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DESARROLLO DE ALEACIONES DE TITANIO A ALTAS TEMPERATURAS

H. L. Gogel y M. Hoch

Los problemas que se han encontrado en la industria del titanio son debidos a su desarrollo histórico.

Históricamente, el desarrollo del titanio se ha dividido en partes representadas por la industria y el gobierno. La industria asume la responsabilidad para el desarrollo, la manufactura y los aspectos de procesamiento de la tecnología del titanio, y el gobierno asume la responsabilidad de la metalurgia física del titanio. Es por estas dos partes que la industria del titanio no ha progresado más rápidamente en su desarrollo hacia una gran variedad de aleaciones de las que el diseñador pueda escoger.

Recientes progresos en el entendimiento de los factores electrónicos que controlan la estabilidad de las fases α y β del titanio provoca ahora una base fundamental para la selección de elementos de aleación. El incremento del conocimiento del defecto y transformación de estructuras y sus efectos sobre las propiedades de resistencia del titanio ofrecen una posibilidad para perfeccionar las aleaciones existentes.

El artículo también discutirá las posibilidades de mejorar las propiedades de creep a altas temperaturas. Importante número de puntos están en la preparación de una matriz β y α verdaderamente estable.

Será descrita la modificación del sistema Ti-Al, por adición ternaria para prevenir la formación del compuesto frágil Ti₃X. Esta matriz tiene mejor resistencia a la oxidación que cualquiera de las aleaciones $\alpha\beta$ y β . Aumento de la resistencia por endurecimiento de la solución sólida, esta matriz puede ser fortalecida por dispersión de partículas duras de la segunda fase.

DESENVOLVIMENTO DE LIGA DE TITANIO PARA ALTAS TEMPERATURAS

H. L. Gogel e M. Hoch

Os problemas que foram encontrados na indústria do titânio são principalmente devidos ao seu desenvolvimento histórico.

Históricamente, o desenvolvimento do titânio foi dividido entre os papéis desempenhados pela indústria e o Governo. A indústria assumiu a responsabilidade de desenvolver os aspectos de manufatura e processamento da tecnologia do titânio, e o Governo assumiu a responsabilidade da metalurgia física do titânio. É por causa desses dois papéis distintos que a indústria do titânio não progrediu mais rapidamente na direção de desenvolver uma variedade maior de ligas que o projetista pudesse escolher.

Processo recente no entendimento dos fatores eletrônicos que controlam a estabilidade das fases α e β do titânio estão agora promovendo uma base fundamental para a seleção de elementos de liga. O aumento de conhecimento dos defeitos e estruturas de transformação e seus efeitos sobre as propriedades de rigidez do titânio oferece a possibilidade de aperfeiçoamento das ligas existentes.

O artigo também irá discutir as possibilidades de aperfeiçoamento das propriedades de creep a alta temperatura. Pontos mais importantes são a preparação de uma fase β verdadeiramente estável e uma matriz α verdadeiramente estável. Será descrita a modificação do sistema titânio-alumínio pela adição ternária para prevenir a formação dos compostos frágeis Ti₃X. Essa matriz α tem melhor resistência à oxidação do que qualquer das ligas $\alpha\beta$ e β . Em adição à resistência pela solução sólida endurecida, essa matriz poderia ser reforçada pela dispersão de partículas duras da segunda fase.

HIGH TEMPERATURE TITANIUM ALLOY DEVELOPMENT

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ABSTRACT

The future needs for titanium alloys are reviewed briefly. Then, against a theoretical background, utilizing presently available data, a new super- α alloy is proposed and developed. The properties (up to 600°C), both mechanical and physical of these alloys are then measured and reported. Development of titanium-base, super- α and super- β alloys for the temperature range 600-1000°C is considered and the difficulties discussed.

INTRODUCTION

Titanium alloys are needed in three general categories:

(1) High strength alloys at temperatures up to 300°C. One potential application is as sheet material for light transportation vehicles. The primary competitor in any application would be the stainless steels.

(2) High strength alloys are also needed for temperatures up to 600°C, but the material must have creep resistance, hot salt stress corrosion cracking resistance, and oxidation resistance as well. These alloys could be used in various engine parts, and would be competing with the stainless steels, copper-base alloys, and possibly the nickel-base materials.

(3) Finally, alloys are needed which have good creep resistance, hot salt stress corrosion cracking resistance, and oxidation resistance at temperatures above 600°C. These alloys would be competitors for the nickel-base alloys, and they could be used in the low temperature section of turbines with significant weight savings.

Alloys in category (1) are already commercially available, and improvements are coming, but alloys for use above 450°C require further development. Some progress has also been made on a 600°C alloy, but titanium alloys which can meet the requirements of category (3) are not yet in sight.

THERMODYNAMIC CONSIDERATIONS

Theoretical Behavior. The alloying behavior of titanium can be adequately described by the regular solution model with an interaction parameter, Ω . The free energy difference between pure β and pure α titanium can then be expressed as

$$\Delta F^\circ = (E^\circ_\beta - E^\circ_\alpha) - T(S^\circ_\beta - S^\circ_\alpha) \quad 1)$$

The free energy for an alloy containing X mole fraction of an addition element is

$$F = E^\circ(1-X) - TS^\circ(1-X) + \Omega X(1-X) + (E_{Me} - TS_{Me})X \quad 2)$$

The free energy difference between β titanium and α titanium, each containing X amount of alloying element, is thus

$$\Delta F = \Delta F^\circ(1-X) + X(1-X)[\Omega_\beta - \Omega_\alpha] \quad 3)$$

if we neglect the term representing the energy difference between the alloying metal in the α and β phases on the assumption it is small.

At the transition temperature of pure titanium $\Delta F^\circ = 0$. If, on alloying, the transition temperature decreases, ΔF° becomes positive and therefore the term in the brackets must be negative. If, on the contrary, the transition temperature increases with addition elements, then ΔF° becomes negative and the term in the brackets becomes positive. Thus for a β stabilizing element where the transition temperature decreases, $\Omega_\beta - \Omega_\alpha < 0$,

whereas for an α stabilizing element where the transition temperature increases, $\Omega_\beta - \Omega_\alpha > 0$.

In the gas phase the systems are ideal, but as the temperature is lowered into the condensed phase region, the deviation from ideality increases with decreasing temperature. It is therefore safe to assume that in a system which can occur in two structures, α and β , with β being the high temperature form,

$$\Omega_\alpha^2 > \Omega_\beta^2 > 0. \quad (4)$$

Thus, for an α stabilizing alloying element,

$$\Omega_\alpha < \Omega_\beta < 0 \quad (5)$$

and for a β stabilizing element

$$\Omega_\alpha > \Omega_\beta > 0. \quad (6)$$

This conclusion was discussed earlier. (1)

Experimental Data. The interaction parameter, Ω , in various binary Ti-X systems has been obtained by thermodynamic activity measurements using a Bendix Time of Flight Mass Spectrometer. Two vapor pressures techniques were used. The first utilized a conventional Knudsen cell configuration where the sample was placed in the cell and the ratio of the titanium signal to the alloying elements signal was determined as a function of composition. The data obtained were then analyzed with the aid of a solution model, and yielded Ω .

If the alloying element was much more volatile, or much less volatile, than titanium the "triple Knudsen cell" technique was used. The triple Knudsen cell consists of two cells within a third cell. One inner cell contains the alloy of interest, and the second contains isotopically enriched pure titanium or a similar sample of the alloying element. Both effuse into the outer cell which is fed into the Time of Flight Mass Spectrometer. The instantaneous ratios measured by the Mass Spectrometer are converted directly into activity values. Details of these experimental methods and calculations have been described earlier (2-7), and the data are summarized in Table 1.

TABLE 1. PHASE-TO-INTERACTION PARAMETER VALUES IN SOME IMPORTANT ALLOYS

System	Temperature Range, °C	Interaction Parameter, Ω	Phase
Ti - Mo	1844 - 1900	+12.7 ± 2.0	4
Ti - Cr	1713 - 1998	+7.9 ± 1.7	1
Ti - V	1723 - 1998	+1.7 ± 0.9	1
Ti - Cu	1423 - 1571	+1.1 ± 0.1	1
Ti - Cu (liquid)	1700 - 1900	+4.8 ± 0.4	2
Ti - Al	1780	-11.7 ± 1.1	3
Ti - Ga	1623 - 1773	-14.8 ± 2.1	1
Ti - Sn	1573 - 1773	-19.8 ± 1.1	7

As expected according to equations 5 and 6, for β stabilizing elements values of $\Omega > 0$ were obtained and for α stabilizing elements, values of $\Omega < 0$. It should be noted that indium and lead are also α stabilizers. The latter, however, are heavy and would increase the density of alloys too much for practical applications.

$\Omega > 0$ indicates a tendency for phase separation, whereas $\Omega < 0$ shows a tendency for short range order and compound formation. In the latter case, as the interaction parameter increases from aluminum to gallium to tin, the highest melting point compound (and thus the most stable compound) moves toward the titanium rich compositions, i.e. from TiAl to Ti₂Ga to Ti₃Sn. In fact, because of the great stability of Ti₃Sn, only a very small amount of tin can be added to titanium base alloys (such as Ti-5Al-2.5Sn) before embrittlement will occur. In an attempt to produce high temperature α -titanium alloys (super- α alloys), titanium alloyed with aluminum and gallium was investigated. The advantages of aluminum and gallium (in equal atomic amounts) as alloying elements are that the density of the alloy is the same as that for pure titanium, (4.5 g/cc) and that they repel each other. (With $\Omega = 3kT/\text{mole}$ (8) their binary system indicates immiscibility.) This repulsion is an advantage because it impedes the formation of the Ti₃Al type ordered structure. If the Ti₃Al structure is to form, then, in addition to ordering between titanium and aluminum-gallium atoms, ordering on the aluminum sublattice between Al and Ga atoms must occur, but it cannot

because the two elements repel each other. It may be, that separate Ti_3Al and Ti_3Ga phases will be formed preferentially.

ALLOY DEVELOPMENT

Preparation. Alloy samples of the desired compositions were prepared by non-consumable arc melting under an argon atmosphere. Buttons weighing from 10 grams to 500 grams were melted and remelted up to 5 times to obtain homogeneity. The melting process was relatively simple, and the gallium loss was negligible, so the nominal composition remain very close to the chemical composition as analyzed. The processing of the materials was done (9) 30°C below the α transus temperature and their processing characteristics (rolling or swaging) were compared to a commercial α alloy, Ti-5Al-2.5Sn, and found comparable as shown in Figure 1.

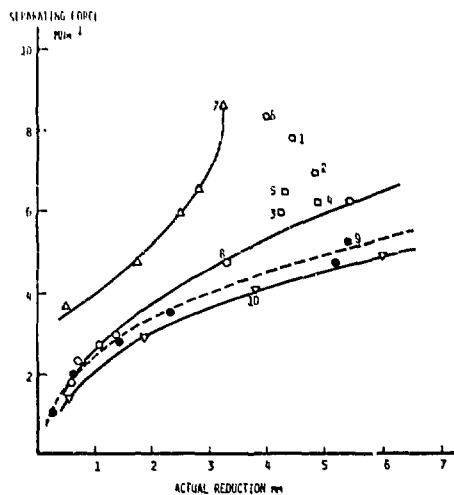


FIGURE 1

Hot Mill Roll Separating Forces vs Inches of Reduction for Six Experimental Ti-Al-Ga Alloys and Standard Ti Alloys

α Transus Measurements. The alloys were observed through a hot stage microscope to determine the α transus temperature. This temperature, as a function of the Al and Ga content is shown in Figure 2 which also

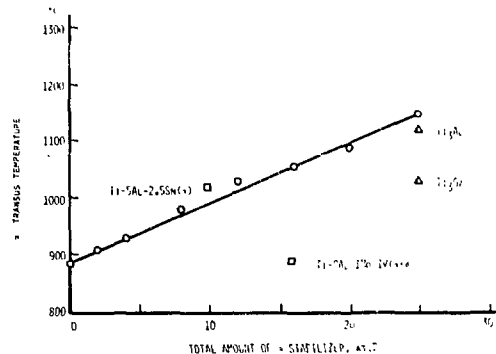


FIGURE 2

contains one data point each for Ti_3Ga and Ti_3Al . In addition, a value for Ti-5Al-2.5Sn (a) is plotted. Finally, the lowest temperature at which the β phase in Ti-8Al-1Mo-1V will not transform is plotted. These results indicate that the α transus temperature increases linearly with α stabilizing content.

The disordering temperature for the DO_{19} structure was also determined, using magnetic susceptibility measurements (10), to be at 640°C for Ti-12.5Al-12.5Ga and 840°C for Ti_3Al .

Mechanical Testing. All mechanical properties were determined on an Instron machine using a head speed of .001 mm/s. Figure 3 shows the

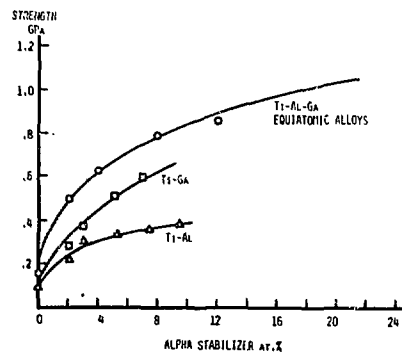


FIGURE 3
Room Temperature Strength of Ti-Al, Ti-Ga and Ti-Al-Ga Alloys

ultimate tensile strength at room temperature of the titanium-aluminum, titanium-gallium and titanium-aluminum-gallium alloys. The strength of titanium-gallium alloys is greater than that of the titanium-aluminum alloys because of their more negative interaction coefficient. The even greater strength of the ternary alloys is thought to be created by the aluminum-gallium positive interaction.

Selected alloys were tested at elevated temperatures and the experimental data are shown in Table 2. The results are somewhat

TABLE 2. MECHANICAL PROPERTIES OF Ti-Al-Ga (base materials)

Composition (wt. %)	Temp. °C	UTS GPa	Elongation %
Ti-6Al-6Ga	25	.835	18
	25	.860	14
	400	.475	13.9
Ti-8Al-8Ga	25	.791	-1
	400	.745	12.8
	510	.690	9.2
Ti-10Al-10Ga	25	.608	2.6
	400	.475	4
	640	.405	2.6
Ti-12.5Al-12.5Ga	25	.581	-1
	400	.580	1.1
	620	.670	18
	620	.515	66

Heat Treatment: All alloys were hot swaged approximately 100% at approximately 900°C to approximately 9.5mm diameter.

Tensile specimens were machined, and then a subsequent heat treatment at 800°C for 160 hours was given. Specimens were unannealed.

surprising. The Ti-6Al-6Ga alloy behaves normally, but the Ti-8Al-8Ga and Ti-10Al-10Ga alloys have very small elongation, and in the former the elongation actually decreases as the temperature is increased. Similarly unexpected behavior in a Ti 12.5Al-12.5Ga alloy has been noted earlier by us⁽¹¹⁾ and also by Goddin et al⁽¹²⁾.

In explanation, Fujishiro and Gegel⁽¹³⁾ showed that the Ti-6Al-6Ga alloy still shows 3 slip systems whereas the Ti-8Al-8Ga and Ti-10Al-10Ga alloys probably show only 1 slip system. Decreasing elongation with increasing temperature is caused by α_2 precipitation under strain at the higher temperatures.⁽¹³⁾

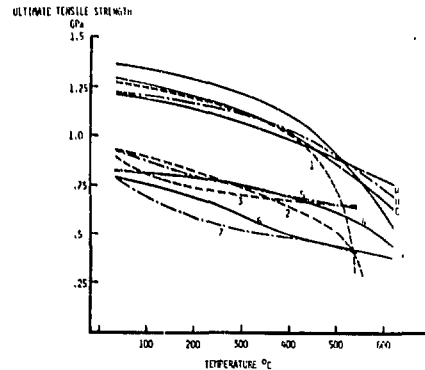
Given these results, the Ti-6Al-6Ga alloy (3.4 wt. % aluminum and 8.7 wt. % gallium) was

taken as base, and different selected elements were added in an attempt to improve the properties. The results are given in Tables 3 and 4.⁽¹⁴⁾ Comparison of those results with

TABLE 3. MECHANICAL PROPERTIES OF TITANIUM-ALUMINUM-BASE ALLOYS

No.	Composition	25°C		400°C		510°C		620°C	
		UTS, GPa	Elong. %	UTS, GPa	Elong. %	UTS, GPa	Elong. %	UTS, GPa	Elong. %
A	Ti-3.6Al-8Ga	1.25	10	930	11.2	660	4.4	510	10.5
B	-12.5Al	1.235	2.4	660	-	660	-	660	-
C	2.25Al	1.245	5.5	1.015	1.5	895	11.7	702	11.7
D	0.5Al	1.245	8.5	745	8.0	25	22.4	515	8
E	-12.5Al	1.240	14.5	1.035	13.5	-	-	495	14.5
F	Ti-7.3Al-8Ga	980	15.0	545	17.5	-	-	485	16.4
G	-25Al	850	15.0	342	17.5	-	-	362	31
H	Ti-1.6Al-8Ga	1.180	1.0	1.105	11.5	895	11.0	515	53.0
I	-12.5Al	-	-	-	-	-	-	-	-
J	-0.5Al	1.255	1.5	-	-	-	-	675	13.5

Heat Treatment: All alloys were hot swaged approximately 100% at approximately 900°C to approximately 9.5mm diameter. Tensile specimens were machined, and then a subsequent heat treatment at 800°C for 160 hours was given. Specimens were unannealed.



data on commercial alloys is done in Figure 4.

TABLE 4. TENSILE DEFORMATION OF A Ti-Al-Ga-BASE ALLOY

Alloy	Test Temp. °C	Yield Stm. GPa	UTS GPa	UTS/YS	Unif. Elong. %	Total Elong. %	Reduction in Area %
1	25	.910	.993	1.091	9.5	10.4	21.4
2	25	1.183	1.270	1.245	8.0	11.1	61.0
3	25	1.025	1.035	1.103	10.3	12.1	16.0
4	25	1.110	1.133	1.240	8.1	9.1	24.5
1	500	.555	.595	.745	16.2	16.2	13.2
2	500	.715	.760	.905	13.6	9.9	21.1
3	500	.595	.650	.775	13.7	11.8	28.1
4	500	.640	.700	.895	12.7	12.4	28.1

Alloy designations (wt. %) are

1. Ti-3.6Al-8Ga-0.5Al
2. Ti-3.6Al-8Ga-0.5Al-1.0Cu-0.5Zr
3. Ti-3.6Al-8Ga-0.5Al-1.0Cu
4. Ti-3.6Al-8Ga-0.5Al-1.0Cu

All alloys annealed in argon 800°C, 24 hrs., furnace cooled to 550°C, anneal at 550°C, 24 hours, furnace cool.

Figure 4

That comparison reveals that our material is significantly better than the commercially available products.

FUTURE DEVELOPMENTS

Our intent is to raise the utilization temperature above 600°C by improving our understanding of the mechanisms occurring in the α alloys Ti-8Al-8Ga and Ti-10Al-10Ga, then introducing small amounts of Si, etc, to improve their properties.

The development of super β -alloys for use above 600°C would also be important, but a number of problems have to be overcome. One is the phase separation tendency indicated by the positive value of the interaction parameter, ω ; experimental evidence of decomposition has been found lately.^(15,16) In a thermodynamic analysis the positive interaction parameter decreases the vibrational σ_D , increases the vibrational entropy, and lowers high temperature strength. For example looking at Figure 4 it is obvious that above 450°C the strength of Ti-6Al-4V, and β III decreases very rapidly. This effect, which is a result of the positive interaction parameter of the alloying element, also appears in alloy K, our basic Ti-6Al-6Ga alloy when it includes a fairly large amount (12.5 wt. %) of molybdenum. It is not certain yet how this problem can be overcome. Certain physical property changes⁽¹⁰⁾ suggest that two additional factors, inherent lattice instability (rapidly changing elastic constants) and the formation of omega phase have to be considered. These problems can perhaps be solved by alloying to high concentration of beta stabilizing elements; this type of alloying with Mo, would produce an alloy with a density of 6.5 g/cc. This density is rather high when compared to pure titanium but it is still less than nickel base alloys. Future research should concentrate on developing a new class of stable super- β titanium alloys.

REFERENCES

- 1) Hoch, M., Hackworth, J.V., Usell, R.J., and Gegel, H.L., "Thermodynamic Properties of the Body-Centered-Cubic

Beta-Phase in the Titanium-Copper and The Titanium-Aluminum Systems", The Science Technology and Application of Titanium, Jaffee, Dr. R. and Promisel, N., Ed., Pergamon Press, New York, 1970, pp. 359-360.

- 2) Hackworth, J.V., Hoch, M., and Gegel, H.L., "Thermodynamics of Titanium Alloys: I. Development of a Triple Knudsen Cell and Its Use to Study the Activity of Copper in the Ti-Cu System", Met. Trans. v 2, 1799-1805, 1971.
- 3) Usell, Jr., R.J., and Hoch, M., "Thermodynamics of Titanium Alloys II. Titanium and Aluminum Activities in the BCC β Phase of the Ti-Al System", Met. Trans. v. 2, 2627-2632, 1971.
- 4) Viswanathan, R. and Hoch, M., "Thermodynamics of Titanium Alloys: III. The Ti-Mo System", Met. Trans., v. 2, 2765-2767, 1971.
- 5) Rolinski, Edmund J., Hoch, M., and Oblinger, Charles J., "Determination of Thermodynamic Interaction Parameters in Solid V-Ti Alloys Using the Mass Spectrometer", Met. Trans., v. 2, 2613-2618, 1971.
- 6) Rolinski, E.J., Hoch, M., and Oblinger, C.J., "Determination of Thermodynamic Interaction Parameters in Solid Vanadium-Titanium-Chromium Alloys Using the Mass Spectrometer", Met. Trans., accepted for publication.
- 7) Oblinger, C.J., and Gegel, H.L. Unpublished results.
- 8) Hultgrén, Ralph, Orr, Raymond L., Anderson, Philip D., and Kelley, Kenneth K., "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley & Son, Inc., New York.
- 9) Chalk, David L., Armco Steel Co., private communication.
- 10) Collings, E.W., Gegel, H.L., and Ho, J.C. "Fundamental Design of Ti-Alloys", Met. Trans., Submitted.
- 11) Gegel, H.L., and Hoch, M., "Strengthening the Ti-Al-Ga System", AIME Meeting, May 12-15, 1969, Pittsburgh, Penna.
- 12) Godden, M.J., Milliken, K.S., and Roberts, W.N., "Ti-Al-Ga Alloys", TMS Meeting, May 16-18, 1971, Atlanta, Georgia.
- 13) Fujishiro, S., and Gegel, H.L., "The Ordered Phase Formation in Ti-Al-Ga Alloys", Proceedings of the Electron Microscope Society of America, C.J. Arceneaux, Edtr, Claitor's Publ. Div., Baton Rouge, La., 1970, p. 440.
- 14) Hoch, M., Sakai, T., Krupowicz, J.J., and Delahanty, M., "The Ti-Al-Ga System", Second International Conference on Ti, Boston, May 2-5, 1972.

- 15) B. A. Wilcox, Battelle Inst., Columbus, Ohio, private communication.
- 16) Narayaman, G.H., and Archibold, T.F., "Decomposition of the Metastable Beta Phase in the All-Beta Alloy Ti-13V-11Cr-3Al", Met. Trans. v. 1, 2281 (1970).
- 17) Williams, J.C., Hickman, B.S., and Leslie, D.H., "The Effect of Ternary Additions on the Decomposition of Metastable Beta-Phase Titanium Alloys", Met. Trans. v. 2, 477 (1971).

