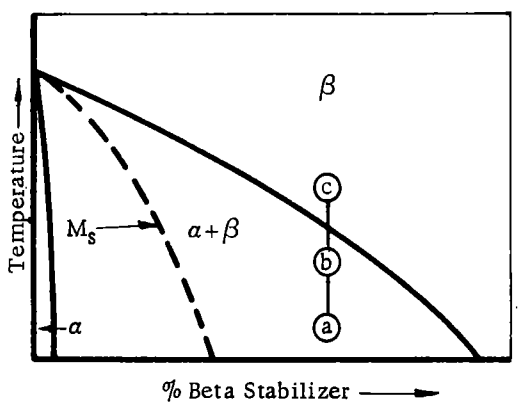
100X N19839

a. Ti-7.5Fe annealed 1 hour at 1380 F, furnace cooled to 1200 F, held for 8 hours, and quenched (1-1/2HF-3-1/2HNO_3)



250X N19560

b. Ti-7.5Fe annealed 4 hours at 1290 F and quenched (1-1/2HF-3-1/2HNO_3)



100X N19561

c. Ti-7.5Fe annealed 1 hour at 1380 F and quenched (1-1/2HF-3-1/2HNO_3)

FIGURE 14. MICROSTRUCTURES OF A Ti-7.5Fe ALLOY FABRICATED IN THE BETA FIELD AND HEAT TREATED IN THE ALPHA-BETA AND BETA FIELDS

(Battelle Memorial Institute)

by the conventional TTT diagram. The microstructures obtained by cooling at different rates from the beta field are shown in Figures 15 and 16 for two typical beta-stabilized alloys. Also included are schematic diagrams showing the cooling rates superimposed on the TTT diagram.

Figure 15 presents the structures typical of a low beta-stabilizer-content alloy. The M_s is above room temperature, so that martensite is formed on a rapid quench (Figure 15a). The specimen quenched in oil at a slower cooling rate transforms partly to alpha phase by a nucleation-and-growth process. This is seen in Figure 15b, where the alpha has formed as fine plates at the prior beta grain boundaries. The structure produced by a still slower cooling rate (Figure 15c) shows a further transformation to alpha; however, there still is an appreciable amount of martensite (alpha prime). At a very slow cooling rate, the transformation to alpha is completed above the M_s temperature. Figure 15d shows the coarse, platelike "basketweave" structure that is typical for the nucleation-and-growth transformation.

Figure 16 shows a similar series of microstructures for an alloy somewhat higher in beta-stabilizer content. The schematic TTT diagram shows that the M_s is below room temperature, but that a second transformation (to omega) occurs at the lower temperatures. The specimens water quenched and oil quenched from the beta field (Figure 16a and b) both appear as equiaxed beta, and there is no microstructural evidence of omega phase. The presence of omega in these specimens was established from hardness measurements. At a slower cooling rate, alpha phase is rejected as fine plates, which appear first at grain boundaries. This is seen in Figure 16c. Beta phase (plus omega) is retained in patches near the center of the grain. At the slowest cooling rate, the transformation to alpha appears complete, and the structure is of the familiar basketweave type (see Figure 16d). Hardness and diffraction data confirm the assumption that the transformation to alpha is completed without the formation of omega phase.

Figure 17 is a composite showing the effects of alloy composition and cooling rate on the microstructures of a single alloy system. The three structures at the top represent the rolled and annealed conditions. The Ti-4Mn and Ti-7Mn alloys are composed of a nearly equiaxed alpha-beta mixture, indicating that the annealing and fabrication were done at a temperature within the alpha-beta field. The Ti-18Mn alloy structure is almost all retained beta phase with a few particles of alpha. This alloy probably was fabricated in the beta field and annealed at a temperature slightly below the beta transus.

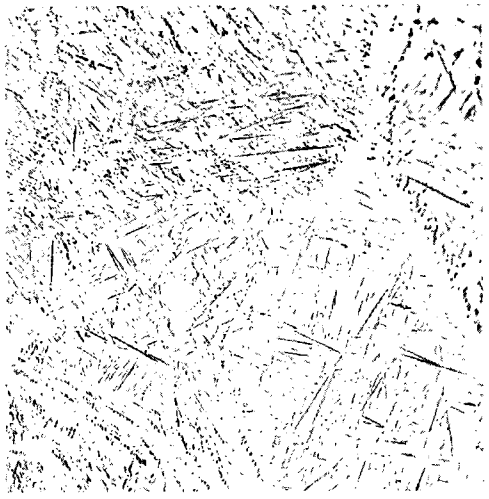
The remaining photomicrographs show the structures obtained for different cooling rates from the beta field. For the Ti-4Mn alloy, the water-quenched specimen transformed to alpha-prime (martensite), as shown

100X N19551

a. Ti-2.6Fe annealed 1/2 hour at 1650 F and quenched (1-1/2HF-3-1/2HNO_3)

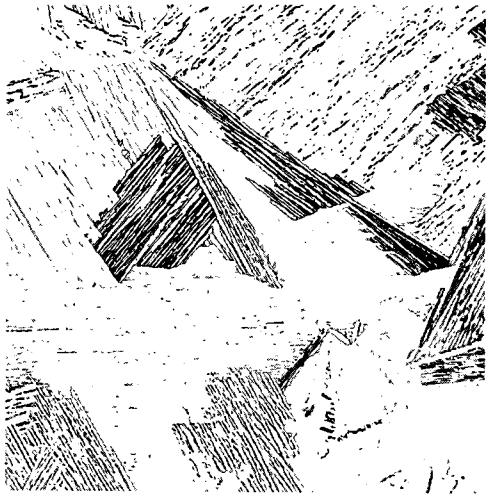
100X N19898

b. Ti-2.6Fe annealed 1/2 hour at 1650 F and oil quenched (1-1/2HF-3-1/2HNO_3)



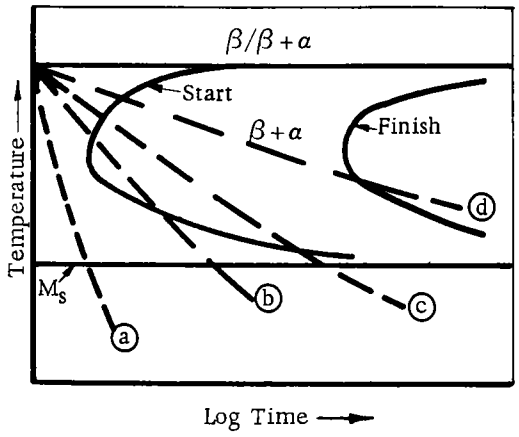
100X N19897

c. Ti-2.6Fe annealed 1/2 hour at 1650 F and air cooled (1-1/2HF-3-1/2HNO_3)



100X N19552

d. Ti-2.6Fe annealed 1/2 hour at 1650 F and furnace cooled (1-1/2HF-3-1/2HNO_3)

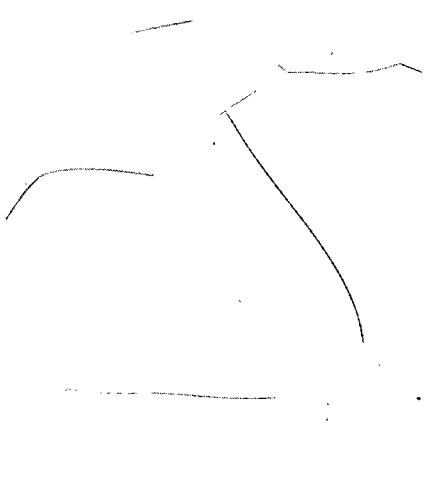


Cooling Rates

(a) Water quench
(b) Oil quench
(c) Air cool
(d) Furnace cool

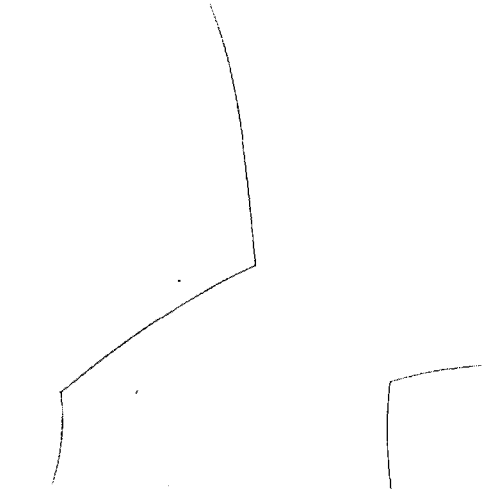
FIGURE 15. EFFECT OF COOLING RATE ON THE MICROSTRUCTURES OF AN ALPHA-BETA ALLOY (Ti-2.6Fe) ANNEALED IN THE BETA FIELD

(Battelle Memorial Institute)



100X N19557

a. Ti-5Fe annealed 1 hour at 1470 F and water quenched (1-1/2HF-3-1/2HNO_3)

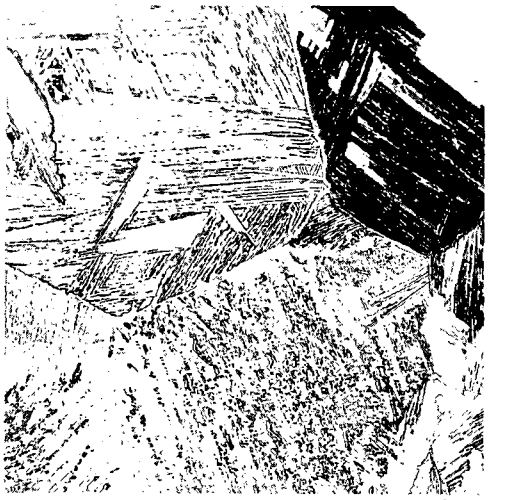


100X N19894

b. Ti-5Fe annealed 1 hour at 1470 F and oil quenched (1-1/2HF-3-1/2HNO_3)

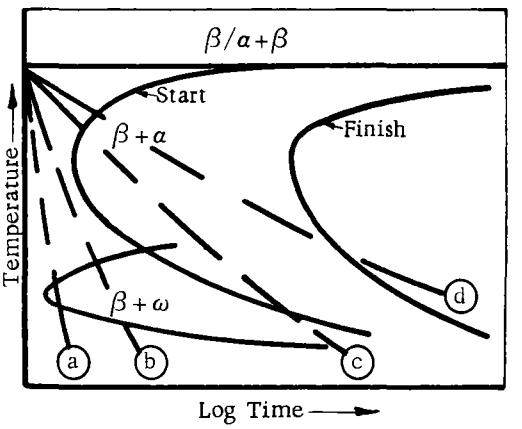
100X N19893

c. Ti-5Fe annealed 1 hour at 1470 F and air cooled (1-1/2HF-3-1/2HNO_3)



100X N19558

d. Ti-5Fe annealed 1 hour at 1470 F and furnace cooled (1-1/2HF-3-1/2HNO_3)



Cooling Rates

(a) Water quench
(b) Oil quench
(c) Air cool
(d) Furnace cool

FIGURE 16. EFFECT OF COOLING RATE ON THE MICROSTRUCTURES OF A LEAN BETA ALLOY (Ti-5Fe) ANNEALED IN THE BETA FIELD

(Battelle Memorial Institute)

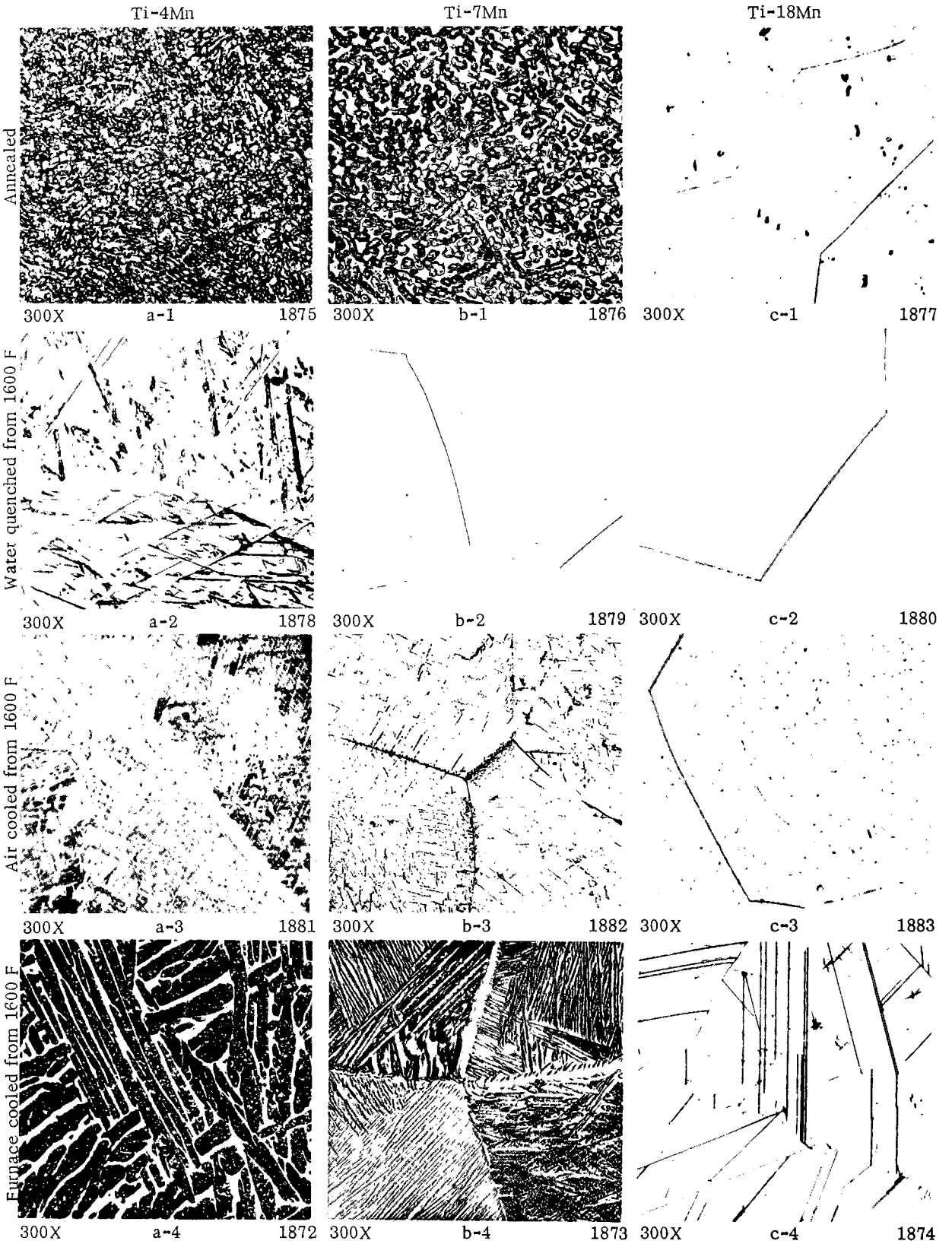


FIGURE 17. EFFECTS OF ALLOY COMPOSITION AND COOLING RATE ON THE MICROSTRUCTURES OF TITANIUM-MANGANESE ALLOYS

2% HF etch

(Rem-Cru Titanium, Inc.)

in Figure 17a-2; it is probable that some beta was retained between the martensite plates, although this is difficult to determine metallographically. On air cooling, the structure contains a mixture of martensite and nucleation-and-growth alpha, whereas for a furnace-cooled specimen, the structure contains a coarse platelike mixture of alpha and beta phases.

Beta phase is retained when the Ti-7Mn alloy was rapidly quenched from the beta field. At slower cooling rates, alpha phase appears as a Widmanstätten precipitate. Air cooling produced a fine, rather uniformly dispersed array of alpha particles, whereas the furnace-cooled specimen has the coarse, basketweave alpha-beta structure.

The water-quenched specimen of the Ti-18Mn alloy contains retained beta. Upon air cooling, a precipitate (presumably alpha) forms in a fine dispersion of particles, with some indication that precipitation occurs preferentially at subgrain boundaries. After furnace cooling from the beta field, the alpha is rejected as thin plates having a distinct orientation to the beta grains.

Isothermal Transformations

Like other nucleation-and-growth processes, the beta transformations in titanium alloys are dependent on the time-temperature path. For example, the equilibrium microstructures obtained by isothermal transformation may differ considerably from those reached by slow cooling, or by a quench-and-temper treatment.

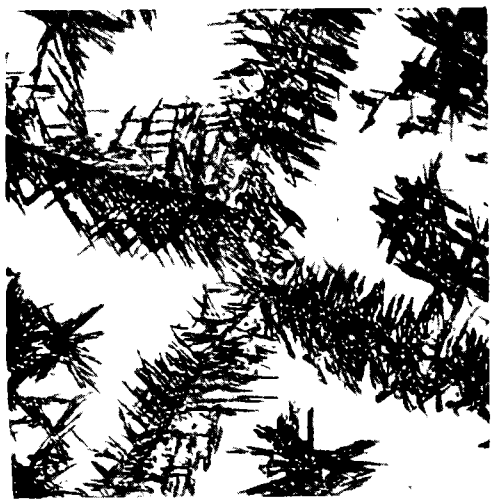
The TTT diagram, which maps the transformation in time-temperature space, usually is constructed from data obtained from isothermally transformed specimens. That is, the specimens are quenched to the transformation temperature and held for various lengths of time. The resulting microstructures are strongly dependent on transformation temperature. At the higher temperatures, nucleation is slow and growth is rapid, so that the transformation product tends to precipitate in massive form. At lower temperatures the reverse is true, resulting in a finer dispersion of precipitated transformation product.

In beta-stabilized titanium alloys, three nucleation-and-growth products may form from the beta phase; these are alpha, eutectoid, and omega. Of these, the omega phase is metastable and cannot be observed by ordinary metallographic methods.

Figure 18 shows the sequence of isothermal transformation from beta-to-alpha in a Ti-3Mo alloy; the TTT diagram is included as a frame of

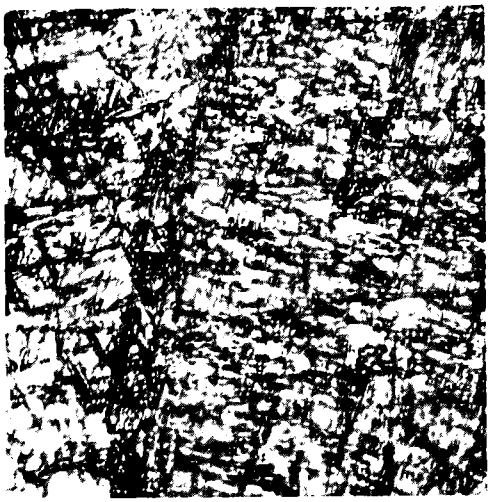
750X 6859

a. 5 minutes (10HF-60HNO_3-30 glycerine)



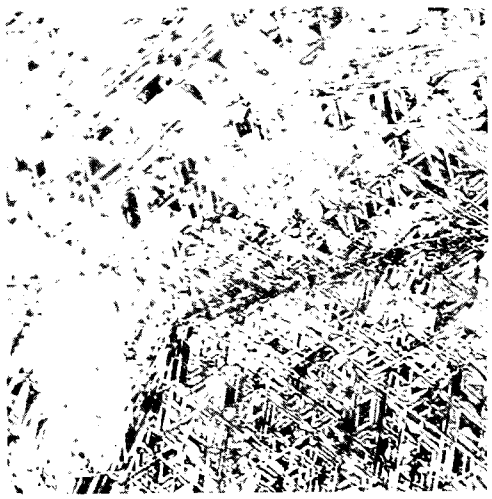
750X 6377

b. 15 minutes (10HF-60HNO_3-30 glycerine)



750X 6376

c. 30 minutes (10HF-60HNO_3-30 glycerine)



750X 6375

d. 60 minutes (10HF-60HNO_3-30 glycerine)

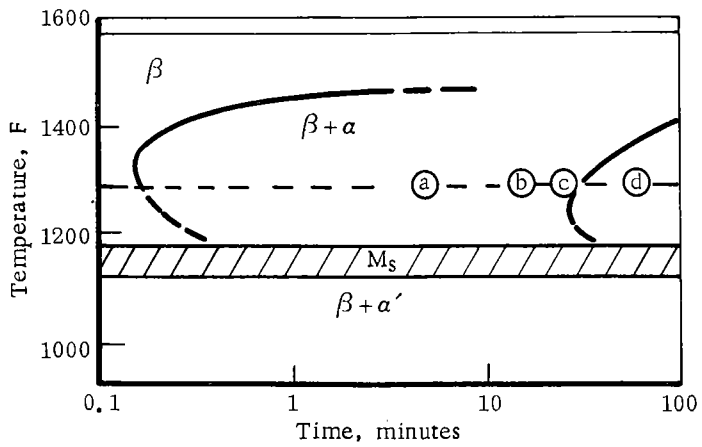


FIGURE 18. EFFECT OF ISOTHERMAL HOLDING TIME ON THE MICROSTRUCTURES OF A Ti-3Mo ALLOY QUENCHED FROM THE BETA FIELD TO 1290 F
(Armour Research Foundation)

reference. At the isothermal holding temperature, the quenched structure is retained beta phase. The transformation of alpha commences at the beta grain boundaries (5 minutes); at longer times, alpha also is nucleated within the beta grains (15 minutes). The background structures in Figure 18a and b are alpha prime, formed during cooling to room temperature after the beta-alpha transformation.

The isothermal transformation products for an alloy richer in beta stabilizer content, Ti-11Mo, are shown in Figure 19. At this composition, the beta phase is retained during quenching at room temperature. The samples were quenched from the beta field to temperatures of 930 to 1290 F and held for 60 minutes before quenching to room temperature. As indicated by the TTT diagram, the transformation to alpha is completed in 60 minutes at 930, 1020, and 1110 F. At these temperatures, nucleation is rapid, and a fine dispersion of alpha particles results. Preferential nucleation at beta grain boundaries is apparent at 1110 F, and, to a lesser degree, at 1020 F. At 930 F, the dispersion appears nearly uniform over the entire structure. At 1200 and 1290 F (Figure 19a and b), the beta-to-alpha transformation is not completed in 60 minutes. There is a marked increase in coarseness, resulting from the decreased nucleation rate at higher temperatures. Again, the preferred nucleation at grain boundaries is apparent at these higher temperatures.

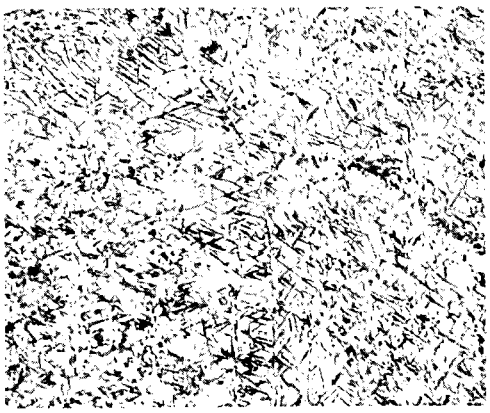
Formation of the Omega Phase

The omega phase is a metastable nucleation-and-growth product that has a potent strengthening and embrittling effect. At alloy compositions near the limit at which the beta phase is retained when the alloy is quenched from the beta field, the omega transformation often is so rapid that it cannot be fully suppressed even by a very rapid quench. Because omega is not observed by ordinary metallographic methods, its formation has been studied by less direct procedures including hardness, X-ray diffraction, and measurements of the elastic modulus. Recent studies using the electron microscope have revealed structures that can be correlated directly with the presence of omega.

Figure 20 shows a series of electron micrographs of a Ti-6.4Mn alloy that was quenched from the beta field and aged at lower temperatures. In this alloy, the omega reaction is not suppressed fully on water quenching except when the specimen is very small. The structures shown in Figure 20a and b are for water-quenched specimens; it may be seen that the structure of the larger specimen (b) contains a number of equiaxed particles, whereas the structure of the smaller specimen is smooth. After aging for 1 hour at 570 F and 750 F (Figure 20c and d), the density of particles is increased.

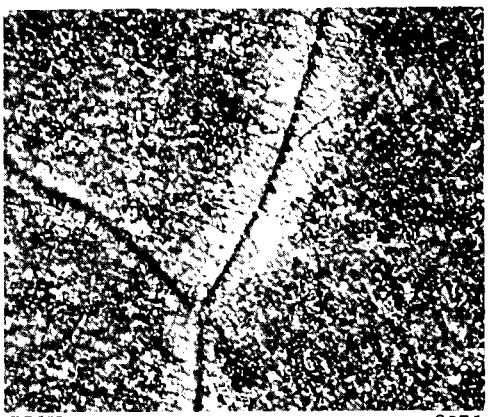
750X 6370

a. Ti-11Mo held 60 minutes at 1290 F and water quenched (10HF-60HNO_3-30 glycerine)



750X 6372

b. Ti-11Mo held 60 minutes at 1200 F and water quenched (10HF-60HNO_3-30 glycerine)



750X 6371

c. Ti-11Mo held 60 minutes at 1110 F and water quenched (10HF-60HNO_3-30 glycerine)

750X 6373

d. Ti-11Mo held 60 minutes at 1020 F and water quenched (10HF-60HNO_3-30 glycerine)

500X 6488

e. Ti-11Mo held 60 minutes at 930 F and water quenched (10HF-60HNO_3-30 glycerine)

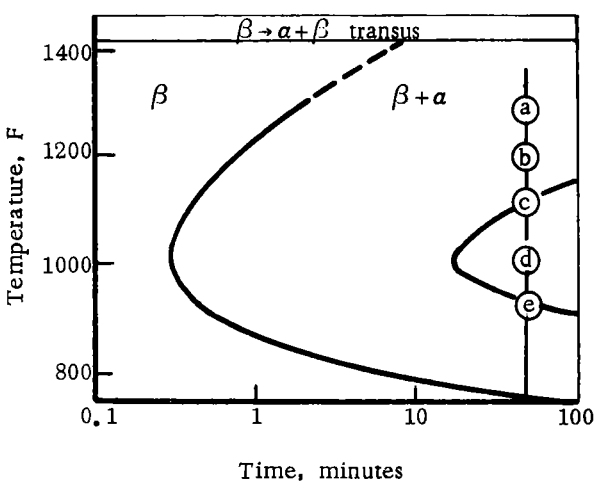
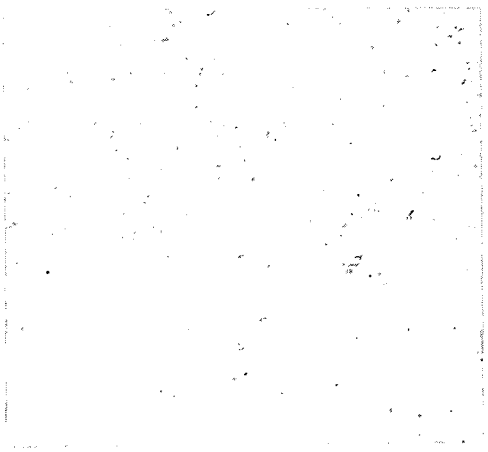


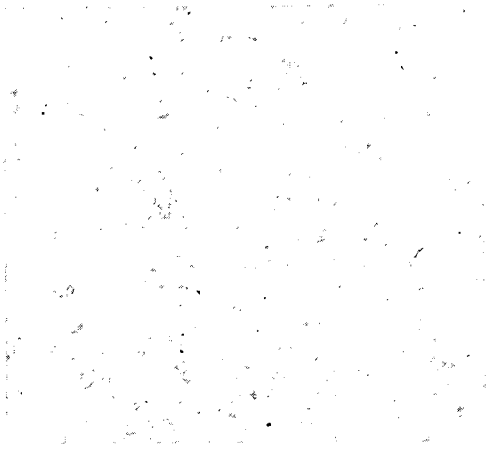
FIGURE 19. EFFECT OF ISOTHERMAL HOLDING TEMPERATURE ON THE MICROSTRUCTURES OF TITANIUM-MOLYBDENUM ALLOYS QUENCHED FROM THE BETA FIELD AND HELD 60 MINUTES AT TEMPERATURE

(Armour Research Foundation)



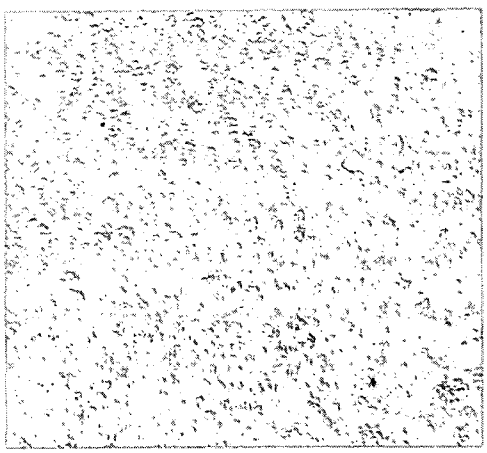
10,000X E5253E

a. Ti-6.4Mn as quenched (very small specimen)



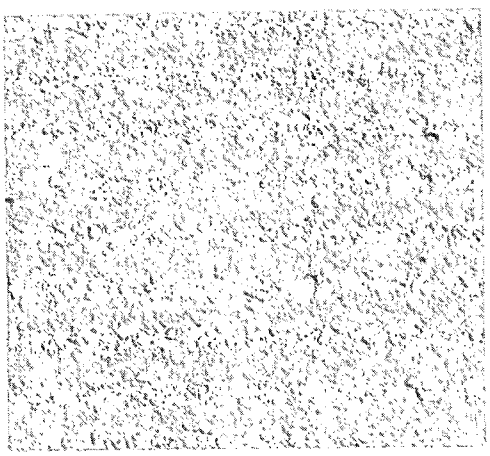
10,000X E5142C

b. Ti-6.4Mn as quenched



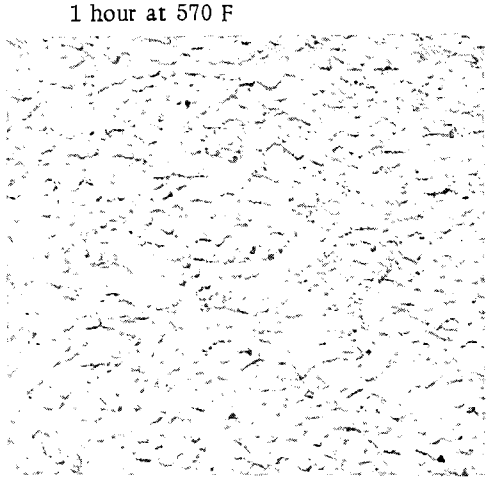
10,000X E5131B

c. Ti-6.4Mn beta quenched and aged 1 hour at 570 F



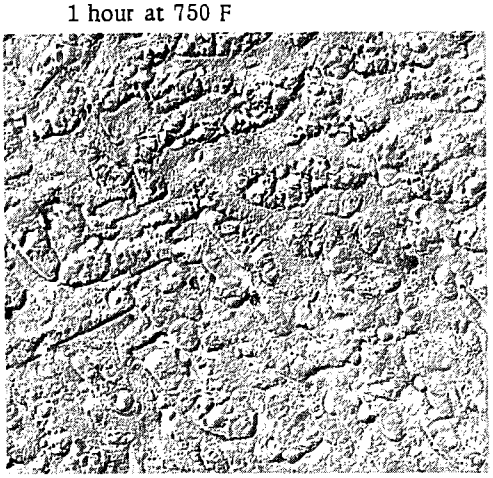
10,000X E5133C

d. Ti-6.4Mn beta quenched and aged 1 hour at 750 F



10,000X E5134B

e. Ti-6.4Mn beta quenched and aged 1 hour at 930 F



10,000X E5135E

f. Ti-6.4Mn beta quenched and aged 1 hour at 1110 F

FIGURE 20. ELECTRON MICROGRAPHS OF A Ti-6.4Mn ALLOY BETA QUENCHED AND AGED

1-1/2HF-3HNO$_3$ etch

(Battelle Memorial Institute)

At higher aging temperatures of 930 and 1110 F, there is a drastic change in the microstructural appearance (Figure 20c and d). The fine, equiaxed particles are replaced by a coarse oriented structure. This change in structure corresponds to the formation of alpha phase, as demonstrated by X-ray diffraction and by ordinary metallographic examination.

Eutectoid Transformation

The transformation from beta to eutectoid is indicated in the constitution diagrams for many of the beta-stabilized titanium alloys. Like the beta-to-alpha transformation, eutectoid products are formed by a nucleation-and-growth process, and the kinetics of the reaction may be described by a TTT diagram. Because the mechanical properties of a titanium alloy usually are affected adversely by the presence of eutectoid products, most of the commercial alloys are designed to avoid the eutectoid transformation. This is done by using alloy elements with low eutectoid temperatures and by compounding the beta stabilizers to depress the eutectoid temperature.

In most instances, the eutectoid products are alpha phase plus an intermetallic compound. Of the eutectoid-forming alloying elements used in present commercial alloys, manganese, chromium, and iron, only chromium and iron have been observed to form eutectoid in the binary alloys. The more active eutectoid-forming elements, nickel, copper, and silicon, have been studied in experimental alloy investigations, but are not used in commercial alloys at the present time.

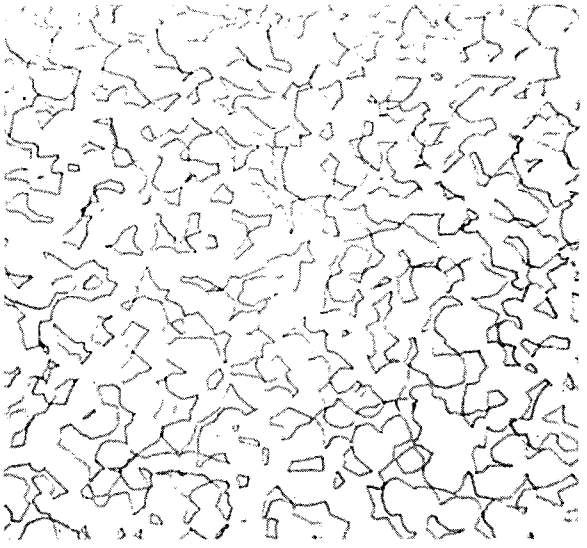
Figure 21 shows the formation of eutectoid products in a binary Ti-5Cr alloy after a 200-hour exposure at 1000 F. The strength and ductility of this alloy were markedly decreased by the presence of the eutectoid products, alpha and $TiCr_2$.

The rapid decomposition of beta to eutectoid products in the Ti-Cu alloy system resulted in the structures shown in Figure 22. The nodular appearance of the eutectoid at 250X actually is shown to consist of fine lamellae by the electron micrograph at 12,000X.

Miscellaneous Structures

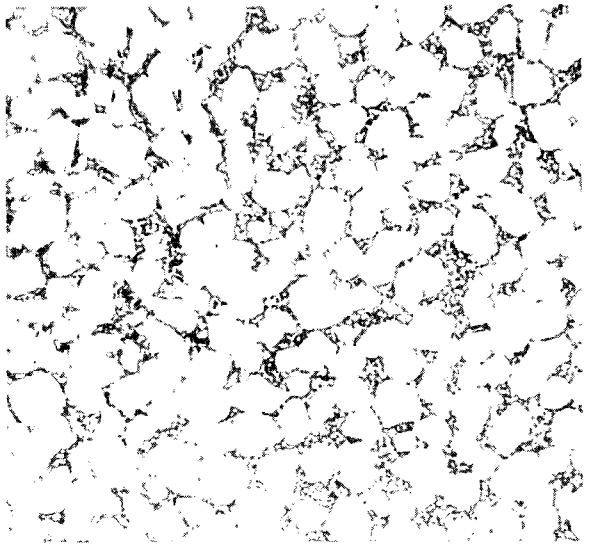
Strain-Induced Martensite

In certain titanium-base beta-stabilized alloy systems there is a composition range where the beta phase obtained on quenching from the beta



1500X N18893

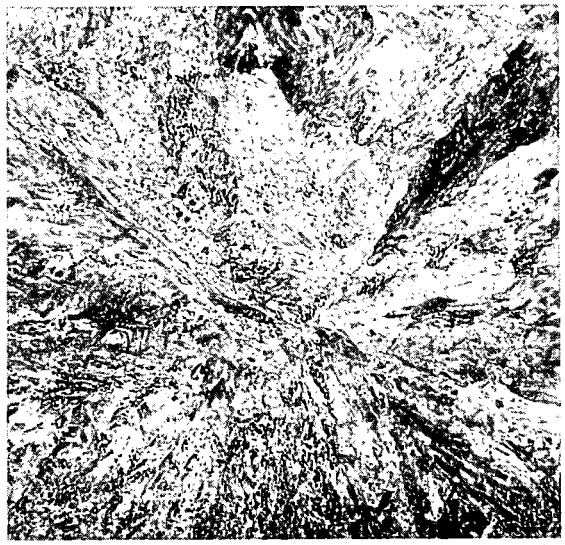
a. As annealed



1500X N18896

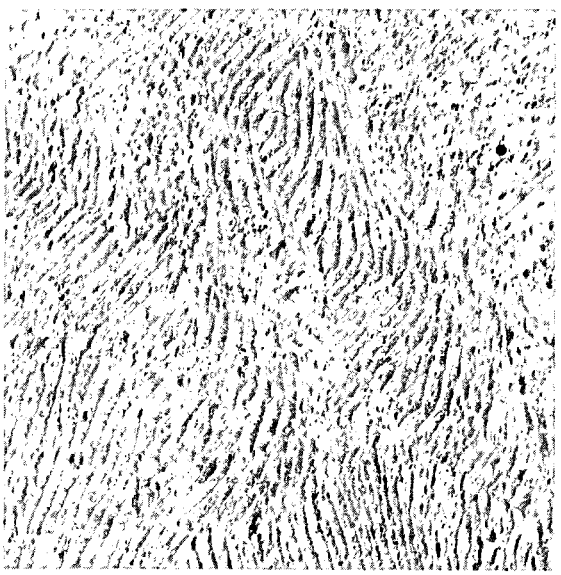
b. Aged 200 hours at 1000 F

FIGURE 21. FORMATION OF EUTECTOID PRODUCTS IN AN ANNEALED Ti-5Cr ALLOY
1-1/2HF-3HNO_3 etch
(Battelle Memorial Institute)



250X N8395

a. Ti-6.8Cu light micrograph showing nodular eutectoid structure



12,000X E4994E

b. Ti-6.8Cu electron micrograph showing lamellar structure of eutectoid

FIGURE 22. LIGHT AND ELECTRON MICROGRAPHS OF A Ti-6.8Cu ALLOY AIR COOLED FROM THE BETA FIELD

1-1/2HF-3-1/2HNO_3 etch

(Battelle Memorial Institute)

field is mechanically unstable. That is, it transforms to martensite (alpha prime) when it is cold worked. The composition range is just beyond the composition at which martensite forms during quenching. In many systems the beta-to-omega reaction is so rapid in this composition range that omega forms during the quench. When this happens the formation of strain-induced martensite is inhibited. In the high-purity Ti-Mo system soft beta, which will transform to martensite on straining, can be obtained by quenching in the composition range of 11 to 14 per cent molybdenum. An example of the structure obtained after straining a Ti-11.7Mo alloy is shown in Figure 23.

Impurity Phases

The chief impurity phases that are found in beta-stabilized alloys are carbides and hydrides. Because of the limited solubility of carbon in both alpha and beta phases of titanium, carbide particles can be seen with carbon contents as low as 0.15 per cent in alpha-beta or beta alloys. Figure 24a and b show carbide particles in an alpha-beta and a beta alloy. The sample of Ti-8Mn alloy shown in Figure 24a had been strained sufficiently to cause fracture at the carbide interface.

The hydride phase is not seen in alpha-beta alloys unless the hydrogen content is abnormally high. When it is seen, it appears as a network, sometimes looking like cracks, as shown in Figure 24c and d. An interesting observation that has been made of the structure of Ti-6Al-4V alloy containing 400 ppm hydrogen is shown in Figure 25. Markings which appear like twins are seen in the beta phase only. This same structure could not be reproduced in low-hydrogen-content material.

Subgrain Structures of Retained Beta

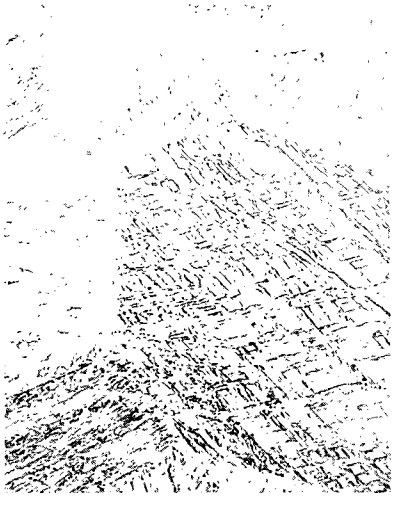
It has been observed by many investigators that retained beta alloys may contain a subgrain structure when quenched from temperatures high in the beta field. An example of such a structure is shown in Figure 26. The subgrain markings are attributed to the high interstitial content of the alloy. Note that they only occur when the beta-annealing temperature is considerably above the beta transus for this alloy.

25X N19217

a. Section through shoulder of tensile-test specimen

250X N19252

b. Start of $\beta \rightarrow \alpha'$ transformation



250X N19253

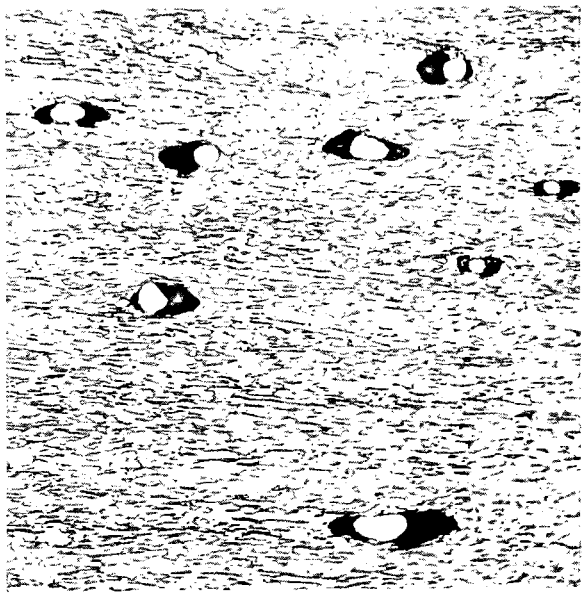
c. $\beta \rightarrow \alpha'$ transformation more complete

250X N19254

d. $\beta \rightarrow \alpha'$ transformation nearly complete

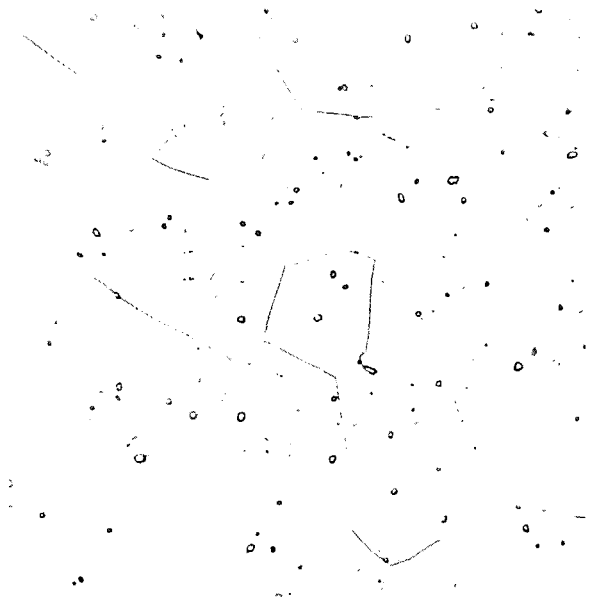
FIGURE 23. FORMATION OF STRAIN-INDUCED MARTENSITE IN A BETA-QUENCHED Ti-11.7Mo ALLOY

1-1/2HF-3-1/2HNO3 etch
(Battelle Memorial Institute)



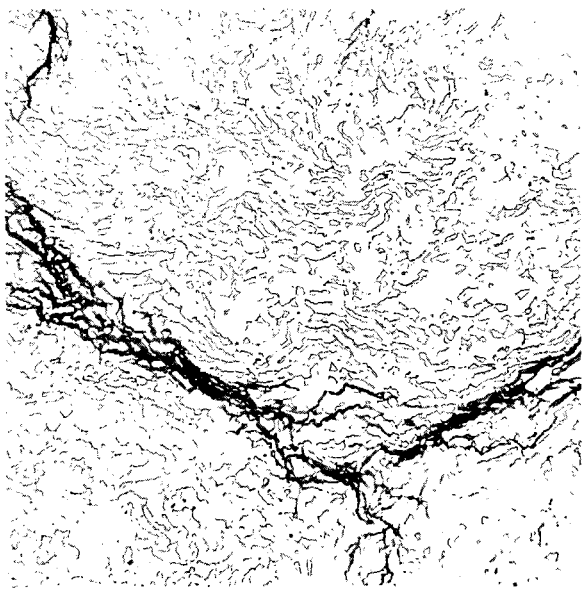
500X N36886

a. Ti-8Mn containing carbide phase fabricated and annealed in the alpha-beta field (1-1/2HF-3HNO_3)



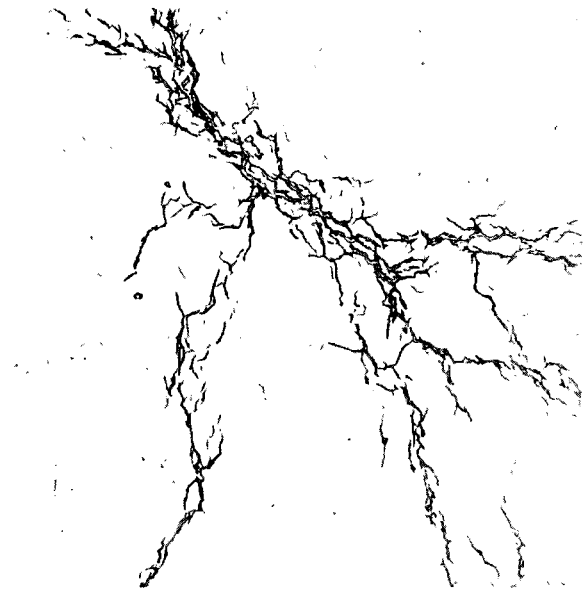
250X N6999

b. Ti-9Mn-0.1C quenched from the beta-carbide field (1-1/2HF-3-1/2HNO_3)



500X N31436

c. Ti-4Mn containing 400 ppm hydrogen (1-1/2HF-3-1/2HNO_3)

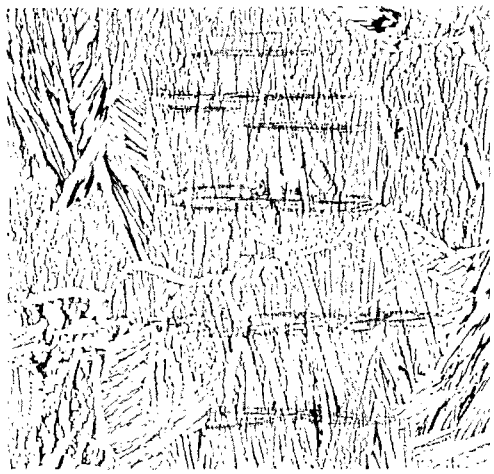


500X N28656

d. Ti-2Mn-2Cr containing 400 ppm hydrogen (1-1/2HF-3-1/2HNO_3)

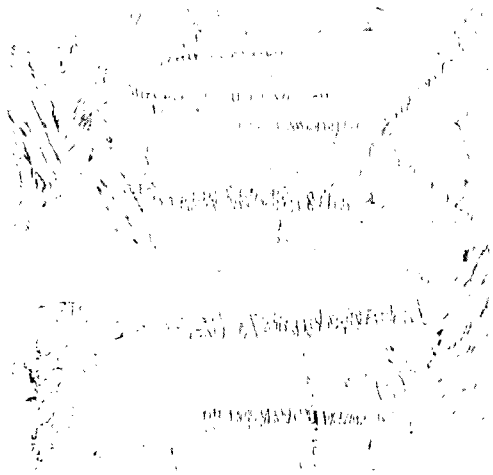
FIGURE 24. MICROSTRUCTURES SHOWING THE APPEARANCE OF HYDRIDE PHASE AND CARBIDE PHASE IN BETA-STABILIZED ALLOYS

(Battelle Memorial Institute)



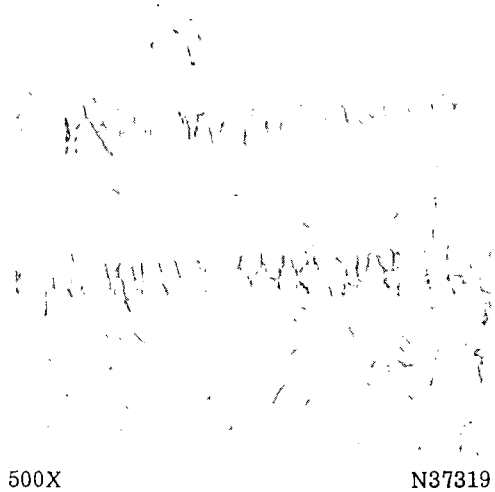
100X N37320

a. Low magnification (1-1/2HF-3-1/2HNO_3)



100X N37318

b. Low magnification (5HF-15HNO_3-30 lactic)

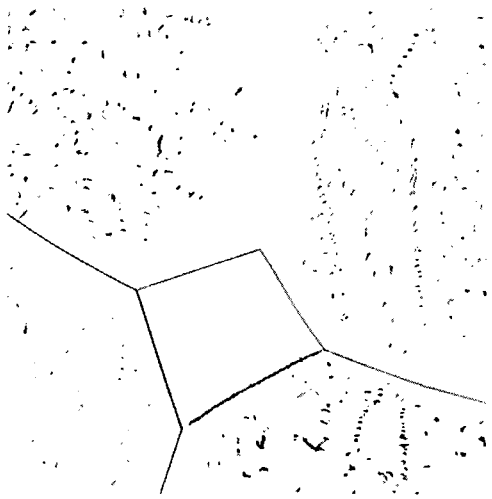


500X N37319

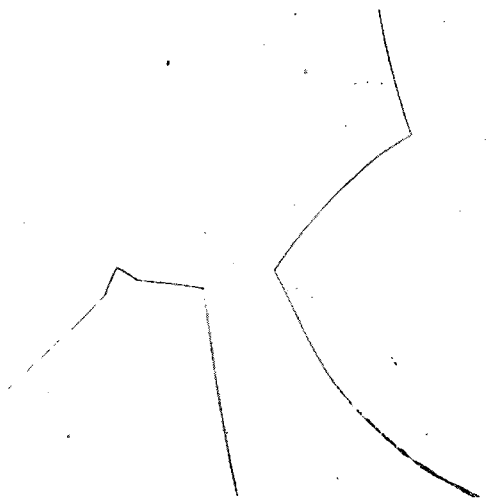
c. High magnification (5HF-15HNO_3-30 lactic)

FIGURE 25. MICROSTRUCTURES OF A Ti-6Al-4V ALLOY CONTAINING 400 PPM HYDROGEN, HEAT TREATED 1 HOUR AT 1900 F, SLOW COOLED TO 1300 F, HELD 1 HOUR AND QUENCHED, FOLLOWED BY AGING FOR 16 HOURS AT 900 F

(Battelle Memorial Institute)



a. Quenched from 1500 F



b. Quenched from 1650 F

FIGURE 26. MICROSTRUCTURES OF A Ti-9Mn ALLOY CONTAINING 0.1 PER CENT NITROGEN, QUENCHED FROM TWO TEMPERATURES ABOVE THE BETA TRANSUS

1-1/2HF-3-1/2HNO_3 etch
(Battelle Memorial Institute)

MICROSTRUCTURES OF COMMERCIAL TITANIUM ALLOYS

There are approximately 18 titanium-base alloys commercially available today or in advanced developmental stages. The microstructures that can be obtained in these alloys are dependent on composition, fabrication history, and thermal history. The previous sections of this report have discussed the general effects of composition and thermal history on the microstructures of titanium alloys. These general effects are applicable to the commercial alloys of the appropriate types. Therefore, this section of the report contains only typical microstructures of the commercial alloys in the annealed or heat-treated conditions. Subsequent sections of this report discuss the effects of fabrication treatments including welding and brazing on the microstructures of titanium alloys.

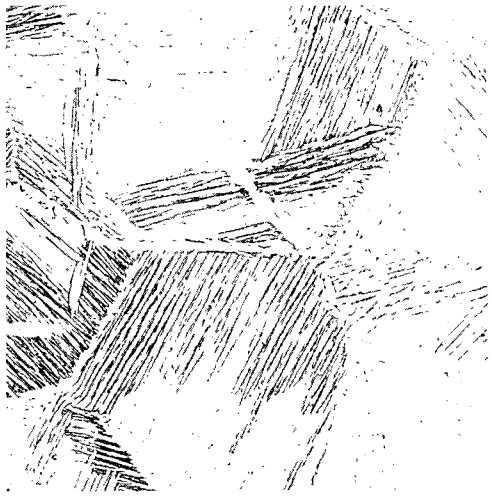
Annealed Alloys

The first series of photomicrographs, shown in Figures 27 through 33, is for alloys in the annealed condition. Each structure is identified as completely as possible including composition, fabrication history, and annealing treatment. All of the structures shown here were obtained on commercially produced alloys. Included in these figures are structures of the following alloys arranged in order of increasing beta-stabilizer content:

Alloy Composition, % (Balance Ti)	Figure
Ti-5Al-2.5Sn	27
Ti-12Zr-4.5Al	27
Ti-8Al-1Mo-1V	28
Ti-8Al-2Cb-1Ta	28
Ti-5Al-3Cr	29
Ti-2.25Al-3.25Mn	29
Ti-6Al-4V	30
Ti-7Al-4Mo	31
Ti-4Al-4Mn	31
Ti-5Al-2.75Cr-1.25Fe	31
Ti-5Al-1.5Fe-1.4Cr-1.2Mo	31
Ti-4Al-3Mo-1V	32
Ti-2.2Fe-2.1Cr-2Mo	32
Ti-8Mn	32
Ti-1Al-8V-5Cr	33
Ti-13V-11Cr-3Al	33

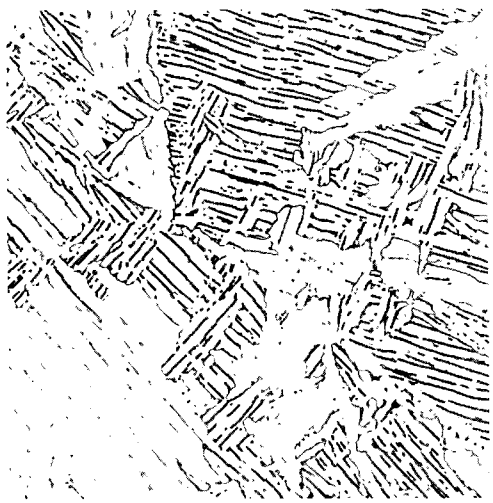
250X BMI N46444

a. Ti-5Al-2.5Sn fabricated and annealed in the alpha field; annealed 50 hours at 1475 F (1-1/2HF-3-1/2HNO_3)



100X BMI N46439

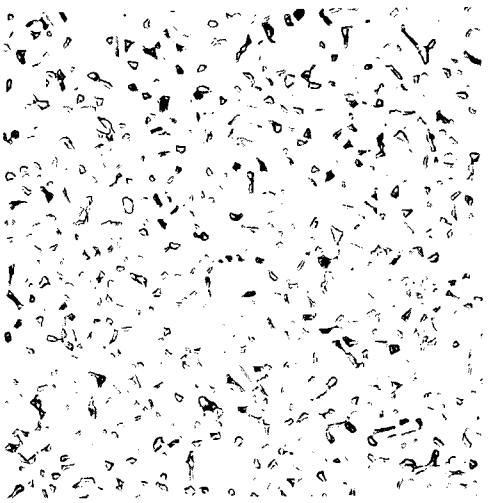
b. Ti-5Al-2.5Sn fabricated in the alpha field; annealed 1/2 hour at 2100 F and air cooled (1-1/2HF-3-1/2HNO_3)



300X Rem-Cru 3000

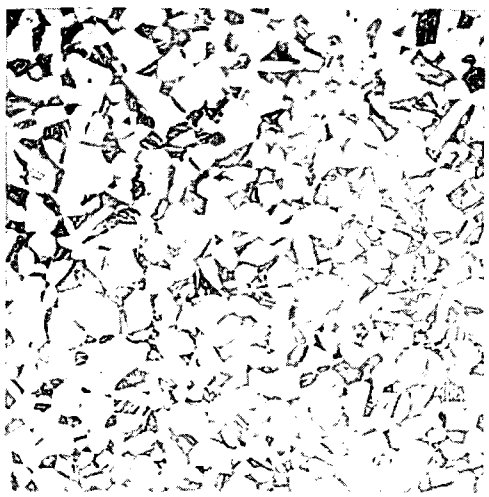
c. Ti-12Zr-4.5Al fabricated in the beta field; annealed 1/2 hour at 1600 F and air cooled (1HF-2HNO_3)

FIGURE 27. MICROSTRUCTURES OF THE COMMERCIAL ALPHA ALLOYS Ti-5Al-2.5Sn AND Ti-12Zr-4.5Al



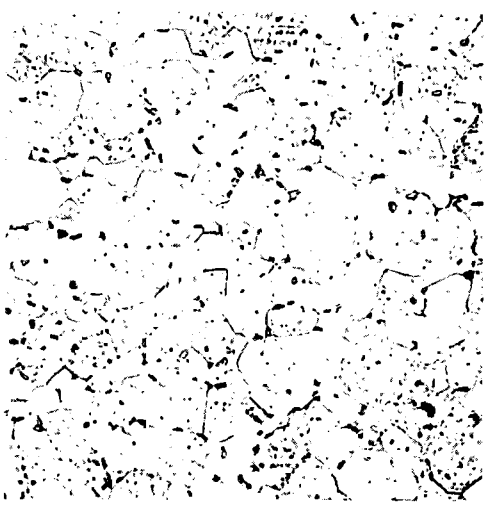
500X TMCA 1

a. Ti-8Al-1Mo-1V annealed 1 hour at 1650 F and air cooled, plus 24 hours at 1100 F and air cooled (Kroll etchant)



500X TMCA 2

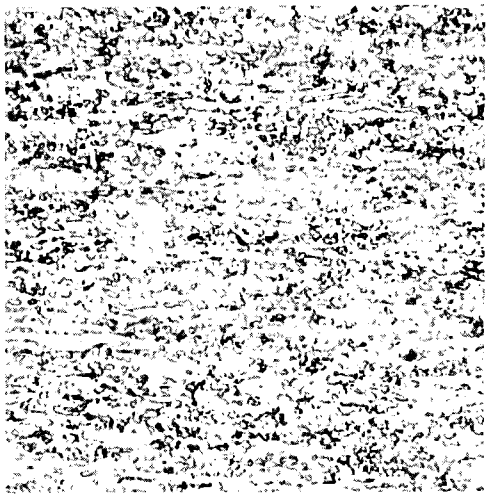
b. Ti-8Al-1Mo-1V annealed 1 hour at 1800 F and air cooled, plus 24 hours at 1100 F and air cooled (Kroll etchant)



500X MSM G 758 UF

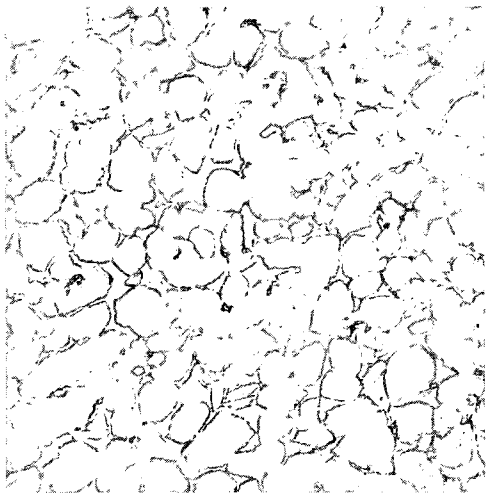
c. Ti-8Al-2Cb-1Ta annealed 1 hour at 1650 F and air cooled (10HF-5HNO_3)

FIGURE 28. MICROSTRUCTURES OF THE ANNEALED COMMERCIAL LEAN ALPHA-BETA ALLOYS Ti-8Al-Mo-1V AND Ti-8Al-2Cb-1Ta



500X Republic

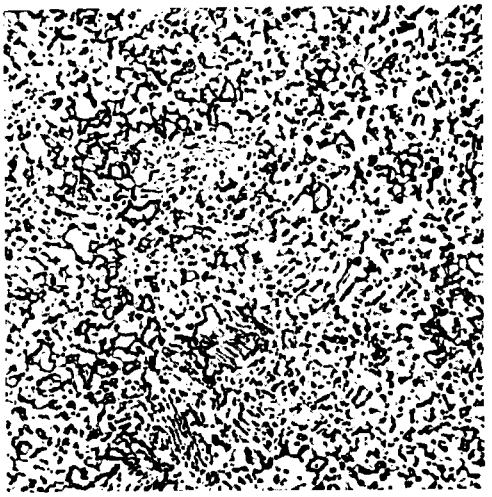
a. Ti-2.25Al-3.25Mn annealed 1/2 hour at 1350 F and air cooled ($2HF-5HNO_3$)



500 X Convair
PMA-495-4

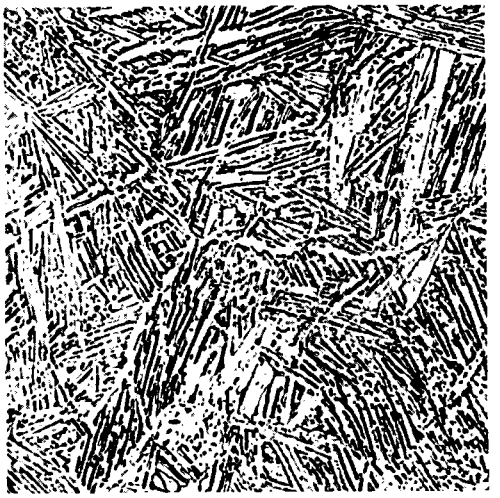
b. Ti-3Al-5Cr fabricated and annealed in the alpha-beta field ($1HF-2HNO_3$)

FIGURE 29. MICROSTRUCTURES OF THE ANNEALED COMMERCIAL ALPHA-BETA ALLOYS Ti-2.25Al-3.25Mn AND Ti-3Al-5Cr



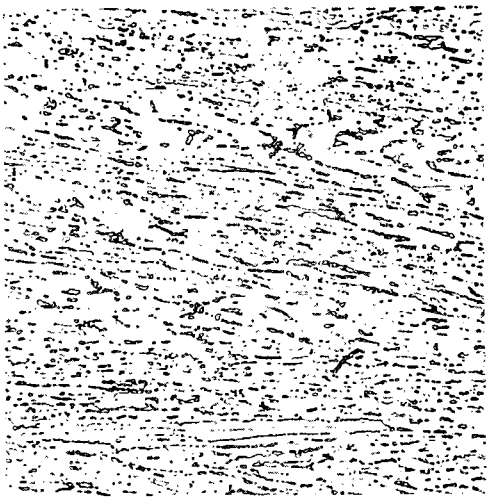
500X MSM
F 363 UF

a. Ti-6Al-4V rolled at 1670 F and annealed at 1525 F for 1 hour, furnace cooled to 1100 F, and air cooled (10HF-5HNO_3)



500X MSM
F 360 UF

b. Ti-6Al-4V rolled at 1870 F and annealed at 1525 F for 1 hour, furnace cooled to 1100 F, and air cooled (10HF-5HNO_3)



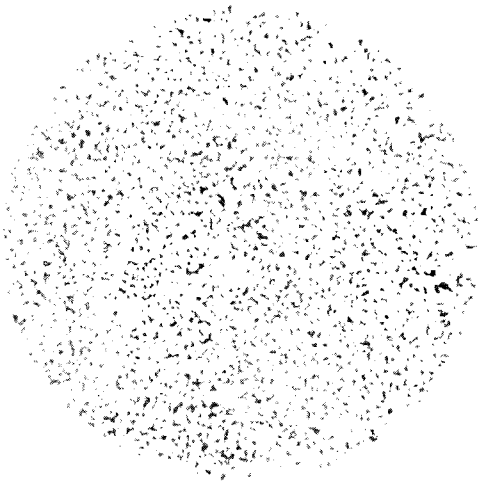
500X TMCA
8

c. Ti-6Al-4V annealed at 1300 F for 2 hours and air cooled (Kroll etchant)

300X Rem-Cru
3001

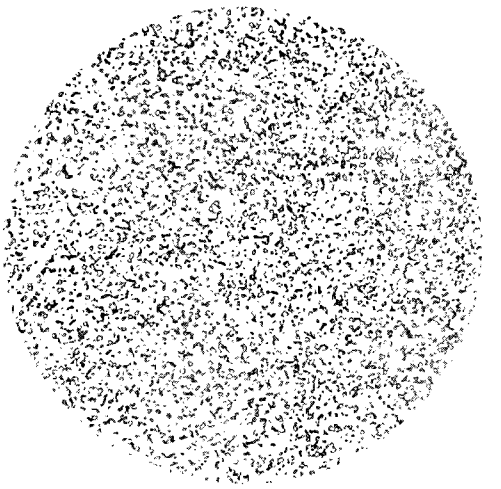
d. Ti-6Al-4V annealed 2 hours at 1550 F, furnace cooled to 1050 F, and air cooled (1HF-2HNO_3)

FIGURE 30. EFFECT OF FABRICATION TEMPERATURE AND ANNEALING TEMPERATURE ON THE MICROSTRUCTURES OF THE COMMERCIAL ALPHA-BETA ALLOY Ti-6Al-4V



300X Rem-Cru 2952

a. Ti-7Al-4Mo annealed 1 hour at 1400 F, furnace cooled to 1050 F, and air cooled (1HF-2HNO_3)

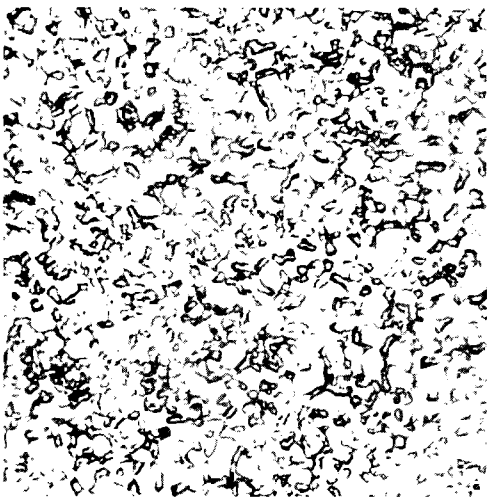


300X Rem-Cru 2892

b. Ti-4Al-4Mn annealed 2 hours at 1300 F, furnace cooled to 1050 F, and air cooled (1HF-2HNO_3)

500X TMCA 5

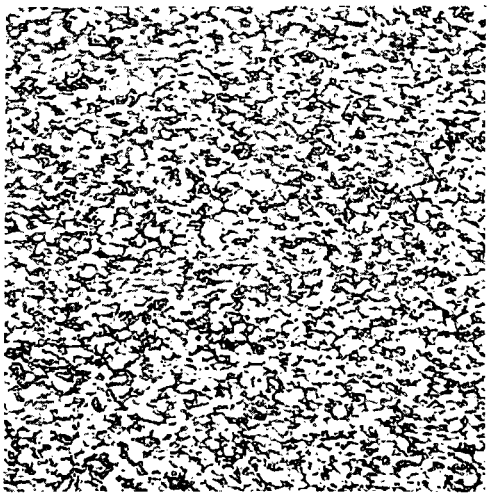
c. Ti-5Al-1.5Fe-1.4Cr-1.2Mo annealed 24 hours at 1200 F and air cooled (Kroll etchant)



750X Republic

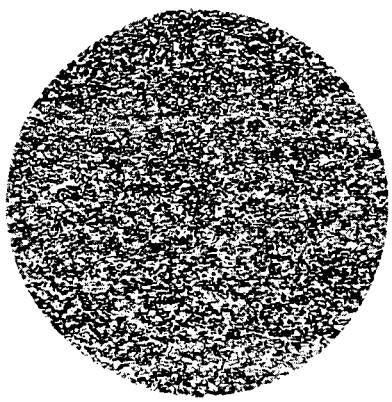
d. Ti-5Al-2.75Fe-1.25Cr annealed 2 hours at 1450 F and furnace cooled to 1000 F (2HF-5HNO_3)

FIGURE 31. MICROSTRUCTURES OF THE ANNEALED COMMERCIAL ALPHA-BETA ALLOYS Ti-7Al-4Mo, Ti-4Al-4Mn, Ti-5Al-1.5Fe-1.4Cr-1.2Mo, AND Ti-5Al-2.75Fe-1.25Cr



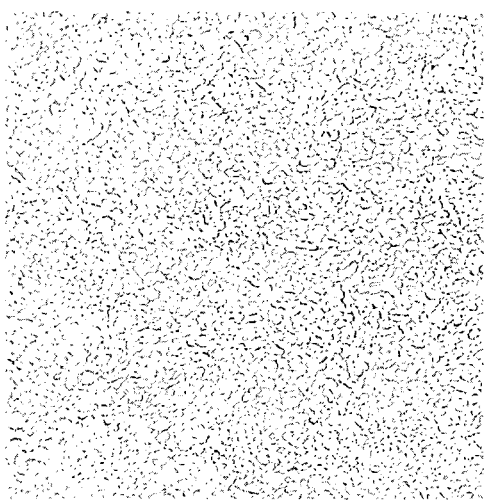
500X TMCA 10

a. Ti-4Al-3Mo-1V annealed 6 hours at 1250 F and air cooled (Kroll etchant)



250X Rem-Cru 450

b. Ti-8Mn annealed 1 hour at 1300 F, furnace cooled to 1000 F, and air cooled (1HF-2HNO_3)



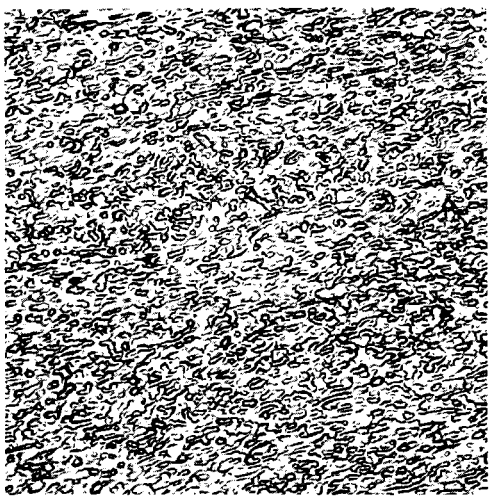
500X BMI N30936

c. Ti-2.2Fe-2.1Cr-2Mo fabricated and annealed in the alpha-beta field (1-1/2HF-3-1/2HNO_3)

500X Republic

d. Ti-8Mn annealed 1/2 hour at 1275 F and furnace cooled to 1000 F (2HF-5HNO_3)

FIGURE 32. MICROSTRUCTURES OF THE ANNEALED COMMERCIAL ALPHA-BETA ALLOYS Ti-4Al-3Mo-1V, Ti-8Mn, AND Ti-2.2Fe-2.1Cr-2Mo



500X MSM
E 6 UF

a. Ti-1Al-8V-5Fe annealed 1/2 hour at 1250 F, furnace cooled to 900 F, and air cooled ($2HF-4HNO_3$)

300X Rem-Cru
2957

b. Ti-13V-11Cr-3Al annealed 1 hour at 1400 F and air cooled ($1HF-2HNO_3$)

FIGURE 33. MICROSTRUCTURES OF THE ANNEALED COMMERCIAL ALPHA-BETA ALLOY Ti-1Al-8V-5Fe AND THE ALL-BETA COMMERCIAL ALLOY Ti-13V-11Cr-3Al

Heat-Treated Alloys

The properties of all of the alpha-beta alloys can be altered to some extent by heat treatment. However, only certain of the alpha-beta alloys have been developed as heat-treatable alloys. Others, developed previously as annealed alloys, are being used in the heat-treated condition. The heat treatment of titanium alloys has been described in detail in TML Report No. 87, and the general effect of the quench-and-age type of heat treatment on microstructures has been described in a previous section of this report. In this section typical structures of specific heat-treatable alloys are given, identified by composition and heat-treatment conditions.

Photomicrographs of the following alloys are given in Figures 34 through 40.

Alloy Composition, % (Balance Ti)	Figure
Ti-6Al-4V	34
Ti-7Al-4Mo	35
Ti-4Al-3Mo-1V	36
Ti-6Mo-3Al	37
Ti-4Al-4Mo-4V	37
Ti-5Al-1.5Fe-1.4Cr-1.2Mo	38
Ti-5Al-2.75Cr-1.25Fe	38
Ti-16V-2.5Al	39
Ti-1Al-8V-5Fe	40
Ti-13V-11Cr-3Al	40

RELATION OF STRUCTURES TO FABRICATION HISTORY

In the preceding section of this report, emphasis was placed on the relationship of microstructure to composition, phase diagrams and thermal history. These are the factors that govern the phases present in the structures and to a large extent the size and shape of the phases. However, in practice ideal microstructures are not always obtained. Microstructure can vary from place to place within an alloy as the result of fabrication history, inhomogeneity, or contamination. Oftentimes it may be difficult to determine what the cause of such differences is using microstructures alone. However, metallography can be used in conjunction with a knowledge of fabrication and heat-treatment history and alloy composition to indicate causes of failures, as quality control, and as a supplement to mechanical testing.

500X TMCA 9

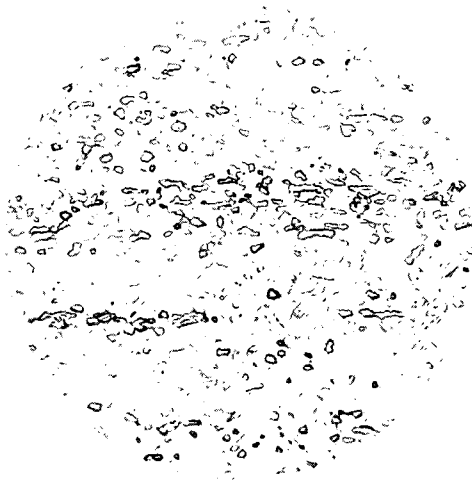
a. Ti-6Al-4V solution treated 1 hour at 1725 F and water quenched (Kroll etchant heat tinted)

500X MSM F 364 UF

b. Ti-6Al-4V solution treated 1 hour at 1700 F, water quenched; aged 2 hours at 1100 F and air cooled (10HF-5HNO_3)

300X Rem-Cru 2950

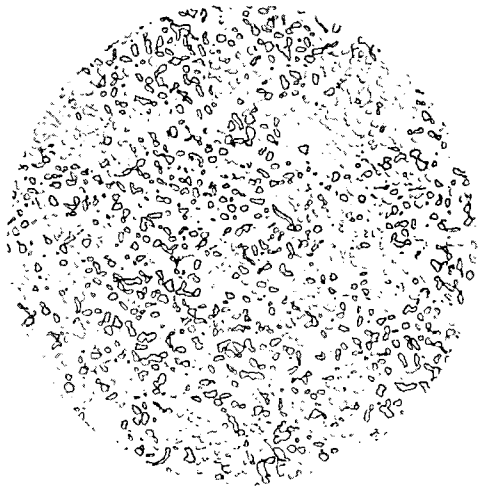
c. Ti-6Al-4V solution treated 1/4 hour at 1700 F and water quenched (1HF-2HNO_3)



300X Rem-Cru 2951

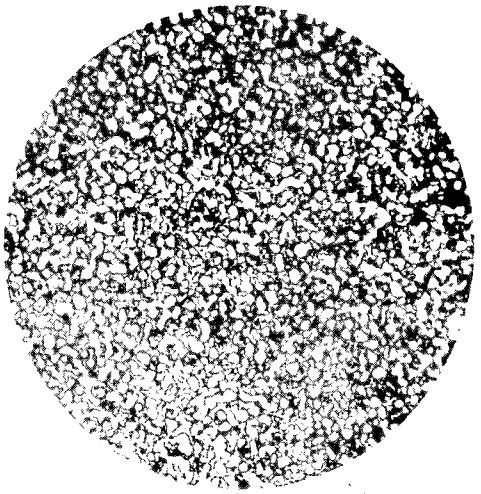
d. Ti-6Al-4V solution treated 1/4 hour at 1700 F, water quenched, and aged 4 hours at 1000 F (1HF-2HNO_3)

FIGURE 34. MICROSTRUCTURES OF THE COMMERCIAL ALLOY Ti-6Al-4V IN TWO SOLUTION-TREATED AND TWO SOLUTION-TREATED AND AGED CONDITIONS



300X Rem-Cru 2953

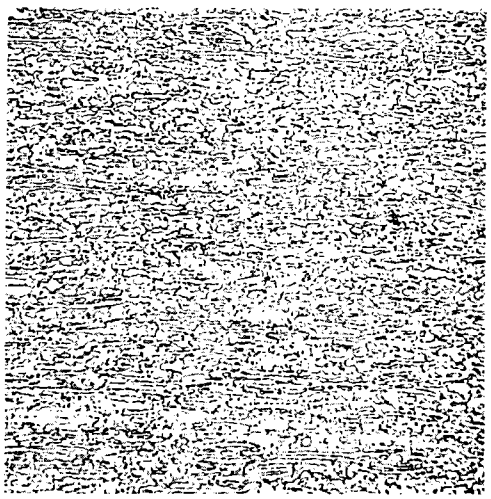
a. Ti-7Al-4Mo solution treated 1 hour at 1750 F and water quenched (1HF-2HNO3)



300X Rem-Cru 2954

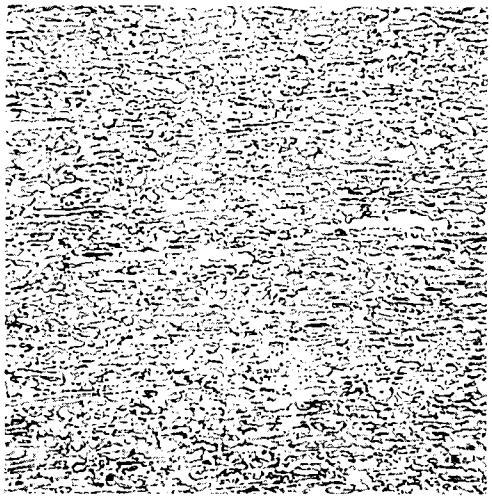
b. Ti-7Al-4Mo solution treated 1 hour at 1750 F, water quenched, and aged 16 hours at 1100 F (1HF-2HNO3)

FIGURE 35. MICROSTRUCTURES OF THE COMMERCIAL ALLOY Ti-7Al-4Mo AS SOLUTION TREATED AND SOLUTION TREATED AND AGED



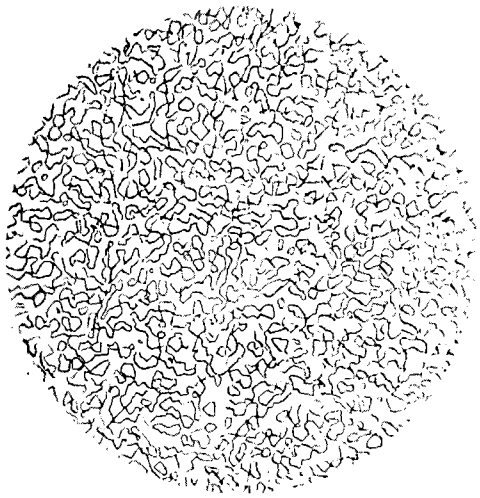
500X TMCA
11

a. Ti-4Al-3Mo-1V solution treated 10 minutes at 1650 F and water quenched (Kroll etchant)



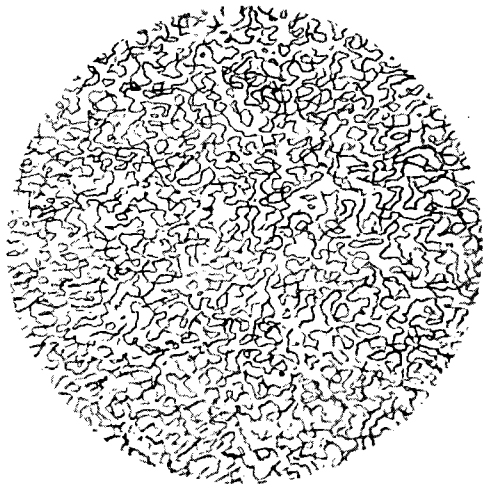
500X TMCA
12

b. Ti-4Al-3Mo-1V solution treated 10 minutes at 1650 F, water quenched; aged 12 hours at 900 F and air cooled (Kroll etchant)



750X Rem-Cru
1597

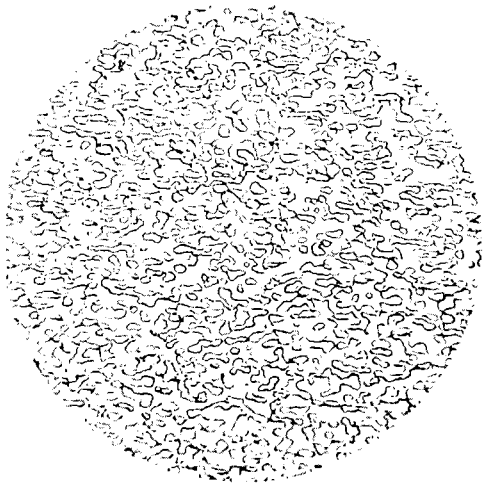
c. Ti-4Al-3Mo-1V solution treated 1/2 hour at 1600 F and water quenched (1HF-2HNO_3)



750X Rem-Cru
1751

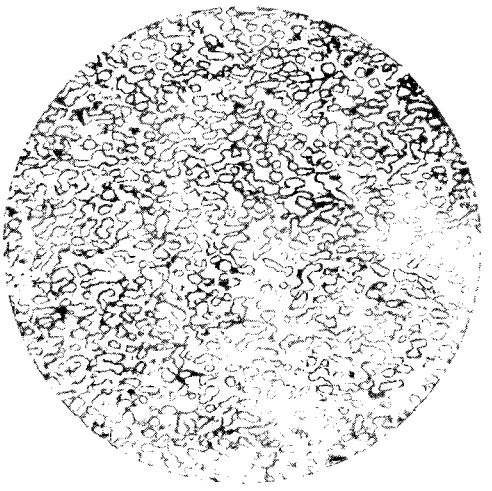
d. Ti-4Al-3Mo-1V solution treated 1/2 hour at 1600 F, water quenched, and aged 24 hours at 1000 F (1HF-2HNO_3)

FIGURE 36. MICROSTRUCTURES OF THE COMMERCIAL ALLOY Ti-4Al-3Mo-1V IN TWO SOLUTION-TREATED AND TWO SOLUTION-TREATED AND AGED CONDITIONS



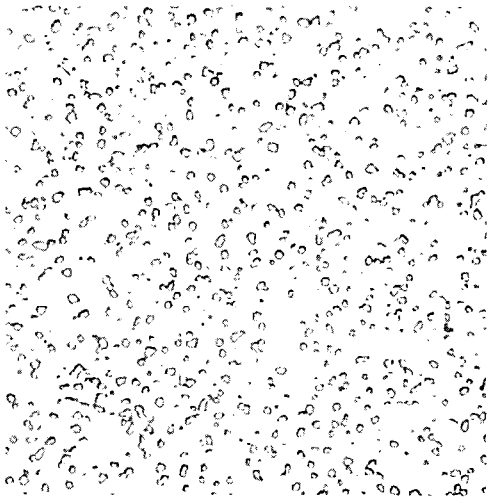
750X Rem-Cru 1589

a. Ti-6Mo-3Al solution treated 1/2 hour at 1550 F and water quenched (1HF-2HNO_3)



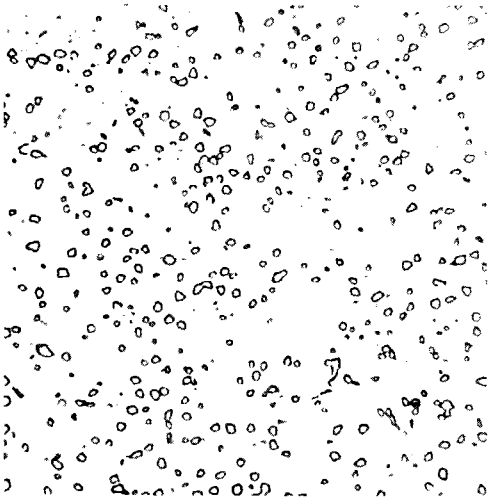
750X Rem-Cru 1815

b. Ti-6Mo-3Al solution treated 1/2 hour at 1550 F, water quenched, and aged 24 hours at 1000 F (1HF-2HNO_3)



1000X TMCA 3

c. Ti-4Al-4Mo-4V solution treated 10 minutes at 1550 F and water quenched (Kroll etchant)



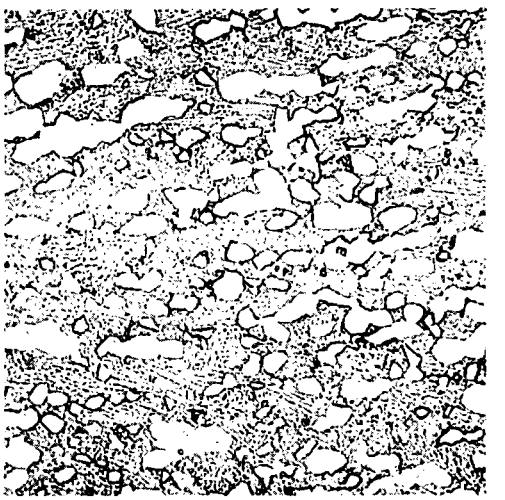
1000X TMCA 4

d. Ti-4Al-4Mo-4V solution treated 10 minutes at 1550 F, water quenched; aged 2 hours at 900 F, then air cooled (Kroll etchant)

FIGURE 37. MICROSTRUCTURES OF THE HEAT-TREATED COMMERCIAL ALLOYS Ti-6Mo-3Al AND Ti-4Al-4Mo-4V

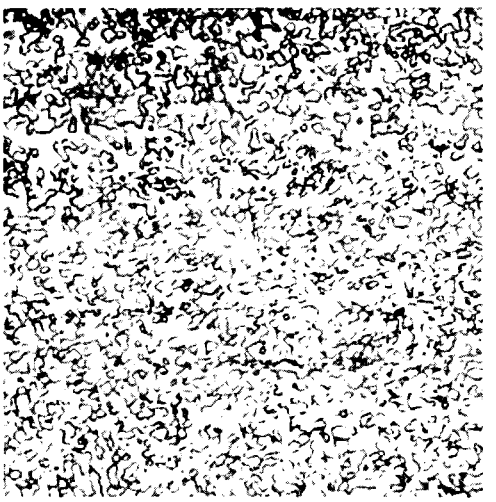
500X TMCA 6

a. Ti-5Al-1.5Fe-1.4Cr-1Mo solution treated 1 hour at 1650 F and water quenched (Kroll etchant)



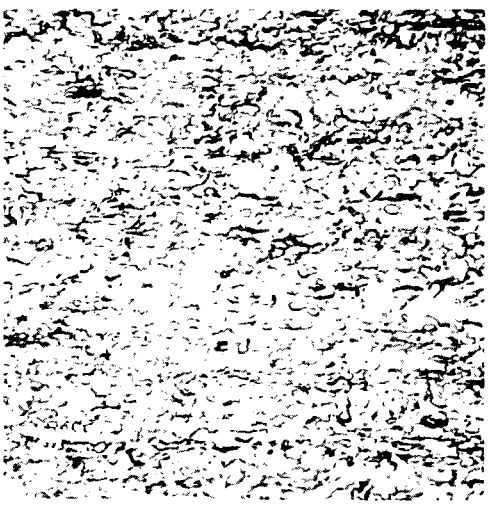
500X TMCA 7

b. Ti-5Al-1.5Fe-1.4Cr-1Mo solution treated 1 hour at 1650 F, water quenched; aged 6 hours at 1000 F, then air cooled (Kroll etchant)



500X Republic

c. Ti-5Al-2.75Cr-1.25Fe hot-rolled sheet (0.010 inch) solution treated 15 minutes at 1425 F and quenched ($2HF-5HNO_3$)



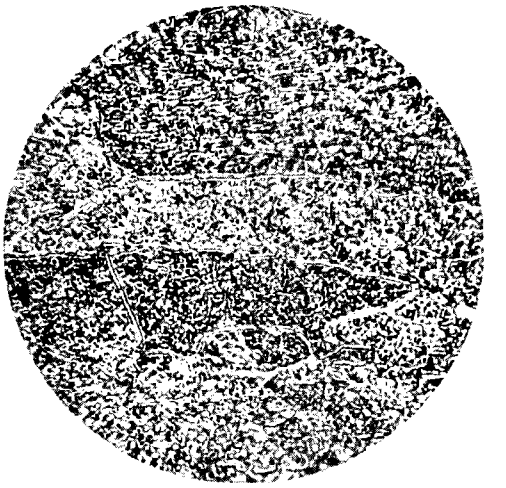
500X Republic

d. Ti-5Al-2.75Cr-1.25Fe hot-rolled sheet (0.010 inch) solution treated 15 minutes at 1425 F, quenched, and aged 6 hours at 1000 F ($2HF-5HNO_3$)

FIGURE 38. MICROSTRUCTURES OF HEAT-TREATED Ti-5Al-1.5Fe-1.4Cr-1Mo AND Ti-5Al-2.75Cr-1.25Fe ALLOYS

750X Rem-Cru 2334

a. Ti-16V-2.5Al solution treated 20 minutes at 1325 F and water quenched (1HF-2HNO_3)

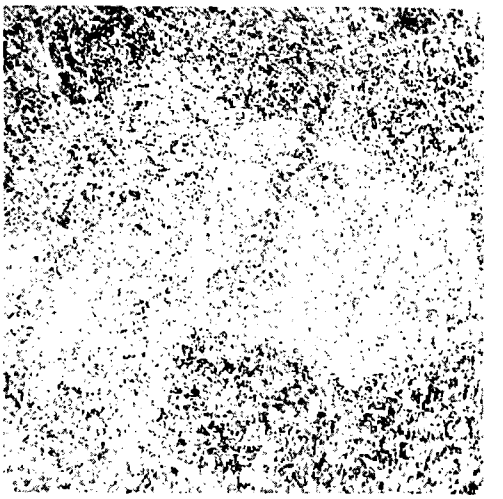


750X Rem-Cru 2335

b. Ti-16V-2.5Al solution treated 20 minutes at 1325 F, water quenched, and aged 12 hours at 900 F (1HF-2HNO_3)

500X MSM G 405 UF

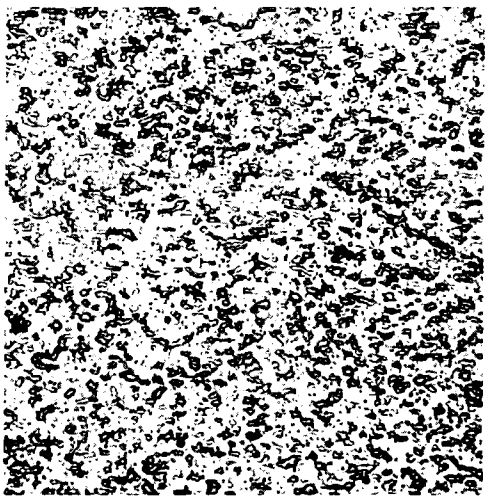
c. Ti-16V-2.5Al solution treated 1-1/2 hours at 1400 F and quenched (10HF-5HNO_3)



500X MSM G 106 UF

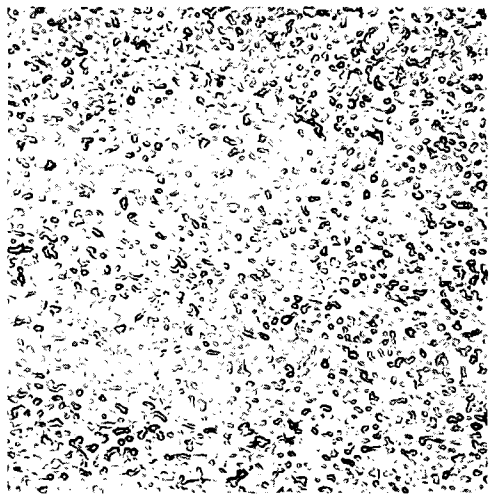
d. Ti-16V-2.5Al solution treated 1/2 hour at 1400 F, water quenched; aged 8 hours at 925 F, then air cooled (1HF-2HNO_3-50H_2O_2)

FIGURE 39. MICROSTRUCTURES OF THE COMMERCIAL ALLOY Ti-16V-2.5Al IN THREE HEAT-TREATED CONDITIONS



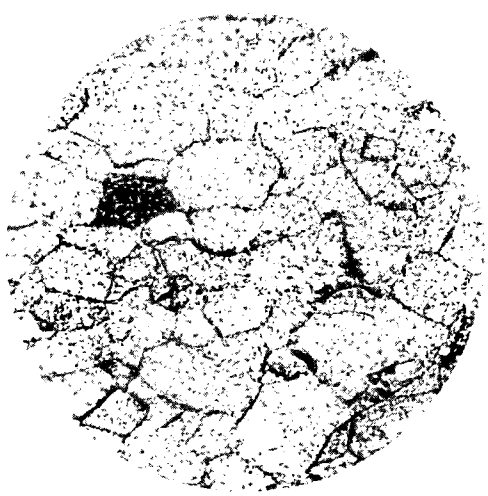
500X MSM
E 3 UF

a. Ti-1Al-8V-5Fe solution treated 1/2 hour at 1375 F and water quenched (2HF-4HNO_3)



500X MSM
E 4 UF

b. Ti-1Al-8V-5Fe solution treated 1/2 hour at 1375 F, water quenched; aged 8 hours at 900 F, and air cooled (2HF-4HNO_3)



300X Rem-Cru
2955

c. Ti-13V-11Cr-3Al solution treated 1/2 hour at 1550 F, water quenched, and aged 100 hours at 900 F (1HF-2HNO_3)

FIGURE 40. MICROSTRUCTURES OF THE COMMERCIAL ALLOYS Ti-1Al-8V-5Fe AND Ti-13V-11Cr-3Al AS HEAT TREATED

In the following sections of this report, the microstructures of many of the commercial alloys are related to prior history. To avoid repetition, these structures have been chosen to represent the types of structures apt to be encountered for selected alloys rather than for all of the alloys.

A general example of the effect of fabrication on microstructure is shown in Figure 41 for the Ti-6Al-4V alloy. The ideal microstructure for the annealed condition is shown in Figure 41a while the same alloy heated into the beta field (Figure 41b) and forged high in the alpha-beta field may have a considerably different structure. The structures shown in Figure 42 were found in two different sections of a part forged in the alpha-beta field after preheating in the beta field. Figure 42a was taken of an area which had considerably more reduction than that of Figure 42b.

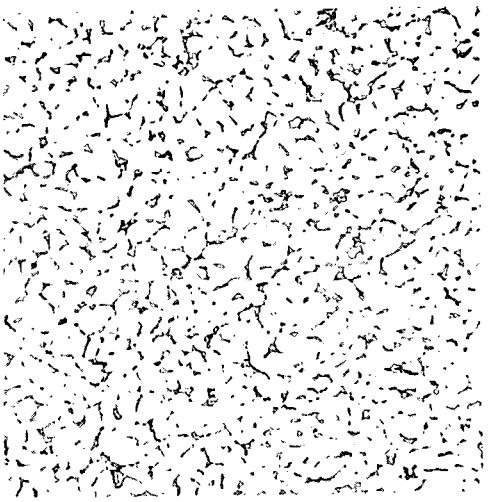
Forging

Of all the fabrication operations, forging probably has the greatest influence on the microstructure of titanium alloys. To obtain heavy reductions during forging it is necessary to use relatively high temperatures so that transformation structures may be encountered. Also, some sections of a forging may be worked to a greater extent than other sections, particularly in die forgings.

In an experimental forging study conducted at North American Aviation, Los Angeles, a variety of microstructures were obtained in a forged billet of Ti-4Al-4Mn alloy. These are shown in Figures 43 and 44. Figure 43 is a macrograph of the forged billet where the flow lines resulting from forging can be seen. The sequence of forging used in this study is also given in Figure 43. The variations in microstructure from Zone 1, where the structure is the result of heating into the beta field, to Zone 5, where the structure is the result of heavy reductions in the alpha-beta field, are shown in Figure 44.

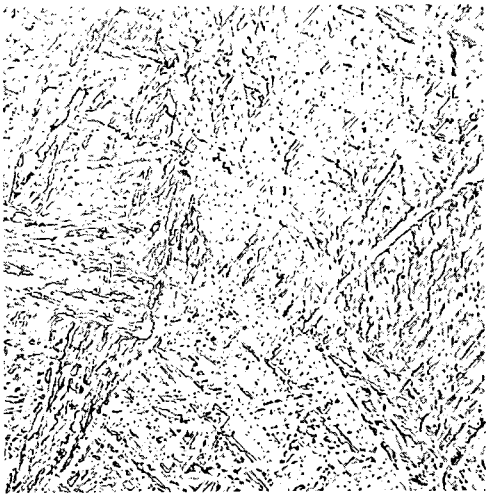
Another example of the effect of forging on the microstructure of the Ti-4Al-4Mn alloy is shown in Figure 45 for a die forging. In this example the forging was conducted in the alpha-beta field on an alloy which originally had a transformed beta structure. The gross structure seen in the macrograph shows the flow of the metal during forging. Microstructures of the various sections in the forging show relatively uniform structures composed of alpha and beta phases which are not significantly different from one section to another.

The microstructures of alpha-beta alloys with a prior history of fabrication and annealing in the alpha-beta field are not altered significantly by



500X N32241

a. Ti-6Al-4V fabricated and annealed in the alpha-beta field; structure is equiaxed alpha with beta in the alpha grain boundaries (1-1/2HF-3-1/2HNO_3)

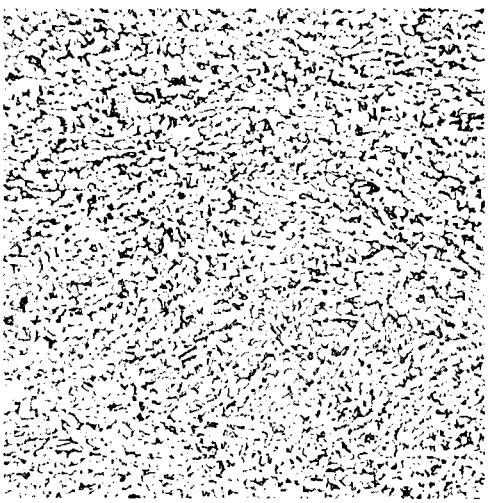


500X N32240

b. Ti-6Al-4V fabricated in the beta field and annealed in the alpha-beta field; structure is acicular alpha (transformed beta) with a small amount of beta dispersed between the alpha plates; large prior beta grain size is visible (1-1/2-HF-3-1/2HNO_3)

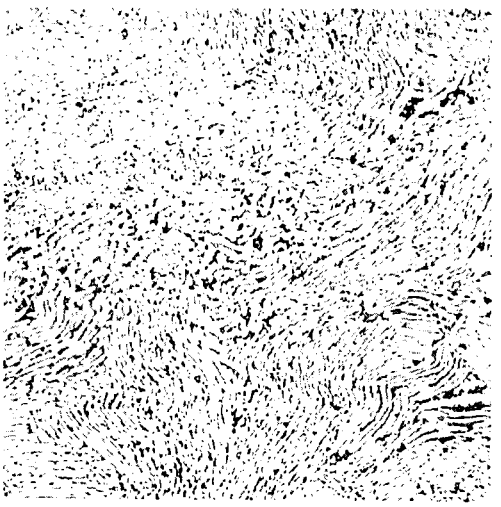
FIGURE 41. MICROSTRUCTURES OF THE COMMERCIAL ALLOY Ti-6Al-4V SHOWING THE EFFECT OF FABRICATION TEMPERATURE

(Battelle Memorial Institute)



250X N28530

a. Ti-6Al-4V forged section which had large amount of reduction in the alpha-beta field; structure is equiaxed alpha-beta (1-1/2HF-3-1/2HNO_3)



250X N28531

b. Ti-6Al-4V forged section which had a small amount of reduction in the alpha-beta field; alpha plates have not been sufficiently deformed to break up the acicular structure (1-1/2HF-3-1/2HNO_3)

FIGURE 42. THE EFFECT OF AMOUNT OF DEFORMATION ON MICROSTRUCTURE OF THE COMMERCIAL ALLOY Ti-6Al-4V

(Battelle Memorial Institute)

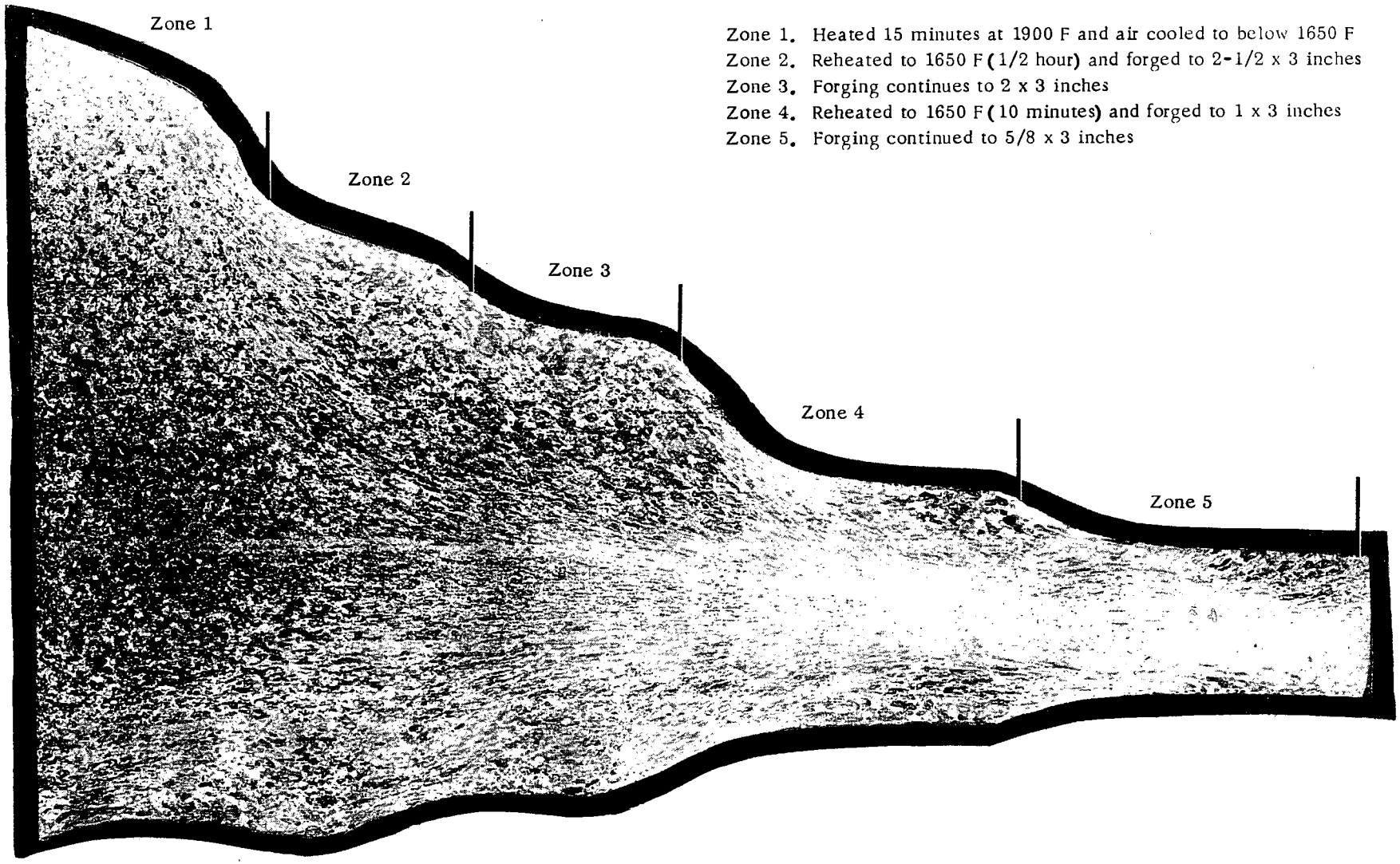


FIGURE 43. MACROSTRUCTURE OF A Ti-4Al-4Mn EXPERIMENTAL FORGING

Forging sequence given above. Initial condition: 9-inch billet forged to 3-1/2 x 3-inch slab at 1900 F. Etchant: 10HF - balance water.

(North American Aviation, Los Angeles)

75X

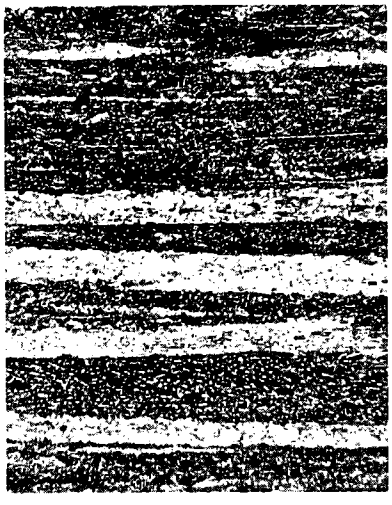
a. Zone 1

75X

b. Zone 2

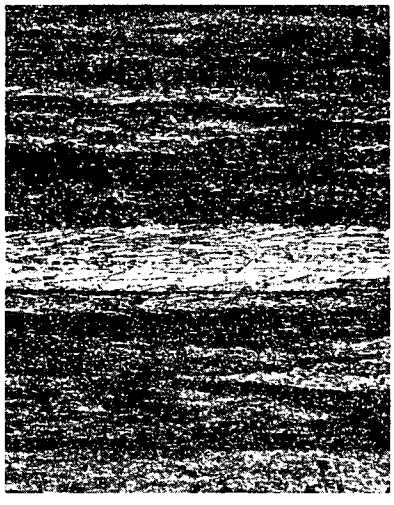
75X

c. Zone 3



75X

d. Zone 4



75X

e. Zone 5

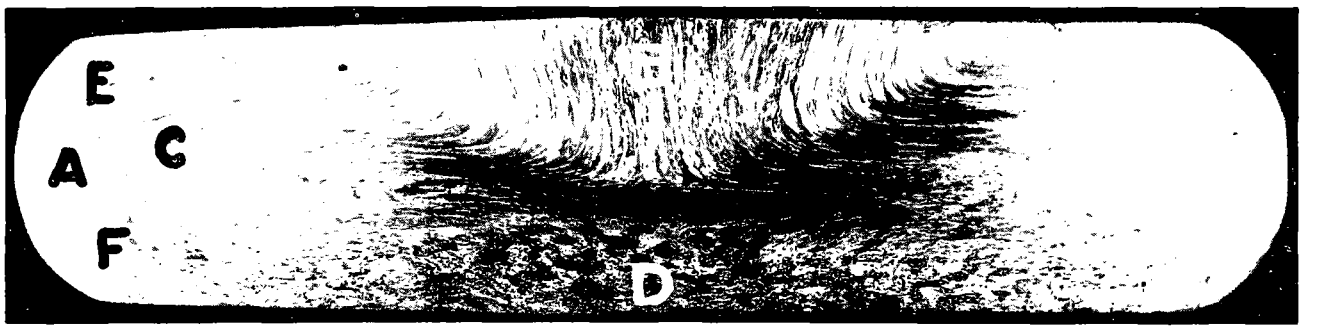
250X

f. Zone 5

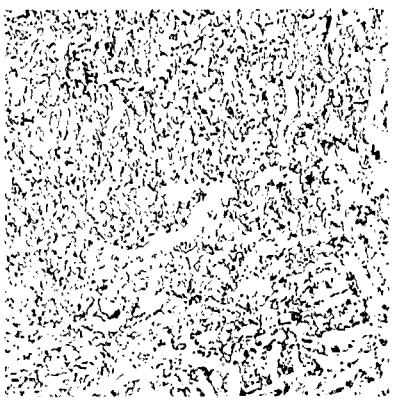
FIGURE 44. MICROSTRUCTURES TAKEN APPROXIMATELY IN THE CENTER OF EACH OF THE FIVE ZONES OF THE Ti-4Al-4Mn FORGING OF FIGURE 43

Etchant: 2HF-5HNO_3 - balance water

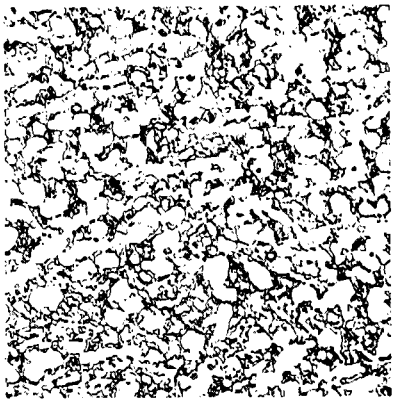
(North American Aviation, Los Angeles)



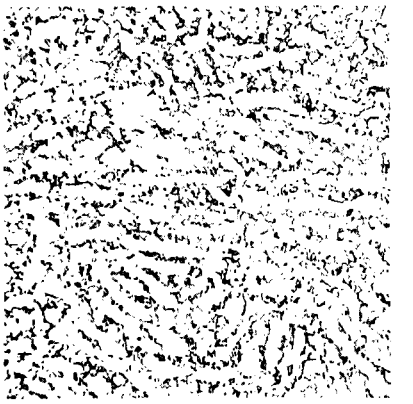
1-1/4X



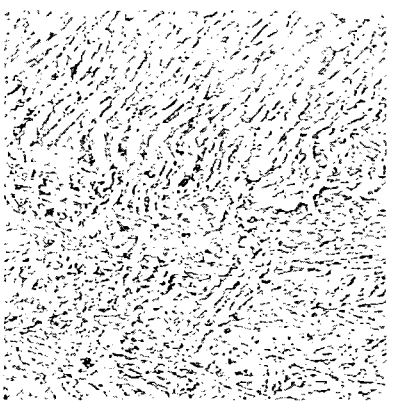
250X A



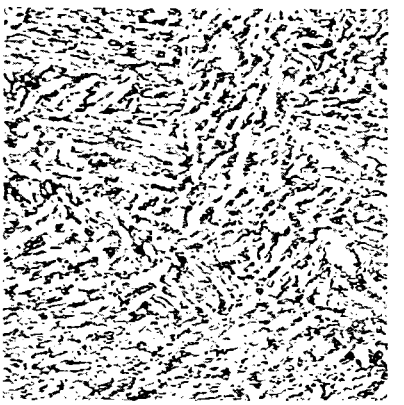
250X B



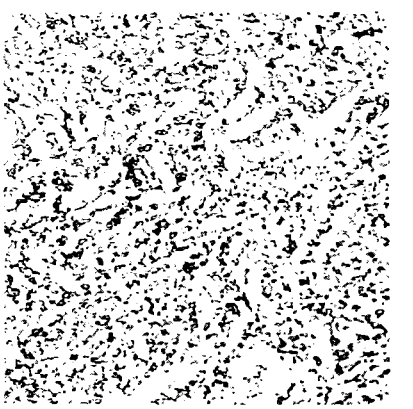
250X C



250X D



250X E



250X F

FIGURE 45. Ti-4Al-4Mn FORGING UPSET AND DIE FORGED AT 1450 F, AND ANNEALED 2 HOURS AT 1300 F AND AIR COOLED

50HF-50 glycerine etch

(Harvey Aluminum)

forging in the alpha-beta field. An example of this is shown in Figure 46 for a Ti-6Al-4V alloy bolt that was heated at 1500 F. Flow lines can be seen in the macrograph, but no significant difference is apparent between the unworked structure and the worked structure other than the better delineation of the beta phase in the unworked structure. Solution treating a bolt in the same condition produces the typical structure found in solution-treated Ti-6Al-4V alloy as shown in Figure 47.

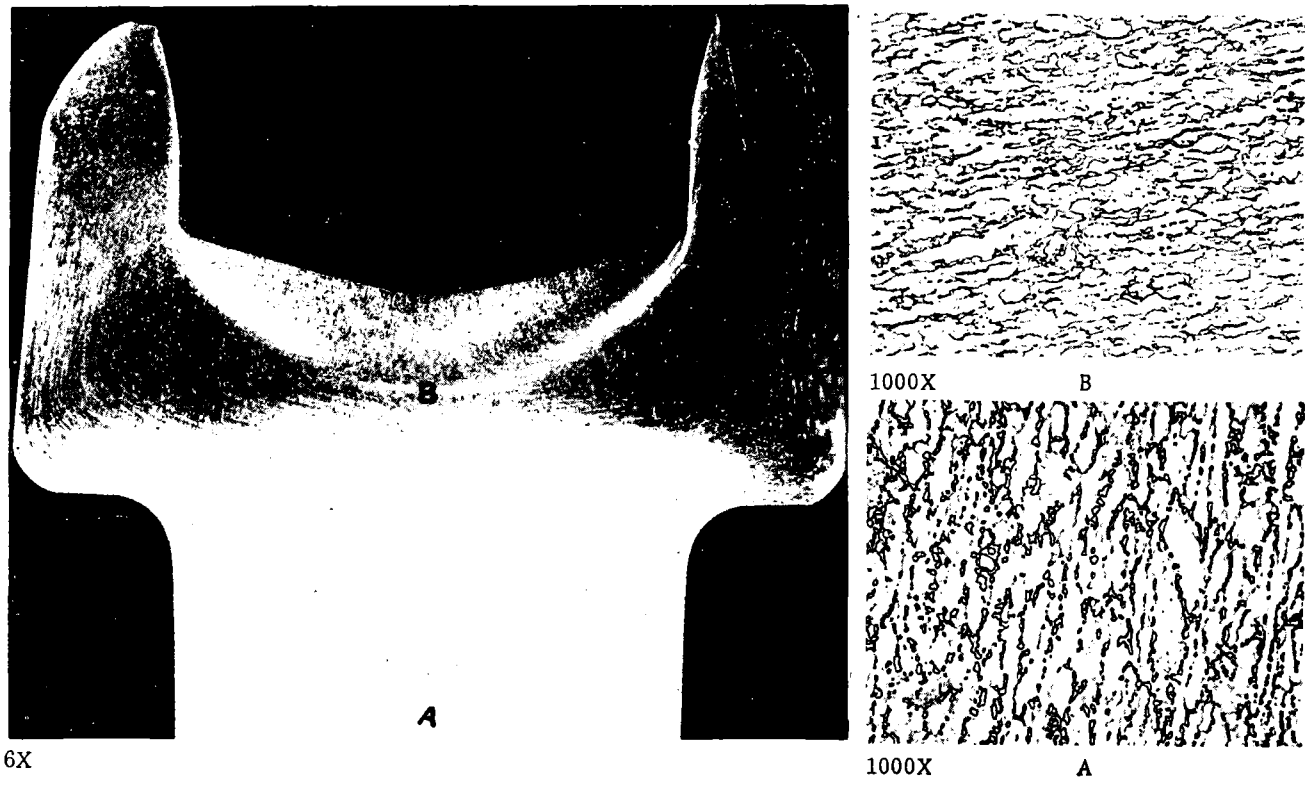


FIGURE 46. MICROSTRUCTURE OF A Ti-6Al-4V ALLOY BOLT HEADED AT 1500 F
1/2HF-1-1/2HCl-2-1/2HNO$_3$ etch
(North American Aviation, Downey, California)

Bolts forged in the alpha-beta field from alloys that have a transformed beta structure initially have structures similar to that shown in Figure 48. The section that has been heavily worked has a much finer grain structure typical of alpha-beta worked material while the unworked metal has the typical transformed beta structure.

Additional microstructures of titanium alloy forgings are shown in Figures 49 and 50. Details of the forging operation and subsequent thermal treatment are given for each structure.

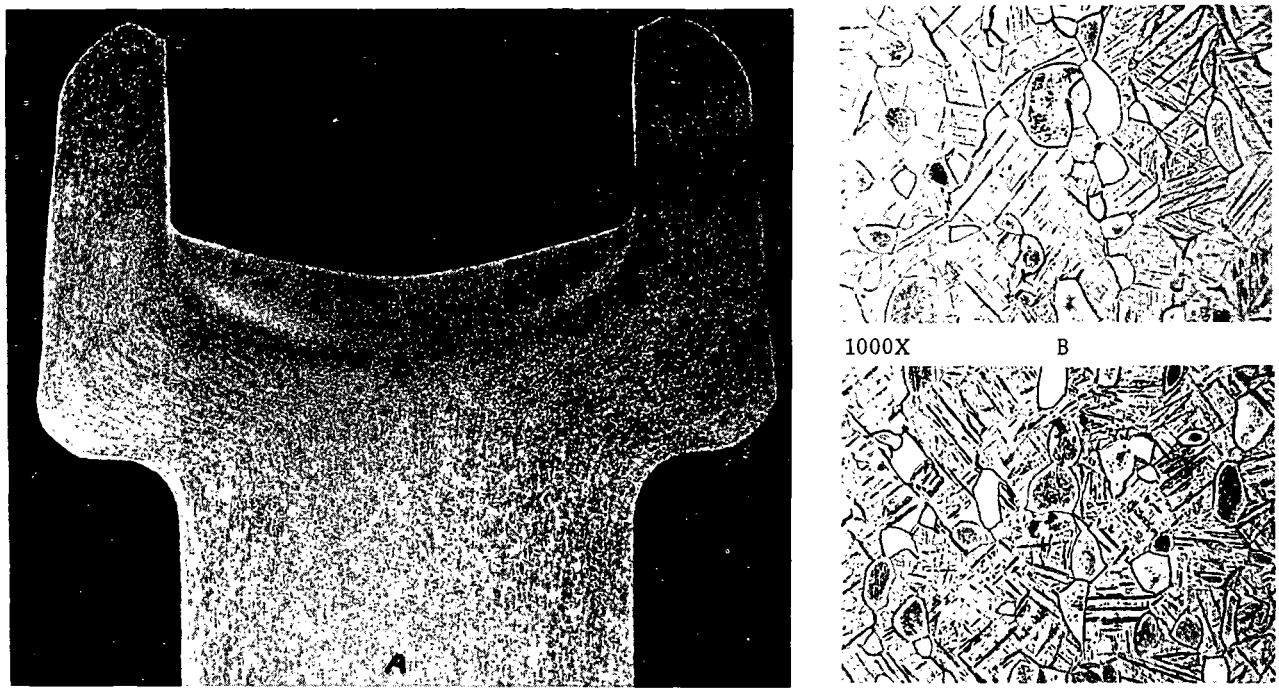


FIGURE 47. MICROSTRUCTURE OF A Ti-6Al-4V ALLOY BOLT HEADED AT 1500 F, AND SUBSEQUENTLY SOLUTION TREATED FOR 1/2 HOUR AT 1700 F AND QUENCHED

1/2HF-1-1/2HCl-2-1/2HNO_3 etch

(North American Aviation, Downey, California)

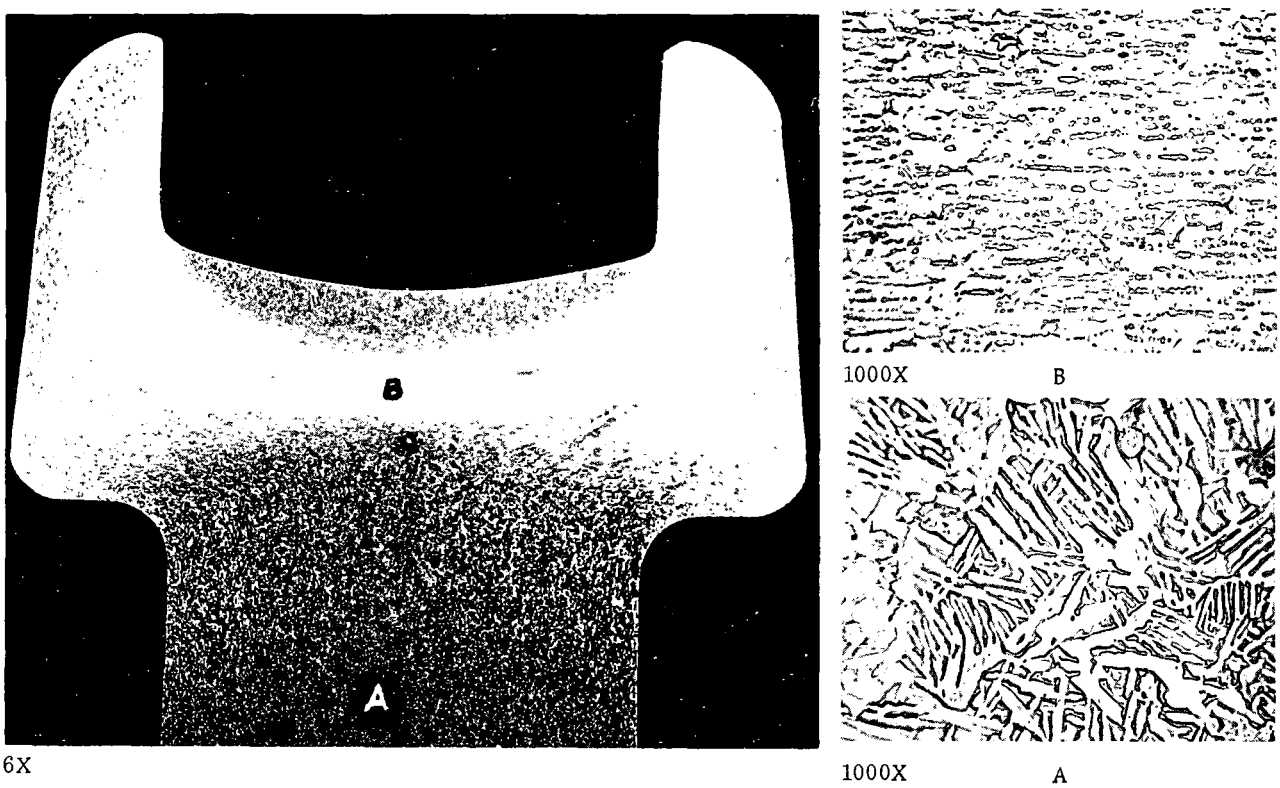


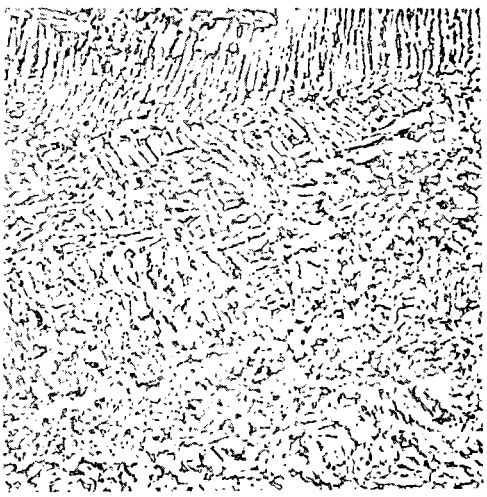
FIGURE 48. MICROSTRUCTURE OF A Ti-5Al-2.75Cr-1.25Fe ALLOY BOLT HEADED AT 1500 F

1/2HF-1-1/2HCl-2-1/2HNO_3 etch

(North American Aviation, Downey, California)

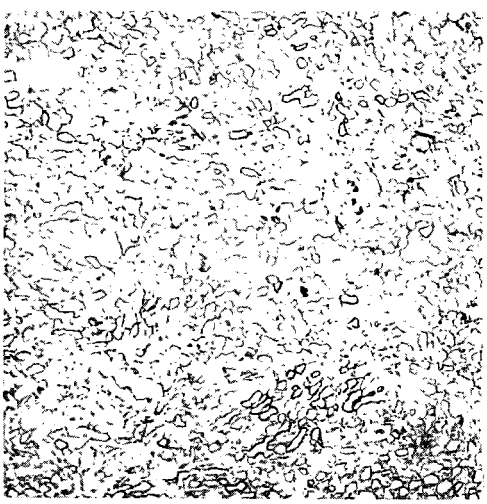
250X A1143

a. Forged at 1720 F



250X A1163

b. Forged at 1720 F and annealed 2 hours at 1300 F, furnace cooled to 1100 F, and air cooled



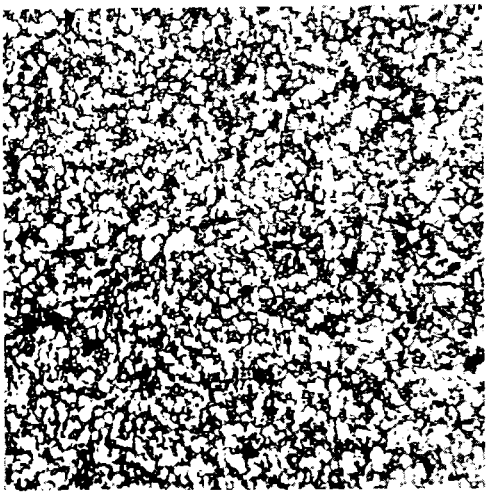
250X A1165

c. Forged, annealed as in b and heat treated 1 hour at 1700 F, quenched, and aged 3 hours at 1000 F

FIGURE 49. MICROSTRUCTURES OF A Ti-6Al-4V FORGING IN SEVERAL HEAT-TREATED CONDITIONS

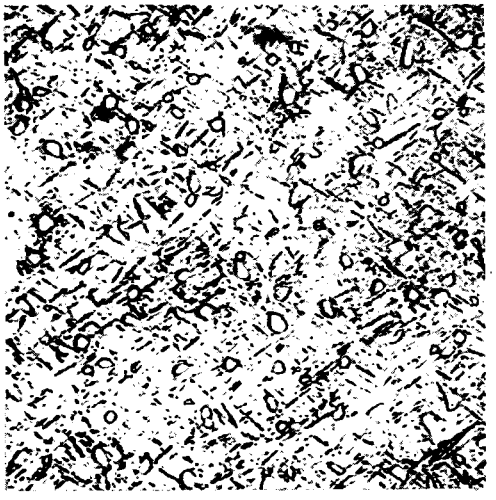
1HF-2HCl etch

(Douglas, El Segundo, California)



250X N76A

a. Forged at 1700 F



250X N76B

b. Forged at 1700 F, solution treated 1 hour at 1900 F, and quenched

250X N76C

Forged at 1700 F, solution treated 1 hour at 1925 F, and quenched

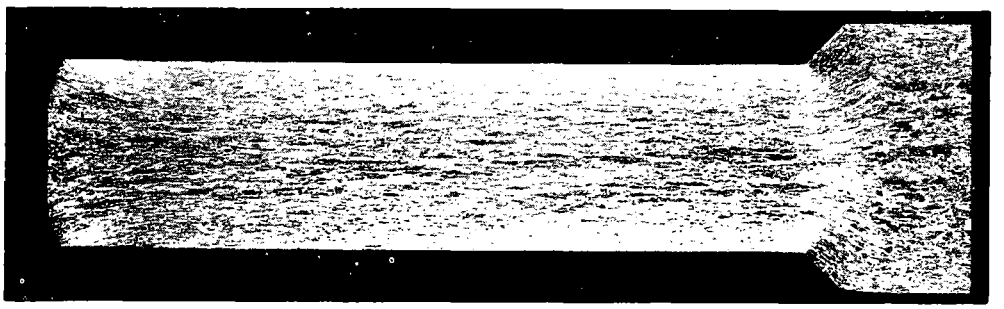
FIGURE 50. MICROSTRUCTURES OF A Ti-7Al-3Mo FORGING IN SEVERAL HEAT-TREATED CONDITIONS

50HF-50 glycerine etch

(Harvey Aluminum)

Extrusions

During extrusion metal is forced unidirectionally through a die so that the grains are elongated in one direction. If the extrusion temperature is below the recrystallization temperature the resulting macrostructure will appear like that shown in Figure 51 for extruded unalloyed titanium. The effect of extrusion temperature on the microstructure of an alpha alloy (Ti-5Al-2.5Sn) is shown in Figure 52. Extrusion in the alpha field (1700 F) produces a heavily worked structure of elongated alpha grains. Extrusion in the alpha-beta field (1800 F) produces a mixture of elongated alpha grains in a background of acicular alpha (transformed beta) while extrusion in the beta field (2000 F) results in an acicular alpha structure with no evidence of directionality. The acicular alpha structures are the result of transformation from beta during cooling after extrusion. It is interesting to note that the prior beta grain size of the alloy extruded at 2000 F is considerably smaller than that obtained in the same alloy annealed at 2000 F. Although recrystallization occurred during extrusion grain growth was considerably retarded.

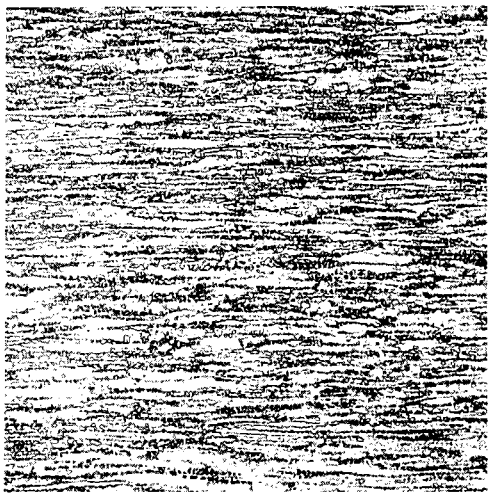


1X N22454

FIGURE 51. MACROGRAPH OF EXTRUDED UNALLOYED TITANIUM
5HF-35HNO3 etch
(Battelle Memorial Institute)

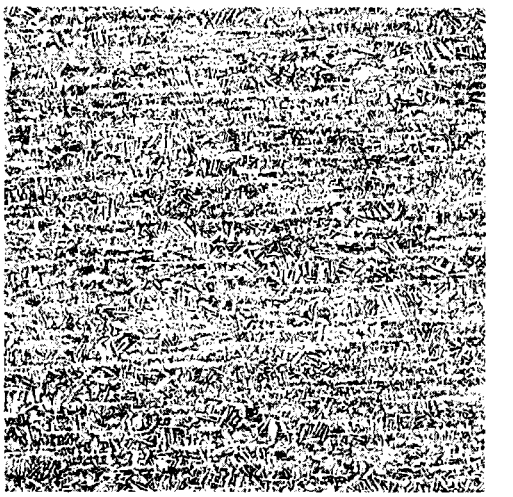
Photomicrographs of an extruded alpha-beta alloy (Ti-4Al-4Mn) are shown in Figure 53. Extrusion in the alpha-beta field (1600 F) produces elongated alpha grains in a matrix of transformed beta. In a transverse section of the same extrusion the alpha grains are more nearly equiaxed. Extrusion in the beta field permits recrystallization to occur, and the resulting structure is the typical transformed beta structure obtained on cooling an alpha-beta alloy from the beta field.

At times an apparently segregated structure may be obtained during extrusion. This can occur when the center of the bar becomes heated to a temperature above the beta transus during extrusion. An example of this is



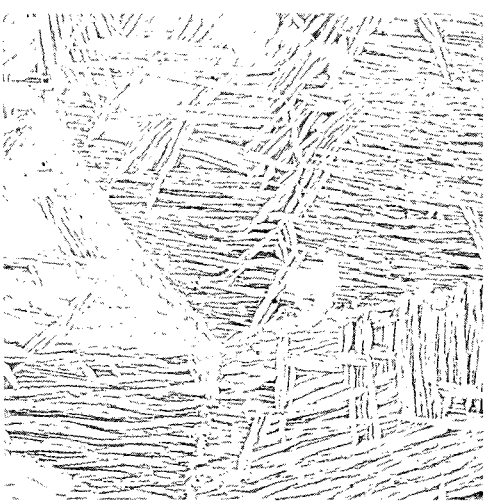
100X 513

a. Ti-5Al-2.5Sn alloy as extruded at 1700 F (25HF-25HNO_3-50 glycerine)



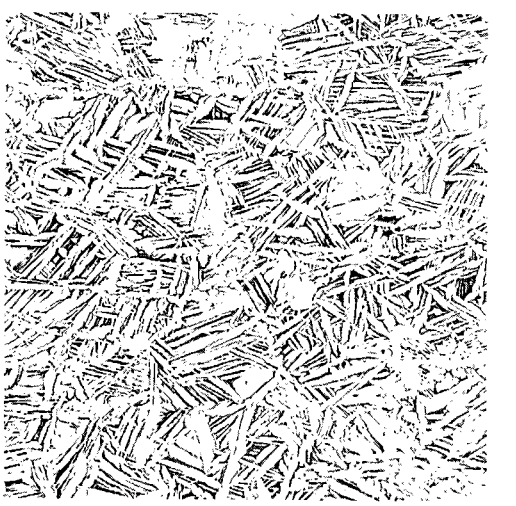
100X 514

b. Ti-5Al-2.5Sn alloy as extruded at 1800 F (25HF-25HNO_3-50 glycerine)



100X 521

c. Ti-5Al-2.5Sn alloy extruded at 1850 F, air-cool annealed at 2000 F for 1 hour, and air cooled (25HF-25HNO_3-50 glycerine)

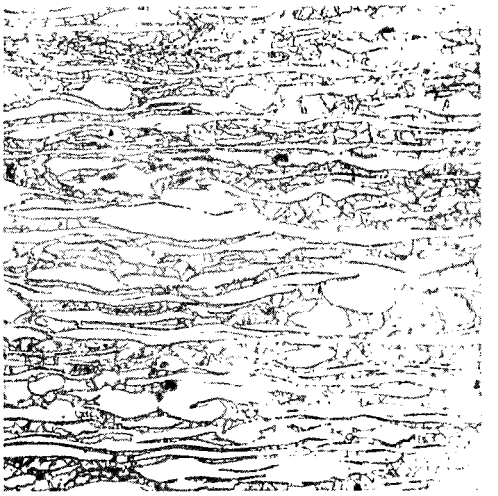


518

d. Ti-5Al-2.5Sn alloy as extruded at 2000 F (25HF-25HNO_3-50 glycerine)

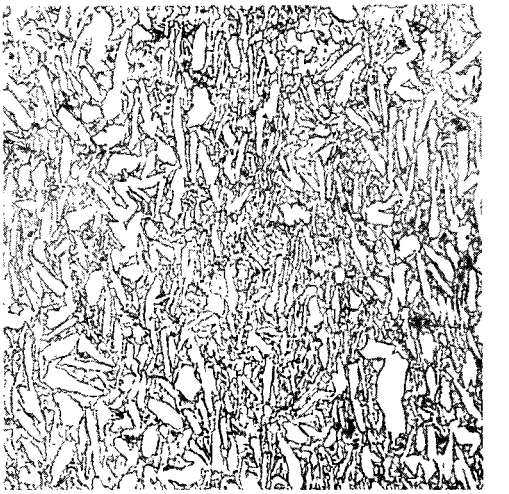
FIGURE 52. MICROSTRUCTURES OF Ti-5Al-2.5Sn ALLOY EXTRUDED AT VARIOUS TEMPERATURES

(Harvey Aluminum)



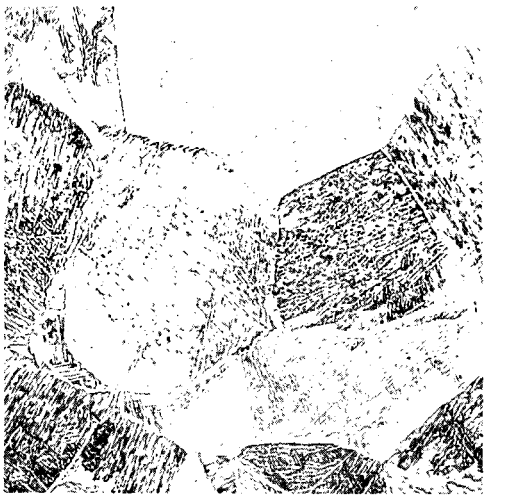
250X 123BL

a. Ti-4Al-4Mn longitudinal section as extruded at 1600 F (20HF-20HNO_3-60 glycerine)



250X 123BT

b. Ti-4Al-4Mn transverse section as extruded at 1600 F (20HF-20HNO_3-60 glycerine)



250X 171L

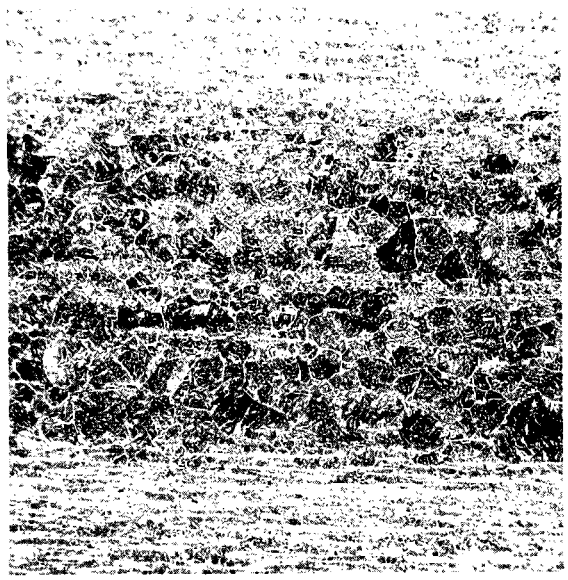
c. Ti-4Al-4Mn as extruded in the beta field at 1750 F (20HF-20HNO_3-60 glycerine)

FIGURE 53. MICROSTRUCTURES OF THE ALPHA-BETA Ti-4Al-4Mn ALLOY EXTRUDED IN THE ALPHA-BETA AND BETA FIELDS

(Harvey Aluminum)

shown in Figure 54. The metal near the surface of the extruded bar has a structure similar to that for the Ti-4Al-4Mn alloy extruded in the alpha-beta field while the center section of the bar has a transformed beta structure similar to the bar extruded in the beta field.

Other examples of extrusions are shown in Figure 55 for the Ti-7Al-3Mo alloy and Figure 56 for the Ti-3Al-5Cr alloy.



50X 147L

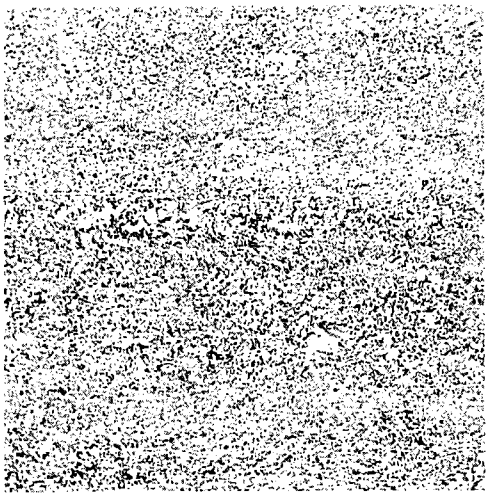
Ti-4Al-4Mn extruded at 1600 F, annealed 1 hour at 1400 F, then furnace cooled at 100 F per hour (20HF-20HNO_3-60 glycerine)

FIGURE 54. MICROSTRUCTURE OF THE ALPHA-BETA Ti-4Al-4Mn ALLOY EXTRUDED IN THE ALPHA-BETA FIELD; CENTER OF THE BAR HEATED ABOVE THE BETA TRANSUS DURING EXTRUSION

(Harvey Aluminum)

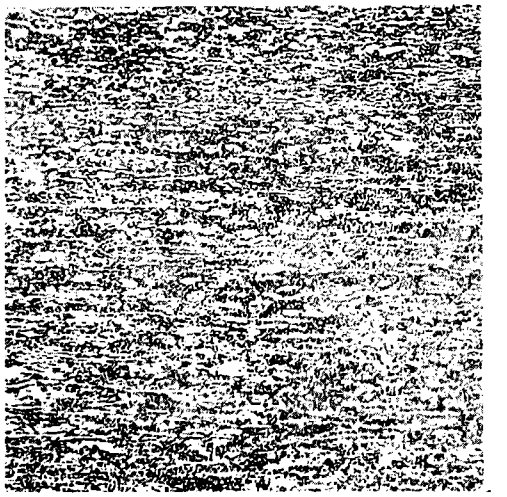
Welding and Brazing

When a metal is welded a portion of the metal becomes liquid for a short period of time and then freezes and cools rapidly to room temperature. The microstructures obtained in such a process are representative of cast structures in the areas which had become molten during the welding operation. During welding the temperature of the solid metal on either side of the fused metal will vary from the melting point of the metal down to room temperature. The microstructure in this zone, known as the heat-affected zone, will vary dependent upon the effects of heating on the microstructure. Thus, in welded alloys, one can expect to find three different structures, the weld zone, the heat-affected zone, and the base metal.



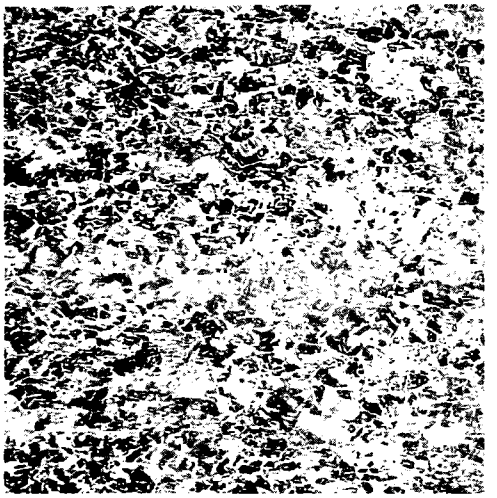
100X 637

a. Ti-7Al-3Mo as extruded at 1600 F (20HF-20HNO_3-60 glycerine)



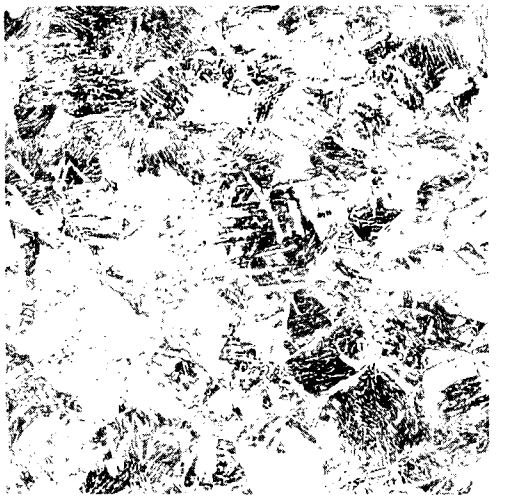
250X 17FB

b. Ti-7Al-3Mo as extruded at 1700 F (20HF-20HNO_3-60 glycerine)



100X 618

c. Ti-7Al-3Mo as extruded at 1800 F (20HF-20HNO_3-60 glycerine)

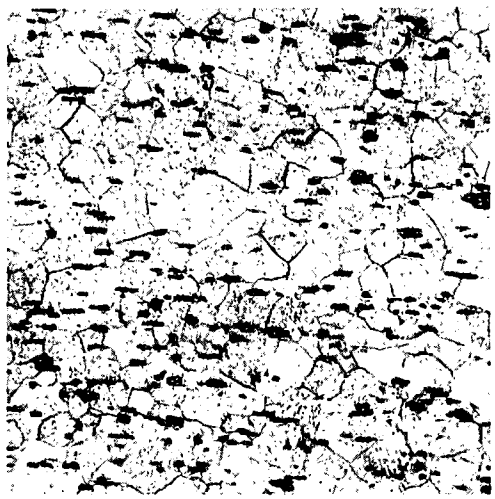


100X 600

d. Ti-7Al-3Mo as extruded at 2000 F (20HF-20HNO_3-60 glycerine)

FIGURE 55. MICROSTRUCTURES OF THE Ti-7Al-3Mo ALLOY EXTRUDED AT FOUR DIFFERENT TEMPERATURES

(Harvey Aluminum)



100X 26L

a. Ti-3Al-5Cr (high carbon) as extruded at 1750 F (25HF-25HNO_3-50 glycerine)

250X 101L

b. Ti-3Al-5Cr (low carbon) as extruded at 1750 F (25HF-25HNO_3-50 glycerine)

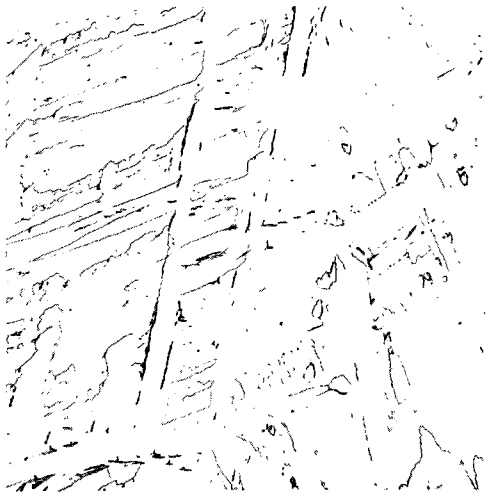
FIGURE 56. MICROSTRUCTURES OF THE Ti-3Al-5Cr ALLOY EXTRUDED AT 1750 F (Harvey Aluminum)

In titanium, which undergoes an allotropic transformation, the structure of the weld zone can be related to some extent to the transformation characteristics of the alloy.

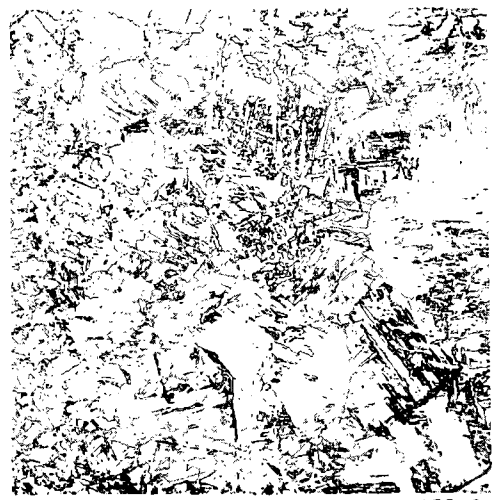
In unalloyed titanium the weld zone may appear as illustrated in Figure 57a. Here, the structure is shown at a high magnification to show the transformation product that is formed on cooling. Note that the grain size is very large, typical of an as-cast structure. At lower magnification the transition between base metal and weld zone can be seen, as illustrated in Figure 57b. In this structure the heat-affected zone is very narrow.

Soluble impurities in titanium have little effect on the structure of welds, at least in the quantities in which they are normally present in titanium. Thus, oxygen and nitrogen contamination of welds cannot be detected by metallographic examination. However, they do have a detrimental effect on the ductility of welds and may cause cracking during cooling. Carbon, on the other hand, is relatively insoluble in titanium compared to oxygen and nitrogen. When titanium containing over about 0.2 per cent carbon is welded, the TiC phase freezes out of the melt in a network pattern which is detrimental to ductility. Structures of the weld zone and heat-affected zone of a Ti-0.5C alloy are shown in Figure 58. The carbide network appears both in the prior beta grain boundaries and within the prior beta grains.

As was shown earlier in this report, transformation structures are dependent on alloy content. Similarly, the structure of welds will be dependent on alloy content because the weld structure is basically an as-cast structure that transforms on cooling through the transformation temperature range. The series of photomicrographs shown in Figure 59 illustrates the weld structures obtained in alpha Ti-Al alloys while those in Figure 60 show the effects of molybdenum content on the microstructure of welds. All of these structures are characterized by large grain sizes and various transformation structures. The change in transformation structure of the Ti-Mo alloys with composition is similar to that shown in Figure 17 where the effect of alloy content on transformed beta structures was described. However, in addition to the transformation structures welds may also show segregation caused by the difference in composition between the liquidus and solidus of the alloy. Such segregation can be seen in the Ti-15Mo alloy in Figure 60e. Another example of segregation is shown in Figure 61 for a weld in a Ti-15Cr alloy which had been reheated into the beta field and quenched to retain the beta phase. The dendritic interstices are lean in chromium and transform while the matrix is rich in chromium and beta is retained during cooling. Also, some $TiCr_2$ particles can be seen in the beta grain boundaries.



a. Weld metal



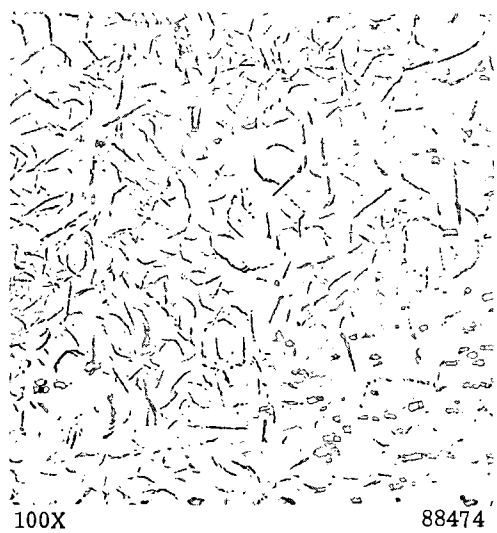
b. Base-metal heat-affected zone and weld metal

FIGURE 57. MICROSTRUCTURES OF WELDS IN UNALLOYED TITANIUM

As-welded condition, welded in inert atmosphere chamber; 1-1/2HF-3HNO_3 etch

(Battelle Memorial Institute)

a. Weld metal

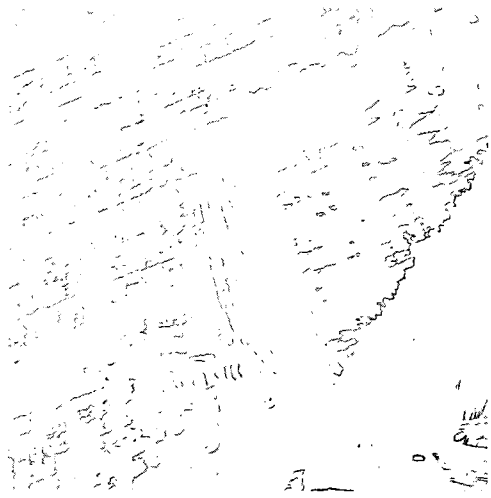


b. Heat-affected zone

FIGURE 58. MICROSTRUCTURES OF WELDS IN TITANIUM CONTAINING 0.5 PER CENT CARBON

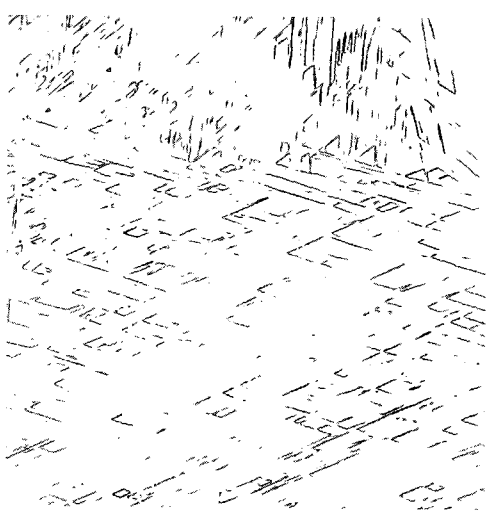
As-welded condition; 1-1/2HF-3HNO_3 etch

(Battelle Memorial Institute)



250X N4683

a. Ti-3Al



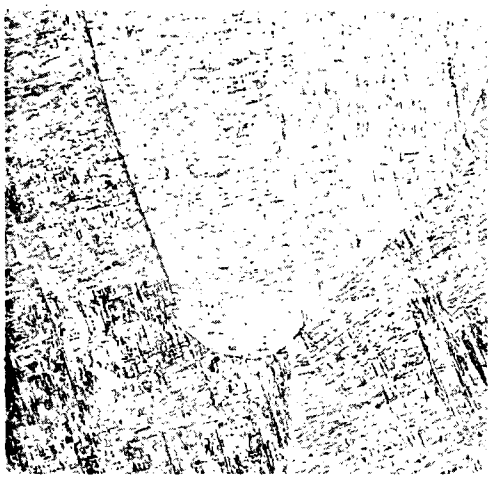
250X N4685

b. Ti-5Al

FIGURE 59. MICROSTRUCTURES OF WELDS IN BINARY TITANIUM-ALUMINUM ALLOYS
As-welded condition; 1-1/2HF-3HNO_3 etch
(Battelle Memorial Institute)

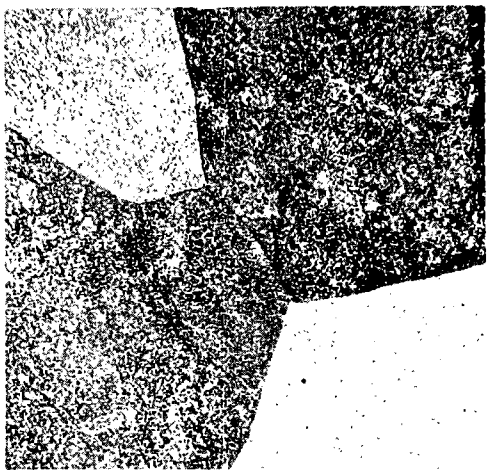
250X 97946

a. Ti-1Mo



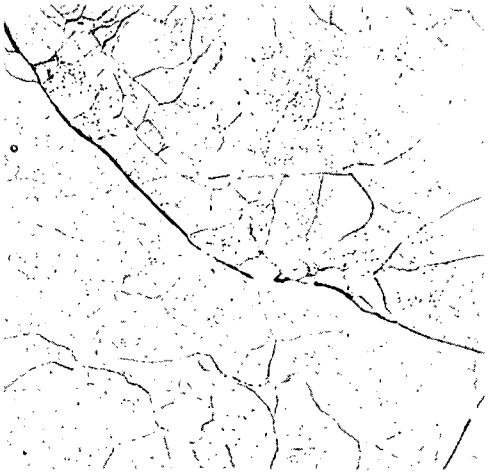
250X 97949

b. Ti-3Mo



250X 97904

c. Ti-6Mo



250X 97915

d. Ti-10Mo

100X 94604

e. Ti-15Mo

FIGURE 60. MICROSTRUCTURES OF WELDS IN BINARY TITANIUM-MOLYBDENUM ALLOYS
As-welded condition; 1-1/2HF-3HNO_3 etch
(Battelle Memorial Institute)

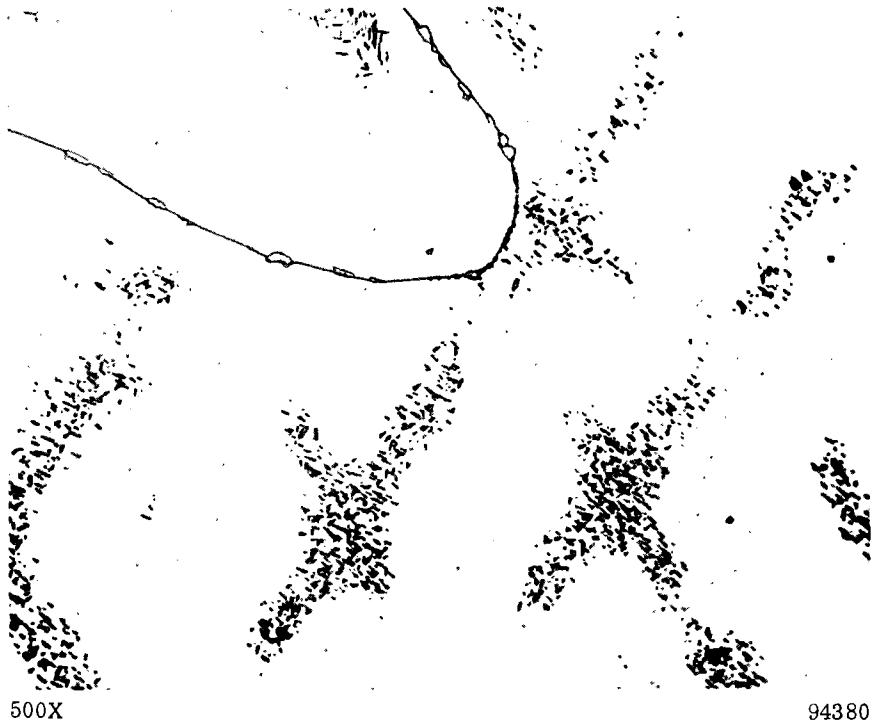
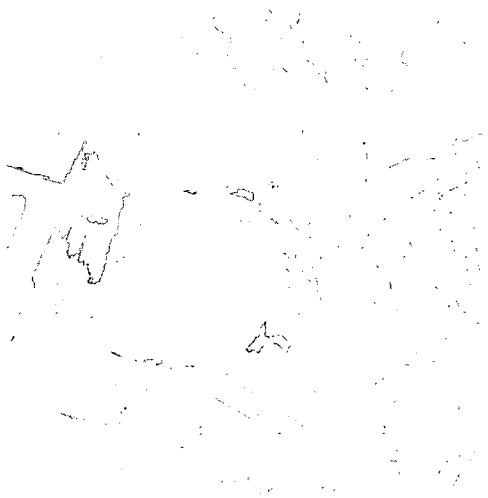


FIGURE 61. MICROSTRUCTURE OF WELD ZONE IN A Ti-15Cr ALLOY HEATED INTO THE BETA FIELD AND QUENCHED AFTER AGING

1-1/2HF-3HNO_3 etch

(Battelle Memorial Institute)

Microstructures of welds in commercial alloys are very similar to those shown previously for experimental alloys. Welds in A-110AT have the same types of structures shown previously for the Ti-Al alloys, characterized by large prior beta grain size and a coarse transformation structure; a typical structure is shown in Figure 62. In alpha-beta alloys a typical sequence of structures going from the base metal to the weld zone is shown in Figure 63 for the Ti-6Al-4V alloy. In this sequence three overlapping micrographs were taken to illustrate the transition in microstructure from the base metal through the heat-affected zone to the weld metal. The heat-affected zone is quite narrow and there is a rapid transition from the equiaxed alpha-beta structure to the coarse-grained transformed beta structure. A similar sequence of photomicrographs (Figure 64) shows the structures encountered in welding RS-110B (Ti-2.25Al-3.75Mn). These micrographs were taken at a very high magnification to show the fineness of the transformation structure. Note the very large difference in beta grain size between Area C, heat-affected zone, and Area D, weld zone. In that part of the heat-affected zone shown in Area C, the temperature did not get high enough to transform all of the alpha to beta phase. The small amount of alpha remaining inhibited beta grain growth.

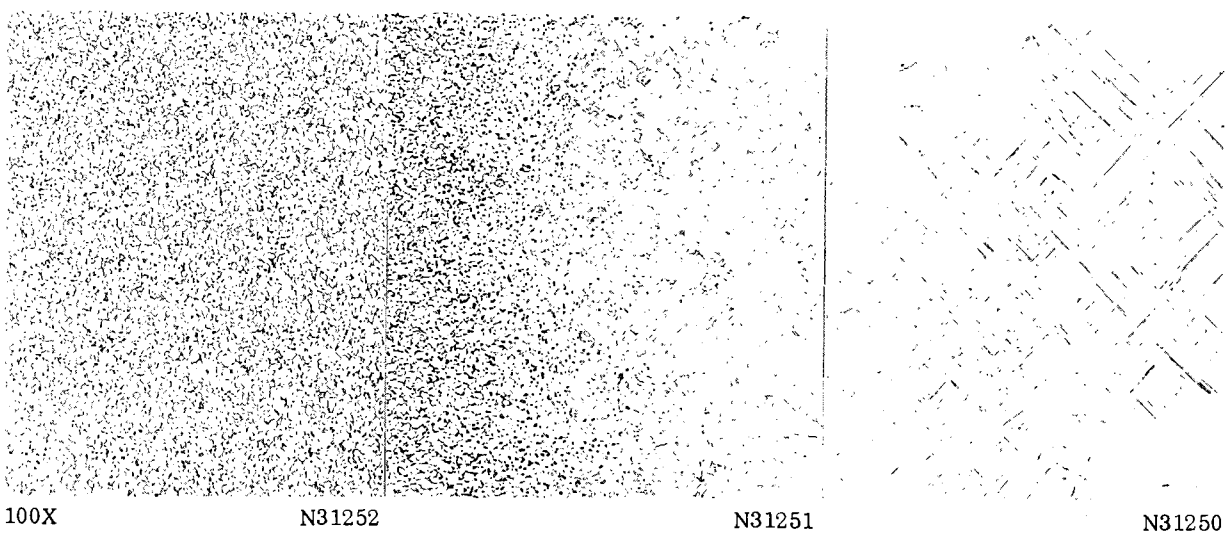


100X N37922

FIGURE 62. MICROSTRUCTURE OF THE WELD ZONE IN AS-WELDED Ti-5Al-2.5Sn

1-1/2HF-3HNO_3 etch

(Battelle Memorial Institute)



100X N31252 N31251 N31250

FIGURE 63. MICROSTRUCTURE OF THE BASE METAL, HEAT-AFFECTED ZONE, AND WELD ZONE IN AS-WELDED Ti-6Al-4V

1-1/2HF-3HNO_3 etch

(Battelle Memorial Institute)

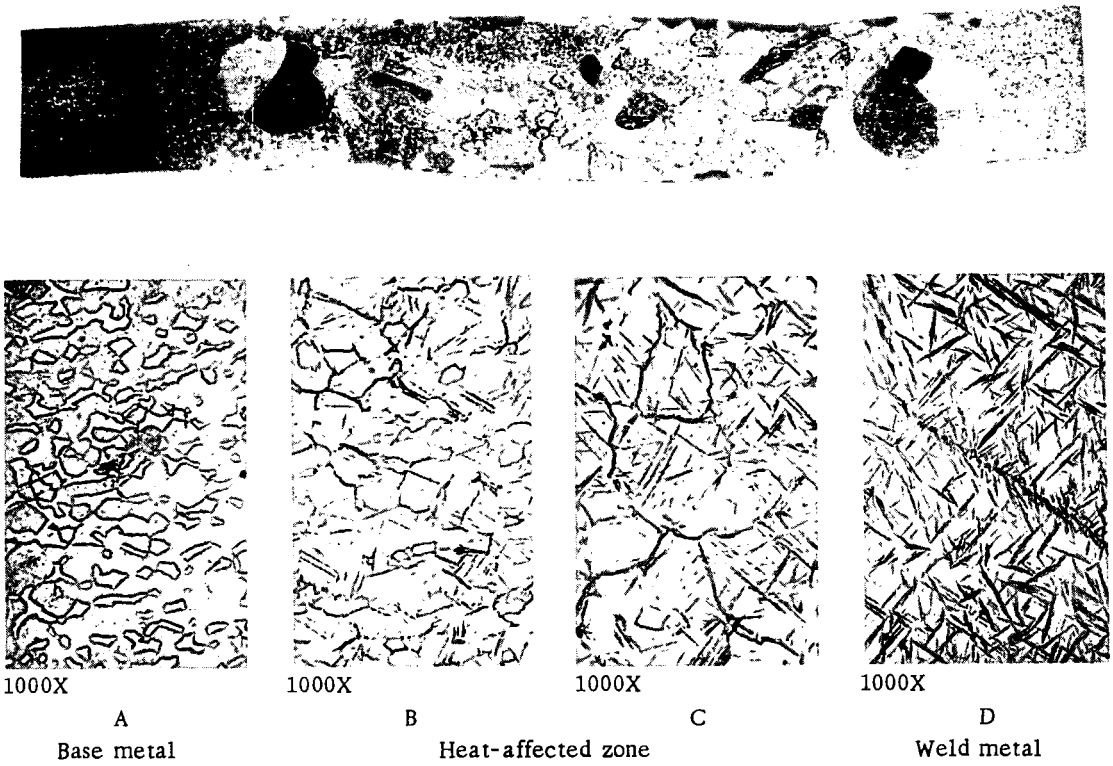
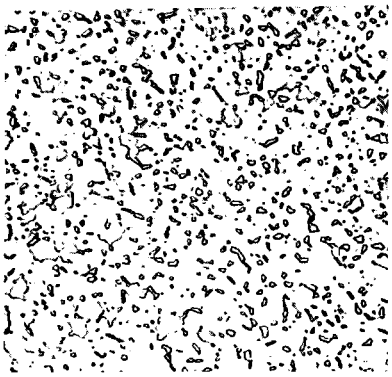


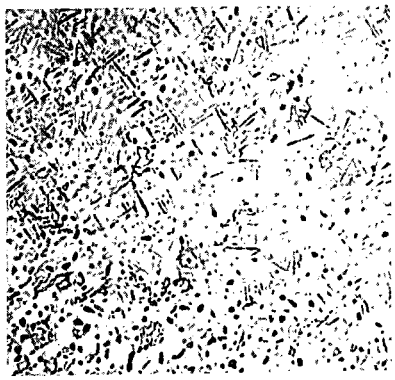
FIGURE 64. MICROSTRUCTURES OF Ti-2.25Al-3.75Mn ALLOY FUSION-HELIARC WELDED
As-welded condition; 1/2HF-1-1/2HCl-2-1/2HNO_3 etch
(North American Aviation, Downey, California)

When two different alpha-beta alloys are joined by welding, the microstructure will depend on the compositions of the two alloys. Generally, there is little difference in structures between alpha-beta alloys except for the quantity of beta phase in the structure and possibly the size and shape of the transformation products. One example of the structures found in a weld joint between RS-110B (Ti-2.25Al-3.75Mn) and Ti-6Al-4V using Ti-6Al-4V filler metal is shown in the sequences of photomicrographs in Figure 65. The chief difference between the two base metal structures is in the quantity of beta phase present. The RS-110B alloy contains more beta phase than does the Ti-6Al-4V alloy. In the weld zone near the RS-110B parent metal, the transformation product is much finer than that near the Ti-6Al-4V parent metal. This probably is the result of the greater beta-stabilizing tendency of manganese as compared to vanadium, giving rise to finer transformation structures.

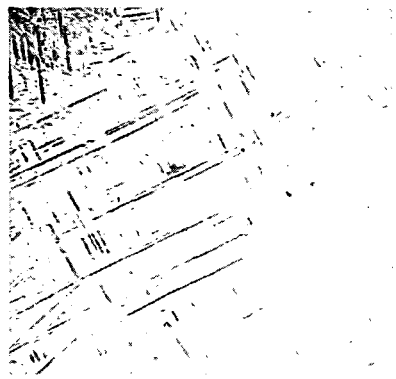
Another example of welds with dissimilar alloys is shown in Figure 66 for a welded Ti-7Mn alloy using unalloyed titanium filler metal. In this structure, the large columnar grains of the weld zone, the recrystallized grains in the heat-affected zone, and the wrought structure of the base metal can readily be seen.



500X
a. Ti-6Al-4V base metal

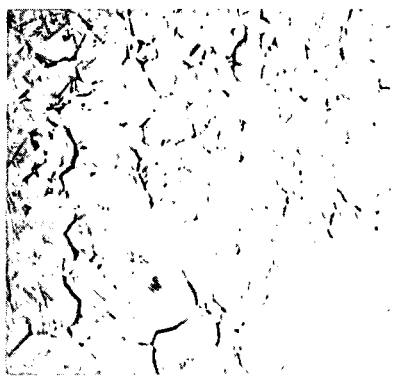


500X
b. Ti-6Al-4V heat-affected zone

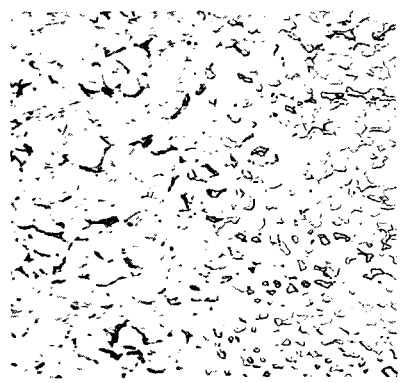


500X
c. Weld metal near Ti-6Al-4V

500X
d. Weld metal near Ti-2.25Al-3.75Mn



500X
e. Ti-2.25Al-3.75Mn heat-affected zone near weld metal

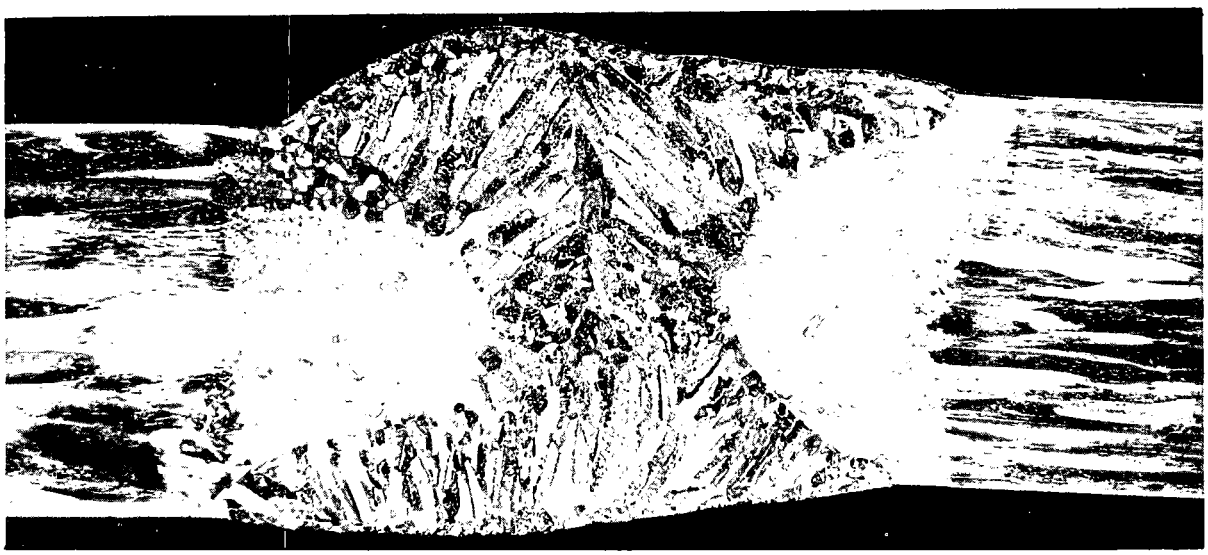


500X
f. Interface of heat-affected zone and Ti-2.25Al-3.75Mn

FIGURE 65. MICROSTRUCTURES OF Ti-6Al-4V WELDED TO Ti-2.25Al-3.75Mn BY THE HELIARC PROCESS USING Ti-6Al-4V FILLER METAL

1/2HF-1-1/2HCl-2-1/2HNO_3 etch

(North American Aviation, Downey, California)



4X 95428

FIGURE 66. MACROGRAPH OF A WELD IN Ti-7Mn USING UNALLOYED TITANIUM FILLER METAL

Welded in inert atmosphere chamber; 5HF-35HNO_3 etch

(Battelle Memorial Institute)

Beta alloys which have sufficient alloying additions to prevent beta-phase decomposition on cooling from the beta field result in somewhat different structures in the welded condition than those described previously. Because of the lack of transformation products, the weld zone has the large as-cast grain structure typical of single-phase alloys. This is shown by the structures in Figure 67 for the B-120VCA alloy (Ti-13V-11Cr-3Al) in the welded condition. The base metal has a relatively small grain size and the weld zone has a very large grain size. The transition from small to large grain size is very evident in the structure shown for the heat-affected zone.

The structures shown thus far have been for welds in the as-welded condition. Heat treatment after welding may be used to relieve stresses, overcome transformation hardening effects, or to strengthen the weld. Such treatments may have an effect on the microstructure of the welded alloys. In alpha alloys annealing after welding to relieve stresses has little effect on the microstructure, as shown in Figure 68. In alpha-beta alloys annealing after welding coarsens the alpha plates formed during cooling after welding, as shown in Figure 69 for a Ti-5V alloy. The objective of annealing welded alpha-beta alloys is to overcome transformation effects and to improve ductility by approaching equilibrium compositions and quantities of alpha and beta phases. For example, the bend ductility of the Ti-5V alloy was increased from about 14 per cent to about 30 per cent elongation in the outer fibers by the postweld anneal. Heat treatments to improve strength of the weld are of the same type as are used to improve the strength of the unwelded alloys. In beta-stabilized titanium alloys this heat treatment consists of solution treating followed by aging. The combined effects of solution treating and aging on a welded microstructure give rise to some complicated structures. The transformation products formed on cooling after welding will be partially dissolved and coarsened by the solution treatment. Subsequent aging will cause precipitation of alpha from beta as well as some decomposition of the alpha plates. An example of this is shown in Figure 70 for RS-110B alloy which had been welded, solution treated at 1250 F for 1 hour, and aged for 25 hours at 800 F. The microstructures in this figure should be compared with the as-welded structures shown in Figure 64. The structure of the base metal is about the same after heat treatment as it was before heat treatment. However, the weld-metal structure is considerably different, consisting primarily of a very fine, almost unresolvable precipitate of alpha in beta with some evidence of the platelike alpha structure. The heat-affected zone structure shows more of the platelike alpha than does the weld zone.

The beta alloy (Ti-13V-11Cr-3Al) has sufficiently sluggish transformation characteristics so that no significant beta decomposition occurs during cooling after welding. Thus, the welded condition can be considered the solution-treated condition. Subsequent aging causes a beta decomposition reaction to occur which is most noticeable in the weld metal and heat-affected zone as shown in Figure 71.

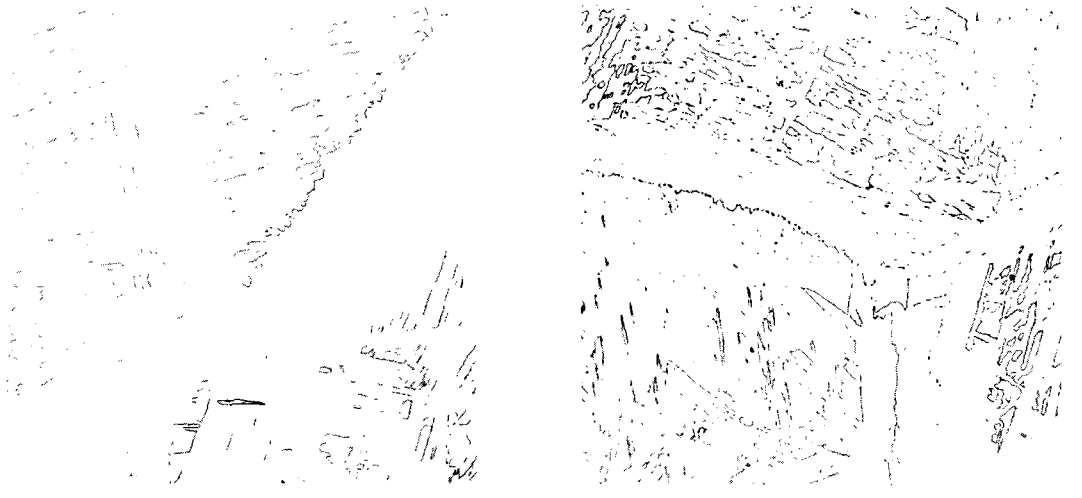
17X

A B C

100X A 100X B 100X C

Base metal Weld metal Heat-affected zone

FIGURE 67. MICROSTRUCTURES OF B-120VCA (Ti-13V-11Cr-3Al) 0.040-INCH SHEET, HELIARC WELDED
1HF-3HNO$_3$ etch
(North American Aviation, Downey, California)

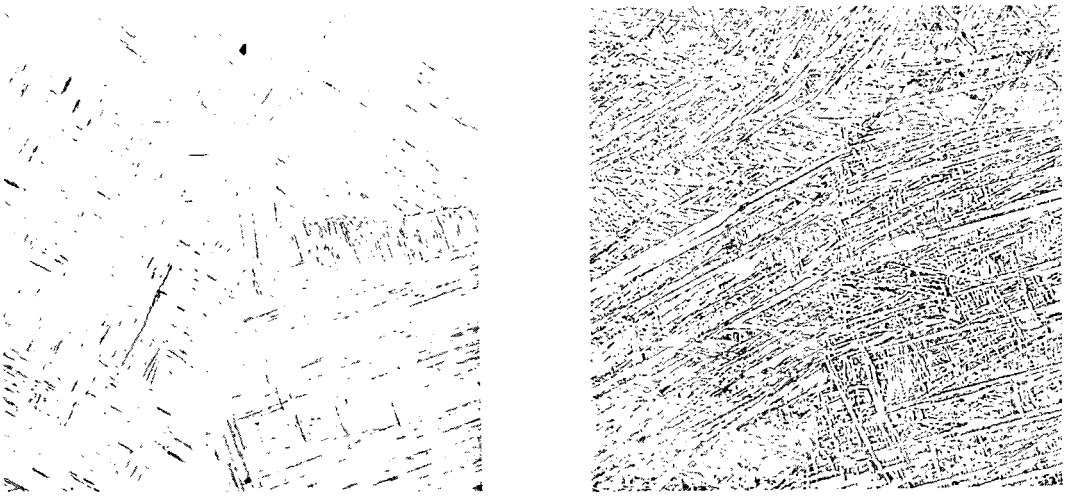


250X N4683 250X N4683

a. As welded

b. Welded plus 1 hour at 1500 F and air cooled

FIGURE 68. MICROSTRUCTURES OF A Ti-3Al ALLOY AS WELDED AND AS WELDED PLUS STRESS RELIEVED
1-1/2HF-3HNO$_3$ etch
(Battelle Memorial Institute)

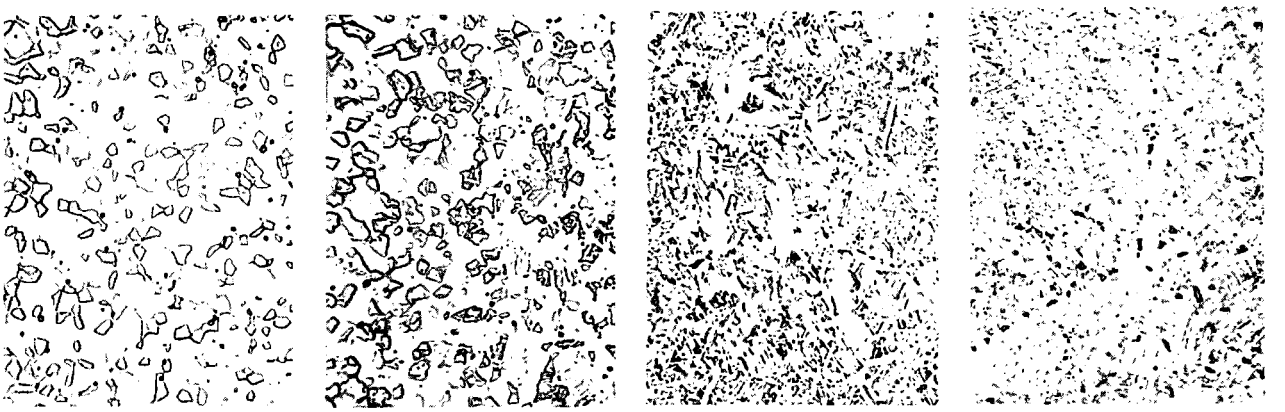


250X N4677 250X N4675

a. As welded b. Postweld annealed

FIGURE 69. MICROSTRUCTURES OF A WELDED Ti-5V ALLOY WITH AND WITHOUT POSTWELD HEAT TREATMENT

1-1/2HF-3HNO_3 etch
(Battelle Memorial Institute)



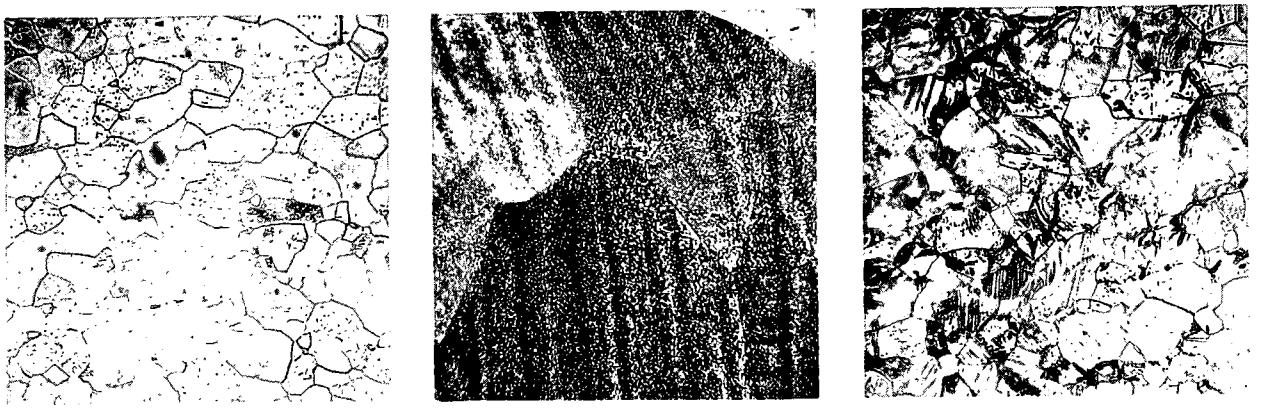
a. Base metal b. Interface between base metal and heat-affected zone c. Heat-affected zone d. Weld zone

FIGURE 70. MICROSTRUCTURES OF RS-110B (Ti-2.25Al-3.75Mn) HELIARC WELDED, SOLUTION TREATED 1 HOUR AT 1250 F, AND AGED 25 HOURS AT 800 F

1/2HF-1-1/2HCl-2-1/2HNO_3 etch
(North American Aviation, Downey, California)

17X

A B C



200X 200X 200X

A B C

Base metal Weld zone Heat-affected zone

FIGURE 71. MICROSTRUCTURES OF B-120VCA (Ti-13V-11Cr-3Al) 0.040-INCH SHEET, HELIARC WELDED AND SUBSEQUENTLY AGED 4 HOURS AT 900 F

1-1/2HF-3HNO_3 etch

(North American Aviation, Downey, California)

The preceding discussion and photomicrographs on welding have been limited to fusion-welded structures only. Flash and spot welding also have been used for titanium alloys, and microstructures of such joints are of interest. In flash welds the grain size of the weld zone is much finer than in fusion welding because of the pressure involved during the welding operation and the small amount of liquid metal involved. An example of the appearance of a flash weld is shown by the macrograph in Figure 72a of flash welded Ti-5Al-2.5Sn alloy. The base-metal structure was coarse-grained transformed beta resulting from previous heating in the beta field. The weld zone has a much smaller beta grain size than the base metal as shown in Figure 72b and c. In both areas, base metal and weld zone, the original beta phase has transformed to a serrated alpha structure.

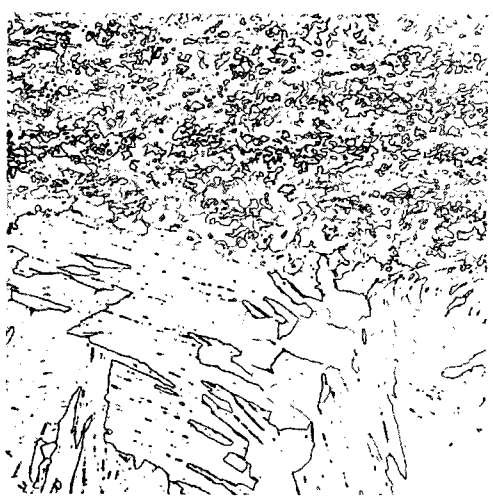
Spot welds are partly pressure welds, with the fusion zone limited to a volume between the two parts being welded. Macrographs showing the gross structure of spot welds in Ti-6Al-4V alloy are shown in Figure 73. The typical large grained cast structure is seen in the weld nugget with no apparent change in structure of the base metal. The heat-affected zone is confined to a very small zone around the molten nugget. The structure of a spot weld in a Ti-7Mn alloy is shown in Figure 74 at two magnifications. At the higher magnification the transformation structure can be seen.

15X N37930

a. Macrostructure of weld zone (1-1/2HF-15HNO_3)

100X N38006

b. Center of weld (1-1/2HF-3HNO_3)

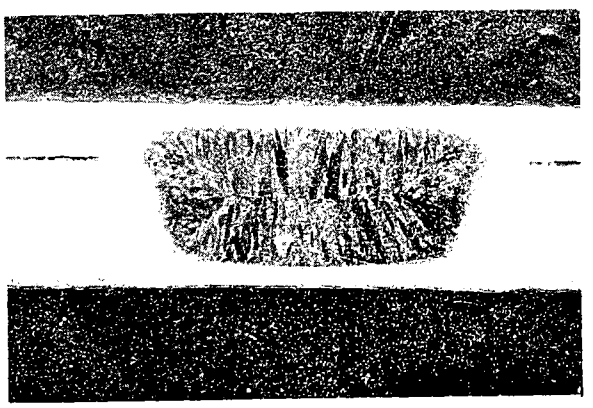


100X N38007

c. Edge of weld zone (1-1/2HF-3HF)

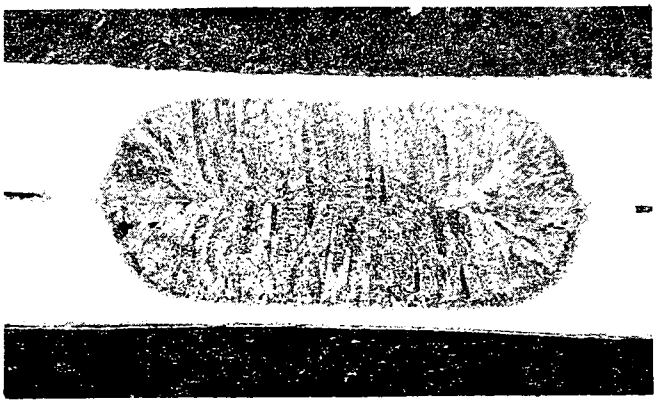
FIGURE 72. MICROSTRUCTURES OF A FLASH WELD IN Ti-5Al-2.5Sn FLASH WELDED AND ANNEALED 30 MINUTES AT 1500 F

(Battelle Memorial Institute)



12.5X PM 1532

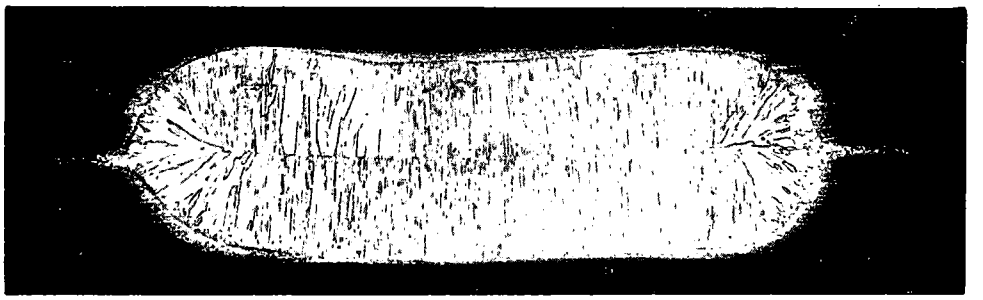
a. Spot-welded 0.025-inch sheet to 0.050-inch sheet



12.5X PM 1533

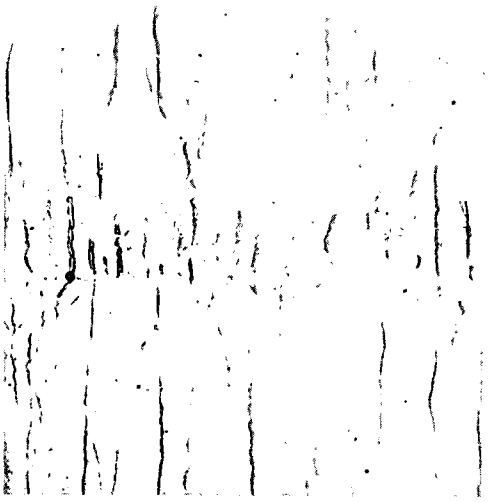
b. Spot-welded 0.050-inch sheet to 0.050-inch sheet

FIGURE 73. MACROGRAPHS IN SPOT WELDS OF Ti-6Al-4V ALLOY
1-1/2HF-3HNO_3 etch
(Convair Division, General Dynamics Corporation, San Diego, California)



15X N11286

a. Macrostructure of spot weld in Ti-7Mn (1/2HF)



500X N11285

b. Microstructure of center of spot weld in Ti-7Mn shown in (a) above (1-1/2HF, 3HNO_3)

FIGURE 74. MACROSTRUCTURE AND MICROSTRUCTURE OF A SPOT WELD IN Ti-7Mn
(Battelle Memorial Institute)

Metallographic examination of brazed joints may be used to check the soundness of the brazed joint and the interdiffusion of the brazing material and metal being brazed. Since the microstructure of the titanium alloy being brazed will be dependent on its composition, and the prior history of the effect of the thermal cycle during brazing, many base metal structures are possible. Prior discussions have described the effects of fabrication and thermal history on the microstructure of titanium alloys. Therefore, this discussion of microstructures of brazed joints will be limited to the joint itself and the effect of brazing materials on the titanium metal.

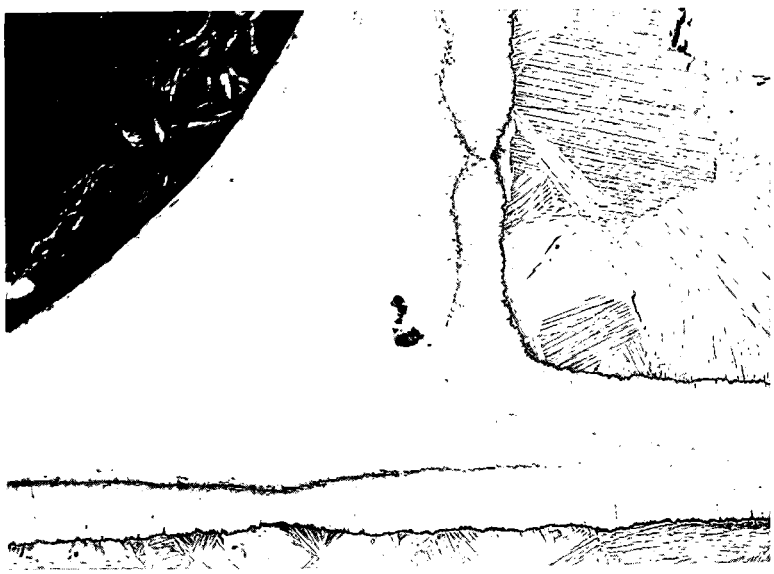
In Figure 75 are microstructures of a brazed joint between two pieces of unalloyed titanium where silver was used as the brazing material. The three zones that can be seen in Figure 75a are the silver brazing material, the diffusion zone between the silver and the titanium, and the titanium metal. The brazing temperature of 1800 to 1850 F used for this sample was above the transformation temperature of titanium, and the structure of the titanium is transformed beta. Figure 75b shows the structure of the diffusion zone at a higher magnification.

One of the difficulties encountered in brazing is the solution of titanium in the molten brazing alloy. Examples of this effect are shown in Figure 76.

Air Contamination

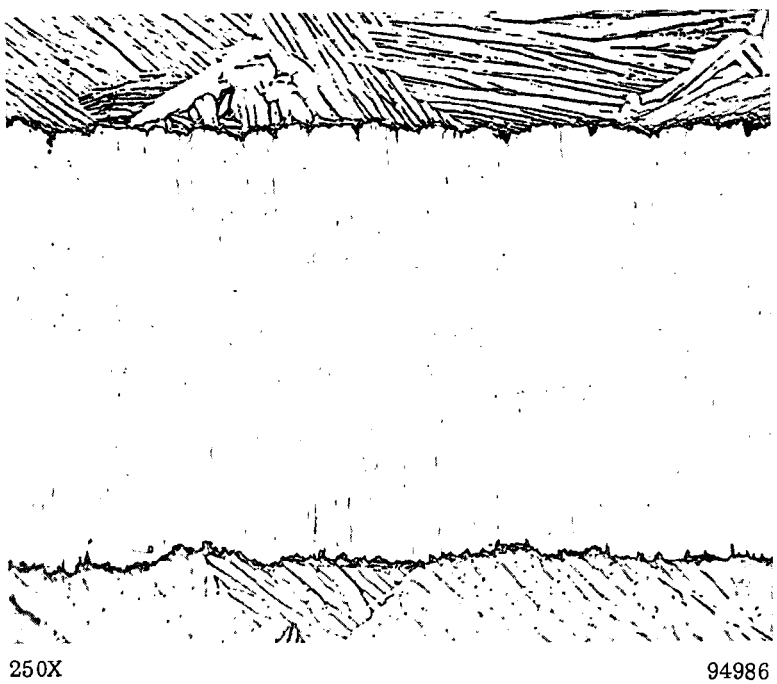
When titanium alloys are heated to temperatures above 1200 F diffusion of oxygen into the metal may occur, resulting in hardening of the surface and in some circumstances the formation of a hard brittle case. In many instances microstructural examination will reveal the presence of contamination, but it cannot be used to determine the specific depth of contamination. For example, the microstructure of a Ti-4Al-4Mn alloy heated for 2 hours at 2000 F shows an alpha case about 9 mils thick (Figure 77), while oxygen diffusion has occurred to a depth of about 40 mils as shown by hardness measurements. A sample of the same alloy heated for 4 hours at 1600 F shows practically no alpha case and is contaminated to a depth of at least 10 mils. A detailed description of the use of hardness in determining air contamination of three titanium alloys has been given in TML Report Number 10.

On the following seven pages are shown microstructures of several titanium alloys which have been exposed to air at elevated temperatures. These particular structures were chosen to illustrate the types of structures that may be attributed to contamination caused by diffusion of gases as a result of heating in air. Microstructural evidence of contamination is most readily observed in samples which have been heated to temperatures above the beta transus of the alloy. Oxygen or nitrogen diffusion into the metal



75X 92756

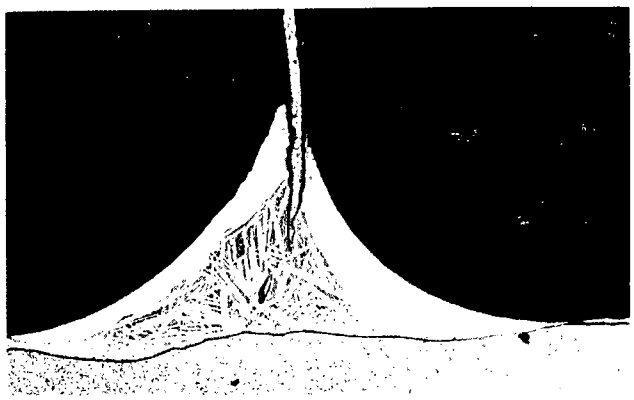
a. Low magnification showing silver fillet and brazed joint



250X 94986

b. High magnification showing diffusion layer between silver and titanium

FIGURE 75. MICROSTRUCTURES OF TITANIUM BRAZED AT 1800 F WITH FINE SILVER
1-1/2HF-3HNO$_3$ etch
(Battelle Memorial Institute)



50X PM 1963

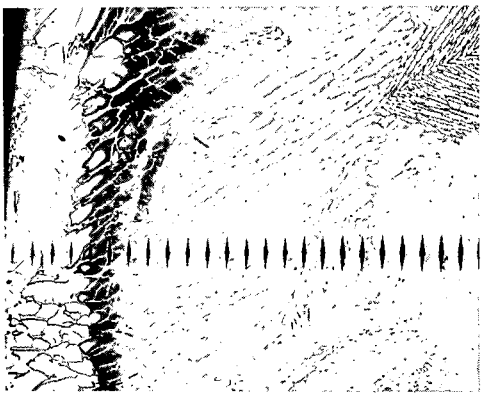
a. Commercial titanium (0.002 inch) core brazed to 0.021-inch Ti-6Al-4V sheet with 72Ag-28Cu alloy heated to flow point and held 1 minute ($1HF-2HNO_3$)

50X PM 1425

b. Commercial titanium (0.0025 inch) core brazed to 0.020-inch titanium sheet with fine silver at 1760 F ($1HF-2HNO_3$)

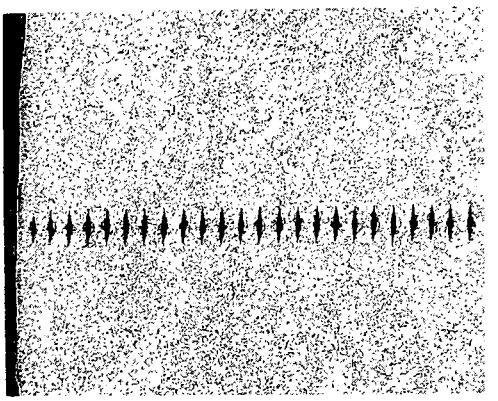
FIGURE 76. MICROSTRUCTURES OF TWO BRAZED JOINTS IN A TITANIUM HONEYCOMB STRUCTURE

(Convair Division, General Dynamics Corporation, San Diego, California)



50X N16727

a. Two hours at 2000 F



50X N16726

b. Four hours at 1600 F

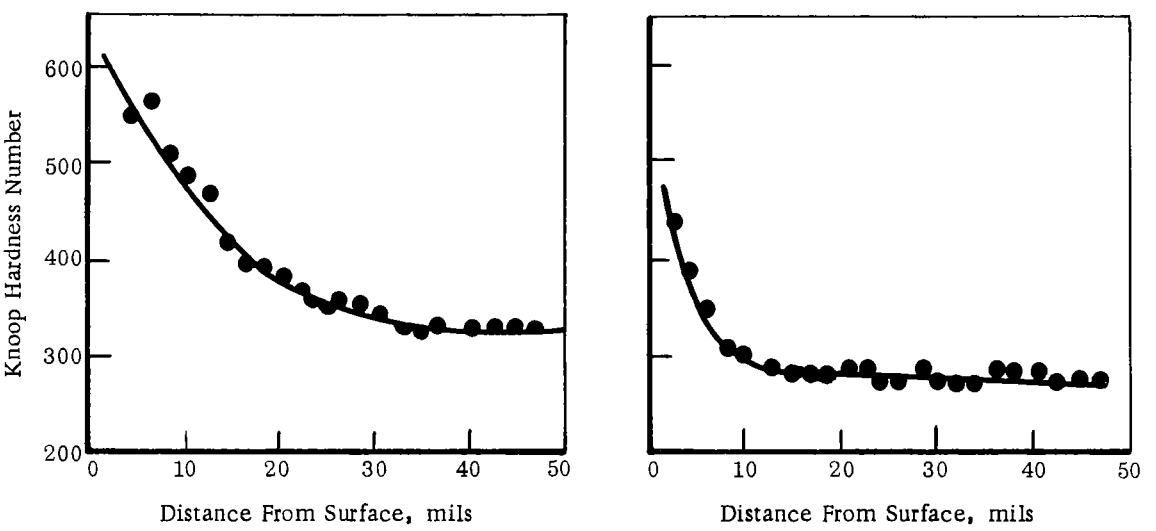
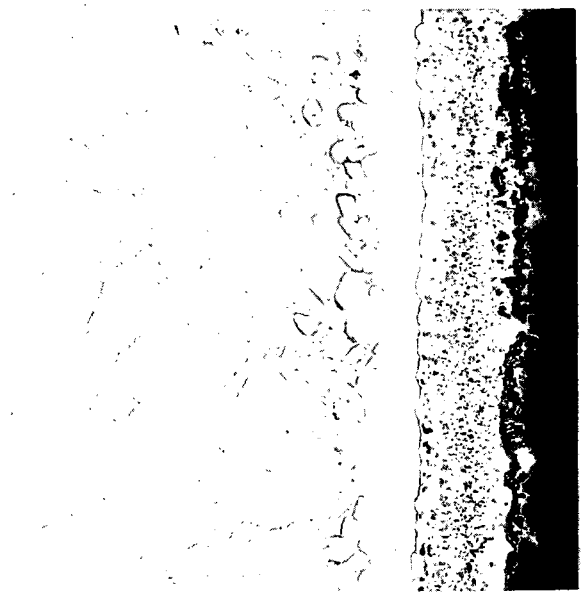


FIGURE 77. MICROSTRUCTURE AND HARDNESS OF SAMPLES OF Ti-4Al-4Mn HEATED IN AIR AT THE TEMPERATURES AND TIMES INDICATED

Metallographic samples etched with the 1-1/2HF-3HNO_3 etchant

(Battelle Memorial Institute)

stabilizes the alpha phase, and the resulting structure consists of an alpha case with a transformed beta core. The structure of the core is dependent on the cooling rate from the exposure temperature and/or subsequent heat treatment of the sample. Figure 78 shows the structure of a sample of the Ti-5Al-2.5Sn alloy heated for 4 hours at 1825 F in a gas-fired furnace. The three zones that can be seen are the oxide scale, the oxygen enriched alpha case, and the transformed core. Figure 79 shows the structure of the same alloy in the same condition where contamination has occurred around a forging lap or fold. The uniform alpha case that is seen above does not always occur as the result of contamination. Often, particularly in alpha-beta alloys, the contaminated area shows up as particles of equiaxed alpha in a matrix of transformed beta (Figure 80).



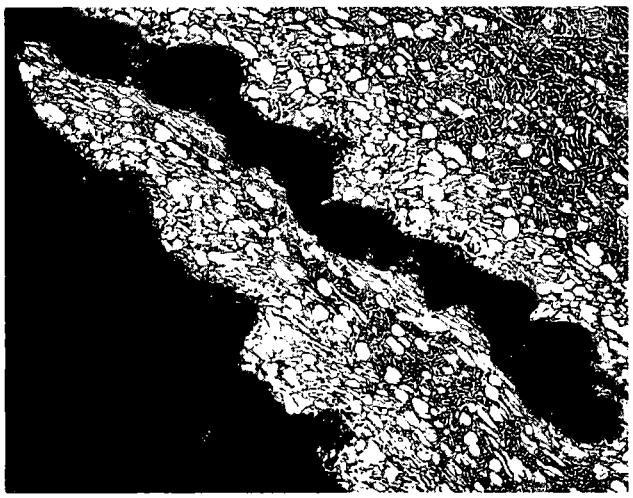
100 X N38005

FIGURE 78. MICROSTRUCTURE OF Ti-5Al-2.5Sn BAR STOCK HEATED IN AIR FOR 4 HOURS AT 1850 F, SHOWING FROM LEFT TO RIGHT: THE TRANSFORMED BETA CORE, ALPHA CASE, AND OXIDE SCALE
1-1/2HF-3HNO_3 etch
(Battelle Memorial Institute)

100X N37925

FIGURE 79. MICROSTRUCTURE OF Ti-5Al-2.5Sn FORGING SHOWING ALPHA CASE AROUND A FORGING LAP
1-1/2HF-3HNO_3 etch
(Battelle Memorial Institute)

Contamination also can occur when titanium alloys are heated for extended periods of time below the beta transus. The changes in microstructure resulting from such contamination are more subtle than for alloys heated above the beta transus as was illustrated in Figure 77b. However, at higher magnifications evidence of surface contamination can sometimes be seen. In an alpha-beta alloy, the area near the surface appears to contain less beta phase than the center of the sample as illustrated in Figure 81 for a sample of Ti-155A exposed for 8 hours at 1450 F in air. Another indication of surface contamination is the light etching characteristic of the sample near

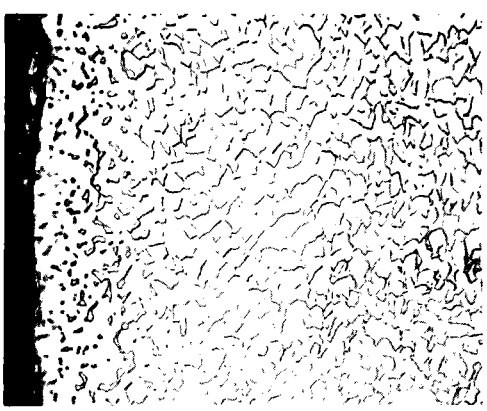


100X

FIGURE 80. MICROSTRUCTURE OF Ti-4Mn-4Al SPAR ATTACHMENT FORGED AT 1850 F, AND ANNEALED 1 HOUR AT 1350 F AND AIR COOLED

Forging lap with particles of alpha in the contaminated layer; 1HF-2HNO_3 etch

(Convair Division, General Dynamics Corporation, San Diego, California)



500X

FIGURE 81. MICROSTRUCTURE OF 5Al-1.5Fe-1.4Cr-1.2Mo HEATED IN AIR AT 1450 F FOR 8 HOURS AND AIR COOLED

Alpha-beta alloy with surface contamination resulting from heat treatment; 1HF-2HNO_3 etch

(North American Aviation, Downey, California)

the surface. The alpha phase with increased oxygen or nitrogen content is attacked more slowly by the etchant than the balance of the sample. Thus, on heavy etching or stain etching the contaminated layer shows up as a light etching area. Figures 82 and 83 show such structures of Ti-6Al-4V that had been exposed to air at 1400 F, 1200 F, and 1000 F for 200 hours. This effect shows up using either the all-purpose HF-HNO_3 etchant or the HF-HNO_3-glycerin stain etch. The mechanical properties of titanium alloys are affected by surface contamination of the type illustrated in the microstructures. Properties available on the Ti-6Al-4V alloy after exposure to air, as shown in Figures 82 and 83, illustrate the detrimental effect of the contamination. These are listed below:*

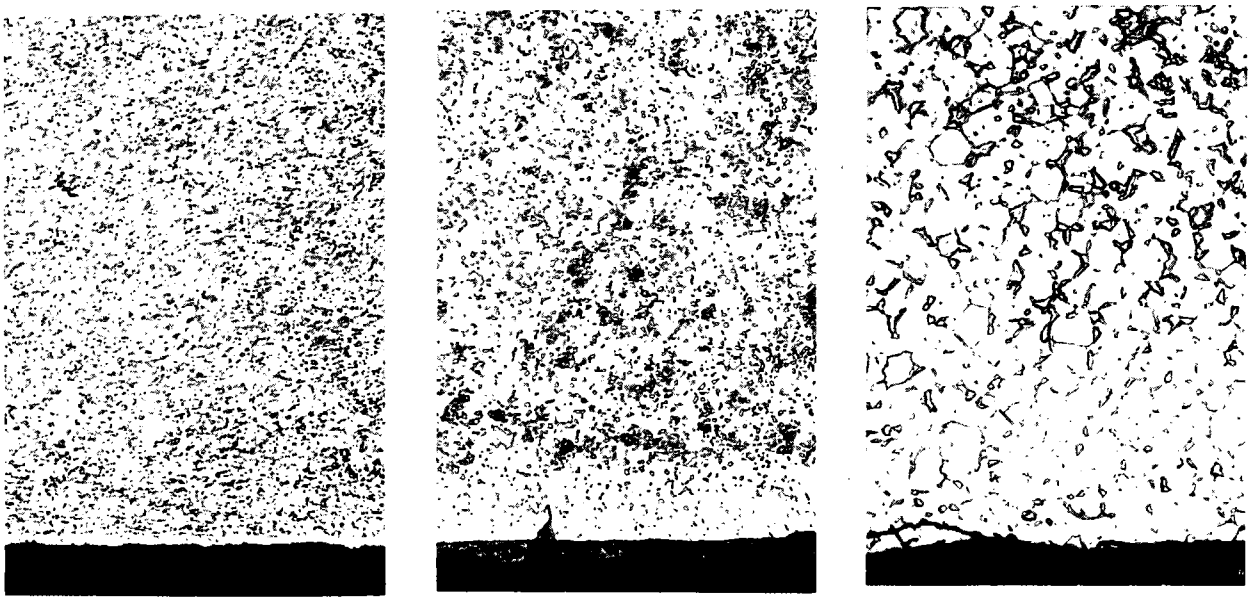
Property	Mill Annealed	Exposed to Air for 200 Hours at Temperature Indicated		
		1000 F	1200 F	1400 F
Yield Strength, 1000 psi	132	128	117	122
Ultimate Strength, 1000 psi	141	138	130	136
Elongation, per cent	10.5	11	10.5	2.5
Depth of Contamination(a), inch	0.0	0.0002	0.001	0.003

(a) As estimated from microstructures.

Many coatings are being investigated as preventives of contamination. An illustration of the effects of such a coating on the microstructure of an alpha-beta alloy is shown in Figure 84 for aluminum painted Ti-155A exposed for 8 hours at 1650 F. The depth of contamination in the uncoated sample is difficult to determine, but it can be seen that the proportion of alpha to beta has greatly increased in comparison with the coated sample; this indicates deep contamination. The surface case on the coated sample is probably aluminum-enriched alpha formed by the diffusion of aluminum from the aluminum paint. Removal of the protective coating after exposure is often difficult. It apparently is unattacked by acids as shown in Figure 85.

It should be realized that metallographic examination is not a reliable method of proving the presence or absence of contaminated surfaces. It is useful for indicating contamination, but it should be used only with other methods such as hardness traverses or bend ductility tests.

*Ryan Aeronautical Company Report No. G-17-94, July, 1957.



280X a. 1000 F

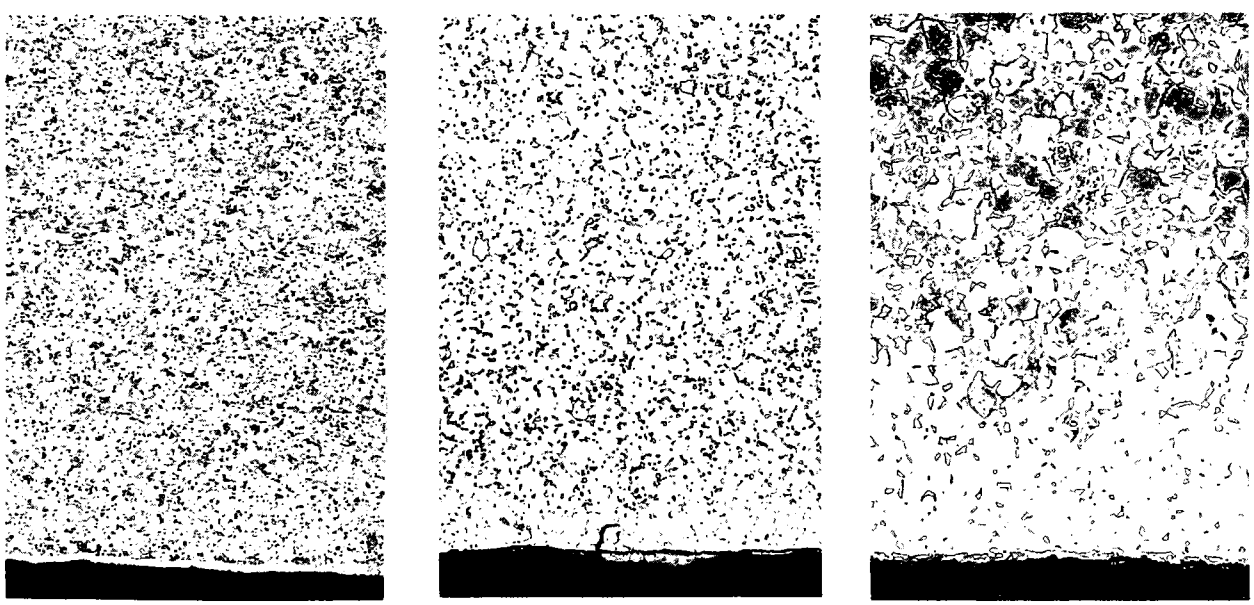
280X b. 1200 F

280X c. 1400 F

FIGURE 82. MICROSTRUCTURE OF SAMPLES OF ANNEALED 0.063-INCH Ti-6Al-4V ALLOY SHEET EXPOSED TO DRY AIR FOR 200 HOURS AT THE TEMPERATURES INDICATED

Etched with 1HF-2HNO_3 in water

(Ryan Aeronautical Company, San Diego, California)



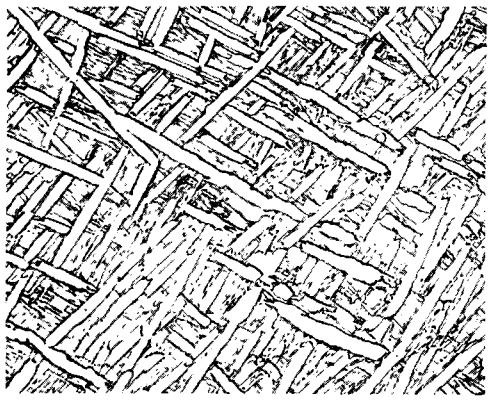
280X a. 1000 F

280X b. 1200 F

280X c. 1400 F

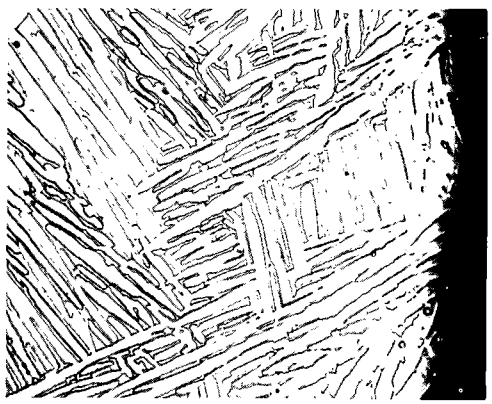
FIGURE 83. Ti-6Al-4V ALLOY GIVEN THE SAME TREATMENT AS IN FIGURE 82 BUT ETCHED WITH 10HF-20HNO_3 IN GLYCERINE TO STAIN THE ALPHA PHASE

(Ryan Aeronautical Company, San Diego, California)



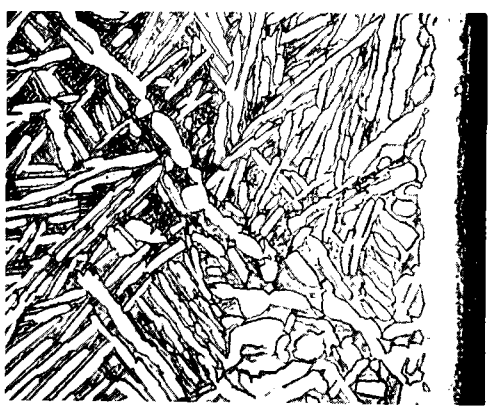
500X

a. Center of specimen showing uncontaminated structure of the alpha-beta alloy



500X

b. Unprotected surface with contamination shown by increase in the alpha phase near the surface



500X

c. Surface protected by aluminum paint; thin aluminum-rich alpha case with no contamination below this area

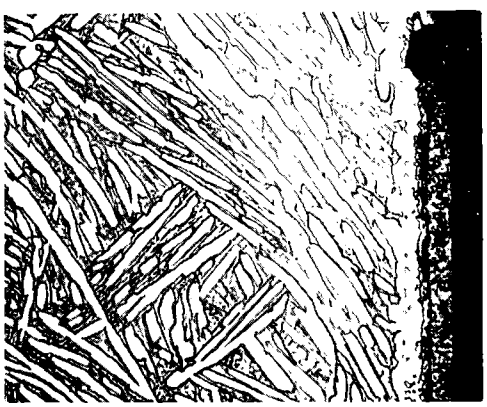
FIGURE 84. MICROSTRUCTURES OF Ti-5Al-1.5Fe-1.4Cr-1.2Mo SHOWING THE EFFECTS OF AN ALUMINUM-PAINTED SURFACE AGAINST CONTAMINATION AFTER EXPOSURE FOR 8 HOURS AT 1650 F

1-1/2HF-3HNO_3 etch

(North American Aviation, Downey, California)

500X

a. Portion of surface which displayed no aluminum paint and apparently was attacked by the acid solutions



500X

b. Portion of surface which exhibited negligible attack from the acid solutions because of the protection afforded by the aluminum paint

c. Portion of surface where there was severe attack by the acids in one location but not in an area adjacent to it

FIGURE 85. MICROSTRUCTURE OF ALUMINUM-PAINTED Ti-5Al-1.5Fe-1.4Cr-1.2Mo HEATED IN AIR AT 1650 F FOR 8 HOURS AND SUBSEQUENTLY IMMERSED IN VARIOUS ACID SOLUTIONS

1-1/2HF-3HNO_3 etch

(North American Aviation, Downey, California)

APPENDIX A

INDEX TO MICROSTRUCTURES OF COMMERCIAL ALLOYS

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APPENDIX B

GLOSSARY OF TERMS USED IN TITANIUM METALLOGRAPHY

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GLOSSARY OF TERMS USED IN TITANIUM METALLOGRAPHY

Acicular alpha - alpha phase formed by the transformation from beta along preferred planes of the beta lattice appearing as needles or plates in the microstructure.

Acicular alpha-beta structure - a two phase alpha-beta structure wherein the alpha phase is acicular in appearance.

Aged structure - a microstructure produced by an aging treatment, it usually refers to the darkening of the beta phase caused by alpha precipitation during aging.

Allotropic transformation - the transformation from the low-temperature phase (alpha) to the high-temperature phase (beta) in pure titanium at about 1625 F.

Alpha - the low-temperature hexagonal-close-packed allotrope of titanium.

Alpha-beta structure - a two phase structure obtained in many titanium alloys composed of alpha and beta phases.

Alpha case - oxygen enriched layer near the surface of contaminated alloys where alpha is stabilized by the contamination.

Alpha-martensite structure - a structure composed of primary alpha and martensite formed by quenching an alpha-beta alloy from a temperature where the composition of the beta-phase component is less than the composition where the Ms temperature is at room temperature.

Alpha prime - a supersaturated solution of alpha formed by quenching alpha-beta alloys from the beta field or alpha-beta field where the composition of the beta phase is less than the composition of Ms at room temperature. Also called martensite.

Alpha stabilizer - an alloying element which dissolves preferentially in the alpha phase and generally raises the alpha-beta transformation temperature of titanium.

Alpha transus - the temperature which designates the phase boundary between the alpha and alpha-plus-beta fields for a given alloy composition.

Banded structure - a structure with bands or layers of two phases (usually alpha and beta or mixtures of the two) produced during fabrication sometimes as a result of ingot inhomogeneity.

Basketweave structure - a term used to designate a structure formed by transformation of beta to alpha wherein the acicular alpha formed appears in a basketweave pattern.

Beta - the high-temperature, body-centered-cubic allotrope of titanium.

Beta-compound structure - a structure composed of beta phase in which a second phase appears that is not alpha but an intermetallic compound such as $TiCr_2$, TiC, etc.

Beta eutectoid - a term used to designate an alloying element which forms a system in which the beta phase undergoes a eutectoid reaction.

Beta fabricated - alloys fabricated in the beta field.

Beta isomorphous - a term used to describe an alloying element which forms a system in which there is complete solubility between the alloying element and beta titanium.

Beta prime - a term used to designate an anomalously hard single phase beta structure formed by quenching alloys which have a beta-stabilizer content slightly greater than the composition of Ms at room temperature from the beta field. This is now known to be caused by the formation of omega.

Beta stabilizer - an alloying element which dissolves preferentially in the beta phase and lowers the alpha-beta transformation temperature of titanium.

Beta transus - the temperature which designates the phase boundary between the alpha-plus-beta and beta fields for a given alloy composition.

Carbide network - a structure of titanium carbide particles arranged in a network pattern formed during freezing. This structure is encountered in castings and welds of high-carbon-content alloys.

Carbide phase - the compound TiC which is formed when the carbon content exceeds the solubility of carbon in titanium.

Contaminated layer - a term used to designate a surface layer that had been contaminated by oxygen diffusion during elevated-temperature treatments (fabrication or heating).

Depth of contamination - the depth from the surface that has been contaminated with oxygen by diffusion during elevated-temperature treatments.

Diffusion zone - the zone that forms by interdiffusion between two dissimilar metal alloys in intimate contact. This is usually restricted to descriptions of structures such as brazed joints, but is sometimes used to designate oxygen contamination.

Elongated alpha - a term used to describe the elongated shape of alpha phase in an alpha-beta alloy that has been formed as a result of fabrication in one direction. This can be seen in longitudinal sections of rolled or extruded material.

Equiaxed alpha - alpha phase in alpha or alpha-beta alloys which has an equiaxed appearance. It is used to describe structures obtained by fabrication and annealing in the alpha or alpha-beta fields.

Equilibration - a term used to describe part of an annealing treatment designed to approach equilibrium quantities and compositions of alpha and beta phases in an alpha-beta alloy. This is usually followed by a stabilization treatment.

Eutectoid structure - the structure formed by the decomposition of beta into eutectoid products, a mixture of alpha phase and an intermetallic compound.

Flowed metal - the worked surface of metallographic samples that occurs during polishing, often giving rise to incorrect microstructures.

Heat-treated structure - a term used to describe the microstructure encountered by heat treatment. Generally used to describe the precipitation of alpha in a beta matrix on aging.

Hydride phase - the phase TiH formed in alpha alloys when hydrogen content is too high.

Hydrogen contamination - hydrogen picked up in the metal during processing resulting in hydrogen contents above specification limits. It may be removed by vacuum annealing.

Interstitial contamination - oxygen, nitrogen, or hydrogen picked up during melting or welding. This term usually is used to designate uniform contamination as distinct from oxygen contamination by diffusion.

Interstitial solute - an element which dissolves in the interstices of the titanium lattice. Oxygen, nitrogen, carbon, and hydrogen are the common interstitial solutes in titanium.

Line markings - a term used to describe the appearance of the hydride phase precipitated in alpha titanium.

Longitudinal section - a metallographic sample in which the surface being examined is parallel to the fabrication direction.

Martensite - the product of the diffusionless transformation of beta to alpha in titanium alloys which results in an acicular alpha-prime structure with well-defined needles or plates. It is often difficult to distinguish from acicular alpha formed by nucleation and growth although the latter is usually less well defined with curved rather than straight sides. Sometimes called alpha prime.

Mechanically unstable beta - beta phase retained by quenching which will transform to martensite during straining at room temperature.

Metastable beta - beta phase retained by quenching which will transform to alpha or eutectoid products on subsequent heating.

Mf temperature - the temperature at which the martensite reaction is complete. Very seldom used in titanium metallography because of the difficulty in determining it.

Ms temperature - the temperature at which martensite starts to form during cooling.

Omega phase - a transition phase that forms during the nucleation and growth transformation of beta to alpha. It is coherent with the beta lattice and cannot be seen under the light microscope. Some evidence of omega has been found using electron microscopy.

Oxide scale - the scale formed on titanium alloys when heated in air or oxygen-bearing atmospheres.

Oxygen contamination - the diffusion of oxygen into titanium alloys during exposure at temperatures above about 1000 F.

Platelike alpha - alpha phase which forms along preferred planes of beta during transformation of beta to alpha. Usually used to describe alpha formed from high beta-stabilizer content alloys as distinct from acicular alpha formed in low beta-stabilizer content alloys.

Primary alpha - alpha phase which was present prior to a heat treatment as distinct from the alpha phase formed during the heat treatment.

Prior beta grain size - the approximate grain size of the beta phase prior to transformation to alpha.

Retained beta - beta phase which is present in the microstructure as a result of quenching. No transformation of the beta has taken place.

Solution-treated structure - the microstructure obtained as a result of the solution-treating portion of the heat-treatment cycle. May consist of an alpha-beta structure, an alpha-martensite structure, a martensite structure, or a retained-beta structure depending on the solution-treating temperature and composition of the alloy.

Stabilization - a term used to describe an annealing treatment which precipitates massive alpha from beta in an alpha-beta alloy rendering the alloy in a condition where no further reaction will take place during exposure at service temperatures.

Strain-induced martensite - product of the transformation of beta to martensite during deformation or straining.

Substitutional solute - an alloying element which dissolves in titanium by substitution for one of the titanium atoms in the lattice.

Titanium carbide - the first intermediate phase in the titanium-carbon system.

Titanium hydride - the first intermediate phase in the titanium-hydrogen system.

Transformed alpha - a term sometimes used to designate alpha formed by the transformation from beta. More commonly called transformed beta.

Transformed beta - alpha phase which is formed by transformation from beta, also called acicular alpha.

Transformed beta core - used exclusively in describing contamination structures where the oxygen contamination has formed an alpha case; the beta core transforms to alpha on cooling from the exposure temperature.

Transverse section - a metallographic sample in which the surface being examined is a plane normal to the fabrication direction.

Unstable beta - beta phase retained at room temperature which will transform partially to alpha or eutectoid products on heating.

Vacuum annealed - material which has been vacuum annealed to remove hydrogen. Usually indicates low-hydrogen-content material.

Widmanstätten alpha - alpha phase formed by transformation from beta in a Widmanstätten pattern.

Widmanstätten pattern - a geometrical pattern resulting from the formation of a new phase along certain crystallographic planes of the parent phase.

APPENDIX C

PREPARATION OF METALLOGRAPHIC SAMPLES

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The primary purpose of preparing metallographic samples is to obtain a surface that will reveal the true structure of the metal when examined under the microscope. Many techniques may be used to prepare titanium samples for metallographic examination, which can provide satisfactory samples. All of these procedures cannot be described here. Rather, the techniques described below are a selection of the more commonly used methods of preparing titanium metallographic samples.

The major difficulty in preparing titanium metallographically is the removal of cold work (mechanical twinning) and flowed metal. Cold work is introduced during sectioning and grinding, whereas flowed metal normally occurs during polishing. The alpha phase in titanium systems is particularly susceptible to cold work and flowed metal. Therefore structures containing primarily the alpha phase must be prepared with the greatest care.

The procedure for the metallographic preparation of titanium and its alloys may be divided into the four conventional steps of all metallographic preparations:

(1) Sectioning and mounting

(2) Grinding

(3) Polishing

(4) Etching.

Sectioning and Mounting

The sectioning of titanium is of importance since severe deformation will cause mechanical twinning, and overheating can cause a highly unstable beta phase to transform to the alpha phase. Sectioning should be done with ample cooling and a slow to moderate feed of the specimen into a silicon carbide cutoff wheel. Other methods of sectioning may be used such as hacksawing, but they are generally more difficult and tend to cold work the metal adjacent to the cut.

The methods of mounting must be considered, because of the increasing solubility of titanium hydride in the alpha phase with increasing temperature.

Mounting in thermal-setting media may cause the solution of existing hydride and, upon cooling, precipitate the hydride in an altered form, usually a fine dispersion. Also, hydrogen contamination is suspected by the diffusion of hydrogen from the mounting material into the specimen, forming the hydride phase. Where the metallographic examination concerns the hydride phase, it is best to leave the samples unmounted, if convenient, or to mount them in such a way as to avoid any heating. The choice of mounting material, therefore, depends on the purpose of the metallographic examination. Suggested mounting materials are:

(1) Epon (for room-temperature mounting)

(2) Bakelite

(3) Lucite.

Grinding

Two steps are involved in grinding:

(1) Coarse grinding on wet 180-grit silicon carbide belts

(2) Fine grinding on 240-, 400-, and 600-grit silicon carbide discs.

The purpose of coarse grinding is to obtain a plane surface and to remove the effects of sectioning. Choose the least coarse grit size to keep cold work resulting from grinding to a minimum. Wet grinding keeps the specimen cool and flushes the belt of loose metal and abrasive particles. Disc grinding may be substituted for belts and should be satisfactory.

Fine grinding is necessary to eliminate any cold-working effects of the coarse grinding and to produce a smoother surface preparatory to polishing. Belts or hand papers may be substituted. However, disc grinding is preferred because less pressure is required, resulting in a finer grind within a given time. During final grinding, the direction of grinding is changed by 90 degrees between the use of each grit size to insure the complete elimination of the previous grind.

Polishing

Polishing is the most important step in the preparation of metallographic samples for it is in this step that the final surface is obtained. Here, there

are many variations in technique, but basically there are two methods for polishing; mechanical and electrolytic polishing. These are discussed separately.

Mechanical Polishing

There are generally two or more steps used in mechanical polishing to obtain a scratch-free surface which is free of flowed metal. The polishing sequence, like the grinding sequence, is done with decreasing size of polishing compound to eliminate the coarser scratches of the preceding operation. The major differences between techniques are the kind of polishing cloth used and the type of abrasive that is used. Most laboratories have found that an etch-polish technique is desirable to speed up the polishing action and to eliminate flowed metal. In using acid in polishing solution, it is desirable to polish a little faster than the etching action to produce a smooth surface.

Listed below are several polishing procedures which have been used satisfactorily in various laboratories:

Battelle Memorial Institute. Polishing is accomplished in three stages:

(1) Rough polishing, using a slurry of 50 g of 600-grit carborundum powder, 60 cc H_2O and 5 cc 20% chromic acid on a low-speed (250 rpm) polishing wheel covered with Buehler silk cloth

(2) Semifinal polishing, using a slurry of 10 g Linde B (Al_2O_3), 35 cc H_2O and 5 cc 20% chromic acid on a high-speed (1750 rpm) polishing wheel covered with Buehler Miracloth

(3) Final polishing, using the above slurry without the chromic acid addition on a medium-speed (500 rpm) polishing wheel covered with Buehler Microcloth.

During rough polishing, hand motion is usually satisfactory although a motor-driven polishing wheel may be used. If the wheel is motor driven, the polishing ordinarily should not exceed 30 seconds on a 250-rpm wheel. If polishing is prolonged, the surface metal will tend to flow and accumulate in tiny piles on the surface.

At the beginning of the semifinal polishing, rather heavy pressure is applied. As polishing progresses, less and less pressure is applied. Alternate etching and polishing (etch polishing) is done at this time to aid in the removal of flowed metal. The etchant used is Kroll's reagent. The etching is light to

avoid pitting around carbides and nonmetallic inclusions, and it is usually necessary to etch polish 3 or 4 times. The specimen is left unetched before proceeding to the final polish.

Final polishing removes very fine polishing scratches left from the previous polish. A light, but firm, pressure is maintained throughout a polishing time of about 1 minute. If it appears necessary, some etch polishing may be done during this step, but relief in the microstructure will result if etch polishing is repeated too often.

Detroit Arsenal. Polishing is done in three stages:

(1) Using either a Fischer Gamal cloth or Buehler Microcloth and diamond compound (4 to 8 microns) as the polishing medium the sample is rotated on the lap. Using heavy hand pressure at the start and gradually diminishing the pressure, the total time consumed is approximately 60 seconds. It is important that the polishing time be held to a minimum to avoid undercutting of the softer phases.

(2) Using a Fischer Gamal cloth or Buehler Microcloth and diamond compound (2 microns) the sample is rotated with heavy pressure being applied for intervals of 1 to 3 seconds. The total time consumed is approximately 90 seconds.

(3) The specimen is then etched lightly and repolished. The final polish is done on a water saturated Buehler Microcloth using "Linde B" as the polishing compound. Observe the sample face to see how quickly the cutting or polishing film dries. For rapid and good polishing the time is 40 to 60 seconds.

Douglas Aircraft Company. Polishing is done in two stages:

(1) After grinding, etch specimens in a solution of 1 to 2% HF, 12% HNO_3, balance water to remove worked metal, scratches, and loose mounting material from the grinding operations.

(2) Use fine alumina and 1% HF in water on a chromium-plated polishing wheel covered with a Gamal polishing cloth. Polish with a positive pressure and slow wheel speeds. Polishing action should be slightly ahead of the etching action. This can be controlled by the amount of HF in the alumina slurry. The specimen must be washed immediately to prevent further etching action by the HF.

Rem-Cru Titanium, Inc. Polishing is done in two stages:

(1) Hand polish with levigated 600-mesh silicon carbide on a lead lap. The lead lap is a piece of lead foil on plate glass. This is an intermediate step between grinding and final polishing.

(2) Final polishing is done on a wax-coated wheel using Buehler Microcloth and gamma alumina with 1% HF. Polishing is done with rotary motion and some pressure. Polish just a little faster than the etching action. If surface is dull, etching is predominant; more dry abrasive should then be added.

Titanium Metals Corporation of America. Polishing is done in four steps:

(1) 45 to 60 seconds using 8 to 10-micron diamond dust compound on an airplane wing covering cloth (or a fine cotton broadcloth).

(2) 45 seconds using 8 to 20-micron diamond dust compound on a Gamal cloth.

(3) 45 seconds using 0 to 2-micron diamond dust compound on a Gamal cloth.

(4) 60 seconds using 0.3-micron aluminum oxide on a Gamal cloth. If fine scratches persist, a fifth step using 0.1-micron aluminum oxide on a Gamal cloth for 60 seconds may be necessary.

It is desirable to repolish the specimen from the last cloth after etching to remove any disturbed metal.

Electrolytic Polishing

Electrolytic polishing may be used in place of mechanical polishing. The preparation steps for electrolytic polishing are the same as for mechanical polishing through grinding. Several electrolytes can be used. Procedures being used by several laboratories are given below:

Mallory-Sharon Metals Corporation. The specimen is ground through No. 0 Emery paper and placed in a Disa Electropolisher. The electrolyte contains:

390 cc methyl alcohol

350 cc ethylene glycol

60 cc perchloric acid (1.41 sp gr).

The temperature of this solution must be kept below 30 C because of its explosive nature. A typical polishing cycle consists of 15 seconds of polishing time at 35 volts and 9 amperes using a 6-mm-diameter polishing surface.

New York University. The nonexplosive electrolyte which is used to polish a variety of titanium alloys consists of the following:

60 ml perchloric acid (sp gr 1.5)

350 ml butyl cellosolve

590 ml ethyl alcohol.

A Uddeholm Company of America proprietary reagent may be added to the above solution (2 ml/liter of electrolyte) to improve the quality of the polish. When the Uddeholm reagent is added polishing occurs over the range of current densities from 0.018 to 0.035 ampere per square millimeter. When the Uddeholm reagent is not used, the polishing range is narrowed and shifted to lower current densities. For iodide titanium this range is 0.0055 to 0.011 ampere per square millimeter. The electrolyte is circulated during polishing to cool the specimens and remove the white oxide film. Polishing times are for 10 to 30 seconds.

Rem-Cru Titanium, Inc. Electropolishing may be done using the following safe (nonexplosive) solution:

90% ethyl (or No. 30 denatured) alcohol

10% n-butyl alcohol, in which is dissolved in the following order for each 100 cc of alcohol

6 g anhydrous $AlCl_3$ (exothermic solution – add slowly)

28 g anhydrous $ZnCl_2$.

This solution is stable for about 1 week. Electropolishing conditions are:

30 to 60 volts dc

1 to 5 amperes per square inch of anode (the specimen) with a stainless steel cathode

1 to 6 minutes

23 to 30 C Solution agitated.

Etching

Nearly all of the etchants used for titanium will contain some concentrations of HF and HNO_3 in either water, glycerin, or lactic acid. In any HF-HNO_3 etch the HF attacks while the HNO_3 brightens the surface. Concentration changes on this basis may be made with any of the etchants.

There is no general rule that can be given as to when to swab or when to immerse. It is definite that swabbing will do more cleansing or brightening of the surface, but the choice of whether to swab or immerse is left to the discretion of the one preparing the specimen. Usually, if swabbing appears unsatisfactory, then immersing is tried, or vice versa.

A list of 13 of the more commonly used etchants is given in Table C-1.

There is a general tendency by those not experienced with titanium to over-etch. It is far better to etch lightly at first, examine under the microscope, and re-etch more heavily if it appears necessary. If there is evidence of flowed metal after final etching, it often may be removed by heavier etching, but in doing so, the microconstituents are usually over-etched and lack definition. In such a case the semifinal polishing stage with etch polishing should be repeated rather than to accept the deeply attacked microstructure resulting from over-etching.

In addition to the swab or immersion etchants described above, some special purpose electrolytic etchants have also been used on titanium alloys. They are generally used for phase identification by the color that various phases are stained. One such procedure that has been found very valuable in distinguishing between intermetallic phases in titanium alloys has been developed by New York University. Starting with a standard polished and etched sample, it is electrolytically etched in a solution of 5 g oxalic acid, 5 g citric acid, 5 ml orthophosphoric acid, 10 ml lactic acid, 35 ml water, and 60 ml ethanol. A modification of this solution is to dilute it with an equal volume of glycerin. Dilution with glycerin increases the time required for etching and thus increases the control over stain etching. Applied voltages range from 20 to 130 volts for areas of 25 to 75 square millimeters. The various phases in the microstructure are tinted, the actual color depending upon the length of time of applied voltage. Colors will vary from brown to violet to blue. Because different phases will react at different rates, distinct color differentiations can occur between phases. This technique has not proved completely satisfactory for alpha-beta alloys, however, because the reaction rates of these two phases appear to be about the same.

TABLE C-1. ETCHANTS FOR TITANIUM AND TITANIUM ALLOYS

Etchant	Remarks
(1) 1 cc HF, 99 cc H_2O	Stain etch for alpha phase
(2) 1 to 3 cc HF, 2 to 6 cc HNO_3[a] H_2O to make 100 cc	General purpose, does not stain and brings out grain boundaries
(3) 1 to 2 cc HF, 12 cc HNO_3 H_2O to make 100 cc	General purpose, slower acting etchant than the one above
(4) 1 to 2 cc HF, 4 to 5 cc H_2O_2 H_2O to make 100 cc	Nonstaining etch
(5) 1 to 4 cc HCl, 1 cc H_2SO_4 H_2O to make 100 cc	Etch 3 to 10 minutes in boiling solution; used for differentiation of phases in alpha-beta alloys
(6) 20 cc HF, 20 cc HNO_3 40 cc glycerin	General purpose, fast acting
(7) 10 cc KOH, 5 cc H_2O_2 20 cc H_2O	General purpose, stains alpha but not beta
(8) 5 cc HF, 10 cc HNO_3 30 cc lactic acid	General purpose, works well on alpha-beta alloys
(9) 1 cc HF, 30 cc HNO_3 30 cc lactic acid	Preferentially outlines hydride phase in some alloys
(10) 10 cc HF, 10 cc HNO_3 30 cc lactic acid	Fast acting etch, tends to remove disturbed metal from surface of polished samples
(11) 5 cc HF, 35 cc HNO_3 60 cc H_2O	General macroetch
(12) 50 cc HCl, 50 cc H_2O	General macroetch for alpha-beta alloys
(13) 1/2 cc HF, 1-1/2 cc HCl, 2-1/2 cc HNO_3, balance water	Kellers etch. General purpose, macro- and microetch.

(a) Probably the most commonly used etchant and often called Krolls etch in honor of the contribution of Dr. W. J. Kroll to titanium.

LIST OF TECHNICAL REPORTS ISSUED

Titanium Metallurgical Laboratory
Battelle Memorial Institute
Columbus 1, Ohio

The technical reports listed below are available for distribution to Government agencies, Government contractors, subcontractors and their suppliers. Others may request copies through the Office of Technical Service, Department of Commerce, Washington 25, D. C. (See PB numbers and prices in parentheses.)

Report Number	Title
* 5A	The Use of Titanium Alloy Sheet in Airframe Components (Superseded by TML Nos. 13 and 24)
* 7	Survey of the Problem of Delayed Cracking in Formed Titanium Parts (PB 124562, Microfilm $3.60, Photo copy $9.30)
* 8	Principles and Practical Aspects of Titanium Heat Treatment (PB 124563, Microfilm $2.70, Photo copy $4.80)
*10	A Study of the Air Contamination of Three Titanium Alloys (PB 124564, Microfilm $3.00, Photo copy $6.30)
*12	Formability Tests on Titanium Alloy Sheet (PB 124565, Microfilm $2.70, Photo copy $4.80)
**13	Selection of Materials for High-Temperature Applications in Airframes (PB 111980 $1.00)
**	Supplement to TML Report No. 13 (PB 121602 $.75)
**15	Engineering Properties of Commercial Titanium Alloys (PB 111981 $2.25)
*18	Analysis and Laboratory Examination of Aircraft Parts Which Failed by Delayed Cracking (PB 124567, Microfilm $3.00, Photo copy $6.30)
**19	General Summary of the Physical Metallurgy of Titanium Alloys (PB 121603 $2.25)
**20	Effect of Carbon, Oxygen, and Nitrogen on the Mechanical Properties of Titanium and Titanium Alloys (PB 111982 $2.75)
*21	The Diffusion of Interstitial and Substitutional Elements in Titanium (PB 124568, Microfilm $2.70, Photo copy $4.80)
*22	Selection, Standardization and Status of Specifications for Titanium Mill Products (PB 124569, Microfilm $2.70, Photo copy $4.80)
**24	The Application of a New Structural Index to Compare Titanium Alloys With Other Materials in Airframe Structures (PB 121605 $1.00)
*25	Beta Transformation in Titanium Alloys (PB 124570, Microfilm $7.20, Photo copy $22.80)
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46A	Department of Defense Titanium Sheet-Rolling Program Status Report No. 1 (PB 121624 $1.25)
46B	Department of Defense Titanium Sheet-Rolling Program Status Report No. 2
46C	Department of Defense Titanium Sheet-Rolling Program Status Report No. 3
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