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[54] **DISPERSOID TITANIUM AND TITANIUM-BASE ALLOYS**  
**11 Claims, No Drawings**

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**C22c 31/04**  
 [50] Field of Search ..... **75/175.5,**  
**201, 202; 148/32, 32.5; 29/182, 182.5, 182.7**

[56] **References Cited**

## UNITED STATES PATENTS

2,797,996	7/1957	Jaffee et al.	75/175.5
3,052,538	9/1962	Jech et al.	75/175.5

**ABSTRACT:** As a new article of manufacture a base metal of the group titanium and titanium base alloys containing a dispersoid of the group consisting of thorium, boron, rare earth elements having an atomic number of 57-71, and elements of groups IIb and IIc of the periodic table of elements, which are substantially insoluble in solid titanium but soluble in molten titanium, and combinations and compounds thereof, preferably in proportions of about 0.1 to 6 percent by weight of the total, and wherein said dispersoid is preferably dispersed in a particle size of several microns and under, said article being characterized by high-elevated temperature creep strength.

## DISPERSOID TITANIUM AND TITANIUM-BASE ALLOYS

This application is a continuation-in-part of my copending application Ser. No. 558,589, filed June 20, 1966, now U.S. Pat. No. 3,379,522.

This invention pertains to titanium and titanium-base alloys containing dispersions of particles essentially insoluble in solid titanium at any temperature but soluble in molten titanium, and to methods of producing such dispersoid alloys.

More particularly the invention pertains to titanium-base alloys containing finely divided particle dispersions of one or more dispersoids selected from the group consisting of boron, thorium, groups IIIb and IIIc of the periodic table of elements set forth inside the forth cover of "The Merck Index," seventh edition, 1960, published by Merck & Co., Inc., Rahway, New Jersey elements having atomic numbers 57 through 71 which may be designated rare earth elements, and compounds of the foregoing such as the sulfides as well as combinations of any of them, which are substantially insoluble in solid titanium at any temperature but soluble in molten titanium. The preferred dispersoids are boron, cerium, thorium, lanthanum and combinations and compounds thereof, such as TiB, CeS, LaS, misch metal and other mixed rare earth sulfides, and the like. The rare earths and especially cerium and lanthanum are most preferably used as the sulfides whereas the boron and thorium are preferably used in the elemental form. The method for producing dispersions of the present invention involves melting the components to form a homogeneous liquid preferably thence extreme chill-casting the liquid as by splashing it in thin layers against a cold solid surface or by spraying the liquid into a cold chamber wherein it freezes as fine shot, and finally consolidating the shot and splashings by pressure, heat and plastic deformation into a product of essentially theoretically full density.

In the extreme chill-casting described, the dispersoid particle components, although soluble in the liquid titanium, are substantially insoluble in solid titanium and are thus forced by freezing of the liquor to separate as particle of extreme fineness because of the very short time available for growth. Thus the dispersoid particles ordinarily appear as submicron-sized dispersions within the shot or splashed flakes which, although fine themselves relative to any standard ingots, are very coarse relative to the dispersoid particles. That is, the shot or flakes may be from perhaps 50 to 100 microns to several hundred microns in mean section, and the dispersed particles therein will be on the order of several microns to less than 1 microns in particles size.

The dispersoid as present in the final solid alloy may appear as a compound with one or more of the materials present in the base alloy. Thus, for example, when elemental boron is added, the final solid alloy may contain the boron as TiB. As used herein, reference to the novel base metal alloys of the present invention as including a given dispersoid is to be understood as meaning the dispersoid as added irrespective of the form in which it appears in the final product.

The advantages of fine particles dispersions in alloys for elevated temperature use are well-known, as are several methods for producing them. Most commonly, dispersions of particles in a base metal are formed as precipitates therein by suitable heat treatment of alloys containing components which are soluble in the solid alloy at high temperatures and less soluble at low. Such systems are very numerous and of great usefulness. Since the precipitate components are soluble at high temperatures, however, they tend to be of limited elevated temperature usefulness generally, and for use beyond their temperature range, dispersoids substantially insoluble in the solid matrix are required.

Alloys containing substantially insoluble, stable and inert particles dispersions, and certain methods of making them are also well-known. The most used conventional method consists of mixing extremely fine powders of base metal and of dispersoids, compacting, sintering and working the mixtures to solidify them. In the case of titanium, the high reactivity of submicron powders thereof and the ready solubility of con-

taminants, as for example, oxygen and nitrogen from the air, make the powder approach impractical. Shot and flake as described herein have several hundred times less surface per unit mass than conventional powders, and handling is therefore not difficult. The micron or submicron particles exist in the shot and flake as made according to the invention and titanium powder of such small particle size is unnecessary.

Another known method of making stable dispersoid systems consists of internal oxidation of solid solutions of active metals in a less reactive base metal, such for example as titanium containing in solid solution, certain rare earth metals which can be oxidized in situ to form stable particles of oxide. The combined requirements of solid solubility of the metallic component of the dispersoid, plus greater reactivity than titanium, essentially limits the possibilities for this approach to the rare earths which are soluble in solid titanium. Also such rare earth oxides are stable only in titanium which of itself contains a substantial oxygen content, which is in some instances undesirable.

The dispersoids above-mentioned with reference to this invention, are all substantially insoluble in solid titanium, and when present as micron or submicron dispersions as produced in accordance with the methods of the invention, impart outstanding elevated temperature creep properties operable to higher temperature levels than is attainable with dispersoid type titanium and titanium-base alloy materials heretofore available insofar as I am aware. Additionally, compositions of the present invention, especially those containing boron as the dispersoid display a substantial resistance to hot salt corrosion cracking. Quick satisfactory results are obtained in this regard at boron inclusions of about 0.25 to about 1 percent.

## EXAMPLE

In the practice of the invention, titanium or titanium alloys in the molten state containing about 0.1 to 6 percent in total amounts of one or more elements, compounds or mixtures as aforesaid which are soluble in the molten base metal but insoluble in the solid state thereof, are shot as described for example, in U.S. Pat. No. 2,897,539. The shot are then consolidated into billets by known methods such as canning and hot pressing. Mill products are made from the hot pressed billets by conventional means as by forging, rolling, extruding, etc.

Maximum usefulness of inert dispersoid-containing alloys as described herein occurs under conditions of very long time and/or high-temperature exposure.

The following table I shows for a Ti-6Al-2Sn-4Zr-2Mo alloy, creep strength with long-term aging without and with an inert submicron dispersoid according to the invention.

Table I

Creep Deformation of Cast Alloys Aged 200 Hours at 1,100° F. And Stressed to 30 Ks.i. at 1,000° F. for 150 Hours

Alloy	Deformation %
Ti-6Al-2Sn-4Zr-2Mo	0.421
Ti-6Al-2Sn-4Zr-2Mo-1.7Ce-0.5S	0.167

Inclusion of the dispersoid thus reduces the creep deformation approximately 60 percent in this alloy.

The effects of dispersoid particle size variation in titanium and titanium base alloys is shown by the following comparative tests. In table II below a dispersoid was produced in a very coarse-grained condition in the two titanium base alloys shown, and the creep deformation measured for the alloy without and with the dispersoid.

TABLE II

Alloy	Deformation, 1,000° F.-30 kp.s.i.-150 hr.
Ti-8Al.....	0.06
Ti-8Al and dispersoid.....	0.20
Ti-8Al-1Mo-IV.....	0.26
Ti-8Al-1Mo-IV and dispersoid.....	0.50

It is thus shown that extremely coarse grained dispersoids are damaging to creep. In contrast in the following table III, there is shown the effect of a fine dispersoid on the order of 1 micron in particle size.

TABLE III

Alloy	Deformation 1,000° F.-30 Kp.s.i.-150 Hr.
Ti-8Al	0.06
Ti-8Al. and dispersoid	0.005

Thus the presence of an inert dispersoid in particle size on the order of several microns and under greatly improves the creep properties.

The following table IV gives the elevated temperature creep properties of various "as cast" base metal and dispersoid alloys according to the invention, wherein the base metal or base metal plus dispersoid additions were melted up and cast into test specimens. The specimens were then aged for about 24 hours at about 1,100° F. before testing.

TABLE IV

Creep Properties of as Cast and Aged Dispersoid Alloys

Composition percent, Bal. Ti	Creep exposure, ° F./K s.i./hrs.	Creep deformation, percent
4Sn-10Zr.....	1,000/30/150	7.8-2.4
4Sn-10Zr+3 Ce.....	1,000/30/150	0-1.3
4Sn-10Zr+1.75 Ce + 0.5 S.....	1,000/30/150	1.7-0.1
4Sn-10Zr+3 U + 0.5 O <sub>2</sub> .....	1,000/30/150	2.2-0
4Sn-10Zr-2Mo.....	1,000/30/150	10.7
4Sn-10Zr-2Mo+3 Ce.....	1,000/30/150	7.9
4Sn-10Zr-2Mo+1.75 Ce + 0.5 S.....	1,000/30/150	2.8
4Sn-10Zr-2Mo+3 Ce + 0.5 O <sub>2</sub> .....	1,000/30/150	1.9
4Sn-10Zr-2Mo+2.4 CeS.....	1,000/30/150	2.9
4Sn-5Zr-11Mo.....	700/110/150	>10.0
4Sn-5Zr-11Mo+0.6 CeS.....	700/110/150	0.9
4Sn-5Zr-11Mo+0.5 Ce + 0.1 S.....	700/110/150	0.9
4Sn-5Zr-11Mo+2 Ce + 0.4 S.....	700/110/150	0.3
4Sn-5Zr-11Mo+5 Th.....	700/110/150	0.6
2Al-2Sn-4Zr-2Mo.....	1,000/30/150	1.09
2Al-2Sn-4Zr-2Mo+5 Th.....	1,000/30/150	0.57
2Al-2Sn-4Zr-2Mo+0.2 Si + 1 Th.....	1,000/30/150	0.45
6Al-2Sn-4Zr-2Mo.....	1,000/30/150	0.42
6Al-2Sn-4Zr-2Mo+3 Ce.....	1,000/30/150	0.33
6Al-2Sn-4Zr-2Mo+3 Ce + 0.5 O <sub>2</sub> .....	1,000/30/150	0.18
6Al-2Sn-4Zr-2Mo+1.75 Ce + 0.5 S.....	1,000/30/150	0.17
6Al-2Sn-4Zr-2Mo.....	1,060/30/24	0.29
6Al-2Sn-4Zr-2Mo+0.2 Si.....	1,060/30/24	0.17
6Al-2Sn-4Zr-2Mo+0.2 Si + 1 Th.....	1,060/30/24	0.07
2Al-4Sn-10Zr-2Mo.....	700/110/150	1.84
2Al-4Sn-10Zr-2Mo+0.5 Ce + 0.1 S.....	700/110/150	0.42
2Al-4Sn-10Zr-2Mo+2 Ce + 0.4 S.....	700/110/150	0.35

It will be seen from the test results of table IV that the dispersoid additions have in each instance greatly increased the creep strength of the base alloy in cast specimens produced as above.

The following table V shows the effects on creep properties of taking as cast alloys produced as above and subsequently working the same as by forging or rolling and thence aging prior to testing. It has been found in this connection that creep properties of such wrought products are developed by working in the alpha-beta temperature field at about 1,700-1,800° F. followed by a lower temperature aging treatment at about

1,100° F. for about 24 hours, although the benefits are not limited to such processing. The specimens for the following table V data were prepared in this way.

TABLE V

Creep Properties of Alpha-Beta Rolled and Aged Dispersoid Alloys

Composition percent, Bal. Ti	Creep exposure, ° F./K s.i./hrs.	Creep deformation, percent
10 6Al-4V.....	800/40/150	0.40
6Al-4V+1B.....	800/40/150	0.13
6Al-4V.....	850/40/24	0.21
6Al-4V+1B.....	850/40/24	1.2
4Al-2Sn-4Zr-2Mo.....	850/70/24	1.0
4Al-2Sn-4Zr-2Mo+0.4 Ce.S.....	850/70/24	0.105
6Al-2Sn-4Zr-2Mo.....	850/70/24	0.145
6Al-2Sn-4Zr-2Mo+0.2 Si.....	850/70/24	0.038
6Al-2Sn-4Zr-2Mo+0.2 Si+1 Th.....	850/70/24	0.960
6Al-2Sn-4Zr-2Mo.....	1,060/30/24	0.316
6Al-2Sn-4Zr-2Mo+0.2 Si.....	1,060/30/24	0.233
2Al-4Zr-Mo.....	1,000/15/150	10.3
2Al-4Zr-4Mo+1 Th.....	1,000/15/150	5.1
2Al-4Zr-4Mo+0.25 B.....	1,000/15/150	2.5

It will thus be seen from the table V data that the dispersoid additions greatly increase the creep properties of these alloys in wrought and aged conditions.

Typical room temperature tensile properties of dispersoid alloys according to the invention after creep testing in wrought form, as in table V supra, are given in the following table VI.

TABLE VI

Room Temperature Tensile Properties of Wrought Ti-Base Dispersoid Alloys After Creep Testing

Composition percent, Bal. Ti	Creep exposure, ° F./K s.i./hrs.	K s.i.		Percent	
		Ult. str.	0.2% Y.S.	Area red.	elong.
6 Al-4V-1B.....	800/40/150	174	160	5	6
6 Al-4V-1B.....	800/40/24	173	161	24	11
4 Sn-5 Zr-11 Mo-5 Th.....	700/100/150	169	166	.....	.....
2 Al-2 Sn-4 Zr-2 Mo-2 Ce. S.....	1,000/30/150	134	119	.....	11
4 Al-2 Sn-4 Zr-0.33 Ce-0.07 S.....	1,060/30/24	129	122	19	9
2 Al-2 Sn-4 Zr-2 Ce.S.....	700/100/150	130	119	.....	10
2 Al-3 Sn-4 Zr-2 Mo-4 Th.O <sub>2</sub> .....	700/110/150	136	117	.....	9
2 Al-3 Sn-4 Zr-2 Mo-4 Th. O <sub>2</sub> .....	1,060/30/150	135	123	.....	9

It will be seen from table VI that the dispersoid alloys according to the invention have good strength and ductility after creep testing.

I have further discovered as an additional feature of the present invention that the alloy thereof containing about 6 percent aluminum, 4 percent vanadium, 1 percent boron and the balance substantially titanium, is substantially more resistant to hot salt corrosion cracking than is the alloy without the boron addition. The boron free, 6 percent Al-4 % V alloy shows severe cracking in less than 100 hours of exposure to salt, NaCl, at 800° F. and under 25 Ks.i. stress. As compared to this, the above boron containing alloy showed no visible cracking such as degraded ductility in tensile tests after 100 hours at 800° F. and at 30, 35, 40 and 50 Ks.i. stresses in separate tests. The following table VII gives the results of a series of creep tests on the aforesaid Ti-6Al-4V-1B alloy both as conducted in an air and in a salt or chloride containing atmosphere.

TABLE VII

Ti-6 Al-4V-1B Beta Worked, Annealed 1,400° F.-1/4 Hr.-AC And Aged 1,100° F.-Hrs.-AC. Exposed as shown. Creep Deformation and Subsequent Tensiles

Exposure	Def., percent	K.s.i.		Percent RA	Percent El
		US	YS		
850/40/24 air.....	0.186	176	163	23	7
850/40/24 air.....	0.180	173	161	24	11
800/40/150 air.....	0.160	173	162	5	6
800/40/150 air.....	0.131	174	160	6	6
800/25/100 salt.....	.....	177	169	23	7
800/35/100 salt.....	.....	176	163	20	7
800/40/100 salt.....	.....	174	162	20	12
800/50/100 salt.....	.....	175	162	23	13

What is claimed is:

1. As a new article of manufacture, a base metal selected

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from the group consisting of titanium and titanium base alloys containing a dispersion of a dispersoid selected from the group consisting of boron, thorium, rare earth elements having an atomic number of 57 to 71, scandium, yttrium, actinium, and compounds and combinations thereof which are substantially insoluble in solid titanium but soluble in molten titanium, the particle size of said dispersoid being predominantly of the order of one micron and under.

2. An article according to claim 1 wherein said dispersoid comprises 0.1 to 6 percent by weight of the total.

3. The article of claim 2 wherein the dispersoid is boron, titanium boride, thorium, cerium, cerium sulfide, lanthanum, or lanthanum sulfide.

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4. The article of claim 1 wherein the dispersoid is boron.

5. The article of claim 1 wherein the dispersoid is thorium.

6. The article of claim 1 wherein the dispersoid is cerium.

7. The article of claim 1 wherein the dispersoid is cerium sulfide.

8. The article of claim 1 wherein the dispersoid is lanthanum sulfide.

9. A cast article according to claim 2.

10. A wrought article according to claim 2.

11. An article according to claim 1 consisting essentially of about: 6 percent aluminum, 4 percent vanadium, 0.25 to 1 percent boron and the balance substantially titanium.

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