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(54) **Titanium aluminum alloys containing niobium, vanadium and molybdenum.**

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Description

The present invention relates to a titanium aluminum alloy and relates more specifically to titanium base alloys of the Ti_3Al (alpha-two) type which have both good elevated temperature properties and sufficient low temperature ductility to make them useful in an engineering sense.

The present invention is an improvement on the alloys described in US-A-4,292,077. As indicated in the patent, the new alloys are comprised of aluminum, niobium and titanium. The compositional ranges for the patented alloys were quite narrow since changes in properties were discovered to be very sensitive to the precise composition. Generally, the patented alloys contain titanium, 24-27 atomic percent aluminum and 11-16 atomic percent niobium. The alloys have at least 1.5% tensile ductility at room temperature and good elevated temperature creep strength, thus permitting their potential substitution for certain nickel base alloys such as INCO 713C.

In an important embodiment of the prior invention, vanadium partially replaces niobium in atomic amounts of 1-4%. This substitution desirably lowers the density of the alloy but at the same time the favorable high temperature properties are retained. An optimum atomic composition range for this embodiment is 24-26% aluminum, 10-12% niobium and 2-4% vanadium.

While the foregoing patented alloys meet the requirement of having creep rupture life at 650 °C/380 MPa which is equal to INCO 713C on a density adjusted basis, the alloys have less tensile strength at temperatures up to 400 °C than does the commercial beta processed alloy Ti-6-2-4-2 (by weight percent Ti-6Al-2Sn-4Zr-2Mo). Consequently, compositional modifications of the patented alloys were evaluated to see if improvements could be achieved. As the general field of titanium alloys indicates, there are many potential alloying ingredients. But, as the prior work demonstrated, the composition of useful Ti_3Al alloys is extremely critical. Many elemental additions which have been common in other titanium alloys were previously shown to be of no advantage in Ti_3Al alloy.

An object of the present invention is to provide Ti_3Al type alloys which have a superior combination of creep rupture life and tensile strength at elevated temperatures in the 600 °C range, but which alloys at the same time have sufficient ductility to enable their use at room temperature and their fabrication by conventional processes associated with titanium base alloys.

The titanium aluminum alloy of the present invention is defined as shown in the claims 1, 3 and 6.

According to a preferred embodiment of the invention, new titanium base alloys contain by atomic percent 25-27 aluminum, 11-16 (niobium + molybdenum) and 0.5-4 molybdenum. Preferably they have 0.5-1.5 Mo. An especially preferred embodiment of the invention is the lighter weight alloy containing vanadium in substitution for a portion of the niobium. Such an alloy contains by atomic percent 25-27 Al, 11-16 (Nb + V + Mo), 1-4 (V + Mo), at least 0.5 Mo, balance titanium. More preferably, the light weight alloy contains 9-11 Nb, 1-3 V and 0.5-3 Mo, balance titanium.

The incorporation of molybdenum substantially increases high temperature ultimate tensile strength and creep rupture properties, compared to the essential alloys of our prior invention which did not contain molybdenum.

The foregoing and other objects, features and advantages of the present invention will become more apparent from the following description of preferred embodiments and accompanying drawings.

Figure 1 is a graph showing the comparative ultimate tensile strength-to-density ratio for various known alloys, compared to the invention.

Figure 2 is a bar chart showing comparative stress rupture properties on a density adjusted basis for the invention compared to various known alloys.

The best mode of the invention is described in terms of atomic percent of elements. Those skilled in the metallurgical arts will recognize the limitations on stating the invention by weight percent and the utility of stating the invention by the preferred atomic percent; they will be able to readily convert from atomic percents to exact weight percents for particular embodiment alloys.

The alloys of the present invention are based essentially on the compositions which is disclosed in US-A-4,292,077. Those alloys contain a critical combination of Ti, Nb and Al. In the patent we showed that the essential invention could be enhanced by including substituting 4% V for Nb, thereby lowering density. In making and disclosing the present invention, the light weight vanadium containing version of our prior invention has been used. The work described herein shows that Mo is a particularly unique and valuable addition to the essential Ti-Nb-Al alloys of the prior patent.

The alloys described herein were manufactured using conventional titanium base alloy technology, basically vacuum arc melting and isothermal forging which is quite familiar (albeit isothermal forging is a recent improvement). Alloys of the Ti_3Al composition have been developed to the extent that large ingots,

weighing up to 245 kg may be procured on a routine basis from commercial sources. In the invention, the alloys are cast, forged and heat treated. The procedures for manufacture and testing of forgings are the same as those described in US-A-4,292,077.

An exemplary alloy demonstrating the invention is Ti-25Al-10Nb-3V-1Mo. (All compositions hereinafter are in atomic percent unless otherwise stated.) The alloy has a density of about 3% greater than that of Ti-25Al-10Nb-4V, which is 4.5 g/cc. The alloy was isothermally beta forged (the cylindrical cast ingot pressed to a disk shape approximately 14% of the original ingot height) at a temperature of about 1120 °C. This is about 40 °C over the beta transus, estimated to be about 1080 °C. Tables 1 and 2 show respectively the tensile and creep rupture properties of the alloy.

Table 1.

Tensile Properties of Isothermally Beta Forged and Heat Treated Ti-25Al-10Nb-3V-1Mo Alloy					
Specimen	Temperature ° C	0.2% Yield Strength MPa	Ultimate Tensile Strength-MPa	El%	RA%
A	25	825	1047	2.2	1.7
B	260	831	1058	9.2	14.1
C	427	729	950	12.1	16.9
D	538	647	967	9.2	13.0
E	650	640	835	9.1	14.3

Table 2.

Creep-Rupture Properties of Isothermally Beta Forged and Heat Treated Ti-25Al-10Nb-3V-1Mo Alloy					
Specimen	Test Conditions ° C/MPa	Time in Hours to			
		0.2% El	0.5% El	1.0% El	Rupture
F	650/380	2.8	31.1	184.5	*
G	650/380	1.4	12.0	66.3	222.8
H	593/413	27.0	405.6	*	*

* Test terminated at 502 Hours without rupture

Figure 1 shows how the ultimate tensile strength to density ratio of the new alloy of the present invention compares with those of a similar alloy lacking molybdenum and two commercial alloys, alloy Ti-6-2-4-2 and nickel base alloy INCO 713C. It is seen that the new alloy provides a significant improvement.

Figure 2 shows how the density-adjusted stress for 300 hr rupture life at 650 °C for the alloy containing molybdenum is substantially improved over the creep rupture life for a similar alloy lacking molybdenum.

Generally, the alloys of the present invention will be characterized in their optimally forged and heat treated condition by a tensile ductility at room temperature of at least 1.5%, typically about 2.5%; an ultimate tensile strength of 1000 MPa at 25 °C; and a 650 °C/372 MPa creep life of at least 150 hours, typically about 300 hours. They have stress-to-density ratios of the order of 2 kPa/m³, compared to less than 1.5 kPa/m³ for the alloys of our prior patent, and compared to even lower values for older alloys.

The new alloys of the present invention also have desirably increased dynamic elastic modulus compared to other alloys, as indicated in Table 3. The Ti-25Al-10Nb-3V-1Mo 650 °C modulus is almost 30% greater than the value for Ti-25Al-10Nb-4V, and a significant improvement over commercial alloys as well. The modulus was measured by mechanically stimulating resonant vibration of a beam of known dimensions and measuring the frequency response thereof. Calculation is made from known dynamics relationships.

Table 3.

Dynamic Modulus of Selected Alloys (10 ⁷ kPa)			
	Temperature - ° C		
	20	315	650
Ti-6Al-2Sn-4Zr-2Mo	11.9	10.4	8.6
Ti-25Al-10Nb-4V	10.1	9.7	8.7
Ti-25Al-10Nb-3V-1Mo	12.6	12.1	11.2

As much as 6-8% Mo may be included in the new alloys of the present invention, since as Mo content rises, creep strength and stiffness rise. However, density and oxidation resistance (necessary for high temperature gas turbine use) decrease. Thus, for such alloys the Mo should be limited to about 4% and preferably it is 0.5-1.5%. The basic Ti-Nb-Al-Mo alloys of the present invention are useful, but they are even more useful when V is used in place of Nb in accord with the prior invention. But since V like Mo decreases oxidation resistance, the total content of (V + Mo) should be maintained at less than 4%. Thus, the new alloys of the present invention will essentially consist of Ti, Al, Nb, Mo. They preferably will contain v. Tungsten may substitute in part or whole for Mo, as indicated below. Other intentional additions may be included in our essential alloys, such as less than 1% C or Si in replacement of Ti.

Table 4 shows the lightest and heaviest embodiments of the present invention in weight percent. This will be provided as a reference for the future.

Table 4.

Weight Percentages (w/o) for the Invention in Atomic Percentages (a/o)						
Alloy		Element				
		Al	Mo	Nb	V	Ti
A	a/o	25	4	12	--	59
	w/o	13.5	7.7	27.3	--	56.5
B	a/o	27	0.5	10.5	--	62
	w/o	15.4	1.0	20.6	--	63
C	a/o	25	1.5	14.5	--	59
	w/o	13.5	2.9	26.9	--	56.7
D	a/o	27	0.5	10.5	--	62
	w/o	15.4	1.0	20.6	--	63.0
E	a/o	25	3.5	12.0	0.5	59
	w/o	13.6	6.7	22.4	0.5	56.8
F	a/o	27.0	0.5	7.0	3.5	62
	w/o	16.0	1.0	14.2	3.8	65.0
G	a/o	25	3	11	1	60
	w/o	13.7	5.9	20.8	1.0	58.6
H	a/o	27	0.5	9	0.5	63
	w/o	15.6	1.0	18.0	0.6	64.8

In the work of the present invention consideration was given to other elements which might be substituted in Ti-Nb-Al-V alloys to achieve the same results as molybdenum. The alloys Ti-25Al-8Nb-X were made, where X was variously 1W, 1Ta, 1Hf, and 1V. No distinction was discerned between the ingredients, all the alloys having poor creep strength. In addition, reference to Table 4 in the US-A-4,292,077 will show that there is no consistent effect of Hf, Zr, or Sn in Ti-24Al-11Nb alloys. The alloys Ti-24Al-11Nb-Z were made, where Z was variously 0.5Hf, 1Zr, (1Zr-0.5Sn-0.5Si), 0.9C, 1.4Hf and (1.5Hf-0.9C), and it was found that compared to Ti-24Al-11Nb the alloys had about the same or inferior creep properties, and about the same tensile properties. Other beta stabilizers, such as iron, chromium or nickel are unsuitable for use in the present invention because they form undesirable phases after high temperature exposure. Their addition also reduces the high temperature properties of the type of titanium alloys of the present invention. Thus,

the studies conclude that molybdenum is unique in the invention, in combination with the narrow ranges of other elements. Since tungsten is known to be metallurgically equivalent to molybdenum in titanium alloys, it will be substitutional for molybdenum in the present invention. However, the use of tungsten will result in an alloy with higher density and therefore, less desirable density-corrected properties than those which result from the use of molybdenum.

The properties of our molybdenum containing alloys were found to be sensitive to microstructure. Based on the prior work, it was felt that the nature of the Widmanstätten platelet array was the key microstructural feature affecting properties. However, in testing it was found that specimens were produced with coarse non-uniform beta grain size. These test bars had associated with them lower tensile ductility, lower fatigue life, and higher creep rupture strength than the other specimens. Analysis showed that in our previous work alloys (Ti-25Al-10Nb-4V) had been redundantly upset and redrawn on a conventional forging press. This working broke up the cast structure and resulted in much finer uniform grain structure than resulted in some of the molybdenum containing alloys. Consequently, it has been concluded that it is desirable with the new alloys to provide some repetitious working prior to isothermally forging the billet to the final desired shape. The desired microstructure will have an ASTM grain size of about 2-4 (0.15-0.20 mm nominal dimension).

The alloy made as described above is best used with limited time exposure at temperatures in the 565-675 °C range. It has been noticed some instability, in that yield strength increased and ductility decreased after several hundreds of hours exposure. Further heat treatment development may avoid the instability.

Generally, the heat treatment which the alloys of the present invention should be given is similar to that disclosed previously in US-A 4,292,077. Solutioning or forging should be conducted above the beta transus, followed by aging between 700-900 °C for 2-24 hours. The cooling rate from the solutioning or forging temperature should be that which produces a fine Widmanstätten structure characterized by acicular alpha two structures of about $50 \times 5 \times 10^{-6}$ m dimension mixed with beta phase lathes, generally as shown in Figure 7(b) of the referenced patent. The conditions necessary to achieve this will depend on the size of the article, but generally cooling in air or the equivalent will be suitable for most small articles. Of course, precautions should be taken to protect the forgings from contamination from the environment, similar to steps followed with the conventional alloys of titanium. An alternative heat treatment comprises solutioning above the beta transus followed by quenching in a molten salt bath maintained about 750 °C, followed by air cooling.

Claims

1. A titanium aluminium alloy consisting (by atomic percent) of 25-27% aluminium, 11-16 % (niobium + molybdenum), 0.5-4% molybdenum, optionally less than 1 % carbon, less than 1 % silicon and the balance titanium plus unavoidable impurities.
2. The alloy of claim 1 having 0.5-1.5% molybdenum.
3. A titanium aluminium alloy consisting (by atomic percent) of 25-27% aluminium, 11-16 % (niobium + molybdenum), 0.5-4% molybdenum, wherein 0.5-3.5 % vanadium is substituted for niobium, the alloy containing 1-4% (molybdenum + vanadium), optionally less than 1 % carbon, less than 1 % silicon and the balance titanium plus unavoidable impurities.
4. The alloy of claim 3 having 1-3% vanadium and 0.5-3% molybdenum.
5. The alloy of claim 3 having 3% vanadium and 1% molybdenum.
6. A titanium aluminium alloy consisting (by atomic percent) of 25-27% aluminium, 11-16 % (niobium + molybdenum), 0.5-4% molybdenum, wherein up to 4 % tungsten is substituted for molybdenum, optionally less than 1 % carbon, less than 1 % silicon and the balance titanium plus unavoidable impurities.
7. The alloy of claim 1 heat treated first at a temperature above the beta transus, then cooled at a controlled rate, sufficient to produce a fine Widmanstätten structure.
8. The alloy of claim 8 further heat treated by aging at 700-900 °C for 4-24 hours.

9. The alloys of claim 1 having a tensile ductility at room temperature of at least 1.5 %.
10. The alloys of claim 1 having a creep stress to density ratio at 650 ° C of greater than 1.6 kPa per kg per m³.
11. The alloy of claim 1 having a 650 ° C dynamic elastic modulus of greater than 9 x 10⁷ kPa.

Revendications

1. Alliage en titane-aluminium consistant en (en pour cent atomique) 25-27% d'aluminium, 11-16% de (niobium + molybdène), 0,5-4% de molybdène, éventuellement moins de 1% de carbone, moins de 1% de silicium, le reste étant du titane plus les impuretés inévitables.
2. Alliage selon la revendication 1, comprenant du molybdène à 0,5-1,5%.
3. Alliage en titane-aluminium consistant en (en pour cent atomique) 25-27% d'aluminium, 11-16% de (niobium + molybdène), 0,5-4% de molybdène, dans lequel on remplace le niobium par du vanadium à raison de 0,5 à 3,5%, l'alliage contenant 1-4% de (molybdène + vanadium), éventuellement moins de 1% de carbone, moins de 1% de silicium, le reste étant du titane plus les impuretés inévitables.
4. Alliage selon la revendication 3, comprenant du vanadium à 1-3% et du molybdène à 0,5-3%.
5. Alliage selon la revendication 3, comprenant du vanadium à 3% et du molybdène à 1%.
6. Alliage en titane-aluminium consistant en (en pour cent atomique) 25-27% d'aluminium, 11-16% de (niobium + molybdène), 0,5-4% de molybdène, dans lequel on remplace le molybdène par une quantité allant jusqu'à 4% de tungstène, éventuellement moins de 1% de carbone, moins de 1% de silicium, le reste étant du titane plus les impuretés inévitables.
7. Alliage selon la revendication 1, que l'on soumet d'abord à un traitement thermique à une température au-dessus du transus bêta, que l'on refroidit ensuite à une vitesse contrôlée, suffisante pour obtenir une structure fine de Widmanstätten.
8. Alliage selon la revendication 8, que l'on soumet à un traitement thermique ultérieur en procédant à un vieillissement à 700-900 ° C pendant 4-24 heures.
9. Alliages selon la revendication 1, qui possèdent une ductilité élastique à la température ambiante d'au moins 1,5%.
10. Alliages selon la revendication 1, qui possèdent un rapport résistance au fluage/masse volumique à 650 ° C supérieure à 1,6 kPa par kg par m³.
11. Alliage selon la revendication 1, qui possède un module d'élasticité dynamique à 60 ° C supérieure à 9 x 10⁷ kPa.

Patentansprüche

1. Titanaluminiumlegierung, bestehend aus (in Atomprozent) 25-27% Aluminium, 11-16% (Niob + Molybdän), 0,5-4% Molybdän, wahlweise weniger als 1% Kohlenstoff, weniger als 1% Silizium, und als Rest Titan plus unvermeidliche Verunreinigungen.
2. Legierung nach Anspruch 1, mit 0,5-1,5% Molybdän.
3. Titanaluminiumlegierung, bestehend aus (in Atomprozent) 25-27% Aluminium, 11-16% (Niob + Molybdän), 0,5-4% Molybdän, wobei 0,5-3,5% Vanadium anstelle von Niob vorgesehen sind und wobei die Legierung 1-4% (Molybdän + Vanadium), wahlweise weniger als 1% Kohlenstoff, weniger als 1% Silizium und als Rest Titan plus unvermeidliche Verunreinigungen enthält.

4. Legierung nach Anspruch 3, mit 1-3% Vanadium und 0,5-3% Molybdän.
5. Legierung nach Anspruch 3, mit 3% Vanadium und 1% Molybdän.
- 5 6. Titanaluminiumlegierung, bestehend aus (in Atomprozent) 25-27% Aluminium, 11-16% (Niob + Molybdän) 0,5-4% Molybdän, wobei bis zu 4% Wolfram anstelle von Molybdän vorgesehen sind, wahlweise weniger als 1% Kohlenstoff, weniger als 1% Silizium und der Rest Titan plus unvermeidliche Verunreinigungen sind.
- 10 7. Legierung nach Anspruch 1, die zuerst bei einer Temperatur oberhalb der Beta-Transus-Temperatur wärmebehandelt und dann mit kontrollierter Geschwindigkeit abgekühlt worden ist, und zwar ausreichend, um ein feines Widmanstätten-Gefüge zu erzeugen.
- 15 8. Legierung nach Anspruch 1, die weiter wärmebehandelt worden ist durch Altern bei 700-900 °C für 4-24 Stunden.
9. Legierungen nach Anspruch 1, mit einer Zugduktilität bei Raumtemperatur von wenigsten 1,5%.
- 20 10. Legierungen nach Anspruch 1, mit einem Verhältnis von Zeitstandfestigkeit zu Dichte bei 650 °C von größer als 1,6 kPa pro kg pro m³.
11. Legierung nach Anspruch 1, mit einem dynamischen Elastizitätsmodul bei 650 °C von größer als 9×10^7 kPa.

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FIG. 1

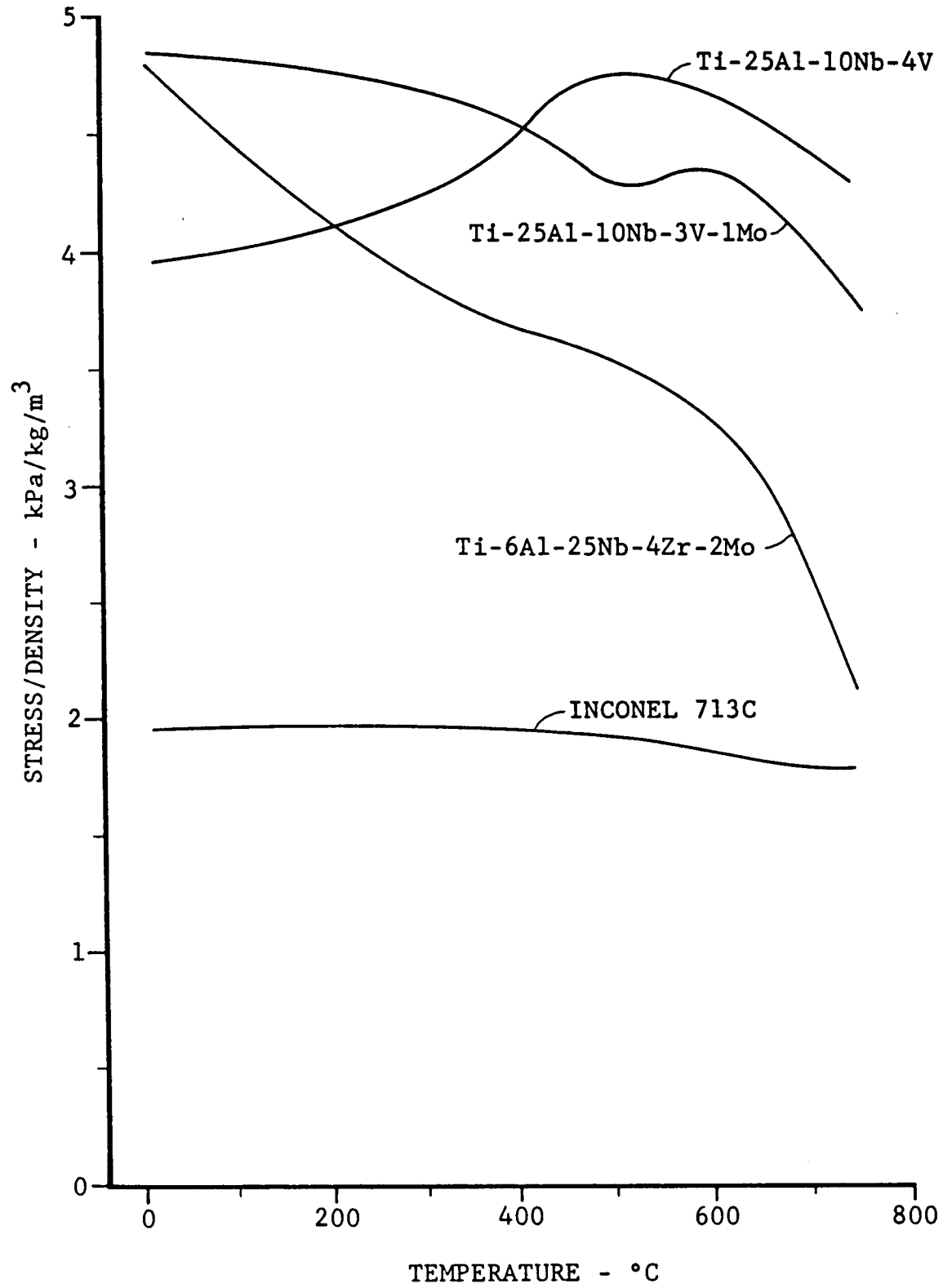


FIG. 2

