STRUCTURAL AND MECHANICAL EFFECTS OF INTERSTITIAL SINKS

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ABSTRACT

The effect of the purity and thickness of titanium interstitial sink on the residual concentrations of interstitials in columbium was considered from a thermodynamic viewpoint. It was concluded that the equilibrium concentrations of interstitials in columbium is not a sensitive function of these parameters.

The structure and hardness of Ti/D-43 diffusion couples were correlated with the partitions of interstitials between the two metals. A reduction in the oxygen and carbon concentration in the D-43 correlates with an increase in the grain size and a change in the grain morphology of this alloy. The equilibrium partition of interstitials between the titanium and the D-43 is believed to account for an increase in the hardness of the titanium, but this partition does not seem to affect the hardness of the D-43.

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I. INTRODUCTION

The term "interstitial sink" is used to describe a metal in which the partial molar free energy of an interstitial element in solution is low relative to that in an adjoining metal so that interstitials tend to concentrate in the metal (sink) where their free energy is lower. In many practical applications it is necessary to place refractory metals, strengthened by interstitial dispersions, in contact with other elements that act as interstitial sinks. Oxidation protective coatings, braze alloys, and diffusion bonding intermediates are three examples of such usage. Under such circumstances the operating temperatures are often sufficiently high so that redistribution of interstitials occurs very rapidly from the refractory base metal into the sink metal. Subsequent dissolution of the interstitial phase in the refractory metal can lead to a serious loss of strength for many refractory alloys.

This is the second quarterly progress report under Contract NAS-7-469, "Structural Effects of Interstitial Sinks". This investigation is a study of the structural changes in columbium base alloys caused by the migration of interstitials to an interstitial sink. The effects of variables such as alloy processing, partition of interstitials between the sink and the alloy, and chemical activity of the sink on the structure of the alloy will be studied and correlated with the creep behavior of the alloy. The refractory metals selected for this study are columbium base alloys such as D-43 (Cb-10W-1Zr-0.1C) and Cb752 (Cb-10W-2.5Zr). The former alloy is carbide strengthened and the latter alloy is oxide strengthened. During the previous quarter the materials necessary for this program were procured. During this quarter the structural changes induced by exposing D-43 sheet to a titanium sink at an elevated temperature were studied, and construction of a high temperature creep facility was continued.

II. THEORETICAL BASIS

For a reaction to occur there must be a driving force, i.e., an overall reduction in free energy. The driving force for the migration of interstitial atoms from a refractory metal to a sink metal is the reduction in free energy gradients caused by differences in the relative activities (the effective concentration) of interstitial solute atoms in the sink metal and the refractory metal. In this regard, the thermodynamic free energy changes are the basic criteria for predicting the feasibility of a reaction without regard to the rate of the reaction. This section is a discussion of the interstitial sink effect from a thermodynamic viewpoint and thus deals quantitatively with equilibrium conditions without considering the rate of approach to equilibrium.

To predict the kinetics of a reaction such as the migration of interstitials from a refractory metal to a sink metal, the rate controlling mechanism must be known (e.g., various interstitial diffusion mechanisms, interstitial reactions at various interfaces or imperfections, etc.). The complexities of refractory alloys such as D-43, however, lead to considerable uncertainty regarding the possible identity of the rate controlling step or steps. Thus, the kinetics of interstitial partition will not be discussed separately in this section. However, when it is deemed appropriate the kinetics of interstitial partition will be discussed together with the experimental data that may yield some insight concerning the rate controlling mechanisms.

The change in free energy when one gram atom of an interstitial is added to a large amount of a metal can be expressed as

$$\mu = \mu^\circ + RT \ln a \qquad (1)$$

where μ is the change in free energy of the solution (chemical potential or partial molar free energy), μ° is the free energy of the solution for unit activity, and 'a' is the activity of the interstitial in solution in the metal. The value of μ° is determined only by the condition of unit activity or the standard state selected for the system.

The equilibrium equation for the formation of the interstitial compound MX from an interstitial, X, and a metal, M, is

$$X + M = MX \qquad (2)$$

for which the free energy of formation is ΔF_1°. The equilibrium equation that determines the composition of the terminal solid solution (i.e., the solubility limit) in equilibrium with MX is

$$\bar{X} + M = MX \qquad (3)$$

where $\overline{X}$ is the interstitial in solution in M. For this equation

$$\Delta F_2^\circ = -RT \ln \frac{1}{a_{\overline{X}}} .$$

Subtracting Eq. (3) from Eq. (2) yields

$$X = \overline{X}$$

and

$$\Delta F_3^\circ = \Delta F_1^\circ - \Delta F_2^\circ = F_1^\circ + RT \ln \frac{1}{a_{\overline{X}}} \tag{4}$$

Since the standard state is chosen so that the activity is unity at the solubility limit, μ° in Eq. (1) is the change in free energy of the metal at the solubility limit caused by the solution of the interstitial. This value is ΔF_3° in Eq. (4) so that:

$$\mu^\circ = F_1^\circ + RT \ln \frac{1}{a_{\overline{X}}} . \tag{5}$$

However, for the selected standard state $a_{\overline{X}}$ in Eq. (4) is equal to one so that

$$\mu^\circ = F_1^\circ .$$

Equation (1) is then

$$\mu = F_1^\circ + RT \ln a . \tag{6}$$

If Henry's law is assumed to apply to the solubility limit ($a = KN_C$ where K is a constant equal to $1/N_S$, and N_C and N_S are the atom fractions of solute and the atom fraction of solute at the solubility limit, respectively),

$$a = N_C/N_S \text{ or simply } a = C/S. \tag{7}$$

In the latter equation, C is the atomic fraction of the interstitial and S is its atomic fraction at saturation. Eq. (6) is then

$$\mu = F_1^\circ + RT \ln C/S. \tag{8}$$

For two metals, A and B in intimate contact and containing an interstitial element X,

$$\mu_{(x \text{ in } A)} = \Delta F^\circ_{AX} + RT \ln \frac{C_A}{S_A} \tag{9}$$

$$\mu_{(x \text{ in } B)} = \Delta F^\circ_{BX} + RT \ln \frac{C_B}{S_B} \tag{10}$$

Assuming negligible interdiffusion of A and B and equilibrium interstitial partition,

$$\Delta F^\circ_{AX} - \Delta F^\circ_{BX} = RT \ln \left(\frac{S_A}{S_B} \cdot \frac{C_B}{C_A} \right). \tag{11}$$

From this equation the equilibrium partitions, C_B/C_A of an interstitial between the two metals can be determined if the free energies of formation of the interstitial compounds and the terminal interstitial solubilities are known.

According to Eq. (11), two factors affect the ratio C_A/C_B (a measure of the effectiveness of an interstitial sink). These are the differences in the free energy of formation of the interstitial compounds AX and BX, and the ratio of maximum interstitial solubilities in the sink metal and in the refractory metal, S_A/S_B. On this basis a metal will be an effective interstitial sink if it has a relatively large negative free energy of formation and a high interstitial solubility However, the solubility of interstitials in the sink metal also influences the effectiveness of the sink in another way.

The interstitial partition between two metals is constant for different concentrations according to Eq. (11) until the solubility limit of the interstitial in one of the metals is exceeded (constant activity in a two phase region). If, for example, $C_A \geqq S_A$, Eq. (11) becomes

$$\Delta F^\circ_{AX} - \Delta F^\circ_{BX} = RT \ln C_B/S_B. \tag{12}$$

If S_B is known, C_B, the equilibrium interstitial concentration remaining in metal B can be determined. The concentration, C_B, is a constant whose value is determined by Eq. (12). This condition may be encountered when metal A is a sink of limited solubility so that its saturation solubility is exceeded at equilibrium interstitial partition between A and B. The partition C_B/C_A under these conditions is no longer constant since C_A can vary while C_B has a fixed value. The use of Eq. (12) will be illustrated for certain metal-sink systems in the following discussion.

In considering the effect of an interstitial sink on the partition of interstitials in commercial alloys it is necessary to idealize the problem somewhat because many of the thermodynamic properties for commerical alloys are not known. For columbium-base alloys in contact with titanium-base interstitial sinks it is useful to consider the simple columbium-titanium system as a guide to predict the behavior of interstitials in the alloys. On this basis various calculations have been made for the titanium-columbium system that may be of use in predicting the effect of certain parameters on the partitions of interstitials in alloys such as D-43 when exposed to interstitial sink environments. However, it should be pointed out that these calculations are intended to indicate general trends in the equilibrium thermodynamic partition of interstitials rather than to predict the precise values that will be attained in real systems.

The changes in free energy as a function of the concentrations of carbon and oxygen in columbium and titanium at 2200°F are shown in Figures 1 and 2. These values were calculated by use of Eq. (8). The partition of interstitials between titanium and columbium (C_B/C_A in Eq. 11) is the concentration shown in these figures for the same value of the chemical potential, μ. The approximate partition ratios calculated according to Eq. (11) for the single phase regions shown in Figures 1 and 2 are

$$O_{Ti(\alpha)}/O_{Cb} = 1200/1 \text{ atomic or } 2300/1 \text{ weight}$$

$$O_{Ti(\beta)}/O_{Cb} = 465/1 \text{ atomic or } 900/1 \text{ weight}$$

$$C_{Ti}/C_{Cb} = 740/1 \text{ atomic or } 1430/1 \text{ weight}$$

These ratios are, of course, only as accurate as the thermodynamic values substituted in Eq. (11).

The interstitial concentration remaining in columbium when the concentration in the titanium sink is that for a two phase region, is determined by Eq. (12). As previously described, the partition ratio when one of the metals is in a two phase region is no longer constant.

The Effect of Foil Thickness

If metal #1 has a thickness t_1, density p_1, and initial and final interstitial concentrations C_1 and C_{1f} respectively, and if metal #2 has a thickness t_2, density p_2, and initial and final interstitial concentrations C_2 and C_{2f} respectively, then

$$C_1 t_1 p_1 + C_2 t_2 p_2 = C_{1f} t_1 p_1 + C_{2f} t_2 p_2 . \tag{13}$$

and

$$\frac{t_1}{t_2} = \frac{p_2}{p_1} \frac{(C_{2f} - C_2)}{(C_1 - C_{1F})} . \tag{14}$$

The most important assumption on which these equations are based is negligible interdiffusion of metals #1 and #2.

Eq. (13) can be used to illustrate the effect of the thickness of the titanium sink on the equilibrium partition of oxygen and carbon between titanium and columbium. Figure 3 shows the variations in the final concentrations of oxygen and carbon in columbium as a function of the relative thicknesses of the two metals. The solution shown in Figure 3 for oxygen is for columbium and titanium with initial oxygen concentrations of 500 and 3000 ppm respectively, where $C_{2f} = 2320 C_{1f}$ and $900 C_{1f}$. The solution for carbon is for columbium and titanium with initial carbon concentrations of 1000 and 500 ppm respectively where $C_{2f} = 1430 C_{1f}$. Although the solution to Eq. (14) in the region where titanium is single phase is not a straight line, it is approximately so where C_{2f} is $\gg$ than C_{1f}.

Figure 3 shows that the final carbon concentration in columbium after exposure to a titanium sink is almost independent of the thickness of the titanium foil relative to that of columbium until the concentration of carbon in the foil reaches that for single phase TiC, i.e., where $t(Cb)/t(Ti) = \sim 66$. In addition, because of the low solubility of carbon in titanium, TiC is likely to form in the titanium sink even for relatively thick foils. In this regard, TiC should be present in titanium foils even if the thickness of the foil is as great as that of the columbium. It is interesting to note that the residual carbon concentration in the columbium is not greatly reduced when the thickness of the titanium approaches that for an infinite sink, i.e., $t_{Cb}/t_{Ti} = 0$.

As shown in Figure 3, the final concentration of oxygen in columbium is more sensitive to the Cb/Ti thickness ratio than is the final concentrations of carbon in columbium. The concentration of oxygen in columbium increases with decreasing foil thickness (large thickness ratio) until the concentration of oxygen is that for the two phase structure. In this regard, titanium appears to be a less effective sink for oxygen than for carbon. This is partly caused by the larger Cb/Ti solubility ratio at saturation for oxygen relative to that for carbon. However, another factor, as indicated in Figure 3, is the high concentration of oxygen that can be taken up by titanium before an oxygen induced two phase structure is formed. These results suggest that a metal with a low terminal solubility for interstitials may be potentially a more effective sink than one with a greater terminal solubility, assuming other conditions are unchanged.

Effect of Foil Purity

Equation (13) can be written as

$$C_{1f} = \frac{-t_2 p_2 (C_{2f} - C_2)}{t_1 p_1} + C_1 \tag{15}$$

so that C_{1f}, the final interstitial concentration in the columbium, can be calculated for varying values of C_2, the initial interstitial concentration in the titanium. The value of C_{1f} will also be a function of the Cb/Ti thickness ratio, t_1/t_2.

The solutions to Eq. (15) where C_{1f} is the residual carbon concentration in columbium for varying values of C_2 and t_1/t_2 are shown in Figure 4. For these solutions, C_1, the initial carbon concentration in columbium, is 1000 ppm and $C_{2f} = 1430\,C_{1f}$. It can be seen that the carbon concentration remaining in the columbium increases with increasing initial carbon concentration in the titanium and reaches a constant value when the concentration of carbon in titanium attains that for the formation of TiC in titanium. The residual carbon concentration in the columbium increases again when the concentration of carbon in the sink is that for single phase TiC. It can be seen that TiC will form in a titanium sink whose thickness ratio, t(Cb)/t(Ti), is 5, even if it contains no carbon initially. However, the effectiveness of titanium as a sink for carbon in columbium is relatively independent of the initial titanium purity, unless the thickness of the titanium with respect to columbium is very large.

The solutions to Eq. (15) where C_{1f} is the final oxygen concentration in columbium for varying values of C_2 and t_1/t_2 are shown in Figure 5. For these solutions, C_1, the initial oxygen concentration in the columbium is 500 ppm and $C_{2f} = 900\,C_{1f}$ and $2300\,C_{1f}$. The oxygen concentration remaining in columbium increases along the diagonal lines shown in Figure 5 as the initial oxygen concentration in the titanium increases and is constant when the oxygen concentration in the titanium is that for a two phase region.

In general, the residual oxygen concentration in columbium is more dependent on the initial titanium purity for different Ti/Cb thickness ratios than is the residual carbon concentration in columbium. However, even for oxygen the effectiveness of the titanium sink is not significantly changed for reasonable variations in both the initial oxygen concentration of the titanium and the Ti/Cb thickness ratio.

III. EXPERIMENTAL PROCEDURES

The D-43 sheet obtained for this program was processed by Fansteel Corporation in the duplex (solution annealed, rolled and aged 2600° F) and standard (solution annealed, rolled, and aged 2300° F) conditions. Further examination of the duplex processed D-43 revealed that the solution annealing temperature (2900° F) may not have been sufficiently high to take the carbide dispersions into solution so that subsequent duplex aging at 2600° F did not induce significant additional carbide precipitation. Tensile tests at 2200° F showed the duplex D-43 to be weaker than the standard heat treated D-43 whereas it had been previously determined that duplex material processed by du Pont using a 3000° F solution anneal was stronger than the standard heat treated D-43. Duplex D-43 which had been processed by du Pont was, therefore, obtained so that the difference in structure induced by the two duplex treatments and the interstitial sink effects on these structures could be investigated. For simplicity, the D-43 in the duplex heat treated condition will be referred to as D-43 (Dup F) and D-43 (Dup D) for material processed by Fansteel and du Pont respectively, while D-43 in the standard heat treated condition will be referred to as D-43 (Std).

Construction of a high temperature vacuum creep facility for use in this program was continued during this period. It is anticipated that this device will be operational within a few weeks. Creep tests will be conducted at constant stress by use of constant-stress lever arm similar to the one described by Fullman, et al (1). This beam loading device is illustrated in Figure 6. When the beam is approximately horizontal a specimen of initial length l_o will be deformed at constant tensile stress if

$$L_3 = \frac{L_1 L_2}{l_o} .$$

A series of Ti/D-43 diffusion couples were prepared by diffusion bonding 2 mil titanium foil to 20 mil D-43 sheet specimens 0.3 inches wide and 2.5 inches long. The titanium foil was bonded to both surfaces of the flat D-43 specimens making a Ti/D-43/Ti sandwich. These diffusion couples were annealed in a vacuum for various lengths of time at 2200° F. After the various heat treatments, the structures were examined metallographically, and the hardnesses were measured using a Knoop indenter and a 100 gram load.

Initially, some difficulty was encountered in diffusion bonding the titanium foil to the D-43 sheet. Bonding was found to be unsatisfactory toward the edges and ends of the diffusion couples. The region toward the edge of a specimen that was soundly bonded near its center is shown in Figure 7. Various combinations of time, temperature, pressure and surface preparations were tested to improve bonding. The bonding conditions selected were 30 seconds at 2200° F using a bonding pressure of 6500 psi and D-43 specimens whose surfaces had been flattened by sanding prior to bonding. Bonding was accomplished using a 0.4 inch by 1.75 inch TZM electrode with a tungsten-rhenium tip.

The concentrations of carbon and oxygen in the diffusion couples was determined by combustion-conductimetric and vacuum fusion analysis, respectively. The nitrogen concentration was also determined by vacuum fusion analysis. However, it is not reported in this investigation because the initial nitrogen concentration of the D-43 is relatively low (~1/12 that of carbon and 1/6 that of oxygen). In addition, the analysis for nitrogen in the presence of titanium is not sufficiently accurate to yield data for a reliable study of the interstitial sink effect.

IV. RESULTS AND DISCUSSION

The results presented in this report are for titanium bonded to D-43 (Std) and D-43 (Dup F). The experimental data for titanium bonded to D-43 (Dup D) will be presented in a later report. The results of a series of chemical analyses for carbon and oxygen in Ti/D-43 diffusion couples, the structures observed metallographically, and the hardness of these structures are presented below.

4.1 THE CONCENTRATION OF INTERSTITIALS IN D-43

After the diffusion couples had been heat treated at 2200° F, selected pieces of each couple were prepared in several different ways for carbon and oxygen analysis. A length of the Ti/D-43/Ti sandwich was analyzed to determine if a loss or gain in overall interstitial concentration had taken place during the vacuum heat treatments. In this regard, specimens of D-43 that had been vacuum heat treated in the "as-received" condition, without titanium bonded to their surfaces, were also analyzed for their carbon and oxygen concentrations. These specimens which will be referred to as standards, were used to check the vacuum atmosphere as a possible interstitial source or sink for the D-43. Another portion of the diffusion couples was analyzed after the titanium had been removed by chemically thinning the couple to 14 mils. This center section was well below the zone of titanium diffusion into the D-43 that could be detected by metallographic examination. This analysis was used as a measure of the final oxygen and carbon concentrations of the D-43 after exposure to the titanium sink.

The results of a series of analysis for D-43 (Std) diffusion couples annealed at 2200° F are listed in Table I. The overall oxygen and carbon concentrations of the Ti/-D-43/Ti sandwich are relatively constant for specimens annealed different lengths of time at 2200° F. The analysis of the Standard suggests that the vacuum heat treatments for 16 and 57 hours may have decreased the carbon concentration of the specimens somewhat. The oxygen concentration of the Standard, however, does not seem to be significantly changed by the vacuum heat treatments, although the analysis shows some scatter. Both the oxygen and carbon concentrations of the D-43 are decreased by annealing it in contact with a titanium sink. This is shown in Table I by the progressive decrease in the oxygen and carbon concentrations of the D-43 (Ti removed) with increasing annealing times. These data are also shown plotted in Figure 8. For these conditions, the carbon is more effectively removed by the titanium sink than is the oxygen. The final concentrations of carbon in D-43 are in good agreement with predictions (Figures 3 and 4) for columbium for similar thickness ratios and purities. However, the final oxygen

TABLE I

CARBON AND OXYGEN CONCENTRATIONS AS A FUNCTION OF ANNEALING TIME AT 2200° F

Time (Hrs) at 2200° F	As Bonded		1/4		1		4		16		57	
Carbon and Oxygen (ppm)	C	O	C	O	C	O	C	O	C	O	C	O
Ti/D-43/Ti	845	1400	825	1620	865	1640	800	1725	815	1380	815	1390
D-43(Standard)	—	—	876	990	—	—	—	—	720	1200	685	890
D-43(Ti removed)	910	630	880	545	670	530	550	510	230	235	3	140

concentration is somewhat larger than the predicted value (Figures 3 and 5).

These analyses show that the concentrations of both oxygen and carbon in the D-43 are significantly decreased by the action of the titanium sink. In this regard, titanium reduces the concentration of carbon in the D-43 more than the concentration of oxygen as predicted for columbium (Figures 3,4 and 5). This decrease in interstitial concentration is not significantly influenced by the effect of the "vacuum" atmosphere during annealing.

4.2 STRUCTURAL STUDIES

The structures of the titanium and the D-43 components of the diffusion couples, as revealed by metallographic examination, were studied separately because of differences in their etching characteristics. The effects of the 2200° F heat treatments on the structure of the titanium sink are presented first. This is followed by a presentation of the structural changes detected in the adjacent D-43. In this discussion, the structural changes are correlated with the decrease in carbon concentration of the D-43 detected by the chemical analysis since this was the interstitial whose partition was primarily affected by the action of the titanium.

4.2.1 The Structure of Titanium

Figures 9 through 14 show the structural changes observed in the titanium foils for specimens annealed various lengths of time at 2200° F. The structure of titanium did not appear to be affected by differences in the initial structure of the D-43 with which it was in contact. Thus, Figures 9 through 14 show titanium structures that are typical of both Ti/D-43 (Std) and Ti/D-43 (Dup F) diffusion couples.

As shown in Figures 9 through 11, both alpha and beta titanium are present in the microstructures of specimens annealed less than four hours at 2200° F. This two-phase structure is believed to have formed when the specimens were cooled from the annealing temperature, since 2200° F is well within the beta phase region for titanium. For the longer annealing times, however, the titanium is single phase. This phase is believed to be beta titanium since diffusion of columbium from the D-43 into the titanium will stabilize the beta phase. The grain boundaries in the titanium tend to be obscured by the initial two-phase titanium structure as shown in Figures 9 and 10. However, as this two-phase structure is replaced by a single phase at longer annealing times, the grain boundaries are more easily detected (Figures 11-14).

As shown in Figures 10 and 14, a new phase which may be TiC (Knoop hardness >2800) is present in all the specimens annealed at 2200° F. This phase appears to form preferentially at the intersections of titanium grain boundaries with the titanium surface, although it was also observed within the titanium matrix away from grain boundaries. For convenience during the following discussion, this phase will be termed, TiC although it has not yet been positively identified. However, reference to Figures 3 and 4 shows that the thickness ratio (5/1) and titanium purity (1000 ppm carbon) of the D-43 are well within the range where TiC can form in the titanium foil. In this regard, titanium saturated with carbon can no longer act as a sink for reactive interstitial compounds such as ZrC since the chemical potential of carbon in TiC is higher than that of carbon in ZrC. Titanium saturated with carbon would be an effective sink only for carbides of lower chemical potential such as columbium carbide and for carbon in solution in excess of that in equilibrium with any ZrC that may form.

The formation of TiC in specimens annealed for only 15 minutes at 2200° F suggests that carbon diffuses very rapidly from the D-43 into the titanium sink. This can be accounted for if the diffusion of carbon in D-43 is considered to be about the same as the diffusion of carbon in its primary constituent, columbium. At 2200° F the volume diffusion of carbon in columbium is several orders of magnitude less than the volume diffusion of carbon in titanium. Thus, the rate controlling step is likely to be the slower volume diffusion of carbon in columbium. It can be shown from a solution of Fick's law that the partition of carbon to titanium will be essentially complete when $Dt/L^2 \simeq 1$. Taking D, the diffusion of carbon in columbium, as 5×10^{-8} cm^2/sec and L, the half thickness of the D-43 sheet, as 0.025 cm (10 mils), the time, t, is found to be about 3 hours. Although many factors such as the grain boundary diffusion of carbon in the D-43 and the dissolution rate of the various carbides in D-43 have been neglected, this simplified calculation is probably good enough to yield an approximate time for the decarburization of D-43 by titanium. On this basis, a rapid migration of carbon from the D-43 to the titanium sink will occur at 2200° F. This is in agreement with the observations of carbides in titanium in contact with D-43 after short annealing times at 2200° F.

Carbides in titanium grain boundaries and at their termination with the surface shown in Figures 11 to 14 are evidence for the prominent role that grain boundary diffusion plays in the diffusion of carbon in titanium. However, as previously discussed, the rate controlling step in the decarburization of D-43 is likely to be the slower diffusion of carbon in D-43.

The migration of the Ti/D-43 interface in this series of specimen can be monitored by observing the migration of the porosity and debris that existed in the original bonded interface. Interfaces distinguished in this way have been used in place of Kirkendall markers for diffusion measurements in Cb/Ti alloys, and these experiments have shown that the intrinsic diffusion of titanium is greater than that of columbium (2). Thus, the Kirkendall markers would be expected to migrate toward the titanium if the Ti/D-43 diffusion couples behave as if they were composed of titanium and columbium. A shift in the markers toward the titanium surface does occur as can be seen in Figures 11 through 14. In these photomicrographs, the Kirkendall interface appears as a horizontal line within the titanium diffusion zone. The observed migration of this interface indicated by the displacement of this line shown in Figures 11 through 14 suggests that the net flow of metal atoms into the D-43 is greater than that out of the D-43. In addition, the displacement of the marker toward the titanium surface is approximately proportional to the square root of time as would be anticipated for marker movement controlled by diffusion. This also implies that porosity formation resulting from vacancy precipitations does not play a significant role in these experiments since marker movement is inversely proportional to the volume of pores formed.

4.2.2 The Structure of D-43

Figures 15 through 22 show the structural changes induced in D-43 (Std) and D-43 (Dup F) by annealing this alloy at 2200° F in contact with a titanium sink. The horizontal edges of the specimens on the top of the photomicrographs were in contact with the titanium during annealing. The additional etching required to reveal the D-43 structure, however, has attacked the titanium foil to such an extent that it is no longer evident in these photomicrographs. For comparison, D-43 specimens without titanium bonded to them were heated together with the Ti -D-43 diffusion couples. In the following discussion the structure of the D-43 heated in contact with titanium for different annealing times is compared with the structure of identically heat-treated D-43 without titanium.

Figure 15 shows the structure of D-43 (Std) prior to annealing, and Figures 16 through 20 show the structure of D-43 (Std) annealed for various lengths of time at 2200° F. The structure shown in Figure 16(a) (D-43 annealed with Ti) appears to have less precipitates toward the edge of the specimen than the structure shown in Figure 16 (b) (D-43 annealed without Ti). This suggests that carbon migration to the titanium sink has reduced the concentration of carbide precipitates in this region. As previously discussed, a new phase believed to be TiC was observed in the titanium foil for this specimen after 15 minutes annealing time at 2200° F.

On further annealing, grain growth in the D-43 is evendent toward the edge of the specimen which was in contact with the titanium sink. This is shown in Figures 17 and 18. Grain growth in these specimens is believed to be induced by the dissolution of the interstitial phases that tend to anchor grain boundaries in this alloy. The effect of the titanium sink on structure is clearly evident in Figures 19 and 20. The specimens annealed in contact with the titanium (Figures 19(a) and 20(a) have large well defined grains with relatively straight boundaries, whereas the specimens annealed without a titanium sink (Figures 19(b) and 20(b) have smaller more irregularly shaped grains.

It is evident that a titanium sink promotes grain growth in D-43 (Std). This is believed to be caused by a reduction in interstitial second phases (primarily carbides) that tend to restrict grain boundary migrations. However, these results show that grain growth or grain boundary migration also occurs in specimens annealed for the same length of time without a titanium sink. This can be seen from a comparison of the structures shown in Figure 15 (as-received material) with that shown in Figure 20(b) (57 hours at 2200° F).

The effect of the titanium sink on the structures of D-43 (Dup F) is much less pronounced than the structural changes observed in D-43 (Std). As shown in Figures 15 and 21, the grains in the D-43 prior to annealing at 2200° F are more distinctly outlined by second phase precipitates and are larger in size in the D-43 (Dup F) than in the D-43 (Std). After the D-43 (Dup F) specimens have been annealed in contact with titanium, the grains are about the same size but the grain boundaries are noticeably straighter than the boundaries prior to annealing. This structural change, shown in Figures 21 and 22(a), is induced by the titanium sink rather than being merely an effect of the additional annealing time. This is evident from a comparison of Figure 22(a) (annealed with a titanium sink) and Figure 22(b) (annealed without a titanium sink). Extending the annealing time to 57 hours did not produce any detectable change in the structure of the D-43 (Dup F).

These observations suggest that the dissolution of interstitial precipitates in the D-43 (Dup F), induced by interstitial migrations to the titanium sink is responsible for the change in grain morphology. A decrease in the concentration of second-phase particles anchoring grain boundaries will permit the boundaries to straighten and thus lower the overall boundary area and energy. However, the initial grain size in D-43 (Dup F) appears to be an equilibrium one since grain growth was not observed in specimens annealed extended time at 2200° F.

4.3 HARDNESS

The hardness changes detected in the titanium were about the same for the Ti/D-43 (Std) and the Ti/D-43 (Dup F) diffusion couples annealed at 2200° F. However, the scatter in the hardness values for the titanium foils made precise comparisons difficult. As shown from a comparison of Figure 23 with 24, the hardness of the titanium sink is increased when the diffusion couple is heat treated 15 minutes at 2200° F. Extending the heat treating time to 57 hours, however, did not significantly increase the hardness of the titanium (Figure 25). The diffusion of carbon from the D-43 into the titanium is believed to contribute to the rapid increase in the hardness of the titanium. As previously discussed, a new phase observed in the titanium after the diffusion couples were heat treated at 2200° F is believed to be TiC. The hardness of this phase (> 2800 Knoop), shown in Figure 26, probably contributes to the overall hardness of the titanium.

The hardness of the D-43 (Std) is initially about 220 while that of the D-43 (Dup F) is about 180. The hardness of the former decreases with increasing annealing time to about the hardness of the latter. This decrease in hardness of the D-43 (Std) induced by annealing it in contact with titanium can be seen from a comparison of the hardness traverses shown in Figures 23 and 25. However, this decrease in hardness cannot be attributed to the interstitial sink effect because it was found that the D-43 (Std) after being heat treated without titanium underwent a similar decrease in hardness. In contrast with this behavior, the hardness of the D-43 (Dup F) was unchanged by the 2200° F annealing treatments for specimens annealed both with and without a titanium sink.

V. FUTURE WORK

Studies of the progressive effects on structure of the gradual removal of interstitials from D-43 to a diffusion bonded titanium sink will be continued for both the standard and duplex heat treated conditions. The alloy will be heated for various lengths of time at 1800° F and 2200° F in contact with a titanium sink to allow interstitial partition to take place. The structural changes observed will be correlated with the creep behavior of these specimens in later tests.

The effects on the partition of interstitials and the accompanying structural changes induced by varying the chemical potential (partial molal free energy) of the interstitial sink will be studied. D-43 will be diffusion bonded to a series of Ti-Cb alloys of different compositions (and thus varying chemical potential). The composites will be annealed under conditions to permit interstitial partition to approach equilibrium values.

Creep tests will be performed on D-43 in the 2200° F temperature range in a vacuum of 10^{-6} Torr to correlate the structural effects noted in the initial phase of this study with primary creep behavior. Creep measurements will be made before and after exposure of the alloy to a titanium sink.

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1. R. L. Fullman, R. P. Carreker and J. C. Fisher, Trans. AIME, 197, 657 (1953).

2. C. S. Hartley, J. E. Steedly and L. D. Parsons, Diffusion in Body-Centered Cubic Metals, American Society for Metals, Metals Park, Ohio, 1964 p. 54.

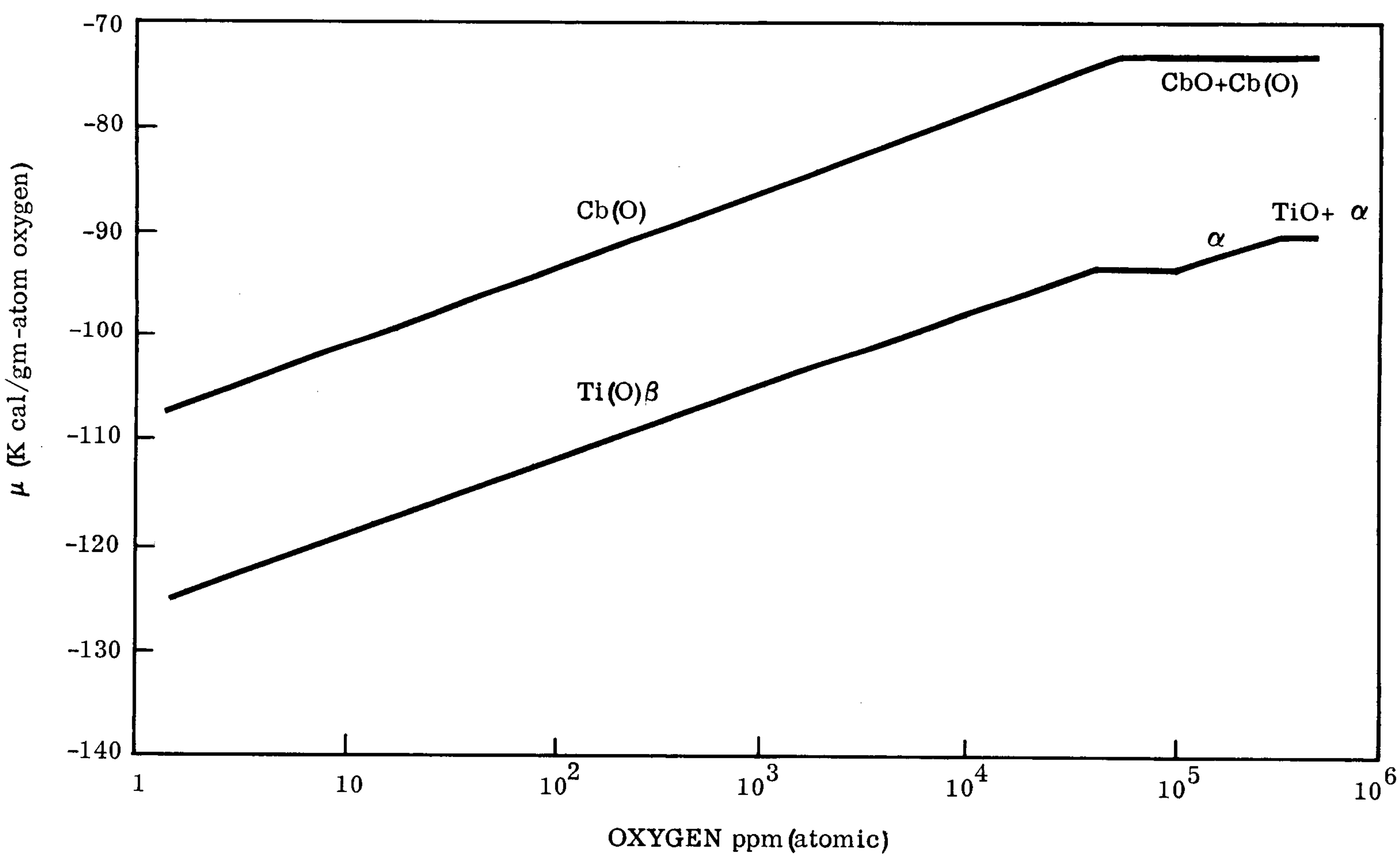


Figure 1. Change in Free Energy as a Function of the Oxygen Concentration of Columbium and Titanium at 2200° F

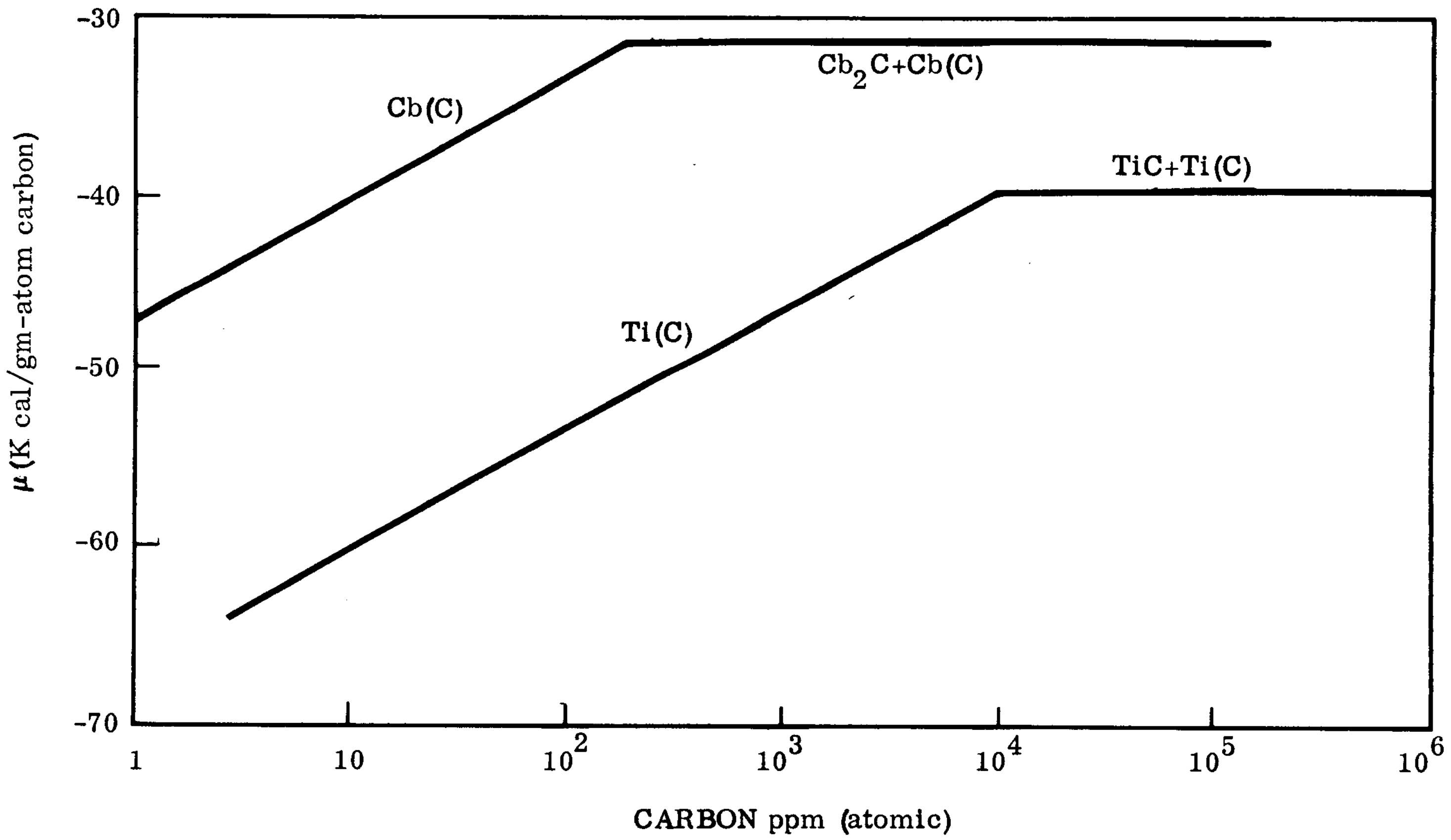


Figure 2. Change in Free Energy as a Function of the Carbon Concentration of Columbium and Titanium

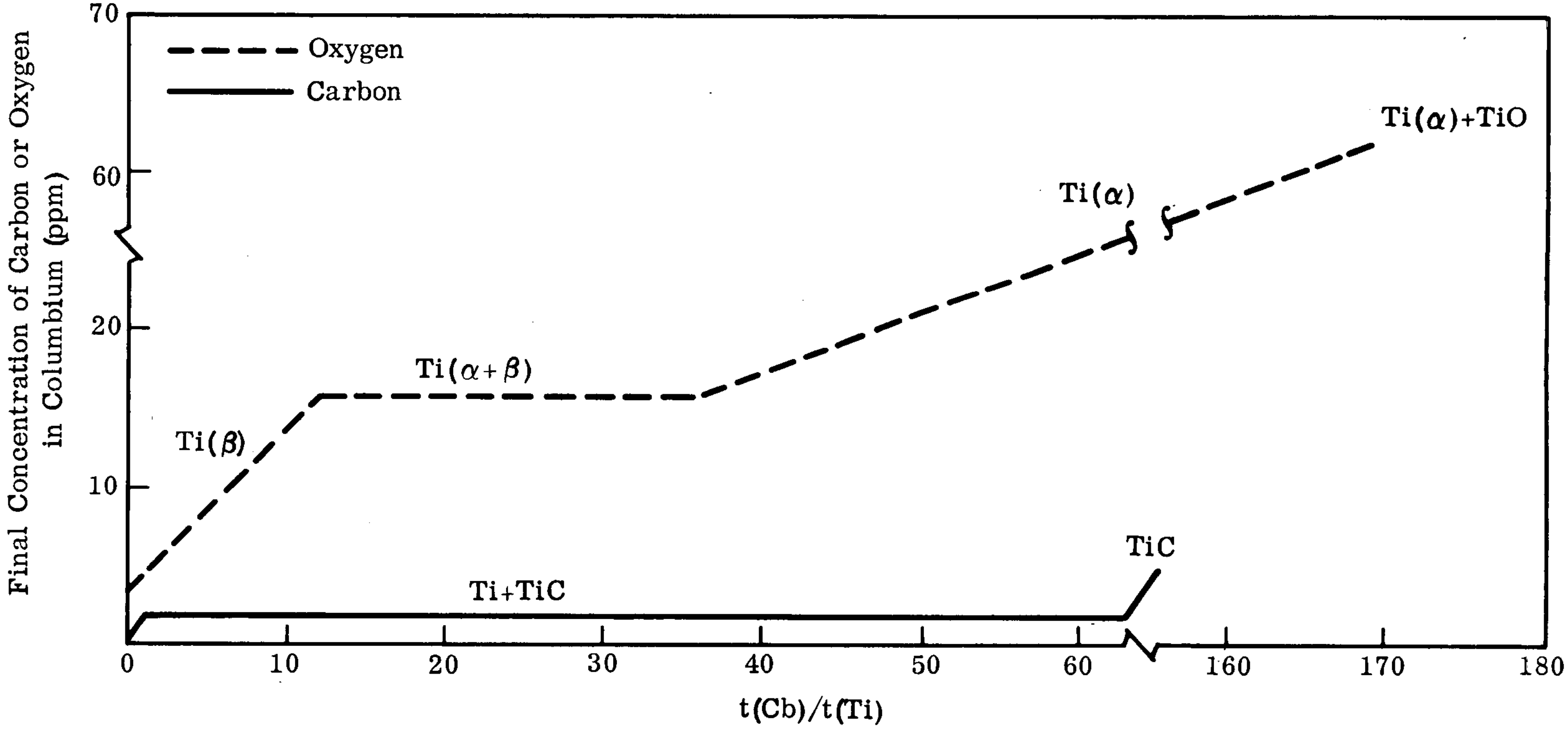


Figure 3. Oxygen and Carbon in Columbium as a Function of the Thickness Ratio, t(Cb)/t(Ti)

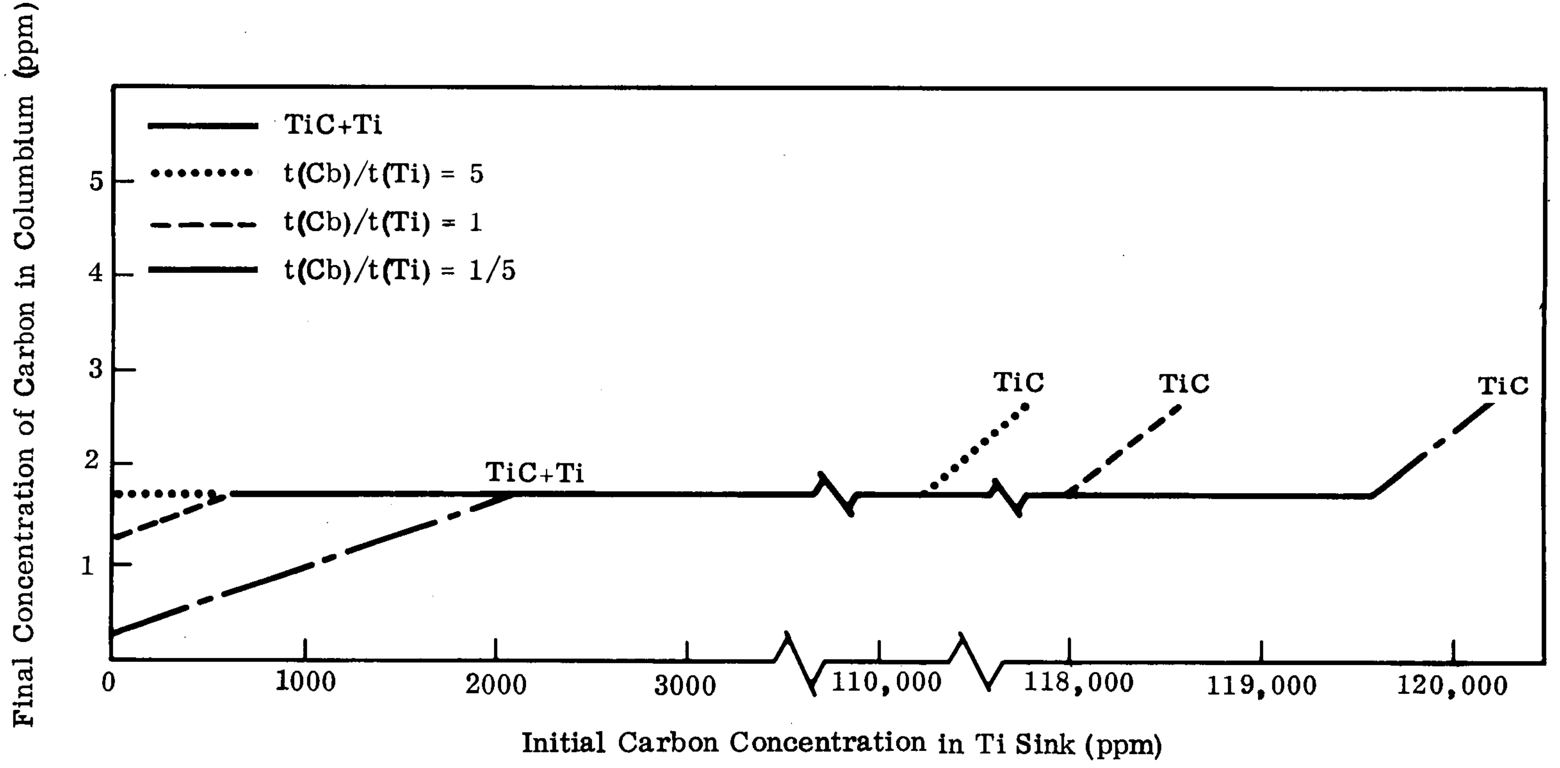


Figure 4. The Influence of the Initial Carbon Concentration in Titanium on the Final Carbon Concentration in Columbium

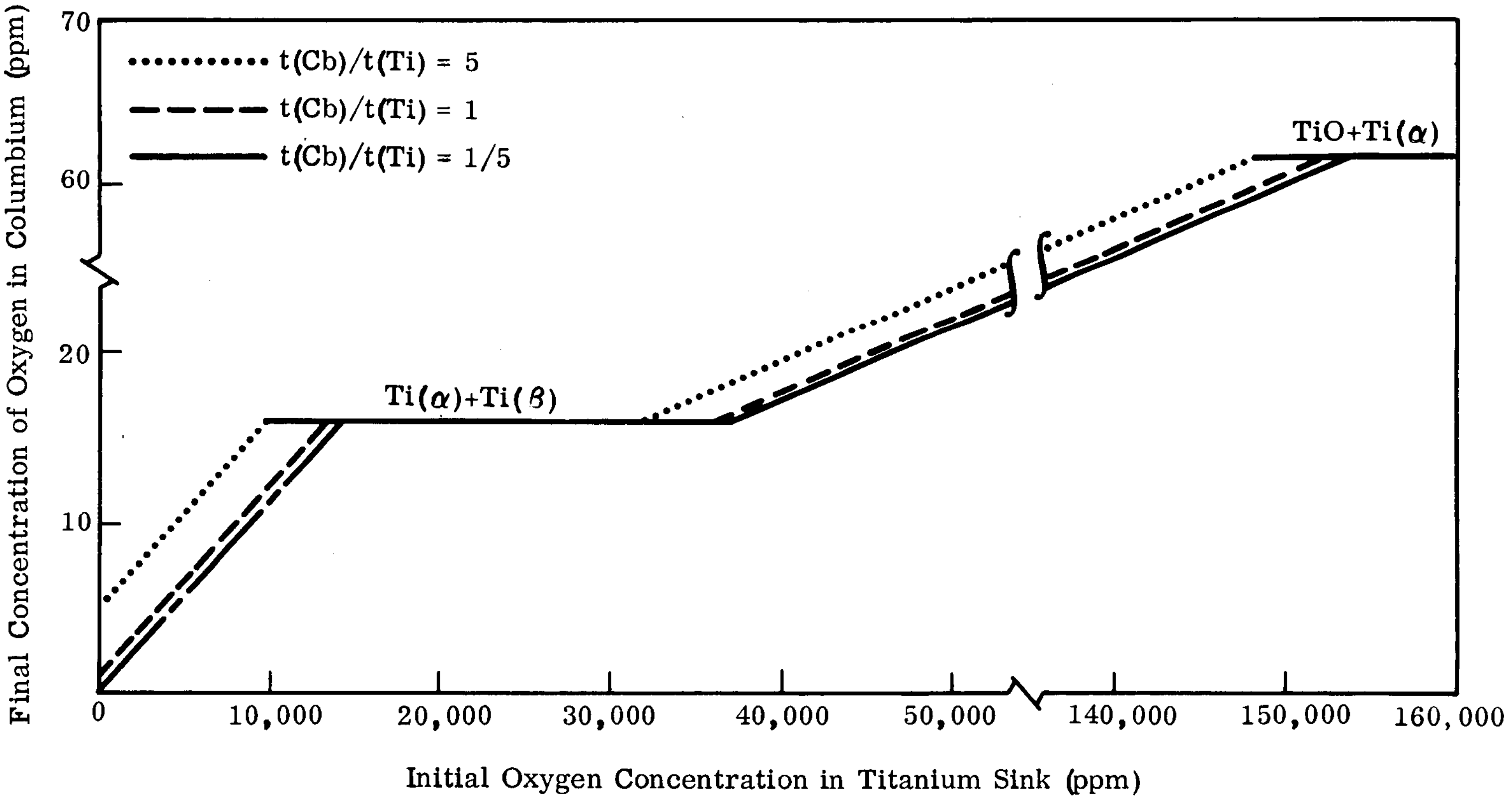


Figure 5. The Influence of the Initial Oxygen Concentration in Titanium on the Final Oxygen Concentration in Columbium

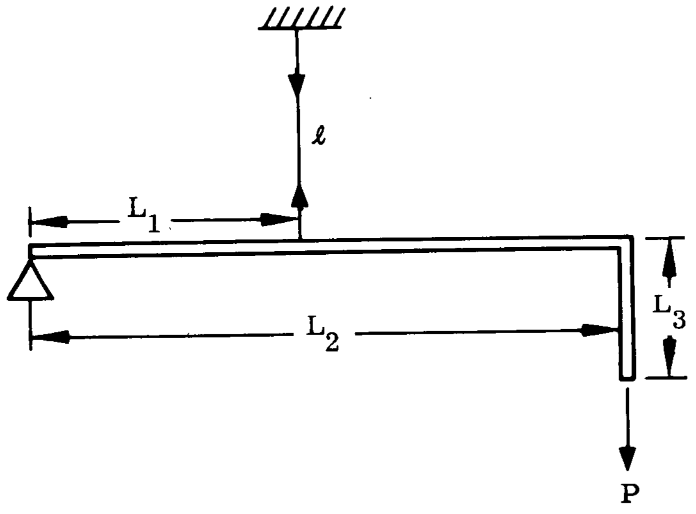
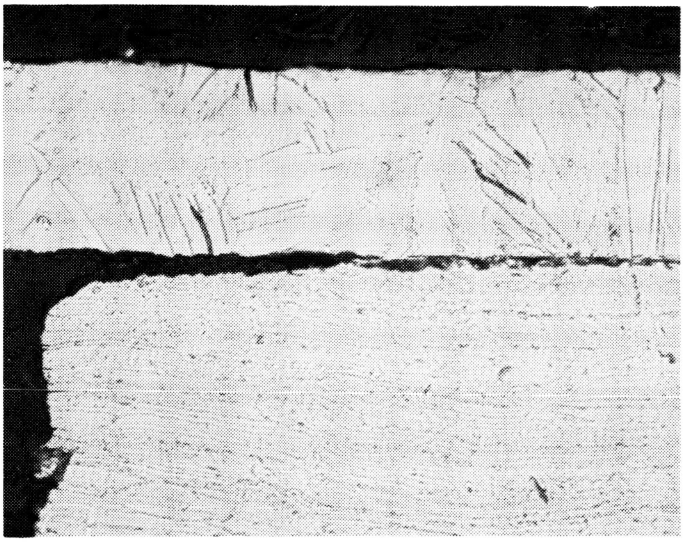


Figure 6. Schematic Diagram of Loading Beam for Constant Stress



(500 X)

FIGURE 7. THE EDGE OF Ti/D-43 DIFFUSION BOND

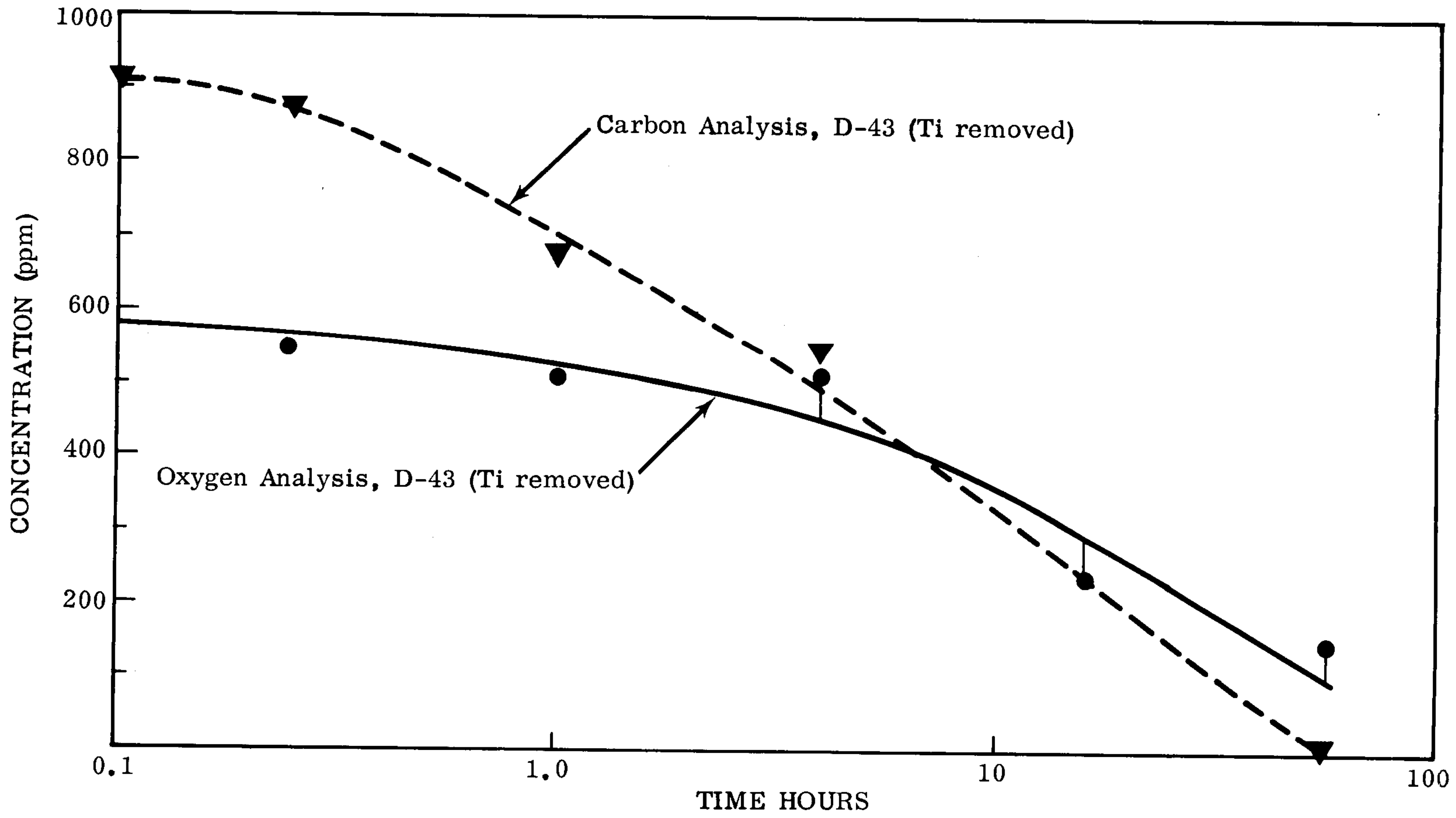
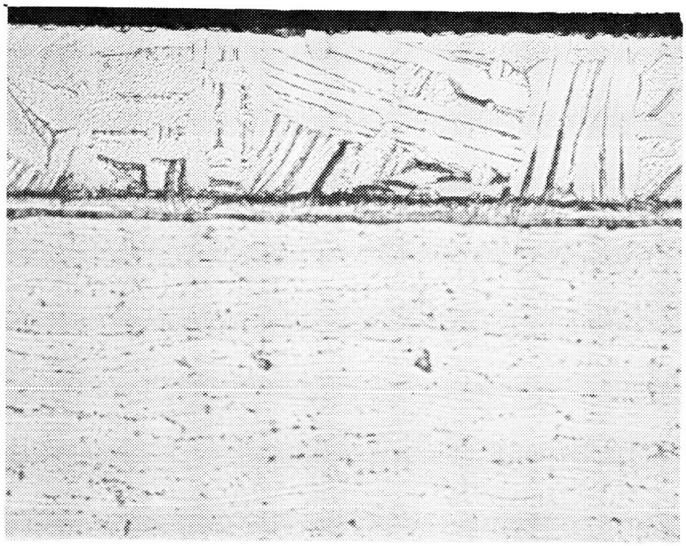
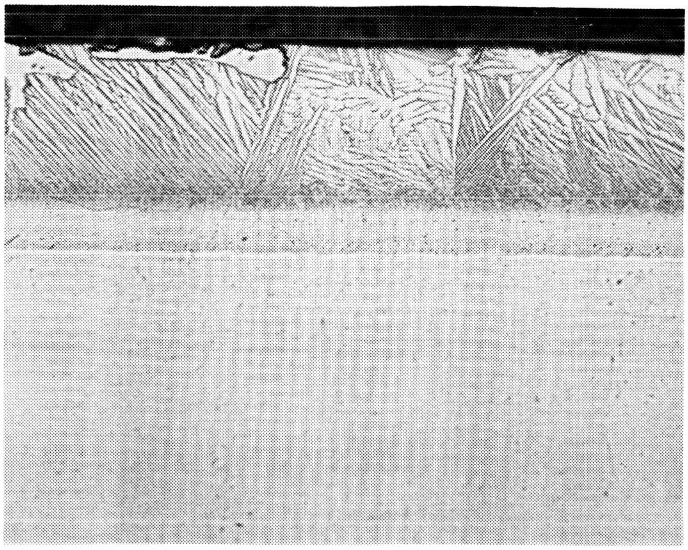


Figure 8. The Effect of a Titanium Sink on the Carbon and Oxygen Concentrations of D-43 (Std)



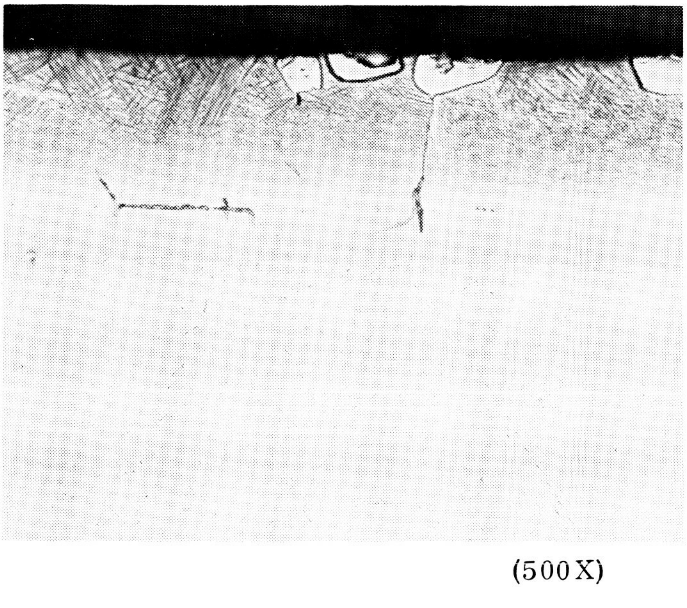
(500 X)

FIGURE 9. Ti/D-43 (CENTER) AS BONDED



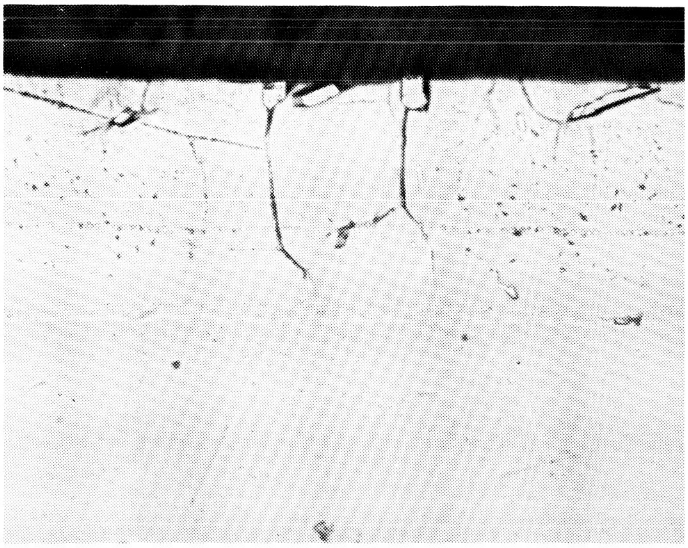
(500 X)

FIGURE 10. Ti/D-43 ANNEALED
15 MIN. at 2200° F



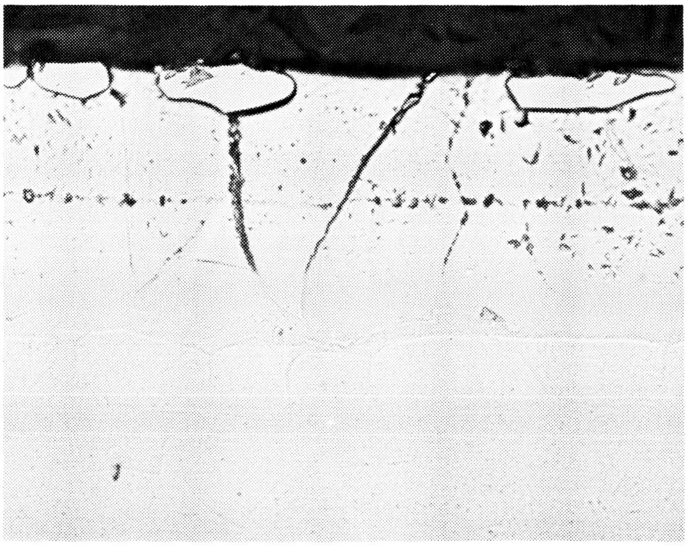
(500 X)

FIGURE 11. Ti/D-43 ANNEALED
1 Hr. 2200° F



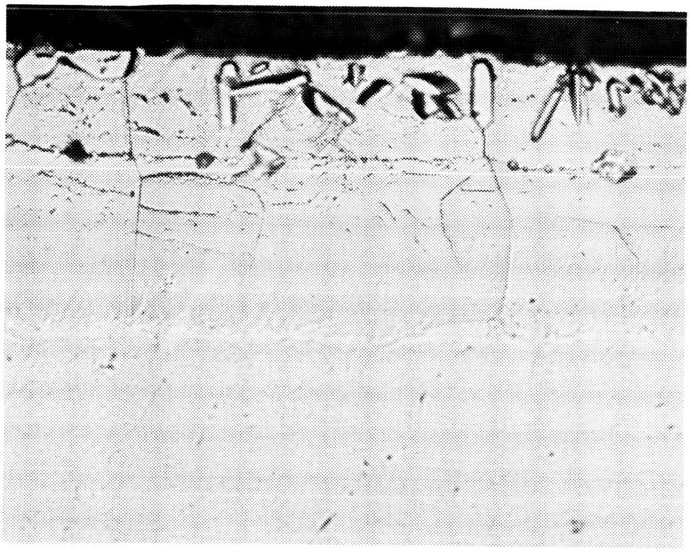
(500 X)

FIGURE 12. Ti/D-43 ANNEALED
4 Hr. at 2200° F



(500 X)

FIGURE 13. Ti/D-43 ANNEALED
16 Hr. at 2200° F



(500 X)

FIGURE 14. Ti/D-43 ANNEALED 57 Hr. at 2200° F

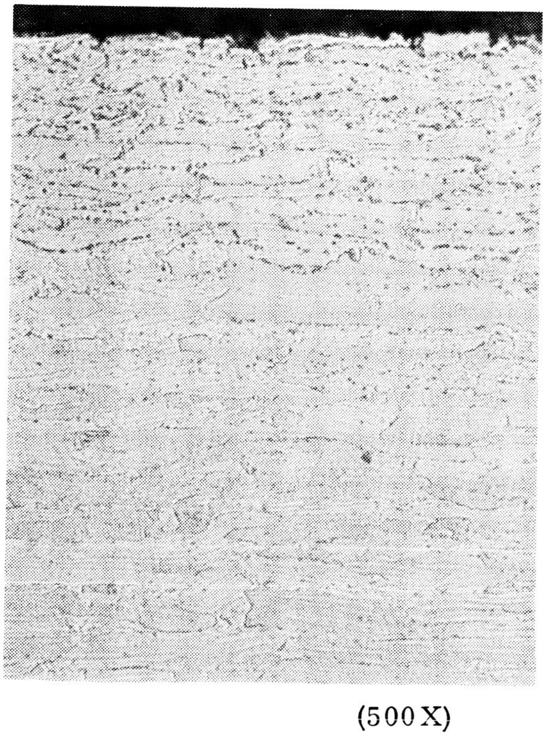
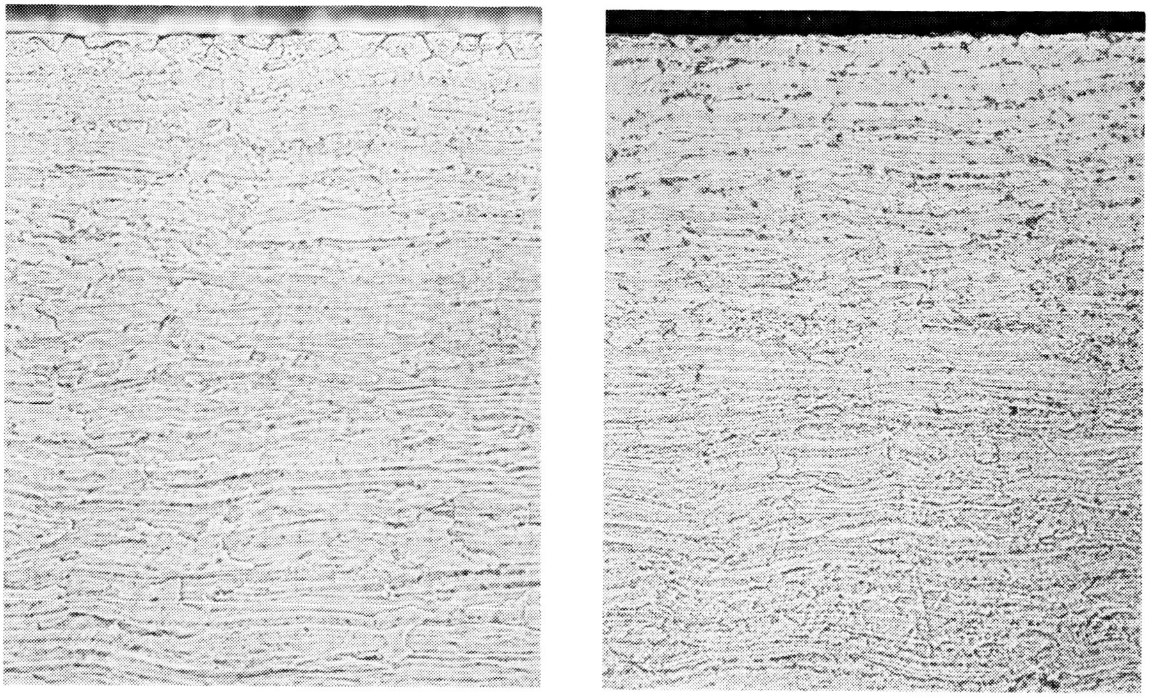


FIGURE 15. THE STRUCTURE OF D-43 (Std) PRIOR TO ANNEALING at 2200° F

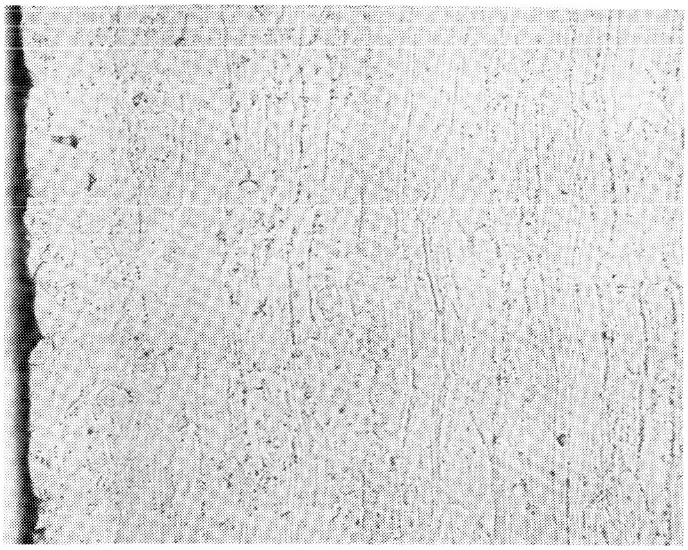
(500 X)



(500 X)

A. B.

FIGURE 16. D-43 (Std) ANNEALED 15 MIN. AT 2200° F
A. In Contact with a Ti Sink
B. Without a Ti Sink



(500X)

FIGURE 17. D-43 (Std) ANNEALED 1 Hr. at 2200° F IN CONTACT WITH A Ti SINK

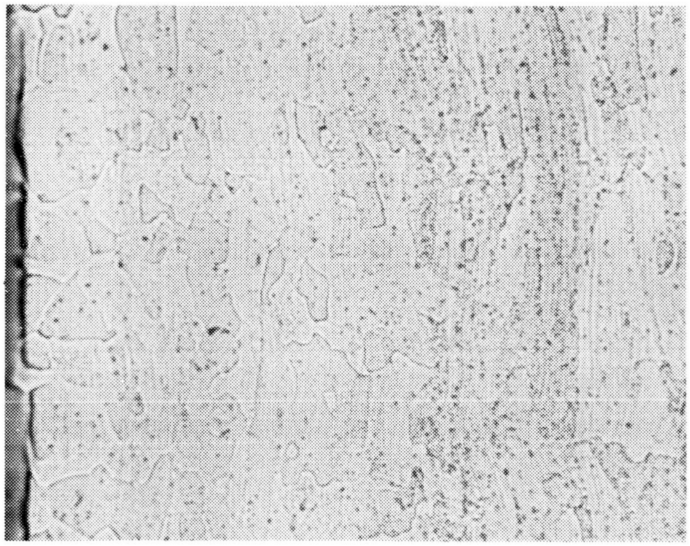


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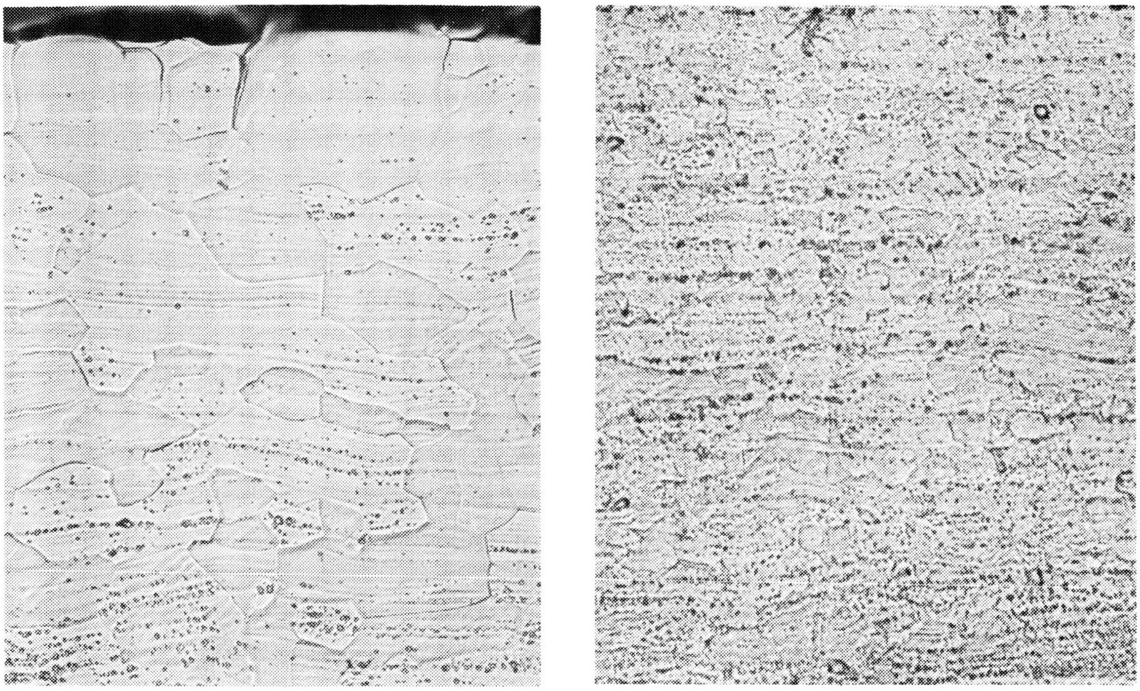
FIGURE 18. D-43 (Std) ANNEALED 4 Hr. at 2200° F IN CONTACT WITH A Ti SINK



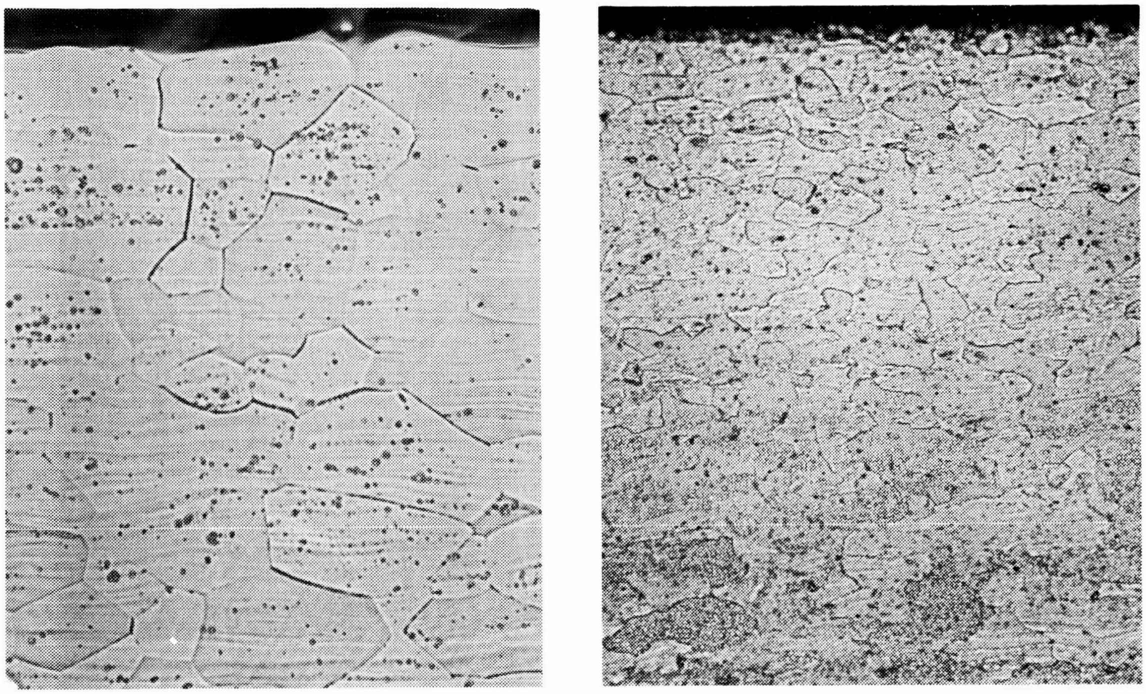
(500 X)

A. B.

FIGURE 19. D-43 (Std) ANNEALED 16 Hr. at 2200° F

A. In Contact with a Ti Sink

B. Without a Ti Sink



(500 X)

A B

FIGURE 20. D-43 (Std) ANNEALED 57 Hr. at 2200° F
A. In Contact with a Ti Sink
B. Without a Ti Sink

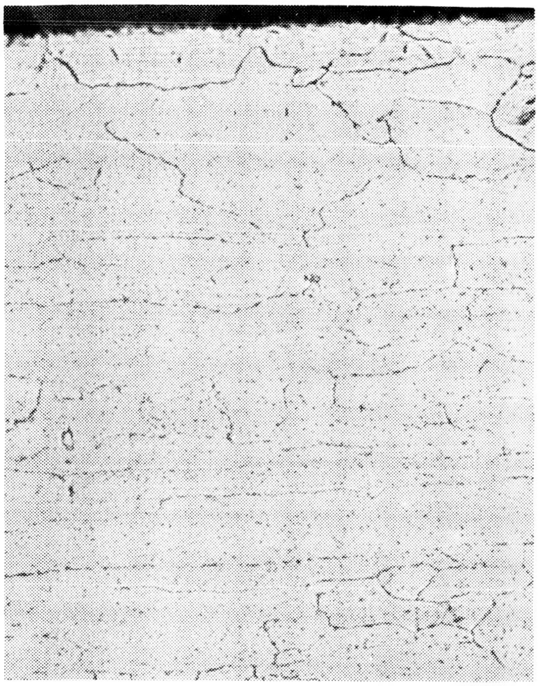


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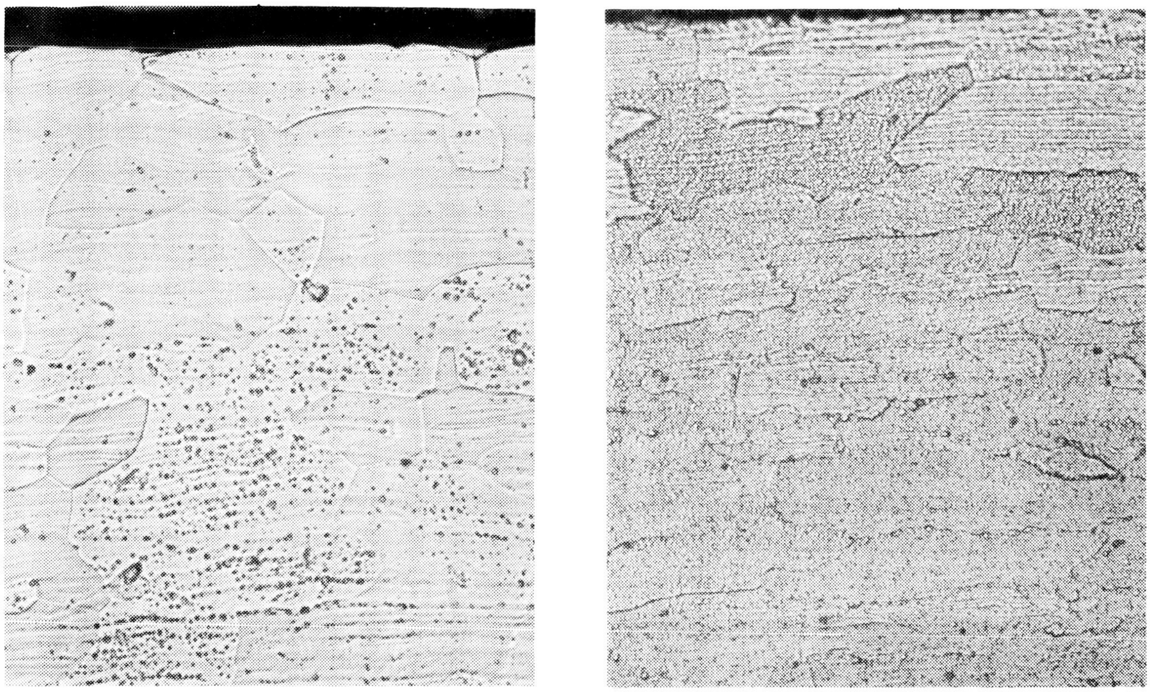
FIGURE 21. D-43 (Dup F) PRIOR TO ANNEALING AT 2200° F



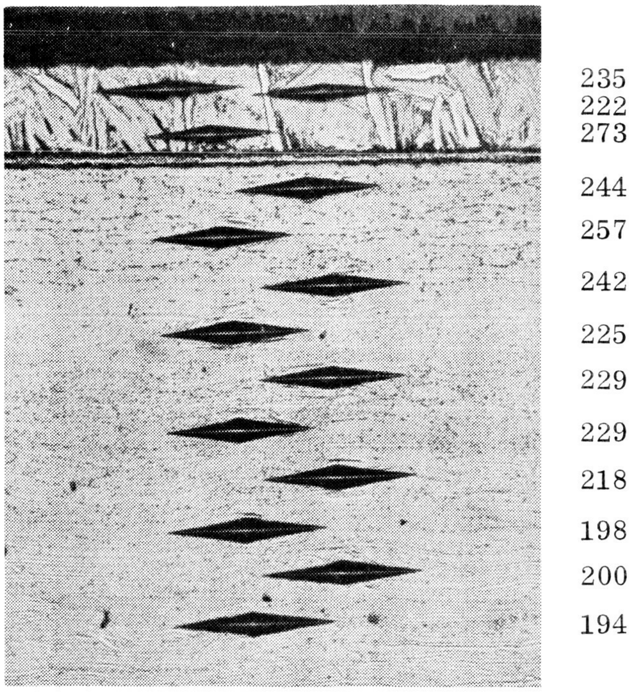
(500 X)

A B

FIGURE 22. D-43 (Dup F) ANNEALED 16 HRS AT 2200° F

A. In Contact with a Ti Sink

B. Without a Ti Sink



(250 X)

FIGURE 23. HARDNESS OF Ti/D-43(Std) IN AS-BONDED CONDITION

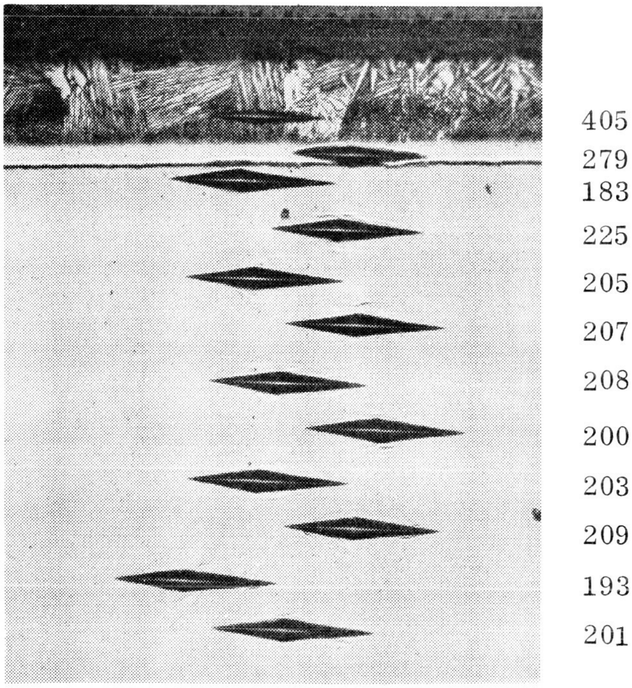


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FIGURE 24. HARDNESS OF Ti/D-43 (Std) ANNEALED 15 MIN. 2200° F

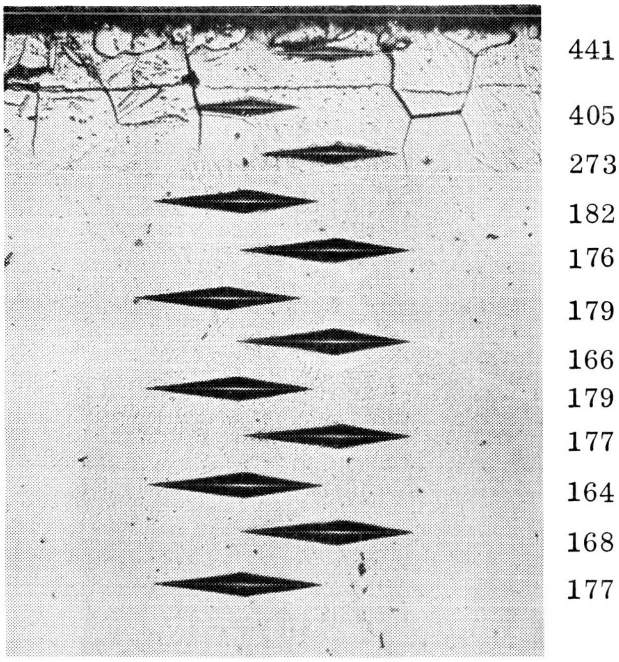

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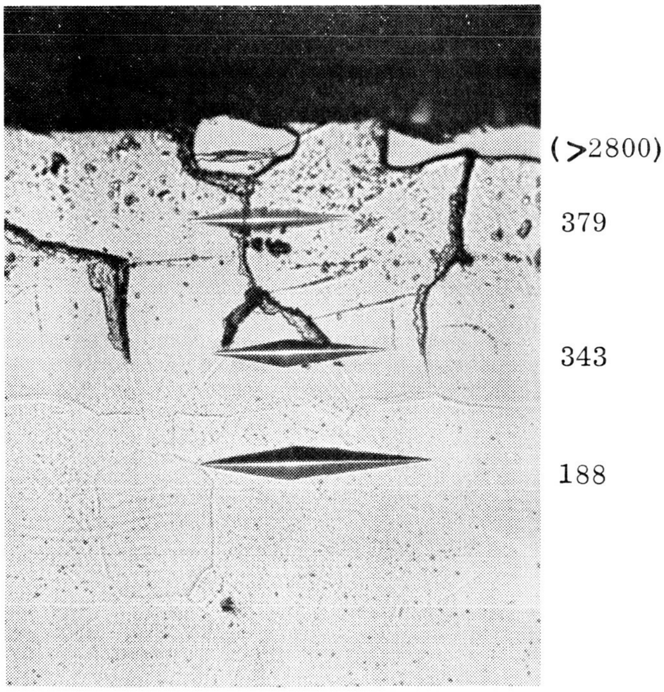
FIGURE 25. HARDNESS OF Ti/D-43 (Std) ANNEALED 57 Hrs at 2200° F



(500 X)

x FIGURE 26. HARDNESS OF SECOND PHASE IN Ti FOIL