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(54) Alloy composition

Legierungszusammensetzung

Composition d'alliage

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Description

Field of the Invention

[0001] The present invention relates to an alloy composition, particularly though not exclusively, to an alloy composition suitable for use in refractory (i.e. high temperature) applications. The invention further relates to a forging die comprising the alloy composition.

Background to the Invention

[0002] Prior alloy compositions comprising molybdenum are known, particularly for use in refractory applications such as fusion and fission reactors, rocket engine nozzles, furnace structural components and forging dies for forming components from high strength alloys. Such applications require high hardness (as measured according to the Vickers hardness test) at a particular operating temperature. However, known molybdenum based alloy compositions have insufficient strength for some applications, particularly at high temperatures such as 1000 to 1100 °C, and may have a high cost of production.

[0003] Examples of compositions of prior molybdenum based alloys are given in table 1, given in terms of weight percentages. TZM is described in further detail in US patent 3275434. Further prior molybdenum based alloys are described in "The Engineering Properties of Molybdenum Alloys" by F F Schmidt and H R Ogden. International patent publication WO9622402 also describes Molybdenum alloys with a range of compositions 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.

[0004] Each of these prior alloys may also comprise an amount of Rhenium. The inclusion of rhenium in a molybdenum alloy is thought to improve ductility, recrystallization temperature and strength. However, rhenium is an expensive elemental addition, due to its relative scarcity in the earth's crust. Rhenium containing alloys may therefore have an unacceptably high cost of production.

[0005] The present invention describes an alloy composition and an article comprising the alloy composition which seeks to overcome some or all of the above problems. All percentage amounts are given in terms of weight percentages unless otherwise specified.

Summary of the Invention

[0006] According to a first aspect of the invention, there is provided an alloy composition consisting of, in weight per cent, between 7% and 14% hafnium between 5% and 10% niobium, between 0.9% and 1.1% titanium, between 0.5% and 2% zirconium, between 0.1% and 0.7% tungsten and 0.05% and 0.3% carbon, and, optionally, an amount less than 2% tantalum wherein the balance consists of molybdenum and incidental impurities, wherein the titanium may be bonded with oxygen to form titanium oxide and wherein the tantalum may be bonded with oxygen to form tantalum oxide.

[0007] Advantageously, the described alloy has a high hardness at temperatures of between 1,000 and 1,100 °C, and is consequently suitable for a wide range of uses, including for example refractory articles. The relatively high amount of hafnium has been found to form hafnium carbide (HfC), which acts as a strengthener. The alloy can also be produced at a lower cost compared to previous high strength molybdenum alloys.

[0008] Preferably, the alloy composition may comprise between 8.5% and 9.5% hafnium, and preferably may comprise between 8.9% and 9.1% hafnium, and may comprise 9% hafnium. The alloy composition may comprise between 0.15% and 0.25% carbon, and may comprise between 0.19% and 0.21% carbon, and may comprise 0.2% carbon.

[0009] The alloy may further comprise between 0.8 and 1.9% zirconium, may comprise between 0.8% and 1.0% zirconium, and may comprise 0.9% zirconium. The zirconium may be bonded with the carbon present in the alloy to form zirconium carbide (ZrC).

[0010] The alloy composition may consist of between 7% and 14% hafnium, between 0.05% and 0.3% carbon and between 0.7% and 2% zirconium, wherein the balance comprises molybdenum. It has been found that a molybdenum based alloy having the above composition has a particularly high hardness and strength, having an ultimate tensile strength (UTS) of up to 984 Mega Pascals (MPa).

[0011] The alloy may comprise 1% Ti. The titanium may be bonded with oxygen to form titanium oxide (TiO_2). TiO_2 has been found to further increase the strength of the alloy by providing dispersion strengthening, and / or solid solution strengthening.

[0012] The alloy may comprise between 5 and 6% Nb, and may comprise between 5.5 and 5.9% Nb, and may comprise 5.7% Nb. The presence of Nb in the alloy composition has been found to form niobium carbide (NbC) with the carbon present in the alloy composition, which acts as a strengthener in addition to the strengthening provided by the HfC. Depending on the application, sufficient strengthening may be provided only by HfC. However, Nb can be used to provide further strengthening at a lower cost compared to further amounts of HfC.

[0013] The alloy may comprise between 0.3% and 0.7% tungsten, and may comprise 0.5% tungsten. The addition of tungsten is thought to act as a solid solution strengthener, thereby increasing the strength of the alloy.

[0014] The tantalum may bond with oxygen in the alloy composition to form tantalum oxide. Tantalum oxide is thought to also act as a solid solution strengthener, thereby increasing the strength of the alloy.

[0015] The presence of metal oxides in the alloy composition is thought to provide dispersion solution strengthening, which will further increase the strength of the alloy.

[0016] The alloy composition may have an ultimate tensile strength of between 680 MPa and 760 MPa at a temperature of 1,000 °C.

[0017] According to a second aspect of the invention there is provided an article comprising an alloy in accordance with the first aspect of the invention.

[0018] The article may comprise a forging die. The alloy is particularly suitable for in use in a forging die, since the alloy provides a very high strength at high temperatures.

[0019] The alloy composition may consist of, in weight per cent, between 8.9% and 9.1% hafnium, between 5.5% and 5.9% niobium, between 0.9% and 1.1% titanium, between 0.8% and 1% zirconium, between 0.3% and 0.7% tungsten and 0.19 and 0.21% carbon, wherein the balance comprises molybdenum and incidental impurities.

Brief Description of the Drawings

[0020]

Table 1 describes prior alloy compositions;

Table 2 describes a first alloy composition in accordance with the present invention;

Table 3 describes a second alloy composition in accordance with the present invention

Table 4 describes a third alloy composition in accordance with the present invention;

Figure 1 is a graph comparing the relationship between the temperature and the ultimate tensile strength of compositions described in tables 1 and 3; and

Figure 2 shows a back scattered electron image of the microstructure of the composition described in table 3.

Detailed Description

[0021] Table 2 shows the compositional ranges of a first alloy composition, while tables 3 and 4 show second and third alloy compositions respectively. A back scattered electron image of the microstructure of the composition of table 4 is shown in Fig. 2. As shown in Fig. 1, the nominal alloy composition is thought to have an ultimate tensile strength (UTS), of between approximately 680 MPa and 760 MPa at a temperature of 1,000 °C, which is supported by evidence from Vicker's hardness tests. This is an improvement in UTS of approximately 350 to 550 MPa at a temperature of 1,000 °C compared to prior molybdenum based alloy compositions such as TZM. Alloy compositions within the claimed range may have a UTS of up to 985 MPa.

[0022] The alloy composition described in table 2 consists essentially of between 7% and 14% hafnium, between 0.05% and 0.3% carbon and between 0.7% and 2% zirconium, wherein the balance comprises molybdenum. The alloy may also contain incidental impurities, such as oxygen, may which be incorporated in the surface of the alloy as the alloy oxidises during manufacture or in use. The hafnium and the zirconium may be present either as elemental hafnium or zirconium, or as hafnium carbide and zirconium carbide respectively, or as a mixture of the two. In some cases, the zirconium could be omitted from the composition, while still resulting in an alloy composition having improved properties compared to prior compositions.

[0023] The presence of hafnium in the range specified in table 2 is thought to increase the strength of the composition by the formation of strengthening hafnium carbide (HfC). It is thought that the hafnium carbide in the composition in the amounts specified in table 2 is responsible for the majority of the strengthening effects provided by the various components of the alloy composition. The amount of hafnium carbide in the composition is much greater than in previous compositions. That such a large amount of hafnium in the composition provides a benefit, was a surprising result from this research.

[0024] The presence of zirconium in the amounts specified in table 2 is thought to further increase the strength of the composition by the formation of particle strengthening zirconium carbide (ZrC).

[0025] Table 3 describes a second compositional range of an alloy composition comprising between 0.19 and 0.21%

carbon, between 0.8 and 1.0% zirconium, and between 8.9 and 9.1% hafnium, with the balance of the composition being molybdenum. The second compositional range further comprises niobium in an amount between 5.5 and 5.9%, titanium in an amount between 0.9 and 1.1%, and tungsten (W) in an amount between 0.3 and 0.7%.

[0026] The niobium may be present as either elemental niobium, or may bond with the carbon present within the alloy composition to form niobium carbides. The presence of niobium in the range specified in table 2 is thought to further increase the strength of the composition at both high and low temperatures, both by forming niobium carbides (NbC) and by solid solution strengthening.

[0027] The presence of titanium in the ranges specified in table 3 promotes the formation of dispersion strengthening titanium dioxide (TiO_2) in combination with oxygen impurities, which has the effect of further increasing the strength of the alloy composition in comparison to alloy compositions which lack titanium.

[0028] The presence of tungsten in the amounts specified in table 3 is also thought to further increase the strength of the composition by the formation of strengthening tungsten carbide (WC). However, it is thought that the tungsten carbide has a relatively small contribution to the strengthening of the composition, and so may optionally be omitted from the composition, particularly in view of the increased processing costs inherent in tungsten containing alloy compositions. Indeed, an alloy comprising only molybdenum, hafnium and carbon in the amounts specified is necessary to provide an alloy having superior tensile strength at high temperatures relative to prior alloys.

[0029] One or more of titanium, niobium and tungsten may be omitted from the alloy, and the remaining components increased accordingly, in order to provide an alloy having the desired balance of material properties and cost.

[0030] Table 4 describes an example of a nominal composition of a molybdenum alloy in accordance with the present invention. The alloy consists of substantially 5.7% niobium, 1.0% titanium, 0.2% carbon, 0.9% zirconium, 9.0% hafnium and 0.5% tungsten, with the balance of the composition (i.e. approximately 82.7%) comprising molybdenum. Incidental impurities may also be present in the alloy composition, such as oxygen for example. Figure 1 shows a graph of the UTS of the alloy at various temperatures, ranging from 0°C to 1400°C. As can be clearly seen, the nominal composition has a UTS of 770 $\pm$ 90 MPa at 1000°C. This is a significant improvement on prior alloy compositions.

[0031] A method of forming the alloy is described below. The alloy is produced by a powder processing method. The powder processing method comprises melting and gas atomisation to form particles having a diameter of less than approximately 5 μm. A billet is then formed by hot isostatic pressing (HIP) of the particles. During the hot HIP step, the powder is subjected to heat at temperatures of approximately 2000°C at approximately 100 Mpa for approximately 4 hours.

[0032] Fig. 2 shows a sample of alloy having the nominal composition described in table 4. The sample was produced using an arc-cast method. The lighter areas of the sample are hafnium carbide precipitates within the alloy matrix. As can be seen, the hafnium carbide precipitates are segregated to the interdentritic regions with molybdenum rich primary dendrites in the sample. More uniform, fine dispersions of hafnium carbide can be produced using a powder metallurgy process. This will be expected to improve the properties of the alloy further.

[0033] While the invention has been described in conjunction with the exemplary embodiments described above, many equivalent modifications and variations will be apparent to those skilled in the art when given this disclosure. Accordingly, the exemplary embodiments of the invention set forth above are considered to be illustrative and not limiting. Various changes to the described embodiments may be made without departing from the spirit and scope of the invention as defined in the claims.

Claims

1. An alloy composition consisting of, in weight per cent, between 7% and 14% hafnium, between 5% and 10% niobium, between 0.9% and 1.1% titanium, between 0.5% and 2% zirconium, between 0.1% and 0.7% tungsten and 0.05% and 0.3% carbon, and, optionally, an amount less than 2% tantalum, wherein the balance consists of molybdenum and incidental impurities, wherein the titanium may be bonded with oxygen to form titanium oxide and wherein the tantalum may be bonded with oxygen to form tantalum oxide.

2. An alloy composition according to claim 1, wherein the composition comprises between 8.5% and 9.5% hafnium, and may comprise between 8.9% and 9.1% hafnium, and may comprise 9% hafnium.

3. An alloy composition according to claim 1 or claim 2, wherein the composition comprises between 0.15% and 0.25% carbon, and may comprise between 0.19% and 0.21% carbon, and may comprise 0.2% carbon.

4. An alloy composition according to any of the preceding claims wherein the composition comprises between 5 and 6% niobium, and may comprise between 5.5 and 5.9% niobium, and may comprise 5.7% niobium.

5. An alloy composition according to any of the preceding claims wherein the composition comprises 1% Ti.

6. An alloy composition according to any of the preceding claims wherein the composition comprises between 0.8 and 1.9% zirconium, may comprise between 0.8% and 1.0% zirconium, and may comprise 0.9% zirconium..

7. An alloy composition according to any of the preceding claims wherein the composition comprises between 0.3% and 0.7% tungsten, and may comprise 0.5% tungsten.

8. An alloy according to any of the preceding claims having an ultimate tensile strength of between 680 MPa and 760 MPa at a temperature of 1,000 °C.

9. An alloy composition according to any of the preceding claims consisting of, in weight per cent, between 8.9% and 9.1% hafnium, between 5.5% and 5.9% niobium, between 0.9% and 1.1% titanium, between 0.8% and 1% zirconium, between 0.3% and 0.7% tungsten and 0.19 and 0.21% carbon, wherein the balance comprises molybdenum and incidental impurities.

Table 1

Prior Compositions (weight per cent)					
	Titanium	Carbon	Zirconium	Hafnium	Molybdenum
TZM	0.5	0.02	0.08	-	Balance
TZC	1.3	0.1	0.3	-	Balance
MHC	-	0.05 - 1.5	-	0.8 - 1.4	Balance
ZHM	-	0.12	0.4	1.2	Balance

Table 2

	wt.%	
	Max	**Min**
Mo	bal.	bal.
C	0.3	0.05
Zr	1.9	0.7
Hf	13.8	7.4

Table 3

	wt. %	
	Max	**Min**
Mo	bal.	bal.
Nb	5.9	5.5
Ti	1.1	0.9
C	0.21	0.19
Zr	1.0	0.8
Hf	8.9	9.1
W	0.7	0.3

Table 4

	wt. %
Mo	bal.
Nb	5.7
Ti	1.0
C	0.2
Zr	0.9
Hf	9.0
W	0.5

Patentansprüche

1. Legierungszusammensetzung, in Gewichtsprozent bestehend aus zwischen 7% und 14% Hafnium, zwischen 5% und 10% Niobium, zwischen 0,9% und 1,1% Titan, zwischen 0,5% und 2% Zirconium, zwischen 0,1% und 0,7% Wolfram und zwischen 0,05% und 0,3% Kohlenstoff, und optional einer Menge von weniger als 2% Tantal, wobei der Rest Molybdän und begleitende Verunreinigungen sind, wobei das Titan mit Sauerstoff verbunden werden kann, um Titanoxid zu bilden, und wobei das Tantal mit Sauerstoff verbunden werden kann, um Tantaloxid zu bilden.

2. Legierungszusammensetzung nach Anspruch 1, wobei die Zusammensetzung zwischen 8,5% und 9,5% Hafnium umfasst, und wobei sie zwischen 8,9% und 9,1% Hafnium umfassen kann, und wobei sie 9% Hafnium umfassen kann.

3. Legierungszusammensetzung nach Anspruch 1 oder 2, wobei die Zusammensetzung zwischen 0,15% und 0,25% Kohlenstoff umfasst, und wobei sie zwischen 0,19% und 0,21% Kohlenstoff umfassen kann, und wobei sie 0,2% Kohlenstoff umfassen kann.

4. Legierungszusammensetzung nach einem der vorstehenden Ansprüche, wobei die Zusammensetzung zwischen 5 und 6% Niobium umfasst, und wobei sie zwischen 5,5 und 5,9% Niobium umfassen kann, und wobei sie 5,7% Niobium umfassen kann.

5. Legierungszusammensetzung nach einem der vorstehenden Ansprüche, wobei die Zusammensetzung 1% Ti umfasst.

6. Legierungszusammensetzung nach einem der vorstehenden Ansprüche, wobei die Zusammensetzung zwischen 0,8 und 1,9% Zirconium umfasst, wobei sie zwischen 0,8% und 1,0% Zirconium umfassen kann, und wobei sie 0,9% Zirconium umfassen kann.

7. Legierungszusammensetzung nach einem der vorstehenden Ansprüche, wobei die Zusammensetzung zwischen 0,3% und 0,7% Wolfram umfasst, und wobei sie 0,5% Wolfram umfassen kann.

8. Legierung nach einem der vorstehenden Ansprüche mit einer Reißfestigkeit zwischen 680 MPa und 760 MPa bei einer Temperatur von 1.000 °C.

9. Legierungszusammensetzung nach einem der vorstehenden Ansprüche, in Gewichtsprozent bestehend aus zwischen 8,9% und 9,1% Hafnium, zwischen 5,5% und 5,9% Niobium, zwischen 0,9% und 1,1% Titan, zwischen 0,8% und 1% Zirconium, zwischen 0,3% und 0,7% Wolfram und 0,19 bis 0,21% Kohlenstoff, wobei der Rest Molybdän und begleitende Verunreinigungen sind.

Revendications

1. Composition d’alliage constituée, en pourcentage en poids, de 7 % à 14 % d’hafnium, de 5 % à 10 % de niobium,

de 0,9 % à 1,1 % de titane, de 0,5 % à 2 % de zirconium, de 0,1 % à 0,7 % de tungstène et de 0,05 % à 0,3 % de carbone, et, éventuellement, d'une quantité inférieure à 2 % de tantale, le reste étant constitué de molybdène et d'impuretés accidentelles, le titane pouvant être lié à l'oxygène pour former de l'oxyde de titane et le tantale pouvant être lié à l'oxygène pour former de l'oxyde de tantale.

2. Composition d'alliage selon la revendication 1, la composition comprenant entre 8,5 % et 9,5 % d'hafnium, et pouvant comprendre entre 8,9 % et 9,1 % d'hafnium, et pouvant comprendre 9 % d'hafnium.

3. Composition d'alliage selon la revendication 1 ou 2, la composition comprenant entre 0,15 % et 0,25 % de carbone, et pouvant comprendre entre 0,19 % et 0,21 % de carbone, et pouvant comprendre 0,2 % de carbone.

4. Composition d'alliage selon l'une quelconque des revendications précédentes, la composition comprenant entre 5 et 6 % de niobium, et pouvant comprendre entre 5,5 et 5,9 % de niobium, et pouvant comprendre 5,7 % de niobium.

5. Composition d'alliage selon l'une quelconque des revendications précédentes, la composition comprenant 1 % de Ti.

6. Composition d'alliage selon l'une quelconque des revendications précédentes, la composition comprenant entre 0,8 et 1,9 % de zirconium, pouvant comprendre entre 0,8 % et 1,0 % de zirconium, et pouvant comprendre 0,9 % de zirconium.

7. Composition d'alliage selon l'une quelconque des revendications précédentes, la composition comprenant entre 0,3 % et 0,7 % de tungstène, et pouvant comprendre 0,5 % de tungstène.

8. Alliage selon l'une quelconque des revendications précédentes ayant une résistance à la traction maximale comprise entre 680 MPa et 760 MPa à une température de 1 000 °C.

9. Composition d'alliage selon l'une quelconque des revendications précédentes constituée, en pourcentage en poids, de 8,9 % à 9,1 % d'hafnium, de 5,5 % à 5,9 % de niobium, de 0,9 % à 1,1 % de titane, de 0,8 % à 1 % de zirconium, de 0,3 % à 0,7 % de tungstène et de 0,19 à 0,21 % de carbone, le reste comprenant du molybdène et des impuretés accidentelles.

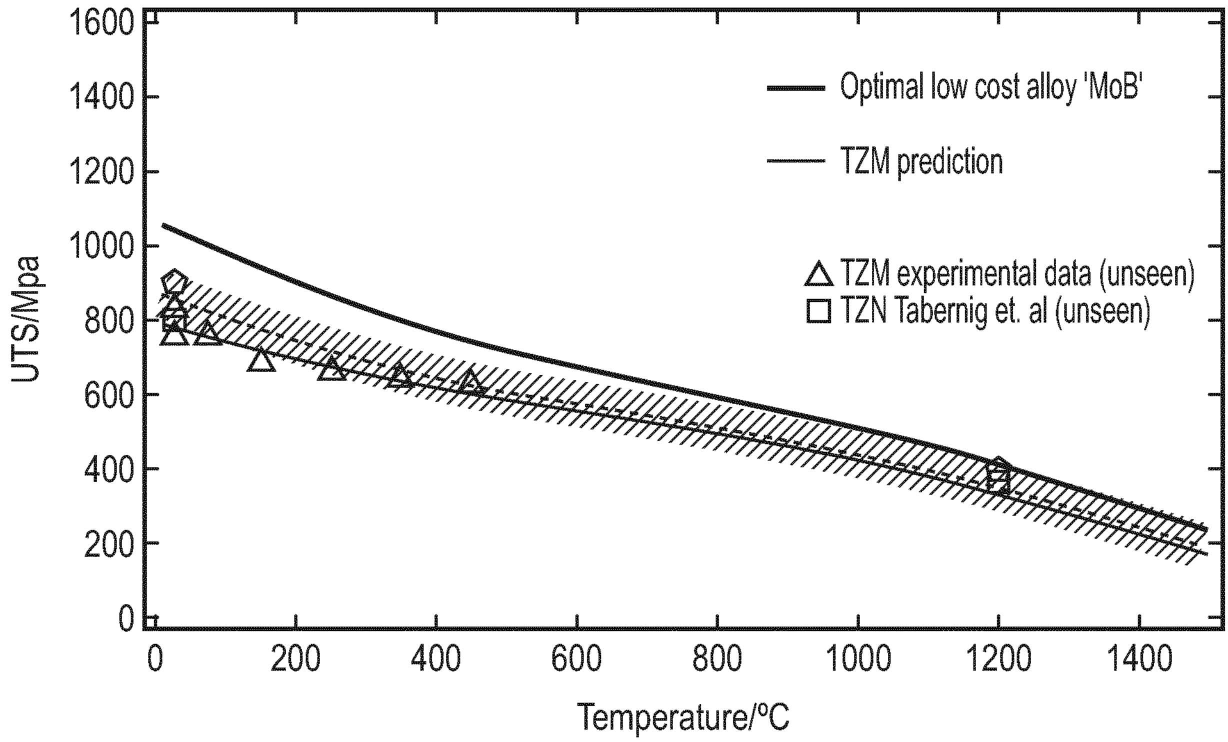
1600
1400
1200
1000
800
600
400
200
0
UTS/Mpa
0
200
400
600
800
1000
1200
1400
Temperature/°C
Optimal low cost alloy 'MoB'
TZM prediction
△ TZM experimental data (unseen)
□ TZN Tabernig et. al (unseen)

FIG. 1

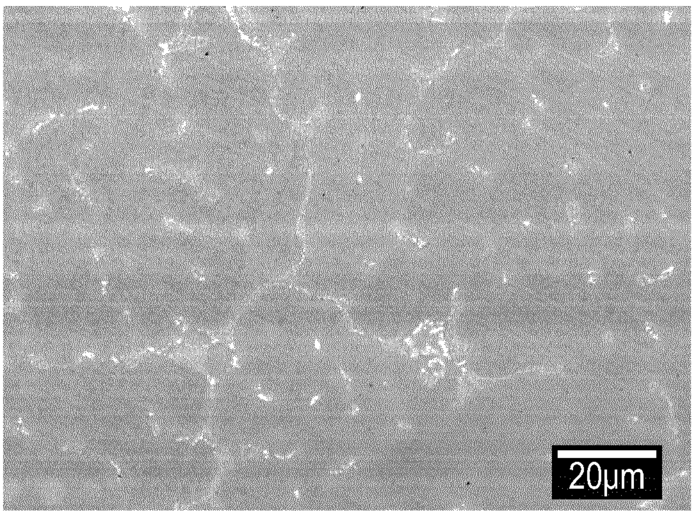
20μm

FIG. 2

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 3275434 A **[0003]**
- WO 9622402 A **[0003]**