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(54) Title: OXIDATION RESISTANT MOLYBDENUM ALLOY		
(57) Abstract Molybdenum alloys are provided with enhanced oxidation resistance. The alloys are prepared by the addition of silicon and boron in amounts defined by the area of a ternary system phase diagram bounded by the points Mo-1.0 % Si-0.5 % B, Mo-1.0 % Si-4.0 % B, Mo-4.5 % Si-0.5 % B, and Mo-4.5 % Si-4.0 B. The resultant alloys have mechanical properties similar to other high temperature molybdenum alloys while possessing a greatly enhanced resistance to oxidation at high temperature. A variety of alloying elements are added to the base composition to modify the alloy properties.		

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OXIDATION RESISTANT MOLYBDENUM ALLOY**BACKGROUND OF THE INVENTION**

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1. **Field of the Invention**

The present invention relates to molybdenum alloys that have been made oxidation resistant by the addition of silicon and boron.

10 2. **Related Art**

Molybdenum metal is an attractive material for use in jet engines and other high temperature applications because it exhibits excellent strength at high temperature. In practice, however, the utility of molybdenum has been limited by its susceptibility to oxidation. When molybdenum or molybdenum alloys are exposed to oxygen at
15 temperatures in excess of about 540°C (1000°F), the molybdenum is oxidized to molybdenum trioxide and vaporized from the surface; resulting in shrinkage and eventually disintegration of the molybdenum or molybdenum alloy article. Most previously disclosed methods of preventing oxidation of molybdenum at high temperature in oxidizing environments (such as air) have required a coating to be applied to the
20 molybdenum alloy. Applied coatings are sometimes undesirable due to factors such as: poor adhesion, the need for extra manufacturing steps, and cost. Furthermore, damage to the coating can result in rapid oxidation of the underlying molybdenum alloy. Thus, there is a need for molybdenum alloys which possess a combination of good strength and enhanced oxidation resistance at high temperature. There is a corresponding need for
25 methods of making these alloys.

SUMMARY OF THE INVENTION

The molybdenum alloys of the present invention are composed of a matrix of body-centered cubic (BCC) molybdenum and dispersed intermetallic phases wherein the composition of the alloys are defined by the points of a phase diagram for the ternary system metal-1.0%Si-0.5%B, metal-1.0%Si-4.0%B, metal-4.5%Si-0.5%B and metal-4.5%Si-4.0%B where metal is molybdenum or a molybdenum alloy. Smaller amounts of silicon and boron will not provide adequate oxidation resistance; larger amounts will embrittle the alloys. All percentages (%) disclosed herein refer to weight percent unless otherwise specified. In the foregoing composition ranges, the molybdenum metal component may contain one or more of the following elemental additions in replacement of an equivalent amount of molybdenum:

	ELEMENT	RANGE IN WEIGHT % OF THE FINAL ALLOY	PREFERRED RANGE
	C	0.01 to 1.0	0.03 to 0.3
5	Ti	0.1 to 15.0	0.3 to 10.0
	Hf	0.1 to 10.0	0.3 to 3.0
	Zr	0.1 to 10.0	0.3 to 3.0
10	W	0.1 to 20.0	0.3 to 3.0
	Re	0.1 to 45.0	2.0 to 10.0
	Al	0.1 to 5.0	0.5 to 2.0
15	Cr	0.1 to 5.0	0.5 to 2.0
	V	0.1 to 10.0	0.3 to 5.0
20	Nb	0.1 to 2.0	0.3 to 1.0
	Ta	0.1 to 2.0	0.3 to 1.0

When the alloys of the present invention are exposed to an oxidizing environment at temperatures greater than 540°C (1000°F), the material will produce a volatile molybdenum oxide in the same manner as conventional molybdenum alloys. Unlike conventional alloys, however, oxidation of alloys of the present invention produces build-up of a borosilicate layer at the metal surface that will eventually shut off the bulk flow of oxygen. For example, an X-ray map of a sample of the alloy Mo-0.3%Hf-2.0%Si-1.0%B after oxidation in air at 1090°C (2000°F) for two hours showed a borosilicate layer about 10µm thick. This is shown in Figure 1. After a borosilicate layer is built up, oxidation is controlled by diffusion of oxygen through the borosilicate and will, therefore, proceed at a much slower rate.

In certain preferred embodiments, it is advantageous to add a reactive element such as titanium, zirconium, hafnium, and/or aluminum to the alloy to: (1) promote wetting of the borosilicate layer once it has formed, (2) raise the melting point of the borosilicate, and (3) form a more refractory oxide layer below the initial borosilicate layer further impeding oxygen transport to the molybdenum matrix. The addition of such elements is particularly advantageous for alloys that are intended to be used at high temperatures (i.e., about 1090°C (2000°F)). In some embodiments, it is advantageous to add carbon to the alloy in order to produce small amounts (less than 2.5 volume %) of carbide to strengthen the alloy. The alloys of the present invention preferably contain 10 to 70 volume % molybdenum borosilicide (Mo_3SiB_2), less than 20 volume % molybdenum boride (Mo_2B), and less than 20 volume % molybdenum silicide (Mo_3Si_3 and/or Mo_3Si). In a still more preferred embodiment, the alloys of the present invention comprise less than 2.5 volume % carbide and less than 3 volume % of non-BCC molybdenum phases, other than the carbide, silicide, and boride phases discussed above. Preferred alloys of the present

invention are formulated to exhibit oxidation resistance such that articles composed of these alloys lose less than about 0.01" (about 0.25mm) in thickness after exposure to air for two hours at the maximum use temperature of the article. The maximum use temperature of these articles is typically between 820°C (1500°F) and 1370°C (2500°F). It is contemplated that the alloys of the present invention be formulated for the best overall combination of oxidation resistance and mechanical properties for each article's particular requirements.

The alloys of the present invention can be produced through a variety of methods including, but not limited to: powder processing (prealloyed powder, blended powder, blended elemental powder, etc.), and deposition (physical vapor deposition, chemical vapor deposition, etc.). Powders of the alloys of the present invention can be consolidated by methods including, but not limited to: extrusion, hot pressing, hot isostatic pressing, sintering, hot vacuum compaction, etc. After consolidation, the alloys can be thermally-mechanically processed by methods used conventionally on molybdenum alloys.

While the alloys of the present invention may be used in less demanding conditions, these alloys are particularly desirable for use in situations requiring both good strength and good oxidation resistance at temperatures in excess of 540°C (1000°F). Particular applications include, but are not limited to, jet engine parts such as turbine blades, vanes, seals, and combustors.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 shows an X-ray map of silica scale (white area) produced on the alloy Mo-0.3%Hf-2.0%Si-1.0%B by oxidation in air at 1090°C (2000°F) for two hours. The magnification is 1000X so that 1cm is equal to 10 microns.

5 Fig. 2 shows the comparison of the oxidation resistance of an alloy of the present invention (Mo-6.0%Ti-2.2%Si-1.1%B) and a conventional (Mo-0.5%Ti-0.08%Zr-0.03%C, TZM) alloy molybdenum which have been exposed to air for two hours at 1370°C (2500°F) and 1090°C (2000°F), respectively.

DETAILED DESCRIPTION OF THE INVENTION

Alloys of the present invention are made by combining elements in proportion to the compositional points defined by the points of a phase diagram for the ternary system metal-1.0%Si-0.5%B, metal-1.0%Si-4.0%B, metal-4.5%Si-0.5%B, and metal-4.5%Si-
5 4.0%B, wherein the metal is greater than 50% molybdenum.

The intermetallic phases of the alloy of the present invention are brittle. Therefore, in order to obtain ductile alloys, the material must be processed so that there is a matrix of ductile BCC molybdenum surrounding discrete particles of intermetallic phase. This structure is obtained, in preferable embodiments of the present invention by: 1) blending
10 molybdenum powder with either a prealloyed intermetallic powder (such as molybdenum borosilicide) or boron and silicon powder, followed by consolidating the powder at a temperature below the melting temperature of the alloy; or 2) rapidly solidifying a melt containing molybdenum, silicon and boron, followed by consolidating the rapidly solidified material at a temperature below the melting temperature. The latter process is
15 more expensive but it produces a material having a finer, more processable microstructure.

In order to obtain desired shape, strength and hardness, alloys of the present invention can be processed in the same manner as other high strength molybdenum alloys. Preferred alloys of the present invention can not be shaped by recasting and slow solidification since slow solidification forms excessively large dispersoids and, as a result,
20 embrittled alloys.

In the most preferable method of making alloys of the present invention, elemental molybdenum, silicon and boron, in the portions defined above, are combined in a melt. Alloy from the melt is rapidly solidified into a fine powder using an atomization device based on U.S. Patent No. 4,207,040. The device from this patent was modified by the

substitution of a bottom pour 250 kilowatt plasma arc melter for the induction heated crucible. The resultant powder is screened to minus 80 mesh. This powder is loaded into a molybdenum extrusion can and then evacuated. The material is then given a pre-extrusion heat treatment of 1760°C (3200°F) for 2 hours and then is extruded at a cross-sectional ratio of 6 to 1 at a temperature of 1510°C (2750°F). The extrusion is then swaged 50% in 5% increments at 1370°C (2500°F). The molybdenum can is then removed and the remaining material is then swaged down to the desired size at temperatures of 1260°C (2300°F) to 1370°C (2500°F). All heat treatments and pre-heating should be done in an inert atmosphere, in vacuo, or in hydrogen.

10 Other elements can replace some of the molybdenum in alloys of the present invention. The use of titanium, zirconium, hafnium and/or aluminum in the alloys of the present invention promotes wetting of the metal surface by the oxide and increases the melting point of the oxide. Larger additions (i.e. 0.3% to about 10%) of these elements creates a refractory oxide layer under the initial borosilicate layer. The addition of
15 titanium is especially preferred for this use.

Because elements such as titanium, zirconium, hafnium and aluminum can have a small deleterious effect on oxidation resistance at temperatures below about 980°C (1800°F); the addition of these elements is undesirable for some low temperature applications.

20 The tensile strength of the alloys of the present invention can be increased by the addition of solid solution strengthening agents. Additions of titanium, hafnium, zirconium, chromium, tungsten, vanadium and rhenium strengthen the molybdenum matrix. In addition to strengthening the material, rhenium can also be added to lower the ductile/brittle transition temperature of the BCC matrix.

Since titanium, zirconium, and hafnium are potent silicide and boride formers, these elements can be added to improve the mechanical properties of the alloys by increasing the fracture strength of the intermetallic phases. In some embodiments, the intermetallic phases are strengthened by the use of carbon as an alloying addition.

5 In certain, preferred embodiments, alloys of the present invention are additionally strengthened through solutioning and aging. In these alloys small amounts of silicon and/or carbon can be taken into solution in the BCC matrix by heating the alloy to over 1540°C (2800°F). A fine dispersion of either silicides or carbides can then be produced in the alloy by either controlled cooling of the material, or by cooling it fast enough to keep
10 the silicon and/or carbon in solution and then precipitating silicides and/or carbides by aging the material between 1480°C (2700°F) and 1260°C (2300°F). Tungsten and rhenium decrease the solubility of silicon in the alloy and when added in small amounts (i.e. about 0.1-3.0%) improve the stability of any fine silicides present. In alloys with an insufficient amount of silicon present for an aging response, vanadium may be added to increase the
15 solubility of silicon in the alloy. The elements titanium, zirconium, and hafnium may be added to improve the aging response by promoting the formation of alloy carbides. In a preferred embodiment, the silicide or carbide fine dispersion particles consist essentially of particles having diameters between 10nm and 1 micron. In a more preferred embodiment, these fine dispersion particles are spaced apart by 0.1 to 10 microns.

20 In preferred embodiments, alloys of the present invention are composed of long grains having an aspect ratio of greater than 6 to 1.

Phases in alloys of the present invention were characterized by scanning electron microscope - energy dispersive x-ray analysis (SEM-EDX) and x-ray back scattering. In alloys containing only molybdenum, silicon and boron, the stable phases are Mo_5SiB_2 .

Mo₂B, and Mo₃Si. Alloys containing more than about 2% of additive elements such as titanium, zirconium or hafnium may have alloyed Mo₅Si₃ present either in addition to or in place of Mo₃Si. In a preferred embodiment, the molybdenum boride, silicide and borosilicide dispersion particles consist essentially of particles having diameters between 5 10 microns and 250 microns.

OXIDATION RESISTANCE

A series of tests were conducted that demonstrated the molybdenum alloys of the present invention to have a far greater oxidation resistance than previously known molybdenum alloys. All of the tests were performed using small arc castings made in an inert atmosphere from metal powders. In a comparative test, TZM, a commercially available molybdenum alloy, lost approximately 0.063mm (2.5 mils) per minute in an air furnace at 1090°C (2000°F). In comparison, an alloy of the present invention, having the composition Mo-6.0%Ti-2.6%Si-1.1%B lost approximately 0.05mm (2 mils) in two hours in an air furnace at 1360°C (2500°F) and formed an oxide layer that would greatly retard further oxidation. The alloy samples resulting from the two hour comparative test are shown in Figure 2.

A set of oxidation tests were performed that demonstrated the effects of various amounts of silicon and boron in molybdenum. These tests were conducted in an air furnace at 1090°C (2000°F) for 1 hour and used identically prepared samples consistly only of molybdenum, silicon and boron. The results of this test are shown in Table 1.

5

10

Si	B	oxidation rate (mils/min)
1.0	0.5	0.7
1.0	4.0	0.07
4.5	4.0	0.02
4.5	0.5	0.5
0.5	0.5	1.6
1.0	0	2.0
5.0	0	1.3
1.0	7.0	0.05
4.5	7.0	0.05

Table 1. Oxidation Rates of Various Molybdenum Alloys at 1090°C (2000°F).

The oxidation rate of 0.018mm (0.7 mils) per minute is one third that of TZM and
 15 represents the practical limit for a material that could survive in a coated condition in a
 short time non-manrated jet engine application where the use time of the material would
 be on the order of 15 minutes. As shown from the test data, the addition of 0.5%B results
 in significantly better oxidation resistance than silicon alone. More importantly, the Mo-
 1.0%Si material did not form a protective oxide and the Mo-5.0%Si formed a voluminous,
 20 porous oxide with extremely poor adherence to the base metal. An alloy containing
 0.5%B and only 0.5%Si exhibited intermittent formation of a non-protective oxide and
 twice the oxidation rate of the alloy containing 0.5%B and 1.0%Si. The materials
 containing excessive boron, Mo-1.0%Si-7.0%B and Mo-4.5%Si-7.0%B, demonstrated good
 oxidation rates but produced highly liquid oxides which flowed over and attacked the
 25 material the specimens were placed on. The oxides would be subject to degradation by
 any flowing media such as air passing over the material and would be easily removed by
 physical contact.

In another set of tests approximately 200 alloy compositions were made up of small arc castings and tested for oxidation resistance. These oxidation tests were conducted at temperatures of 820°C (1500°F), 1090°C (2000°F) and 1370°C (2500°F). The tests were done for 2 hours in an air furnace. The specimens were rectangles approximately 1¼ x 3⅛ x 3¼ inches long. It was found that as the amount of silicon and boron increased, the amount of intermetallic present also increased, and the better the oxidation became. However, increasing amounts of silicon and boron also made the material difficult to process for useful mechanical properties. At 2% silicon and 1% boron there is approximately 30 to 35 volume % intermetallic in the material. Additions of titanium, zirconium and hafnium improve the oxidation resistance of the material at 2000°F without causing an increase in the amount of intermetallic. These elements caused a slight but acceptable decrease in the oxidation resistance at 820°C (1500°F). They caused a significant increase in the oxidation resistance at 1370°C (2500°F).

The following compositions are examples of alloys that were found to be highly oxidation resistant at 1500, 2000, and 1360°C (2500°F): Mo-2.0%Ti-2.0%Si-1.0%B; Mo-2.0%Ti-2.0%Si-1.0%B-0.25%Al; Mo-8.0%Ti-2.0%Si-1.0%B; Mo-0.3%Hf-2.0%Si-1.0%B; Mo-1.0%Hf-2.0%Si-1.0%B; Mo-0.2%Zr-2.0%Si-1.0%B; and Mo-6.0%Ti-2.2%Si-1.1%B. Mo-6.0%Ti-2.2%Si-1.1%B showed particularly excellent oxidation resistance at 1090°C (2000°F) and 1370°C (2500°F).

20 STRENGTH

The tensile properties of Mo-0.3%Hf-2.0%Si-1.0%B are shown in Table 2. The alloy used in testing was prepared by rapid solidification from the melt followed by extrusion as described above with reference to the most preferred embodiment. Tensile strength testing was conducted on bars 0.38cm (0.152") in diameter, 2.5cm (1") long with

threaded grips and 0.63cm (0.25") radius shoulders. For comparison, the yield strength of TZM at 1090°C (2000°F) is 70 ksi and the yield strength of a single crystal nickel superalloy at 1090°C (2000°F) is 40 ksi. For a review of molybdenum alloys and their strengths; see J.A. Shields, "Molybdenum and Its Alloys," Advanced Materials &

5 Processes, pp. 28-36, Oct. 1992.

10

Temperature	Yield Strength	Ultimate Strength	%El	%RA
RT	115.3	115.7	.2	0
1000°F	112.5	140.2	2.5	0.8
1500°F	103.4	148.0	2.6	1.6
2000°F	68.4	77.0	21.5	29.4
2300°F	36.3	43.3	28.2	36.0
2500°F	24.6	29.5	31.6	39.8

15

Table 2. Tensile Properties of Mo-.3%Hf - 2%Si - 1% B.

Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and variations that fall within the spirit and scope of the appended claims.

WHAT IS CLAIMED IS:

1. Molybdenum alloys comprising a matrix of body centered cubic molybdenum and intermetallic phases wherein said alloys comprise a composition defined by the area described by the compositional points of the phase diagram for a ternary system: metal-1.0%Si-0.5%B, metal-1.0%Si-4.0%B, metal-4.5%Si-0.5%B, and metal-4.5%Si-4.0%B; wherein percentages are weight % and wherein said metal comprises molybdenum as the major component.
2. The molybdenum alloys of claim 1 wherein said intermetallic phases are discontinuous and dispersed in said matrix of body centered cubic molybdenum.
3. The molybdenum alloys of claim 2 comprising 10 to 70 volume % molybdenum borosilicide, less than 20 volume % molybdenum boride, and less than 20 volume % molybdenum silicide.
4. The molybdenum alloys of claim 3 further comprising up to 2.5 volume % carbides.
5. The molybdenum alloys of claim 4 having a resistance to oxidation such that said alloys lose less than about 0.025 cm (0.01") of thickness from each surface of said alloy when heated to 1090°C (2000°F) in air for 2 hours.

6. The molybdenum alloys of claim 5 having a yield strength of greater than 60 ksi at 1090°C (2000°F); wherein said yield strength is measured on a round specimen formulated and tested per ASTM E21-79.

7. The molybdenum alloys of claim 2 comprising:

Mo	50-98.5%
C	0.0-1.0%
Ti	0.0-15.0%
Hf	0.0-10.0%
Ti	0.0-15.0%
Hf	0.0-10.0%
Zr	0.0-10.0%
W	0.0-20.0%
Re	0.0-45.0%
Al	0.0-5.0%
Cr	0.0-5.0%
V	0.0-10.0%
Nb	0.0-2.0%
Ta	0.0-2.0%

wherein % is weight %.

8. The molybdenum alloys of claim 7 comprising at least one element in the stated quantity selected from the group consisting of:

C	0.01-1.0%
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Ti	0.1-15.0%
Hf	0.1-10.0%
Ti	0.1-15.0%
Hf	0.1-10.0%
Zr	0.1-10.0%
W	0.1-20.0%
Re	0.1-45.0%
Al	0.1-5.0%
Cr	0.1-5.0%
V	0.1-10.0%
Nb	0.1-2.0%
Ta	0.1-2.0%

wherein % is weight %; and wherein the remainder of said alloys consists essentially of molybdenum, boron and silicon.

9. The molybdenum alloys of claim 8 comprising molybdenum and at least one element selected from the group consisting of:

C	0.03-0.3%
Ti	0.3-10.0%
Hf	0.3-3.0%
Zr	0.3-3.0%
W	0.3-3.0%
Re	2.0-10.0%
Al	0.5-2.0%

Cr	0.5-2.0%
V	0.3-5.0%
Nb	0.3-1.0%
Ta	0.3-1.0%

wherein % is weight %.

10. The molybdenum alloys of claim 9 having a resistance to oxidation such that said alloys lose less than about 0.025cm (0.01") of thickness from each surface of said alloy when heated to 1090°C (2000°F) in air for 2 hours.

11. The molybdenum alloys of claim 8 having a resistance to oxidation such that said alloys lose less than about 0.025cm (0.01") in thickness from each surface of said alloy when heated to about 1370°C (2500°F) in air for 2 hours.

12. The molybdenum alloys of claim 10 having a yield strength of greater than 60 ksi at 1090°C (2000°F); wherein said yield strength is measured on a round specimen formulated and tested per ASTM E21-79.

13. The molybdenum alloys of claim 8 comprising 10 to 70 volume % molybdenum borosilicide, less than 20 volume % molybdenum boride, and less than 20 volume % molybdenum silicide.

14. A method for enhancing the oxidation resistance of a molybdenum alloy comprising the step of adding silicon and boron to a molybdenum composition comprised

of more than 50 weight % molybdenum; wherein said step of adding is selected from the group consisting of: blending a powder comprising silicon and boron with a powder comprising molybdenum, followed by consolidation to achieve a dense alloy; and adding said silicon and boron to a melt comprising molybdenum followed by rapid solidification;

and further wherein said silicon and boron are added in amounts such that the molybdenum alloy having enhanced oxidation resistance that results from said step of adding, comprises a composition defined by the area described by the compositional points of the phase diagram for a ternary system: metal-1.0%Si-0.5%B, metal-1.0%Si-4.0%B, metal-4.5%Si-0.5%B, and metal-4.5%Si-4.0%B; wherein percentages are weight % and wherein said metal comprises molybdenum as the major component.

15. The method of claim 14 wherein said step of adding comprises adding silicon and boron to a melt comprising molybdenum followed by rapid solidification of the resulting mixture into a fine powder; and further comprising consolidation of said powder by a method selected from the group consisting of extrusion, hot pressing, hot vacuum compaction, hot isostatic pressing, and sintering.

16. The method of claim 15 wherein said metal of the molybdenum alloy comprises molybdenum and at least one element in the stated quantity selected from the group consisting of:

C	0.1-1.0%
Ti	0.1-15.0%
Hf	0.1-10.0%
Ti	0.1-15.0%

Hf	0.1-10.0%
Zr	0.1-10.0%
W	0.1-20.0%
Re	0.1-45.0%
Al	0.1-5.0%
Cr	0.1-5.0%
V	0.1-10.0%
Nb	0.1-2.0%
Ta	0.1-2.0%

wherein % is weight %.

17. A method of making the alloy of claim 1 comprising the step of consolidating a powder comprising a composition defined by the area described by the compositional points of the phase diagram for a ternary system: metal-1.0%Si-0.5%B, metal-1.0%Si-4.0%B, metal-4.5%Si-0.5%B, and metal-4.5%Si-4.0%B; wherein percentages are weight % and wherein said metal comprises molybdenum as the major component.

18. The method of claim 17 wherein said step of consolidating is selected from the group consisting of extrusion, hot pressing, hot vacuum compaction, hot isostatic pressing, and sintering.

19. The method of claim 18 wherein said powder is a prealloyed powder comprising an intermetallic phase comprising Mo, Si and B and a BCC molybdenum matrix phase; and further wherein said prealloyed powder is made by rapid solidification from a melt.

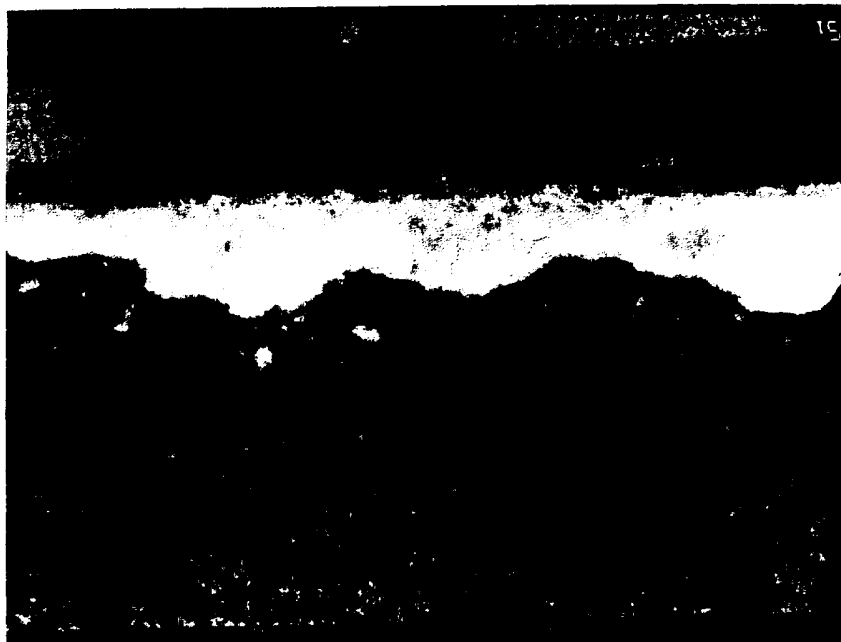


FIG. 1

	TZM after	Exp. Alloy
TZM blank	2000° F/2hrs	After 2500° F/2hrs

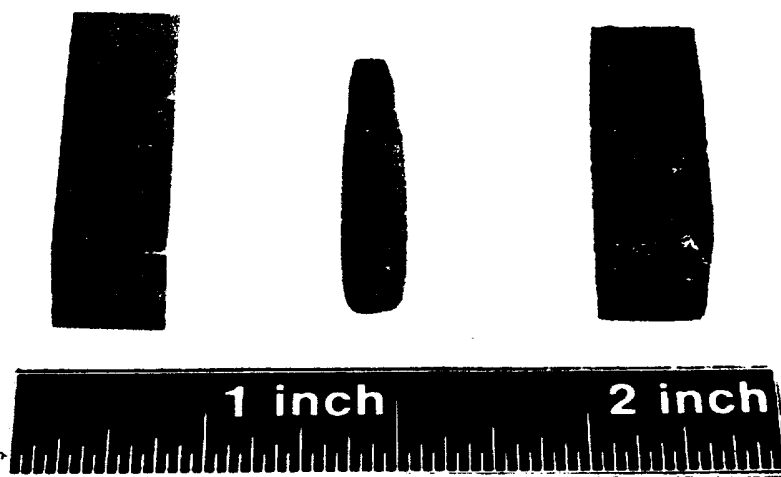


FIG. 2

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 96/00870

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22C27/04 C22C32/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 949 836 (KRAUSS-MAFFEI A.G.) 21 August 1990 see column 1, line 44 - column 1, line 57; claim 1; examples 1,2,4 ---	1-9
X	US,A,3 690 686 (H.F. PRASSE) 12 September 1972 see column 5, line 41 - column 6, line 37 ---	1-9
A	WO,A,85 03953 (METALLWERK PLANSEE G.M.B.H.) 12 September 1985 see page 6, line 19 - page 7, line 19; claims 1,2,5 -----	1-19

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

23 May 1996

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07.06.96

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Information on patent family members

International Application No

PCT/US 96/00870

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4949836	21-08-90	DE-A- 3718779	22-12-88
US-A-3690686	12-09-72	CA-A- 924932	24-04-73
		DE-A- 2032722	25-02-71
WO-A-8503953	12-09-85	AT-A- 386843	25-10-88
		EP-A,B 0172852	05-03-86
		JP-T- 61501714	14-08-86