

# Microstructural Control of Thin-Film Diffusion-Brazed Titanium

*Simple diffusion calculations can be used to control the compositions of thin-film diffusion brazements*

BY R. R. WELLS

**ABSTRACT.** The mechanical behavior of a brazed joint depends upon both the properties of the joining material and the adjacent base metal. This is particularly true for thin-film diffusion brazing systems, since the joint becomes an extension of the base metal.

The work described in this paper was designed to determine what parameters should be controlled to achieve quality joints of good toughness and high strength in titanium alloys. Emphasis was placed upon studying those parameters which provided tough joints compatible with the titanium base metal being joined. This paper is concerned with thin-film diffusion brazing based upon the eutectic system formed between copper and titanium.

In order to control the joint microstructure, the copper diffusion rates and the beta-phase decomposition kinetics were studied in detail. This information was used to produce various types of microstructures in test specimens. These were then evaluated to select the best microstructures for toughness and strength which were compatible with the titanium alloys.

The results of this work show that it is possible to accurately control properties of joints produced by thin-film diffusion brazing. This is done by controlling the initial copper content and the time-temperature parameters used in processing.

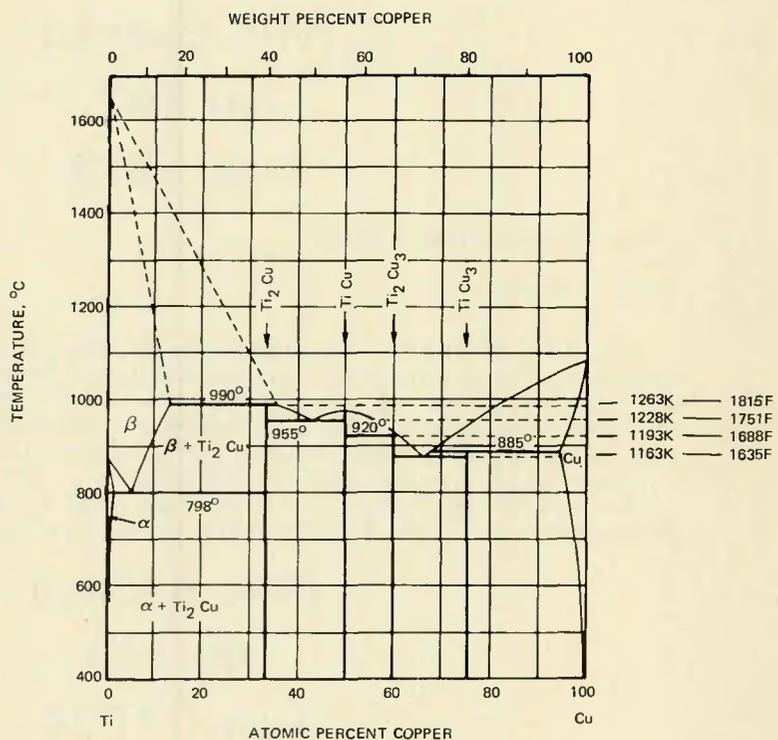


Fig. 1 — Titanium-copper phase diagram

## Introduction

Thin-film diffusion brazing systems differ from normal brazing systems in that only a thin layer of liquid will be formed at the joining temperature. Usually, neither the base metal nor the thin film melt by themselves at this temperature. The liquid is formed due to either a eutectic or peritectic reaction or, in a few cases, the formation of a minimum melting point in an isomorphous system. These systems

owe their joining characteristics to the formation of a eutectic, peritectic, or minimum melt-point liquid after solid state diffusion has occurred between the base metal and the thin film to create the proper composition for melting.

When these systems are used for brazing, the quantity of the thin film must be carefully controlled. If excess thin-film material is used, then the reaction will create a large quantity of liquid which could cause erosion of

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This paper was presented at the Sixth Inter-Agency AWS-WRC Brazing Conference in Cleveland, Ohio, during April 22-

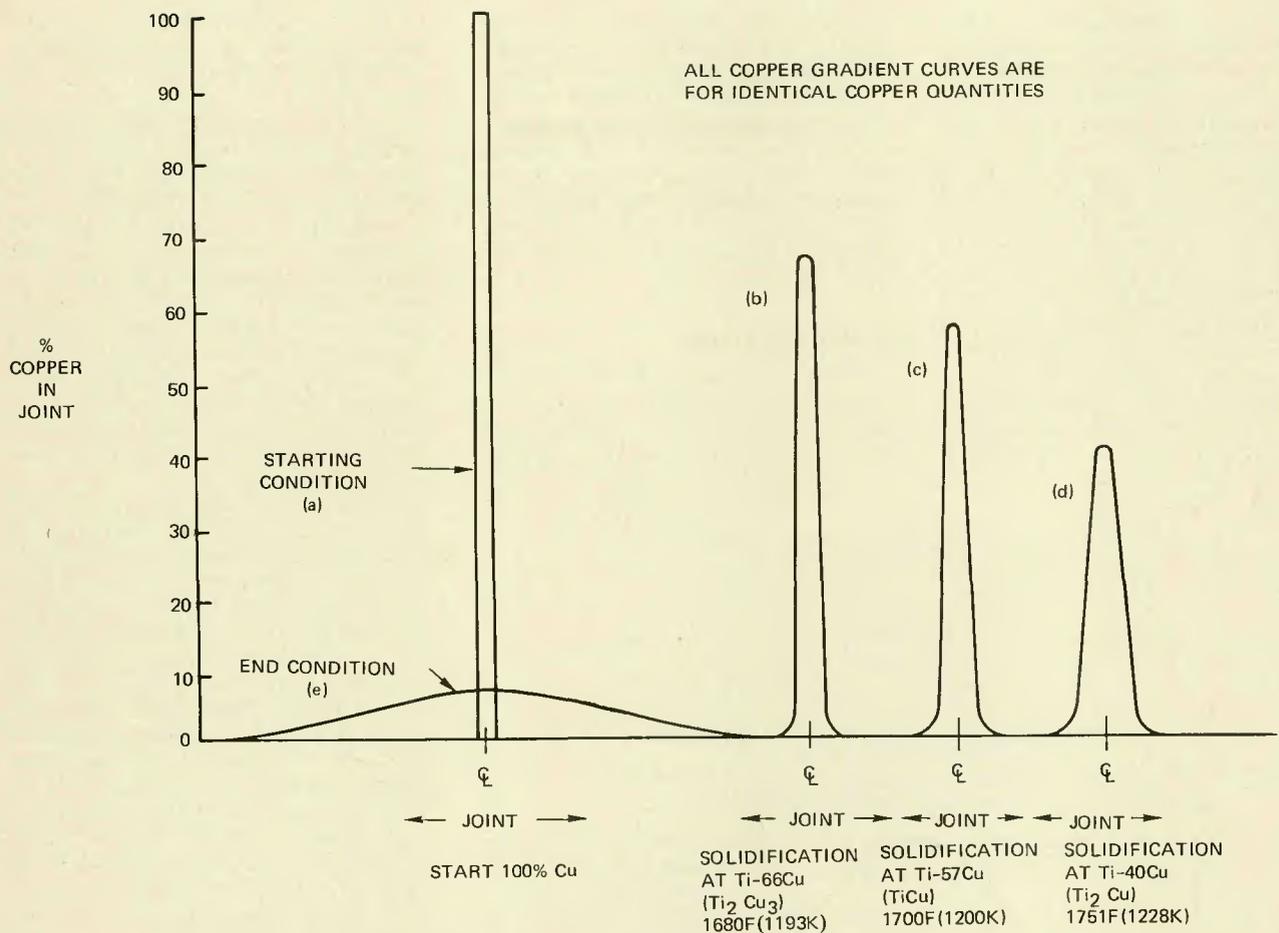


Fig. 2 — Copper distribution through titanium joint at various stages during the eutectic reaction cycle

the base metal and form thick joints. The composition of these thick joints is difficult to alter, and the diffusion times and temperatures become excessive. Conversely, a very thin layer of intermediate material may not form sufficient liquid to fill voids and create sound joints. The selection of the proper quantity of thin-film material is further complicated by solid state diffusion during slow heating rates and by fit-up tolerances.

Potential eutectic joining systems can be identified by studying phase diagrams. However, only experimentation can determine whether (a) a particular system will diffuse rapidly enough to be of practical value, (b) stable intermetallic compounds will form and produce brittle joints, (c) grain boundary liquation occurs, and (d) strong, tough joints can be fabricated.

The mechanical behavior of thin-film diffusion brazed joints depends upon both the properties of the joint and the adjacent base metal. Therefore, a detailed understanding of the metallurgy of the system is required to form a sound, high-strength, tough joint which is compatible with the base metal and its heat treatment. The joint microstructure and me-

chanical properties can be controlled by proper control of the quantity of the thin-film material and the time and temperature parameters.

### Titanium — Copper Eutectic Joining

In this work, the titanium-copper eutectic system was used as a model, since sufficient work (Ref. 1) has been performed to characterize it in detail. Figure 1 shows the titanium-copper binary diagram from Hansen (Ref. 2). For a starting condition, assume that a thin-film of electroplated copper is sandwiched between two pure titanium surfaces. This yields a copper gradient across the joint, as shown in Fig. 2(a).

When these two metals are heated in intimate contact, significant solid state diffusion starts to take place between them at approximately 1300 F (977 K). Thus, by the time 1600 F (1144 K) is reached, a complete range of compositions and phases (see Fig. 1) from pure copper to pure titanium exists. Then, as the eutectic temperature of approximately 1635 F (1163 K) is exceeded, that portion of the interface region which is at the eutectic composition  $Ti-72Cu$  melts.

Diffusion takes place some 100 to 1000 times faster in liquid than in solid. Because of this, the interface broadens rapidly by dissolving more base metal until all of the copper is consumed to form eutectic liquid. At this time, the eutectic liquid becomes a brazing filler metal and wetting and flow take place.

Two different phenomena take place next, each of which becomes a part of the final joining parameters. First, the eutectic liquid tends to form fillets and fill voids; this causes localized concentrations of the eutectic material. The second and somewhat concurrent action is that diffusion continues to take place between the eutectic liquid and the titanium, resulting in an increase in melting-temperature range.

Unless the temperature is increased above 1688 F (1193 K), the eutectic liquid will quickly dissolve additional titanium and solidify at  $Ti-66Cu$ , producing the copper gradient shown in Figure 2(b). However, if the temperature is increased to 1700 F (1200 K), then the liquid composition range is expanded by a peritectic reaction (Fig. 1), and solidification will occur at  $Ti-57Cu$ , producing the copper gradient shown in Fig. 2(c).

This is advantageous because this peritectic adds liquid for brazing purposes while reducing the copper concentration in the joint which otherwise must be reduced by much slower solid state diffusion.

If a temperature of 1700 F (1200 K) is held, the liquid will solidify with a composition of Ti-57Cu. Additional time at 1700 F (1200 K) results in a further reduction in the maximum copper concentration in the joint by solid state diffusion between TiCu and the beta titanium. If the temperature is raised above 1751 F (1228 K), then solidification occurs at the composition Ti-40Cu with the copper gradient shown in Fig. 2(d). The remaining

compositional change takes place through solid state diffusion between Ti<sub>2</sub>Cu and the beta titanium phase.

Above the 1815 F (1263 K) peritectic temperature, the liquid plus solid region extends to the beta titanium phase containing about 15% copper. However, 1815 F (1263 K) is above the beta transus temperature of most titanium alloys; this is undesirable in most cases.

### Diffusion Kinetics

For this discussion, 1800 F (1255 K) is used as the maximum temperature at which solid state diffusion becomes the controlling factor. The next step

taken in developing a practical solution was made by substituting alloys Ti-6Al-4V and Ti-8Al-1Mo-1V for pure titanium.

Once a temperature has been selected, the solidification composition of the joint is determined. The problem of composition control then becomes one of knowing the starting quantities of copper and the final chemical composition desired. A parallel portion of this work indicated that, as a first approximation, a joint containing between 5 and 10% copper was desired. Knowing what composition is desired and the diffusion kinetics, one can then select the proper diffusion time to create the desired joints.

Diffusion couples were used to determine the diffusion rates. The formation of the eutectic liquid, the subsequent dissolving of titanium, and final solidification of this liquid take place very rapidly. Therefore, the diffusion experiments were designed, assuming that this portion of the process took place instantaneously upon reaching a holding temperature. Solid state diffusion then takes place between the infinite supply of titanium and the limited quantity of Ti<sub>x</sub>Cu<sub>y</sub> compound. The diffusion couples were made by sandwiching a thin layer of copper between titanium alloy layers, thus forming a thin-film type of diffusion couple.

Various quantities of copper were used in the diffusion couples, and these were heated to temperatures between 1500 and 1800 F (1090 and 1255 K) and held for different times. Fast heating and cooling rates were used to minimize diffusion effects at lower temperatures. Electron microprobe analyses were conducted for

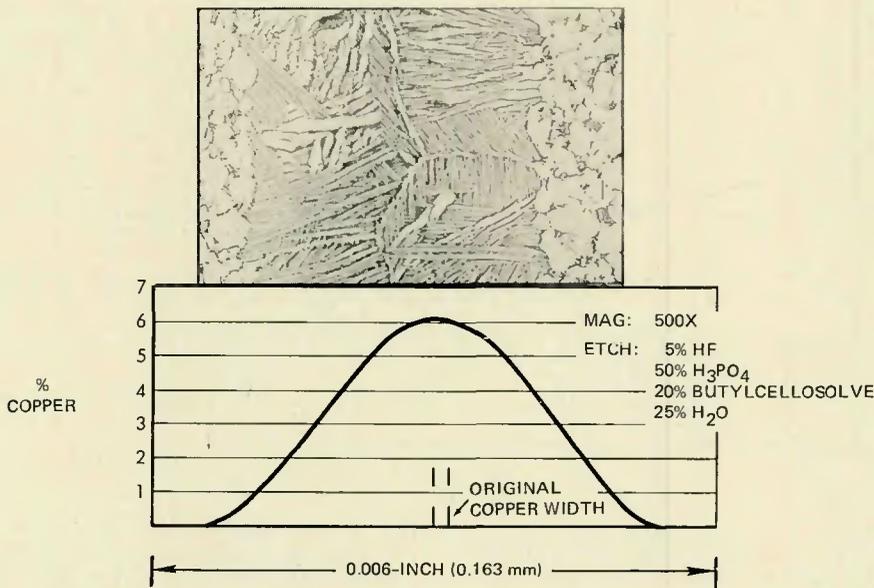


Fig. 3 — Comparison of microstructure and chemical gradient in a Ti-8Al-1Mo-1V joint held at 1700 F (1200 K) for 20 min (photomicrograph reduced 27% in reproduction)

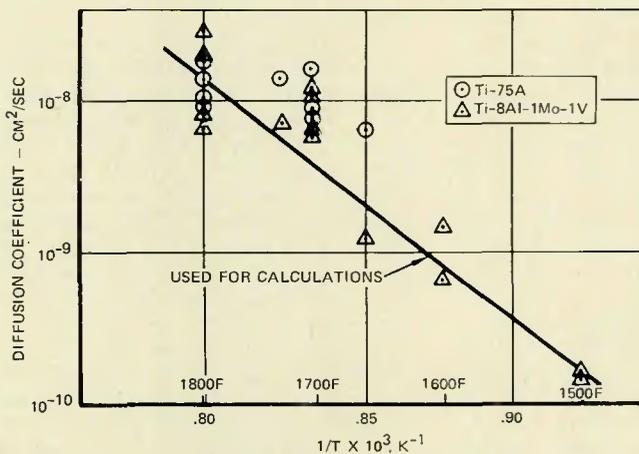


Fig. 4 — Diffusion coefficients for diffusion of copper into titanium joints

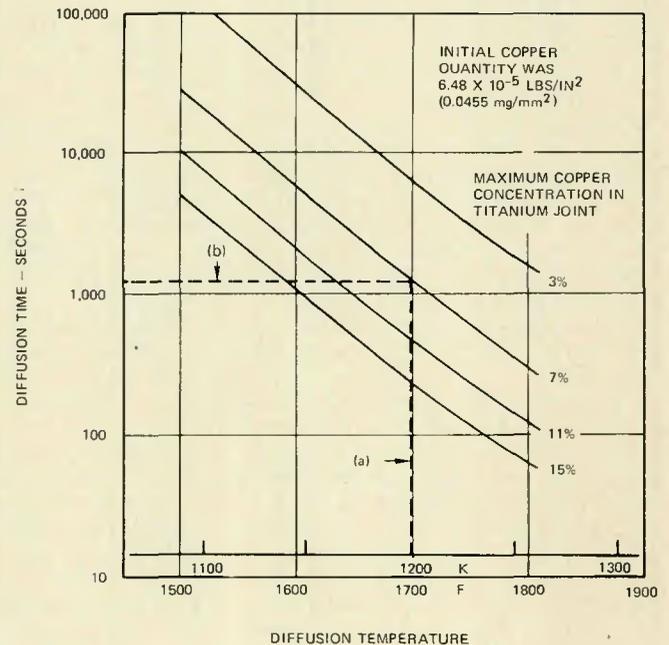


Fig. 5 (right) — Time, temperature, copper concentration curves

copper content as a function of joint position.

If 0.0004 in. (0.010 mm) thick copper is taken as the initial condition for a diffusion couple, then the joint has an initial copper concentration as depicted in Fig. 2(a). After the diffusion cycle, the copper is dispersed over a broad band and the maximum copper content is low, as shown in Fig. 2(e).

Both the microstructure and the microanalysis of an actual joint are shown in Fig. 3. This joint was fabricated at 1700 F (1200 K) for 20 min (1200 sec) with an initial copper thickness of 0.0004 in. (0.010 mm). Other thin-film diffusion couples were made using similar copper quantities but with other diffusion conditions.

These diffusion couples were then analyzed for effective diffusion rates using the Boltzmann-Matano (Ref. 3) method of analysis. These effective diffusion rates were plotted as a function of reciprocal temperature, as shown in Fig. 4. The straight line shown in Fig. 4 was drawn as a reasonable approximation of the diffusion coefficients (D). Values of D from this line were used for all subsequent calculations.

Diffusion couples have an intermediate layer which starts with pure copper and ends with a low copper concentration. Therefore, the thin-film diffusion equation (Ref. 4) was used for subsequent calculations to predict joint behavior. This equation is:

$$c = \frac{\alpha}{2\sqrt{\pi Dt}} \exp\left(-\frac{X^2}{4Dt}\right) \quad (1)$$

where  $c$  is concentration of solute (%);  $\alpha$  is quantity (cm%) of solute (thin-film);  $X$  is distance normal to the initial solute film (cm from the center of the joint);  $t$  is time (seconds or s);  $D$  is diffusion coefficient (cm<sup>2</sup>/second).

For these joints, the maximum copper content of the joint governs the final microstructure and mechanical properties. Since only the maximum copper quantity is important and this maximum occurs at the center of the joint, eq (1) reduces to:

$$C_{\max} = \frac{\alpha}{2\sqrt{\pi Dt}} \quad \text{at } X = 0 \quad (2)$$

Equation (2) was then used to construct the family of curves in Fig. 5. The curves relate maximum residual copper content at the center of the joint with diffusion times and temperatures for a given starting quantity of copper. By determining the quantity of copper necessary to form the joints with a given heating rate and joint configuration, and by determining the maximum joining temperature desired — in this case 1700 F (1200 K)

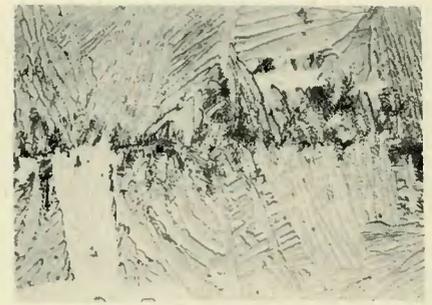
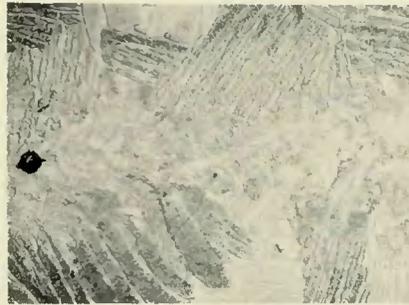


Fig. 6 — Typical microstructures for thin film diffusion brazed joints between pure titanium alloys. Left — Ti-55A, 1700 F (1200 K) — 20 min, 1450 F (1060 K) — 15 min. Right — Ti-75A, 1700 F (1200 K) — 20 min, 1375 F (1020 K) — 15 min. Etch: 5% HF, 50% H<sub>3</sub>PO<sub>4</sub>, 20% butylcellosolve. X500 (reduced 48% on reproduction)

— one can determine the diffusion time by following the vertical 1700 F (1200 K) line, (a) in Fig. 5, up to the desired maximum copper level (7%) and find the time required on the horizontal scale (1200 s). These values apply to joints of uniform copper thicknesses; some additional time will be required to reach the desired chemistry in localized areas where the eutectic liquid may be more concentrated, i.e., fillets and voids.

These concentration curves can be used to calculate the effects of multiple times and temperatures on diffusion of copper from the joint. To do this, one must start with the copper concentration after a joining cycle. For example, a joining cycle of 250 at 1700 F (1200 K) would result in a maximum copper concentration of 15%. If the temperature is then lowered to 1500 F (1090 K), the 15% copper concentration becomes equivalent to a diffusion cycle of 5,000 s at 1500 F (1090 K). An additional 25,000 s of diffusion time would be required to reach a final copper concentration of 7% at 1500 F (1090 K).

The accuracy of the curves shown in Fig. 5 was checked over a period of years by analyzing many different specimens. The only significant deviation from predicted values occurred due to joint thickness variations resulting from poor fit-up. However, experience showed that a given quantity of copper generally required the predicted time and temperature to reach the desired maximum copper concentration at the center of the joints.

### Beta-Phase Decomposition

The eutectoid decomposition of copper-containing beta-phase titanium to alpha-phase plus the compound Ti<sub>2</sub>Cu (Fig. 1) was studied to determine the reaction kinetics and the influence of phase morphology upon joint ductility and joint strength.

The work of Margolin *et al*, (Ref. 5) provided some data on the eutectoid

transformation of copper-containing titanium alloys. The joints in this study consisted of titanium alloys and quantities of copper different from those studied by Margolin. This study used small lap-joints joined at 1700 F (1200 K) which were then continuously cooled at varying cooling rates or to a predetermined temperature and held. The joints were analyzed using hardness transverses and optical microscopy. These data were then used to establish approximate time-temperature-transformation kinetics for pure titanium (Ti-75A and Ti-55A), Ti-6Al-1Mo-1V, and Ti-6Al-4V. Since the copper composition of the joints varied from the center outward, it was necessary to construct several diagrams representing the transformations at the center of the joints and at various distances from the center.

### Beta Decomposition in Pure Titanium

The continuous cooling rates used for transforming joints of Ti-55A and Ti-75A varied between 60 and 500 F per minute (0.5 and 4.6 K s); these covered the practical ranges obtainable in a brazing facility. Neither microstructure nor hardness measurements of these samples indicated a significant difference between the various cooling rates.

Transformation of the pure titanium from beta to alpha plus compound was complete prior to the time that the M<sub>s</sub> temperature was reached, so that no evidence of martensite was seen. Isothermal transformation studies were also conducted. Again, no significant decomposition differences were noted. Since these joints in the pure titanium were made above the beta transus, large columnar alpha grains formed along with the eutectoidal alpha-plus-compound structure.

Figure 6 shows the microstructures of two typical joints resulting from the isothermal transformation of the beta titanium plus copper in the

joint region. These photomicrographs show a small difference in the size and distribution of the  $Ti_2Cu$  compound which is typical for isothermal temperature differences in most systems which transform by a eutectoid reaction.

#### Beta Decomposition in Ti-8Al-1Mo-1V

The aluminum, molybdenum, and vanadium in this alloy are present in the joint as well as the base metal. This led to substantially different transformation kinetics than those seen in the pure titanium joints.

Figure 7 shows the most representative transformation curve for a joint in the Ti-8Al-1Mo-1V alloy, which contains a maximum of 7% copper. To construct this curve, a continuous cooling rate of 500 F/min (4.6 K/s) was used during cooling from the diffusion temperature of 1700 F (1200 K) down to the transformation temperature, at which time the specimen was held at temperature.

Microstructures illustrating the phase morphology resulting from various holding times at 1400 F (1030 K), 1450 F (1060 K), and 1500 F (1090 K) are also shown in Fig. 7. The data indicate that the transformation from beta to alpha plus compound occurs in the region of 1375-1500 F (1020-1090 K) in times from 60 to 10,000 s. For practical holding times which will produce complete transformation, the temperature should be below 1460 F (1065 K). To avoid martensite forma-

tion, the holding temperature should be above 1375 F (1020 K).

#### Beta Decomposition in Ti-6Al-4V

Joint transformation studies for the Ti-6Al-4V alloy indicated that the optimum transformation temperatures occurred between approximately 1275 and 1400 F (960 and 1030 K) with holding times between 60 to 1,000 s. The nose of the curve occurred at approximately 1325 F (990 K), and the  $M_s$  at approximately 1250 F (950 K).

Figure 8 illustrates the effect of the varying copper and aluminum content in the joint on the beta transformation characteristics. These curves show that joints of varying composition will transform differently, resulting in microstructural variations. A holding time greater than 200 s at 1350 F (1003 K) would form a more uniform microstructure than the one illustrated in Fig. 8.

The beta decomposition studies showed that little control could be exercised over the phase transformations in pure titanium joints. However, considerable control can be exercised over joints made with titanium alloys. In the latter cases, the joint microstructure could be varied from a structure consisting of coarse alpha needles plus compound to a precipitate-like dispersion of compound in an alpha matrix or a martensite structure. Thus, a range of phase morphologies similar to the

pearlite, bainite, and martensite structures in steels can be formed with the titanium-copper joints.

Tests have shown that the mechanical properties corresponding to these structures are also similar to those in steels — that is, good toughness with the pearlitic-like structure and poor toughness with the martensite structures. Even the pearlitic-like joints with the titanium-copper alloys have strengths near base-metal strength. Our studies emphasized attainment of good toughness in the joints.

#### Phase Morphology and Mechanical Properties

As stated previously, it is possible to relate joint properties to both retained copper content and the microstructure resulting from decomposition of the beta phase. Three examples of this interrelationship between joint morphology and mechanical properties are briefly described here.

In the first evaluation, small changes in microstructure were produced by fabricating lap-shear specimens of Ti-8Al-1Mo-1V and transforming the beta phase at either 1420 or 1450 F (1045 or 1060 K). These specimens were tested in shear at various temperatures between -320 and 600 F (77 and 590 K). As seen in Fig. 9, there is no significant difference in the high lap-shear strengths caused by these minor

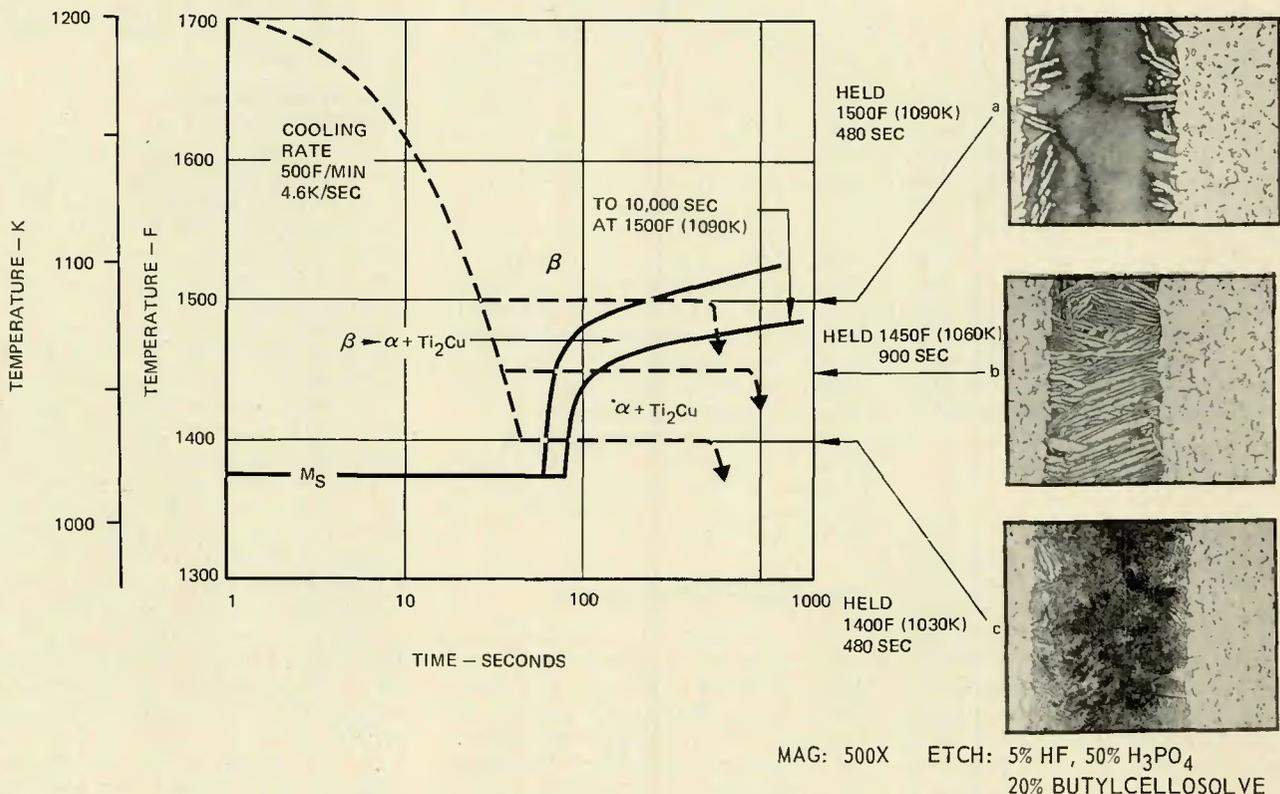


Fig. 7 — Time-temperature-transformation diagram for 7% maximum copper content joints in Ti-8Al-1Mo-1V.

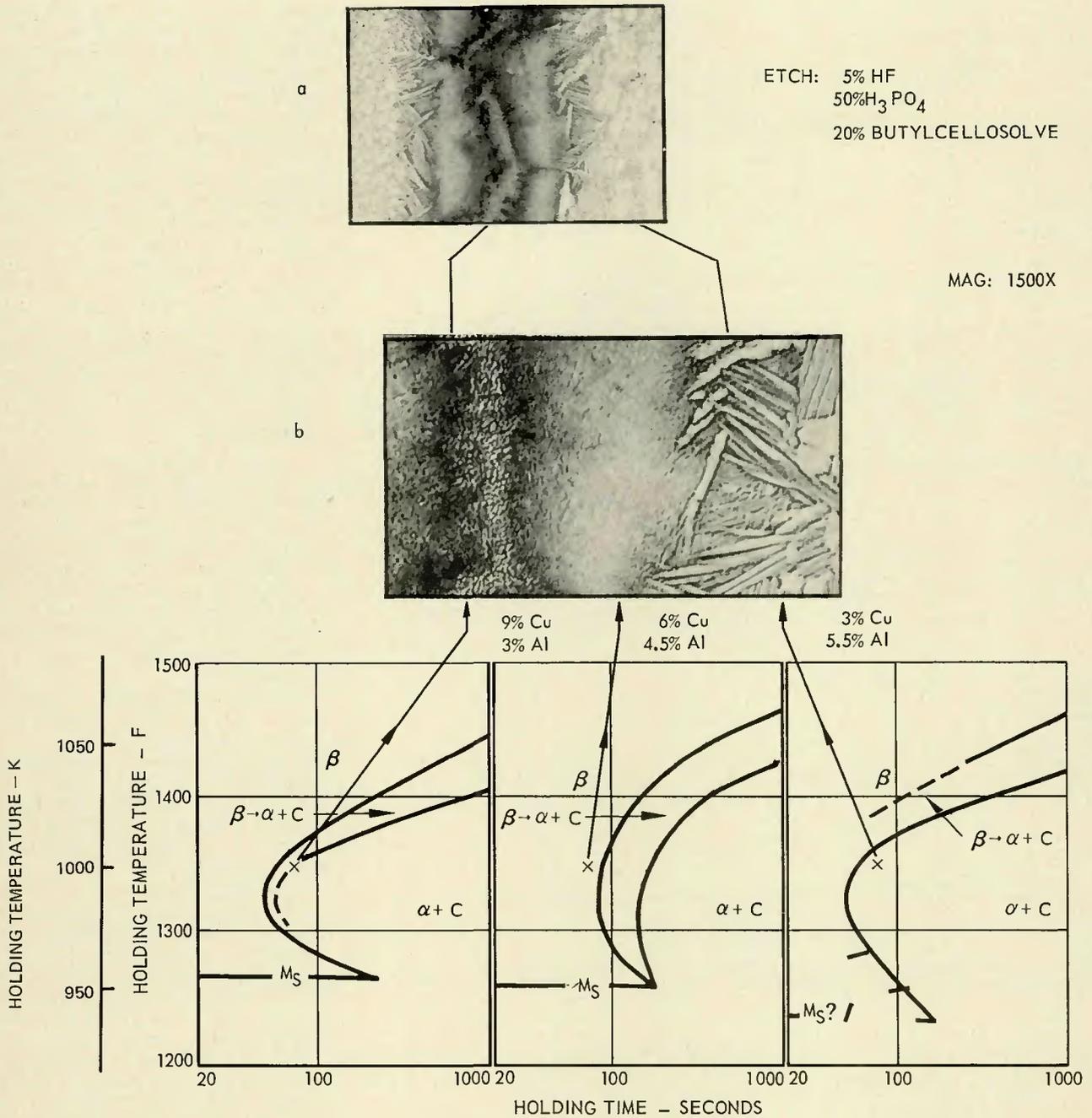


Fig. 8 — Influence of copper content on transformation rates and phase morphology of Ti-6Al-4V joints

microstructural differences.

A third set of lap shear specimens was transformed at 1375 F (1020 K), which is very close to the  $M_S$  temperature. This transformation resulted in the formation of a fine dispersion-type of microstructure. The lower ductility of this microstructure reduced the lap-shear strength at room temperature, as seen in Fig. 9. The higher test temperatures decreased the strength sensitivity of these lap-shear joints to joint ductility. Joints transformed to martensite were not evaluated because Margolin's work indicated that this transformation product produced high strength, poor

ductility, and, presumably, poor toughness.

In the second evaluation, sheets of Ti-75A, Ti-6Al-4V, and Ti-8Al-1Mo-1V were coated on one side with a thin-film of copper, diffusion treated to approximately 7% maximum copper content, and cooled under varying conditions to change decomposition products of the beta-phase. Figure 10 shows the amount of bend deflection which each specimen could withstand before it cracked or, in a few cases, bent far enough to be pushed through the supports. These data provide a sensitive measure of ductility; they support the above conclusion

concerning low ductility in Ti-8Al-1Mo-1V lap shear joints transformed at 1375 F (1020 K).

In the third evaluation, a substantial effect of copper content on fracture toughness was observed in the work by Freedman (Ref. 6). Similar Ti-6Al-4V specimens were given different diffusion times to vary the residual copper level, but each was given an equivalent beta-phase transformation cycle.

As seen in Fig. 11, the fracture toughness is strongly dependent upon the copper content. Thus, joints containing more than 7% copper should be avoided if high toughness

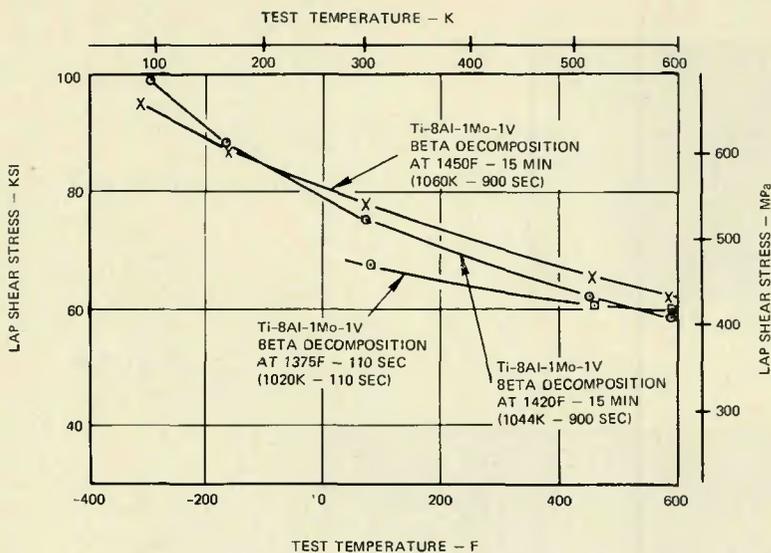


Fig. 9 — Lap shear tensile strength for three phase morphologies in Ti-8Al-1Mo-1V joints

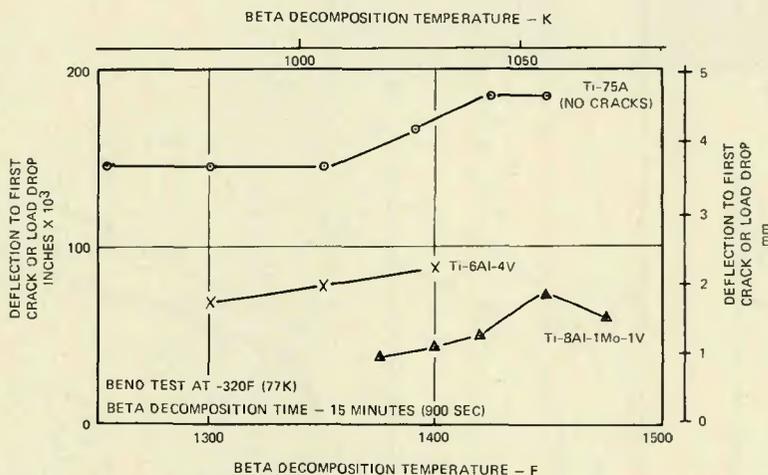


Fig. 10 — Bend deflection versus beta decomposition temperature for Ti-75A, Ti-6Al-4V, and Ti-8Al-1Mo-1V brazements

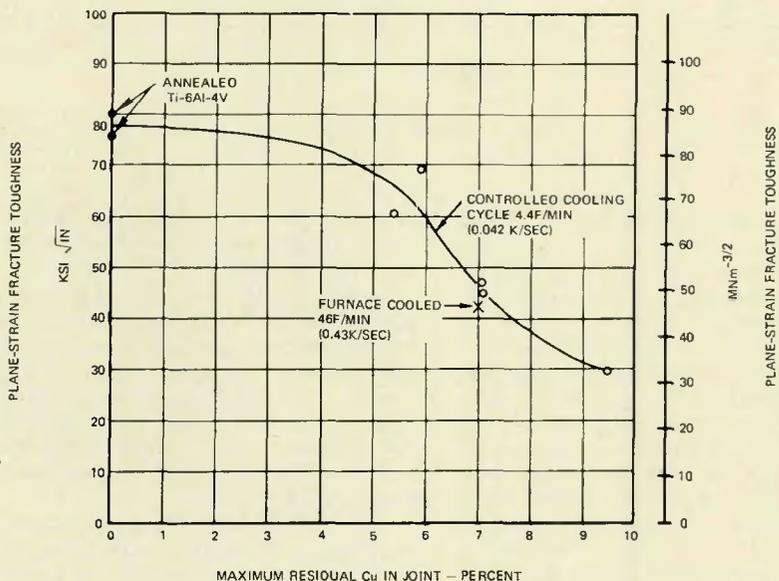


Fig. 11 — Effect of residual copper content on fracture toughness of thin film diffusion brazed joints of Ti-6Al-4V

is desired. The microstructures of these joints varied from pearlite-like (similar to the area of 3% Cu-5.5% Al of Fig. 8) for the 6% copper content specimens to a bainite-like (9% Cu-3% Al area of Fig. 8) structure for the 9.5% copper content specimens.

One specimen with 7% copper was cooled at a faster rate to form a structure with finer alpha needles. This microstructure had a slightly lower toughness than the coarse alpha-needle structure with the same copper content. These data indicate a stronger dependence of toughness on copper content than on microstructure. However, for a given copper content, the proper beta transformation cycle can then provide some increase in toughness.

## Summary

This work has shown that there is a relationship between phase morphology and mechanical behavior in thin-film diffusion-brazed joints. Further, it is shown that the microstructure and mechanical properties of the joints can be varied in a controlled manner by applying diffusion calculations and transformation kinetics to the practical fabrication of components.

The optimum copper quantity required for joining a specific component depends upon fit-up and thus the voids which must be filled with brazing liquid — that is, the smaller the voids and the more intimate the contact between the titanium surfaces, the less copper required to obtain a sound joint.

The amount of solid state diffusion which takes place on heat-up is a function of heating rate and intimacy of contact between the thin-film of copper and the titanium. Slow heating rates allow more solid state diffusion to take place during heating so that additional copper must be used to provide sufficient liquid to fill the joint. Conversely, if a large quantity of copper is used with a very fast heating rate, excess liquid is formed, run-out or erosion may occur, and thick joints are formed which require long diffusion times. Thus, the optimum quantity of copper to be used depends upon fit-up tolerances and heating rates which are compatible with reasonable diffusion cycles to produce the desired final joint composition.

Given the correct copper quantity for a specific titanium component, the proper diffusion time and temperature can be calculated to produce a joint of low residual copper; this can then be transformed into a strong, tough joint compatible with the properties of the titanium alloy being formed.

## Conclusions

1. Simple diffusion calculations

can be used to control the compositions of thin-film diffusion brazements.

2. Transformation kinetic studies (when applicable) are useful in optimizing the mechanical properties of thin-film diffusion-brazed joints.

3. These diffusion control principals can be used with brazing filler metals as well as solid state diffusion-welding systems where thin layers of intermediate are used, or in any joining system in which extensive diffusion is required.

#### Acknowledgments

The author gratefully acknowledges the technical guidance provided by Dr. E. B. Mikus and the assistance of Messrs. T. A. Krinke, L. H. Stone, R. E. Herfert, H. E. Langman, B. J. Mays, and A. H. Freedman in conducting this program.

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## WRC Bulletin 203 February 1975

### "Niobium and Vanadium-Containing Steels for Pressure Vessel Service"

by J. N. Cordea, Armco Steel Corp.

The effects of niobium (Nb) and vanadium (V) additions on the properties of plain carbon (C) steel have been well known for some years now. Recently, through refinements and processing technology, very effective use has been made of relatively small amounts of Nb or V (up to 0.2 wt-%) to significantly increase yield strength and improve notch toughness. These improvements have resulted through optimization of Nb and V carbonitride precipitation hardening, ferrite grain size refinement, and a reduction in C content. The latter item also significantly improves weldability.

Nearly all of the industrialized countries of the world have taken advantage of the economy of producing higher strength steels with a minimum of extra alloying cost. This is especially true for structural applications where weight saving is so important. Many countries have also made effective use of these steels for pressure vessel applications. Although the United States is very active in high-pressure line-pipe development, very little activity has been directed toward using Nb and V steels for pressure vessels and other containers. The principal reason is that allowable-stress calculation as specified by the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code is usually governed by tensile strength. While yield strength is increased significantly by Nb and V additions, there is a relatively small effect on tensile strength. Consequently, no direct advantage can be gained in pressure vessel design by an increase in yield strength.

It is the purpose of this report to summarize the state of the art of Nb- and V-containing C-Mn steels for pressure vessel applications and to identify areas needing further research. Specifically, this report covers low-alloy steels with an upper yield-strength range of about 75 ksi (53 kg/mm<sup>2</sup>). A brief summary of the pressure vessel codes around the world is presented in order to provide a basis for important material properties in the design of pressure vessels. Available steels, their mechanical properties and the technology for producing them are covered in detail. Although a few structural grades and pipeline steels from the United States are discussed, the main emphasis is directed toward foreign steels produced for pressure vessel applications. Where appropriate, comparisons are made to similar composition structural grades produced in the United States. Weldability and other important properties necessary for satisfactory fabrication and service are evaluated. This work was initiated and sponsored by the Pressure Vessel Research Committee of the Welding Research Council, Fabrication Division, Subcommittee on Thermal and Mechanical Effects.

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