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(54) Molybdenum Alloy Composition

Molybdänlegierung

Composition d'alliage en molybdène

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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 component and forging dies. 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.

[0004] European patent publication EP 2065479 discloses a ternary nickel eutectic alloy consisting of 4.5 to 11wt% chromium, 1 to 6wt% cobalt, 1 to 4wt% aluminium, 0 to 1.5wt% titanium, 0 to 3wt% tantalum, 16 to 22wt% niobium, 0 to 3wt% molybdenum, 0 to 4wt% tungsten, 0 to 1wt% hafnium, 0 to 0.1wt% zirconium, 0 to 0.1wt% silicon, 0.01 to 0.1wt% carbon, 0 to 0.01wt% boron and the balance nickel plus incidental impurities.

[0005] German patent application DE3530837 describes a welding rod alloy comprising less than 0.5% carbon, less than 10% iron, less than 1% chromium, and optionally, 40% or more molybdenum or more than 5% niobium. US patent publication US 5,316,723 discloses an alloy comprising about 55-75% Mo, 6-16% Cb [Nb], 1-15% Al, 0.1-5% Si, 0-1% O_2, 0-1% C, 0-1% N_2 and balance Ti.

[0006] 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.

[0007] 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

[0008] According to a first aspect of the invention, there is provided an alloy composition comprising molybdenum, wherein the composition consists of between 15% and 20% niobium and 0.05% and 0.25% carbon, 0.5% and 4% hafnium, between 1% and 3% titanium, between 1% and 10% tungsten, wherein the balance consists of molybdenum and incidental impurities, wherein the titanium may be in the form of titanium oxide (TiO_2).

[0009] 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 niobium compared to prior compositions has been found to form niobium carbide (HfC), which acts as a strengthener. Furthermore, niobium is a relatively inexpensive element in comparison to other strengtheners, resulting in an alloy composition having a high strength at the required temperatures, and a relatively low overall cost.

[0010] Preferably, the alloy composition may comprise between 16% and 17% niobium, and may comprise between 16.1 and 16.5% niobium, and preferably may comprise 16.3% niobium.

[0011] The alloy may comprise between 0.7% and 0.9% hafnium, and preferably may comprise 0.8% hafnium. The inclusion of hafnium in the alloy composition has been found to form hafnium carbide (HfC), which acts as a strengthener in addition to the strengthening provided by the niobium carbide. Depending on the application, sufficient strengthening may be provided only by niobium. However, hafnium can be used to provide further strengthening, though at a comparatively high cost.

[0012] The alloy may comprise between 1.3% and 1.5% titanium, and may comprise 1.42% titanium.. TiO_2 has been found to further increase the strength of the alloy by providing dispersion strengthening, and / or solid solution strengthening.

[0013] The alloy may comprise between 2.7% and 2.9% tungsten, and may comprise 2.8% tungsten. The addition of tungsten is thought to act as a solid solution strengthener, thereby increasing the strength of the alloy.

[0014] The alloy composition may have an ultimate tensile strength of between 380 MPa and 460 MPa at a temperature of 1,000 °C.

[0015] According to a second aspect of the invention there is provided an article comprising an alloy composition in accordance with the first aspect of the invention.

[0016] 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.

Brief Description of the Drawings

[0017]

Table 1 describes prior alloy compositions;

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

Table 3 describes an example of an 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

[0018] Table 2 shows the compositional ranges of an alloy composition, while table 3 shows an example composition of the first alloy composition. A back scattered electron image of the microstructure of the composition of table 3 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 380 MPa and 460 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 50 to 250 MPa at a temperature of 1,000 °C compared to prior molybdenum based alloy compositions such as TZM. In general, it has been found that an alloy composition comprising molybdenum, between 15% and 20% niobium and 0.05% and 0.25% carbon provides advantages over prior molybdenum alloy compositions.

[0019] The presence of niobium in the amounts specified in table 2 is thought to increase the strength of the composition by the formation of strengthening niobium carbide (NbC). In the example composition, it is thought that the niobium carbide in the composition is responsible for the majority of the strengthening effects.

[0020] The presence of hafnium in the amounts specified in table 2 is thought to further increase the strength of the composition at both high and low temperatures, both by forming hafnium carbides (HfC) and solid solution strengthening.

[0021] The presence of titanium in the specified amounts promotes the formation of dispersion strengthening titanium dioxide (TiO_2), which has the effect of further increasing the strength of the alloy composition.

[0022] The presence of tungsten in the amounts specified in table 2 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.

[0023] The composition may further comprise a trace amount of zirconium.

[0024] 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.

[0025] Fig. 2 shows a sample of alloy having the composition described in table 3. 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.

[0026] The alloy may be formed using different processes.

Claims

1. An alloy composition comprising molybdenum, wherein the composition consists of between 15% and 20% niobium and 0.05% and 0.25% carbon, 0.5% and 4% hafnium, between 1% and 3% titanium, between 1% and 10% tungsten, wherein the balance consists of molybdenum and incidental impurities, wherein the titanium may be in the form of titanium oxide (TiO_2).

2. An alloy composition according to claim 1, wherein the alloy composition comprises between 16% niobium and 16.5% niobium, and may comprise between 16.1 and 16.5% niobium, and may comprise 16.3% niobium.

3. An alloy composition according to any of the preceding claims, wherein the composition comprises between 0.19% carbon and 0.21% carbon, and may comprise 0.2% carbon.

4. An alloy composition according to any of the preceding claims comprising between 0.7% and 0.9% hafnium, and may comprise 0.8% hafnium.

5. An alloy composition according to any of the preceding claims further comprising, and may comprise be-

tween 1.3% and 1.5% titanium, and may comprise 1.42% titanium.

6. An alloy according to any of the preceding claims, wherein the alloy comprises, and may comprise between 2.7% and 2.9% tungsten, and may comprise 2.8% tungsten.

7. An alloy according to any of the preceding claims having an ultimate tensile strength of between 380 MPa and 460 MPa at a temperature of 1,000 °C.

8. An article comprising an alloy composition according to any of the preceding claims.

Patentansprüche

1. Legierungszusammensetzung, umfassend Molybdän, wobei die Zusammensetzung aus zwischen 15 % und 20 % Niobium und 0,05 % und 0,25 % Kohlenstoff, 0,5 % und 4 % Hafnium, zwischen 1 % und 3 % Titan, zwischen 1 % und 10 % Wolfram besteht, wobei das Gleichgewicht aus Molybdän und zufälligen Verunreinigungen besteht, wobei das Titan in der Form von Titanoxid (TiO_2) vorliegen kann.

2. Legierungszusammensetzung nach Anspruch 1, wobei die Legierungszusammensetzung zwischen 16 % Niobium und 16,5 % Niobium umfasst und zwischen 16,1 und 16,5 % Niobium umfassen kann und 16,3 % Niobium umfassen kann.

3. Legierungszusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Zusammensetzung zwischen 0,19 % Kohlenstoff und 0,21 % Kohlenstoff umfasst und 0,2 % Kohlenstoff umfasst.

4. Legierungszusammensetzung nach einem der vorhergehenden Ansprüche, die zwischen 0,7 % und 0,9 % Hafnium umfasst und 0,8 % Hafnium umfassen kann.

5. Legierungszusammensetzung nach einem der vorhergehenden Ansprüche, die ferner umfasst, und kann zwischen 1,3 % und 1,5 % Titan umfassen und kann 1,42 % Titan umfassen.

6. Legierung nach einem der vorhergehenden Ansprüche, wobei die Legierung umfasst, und zwischen 2,7 % und 2,9 % Wolfram umfassen kann und 2,8 % Wolfram umfassen kann.

7. Legierung nach einem der vorhergehenden Ansprüche mit einer Zugfestigkeit von zwischen 380 MPa und 460 MPa bei einer Temperatur von 1.000 °C.

8. Artikel, der eine Legierungszusammensetzung nach einem der vorhergehenden Ansprüche umfasst.

Revendications

1. Composition d'alliage comprenant du molybdène, ladite composition comprenant entre 15 % et 20 % de niobium et 0,05 % et 0,25 % de carbone, 0,5 % et 4 % de hafnium, entre 1 % et 3 % de titane, entre 1 % et 10 % de tungstène, le reste étant constitué de molybdène et d'impuretés accidentelles, ledit titane pouvant être sous forme d'oxyde de titane (TiO_2).

2. Composition d'alliage selon la revendication 1, ladite composition d'alliage comprenant entre 16 % de niobium et 16,5 % de niobium et pouvant comprendre entre 16,1 et 16,5 % de niobium et pouvant comprendre 16,3 % de niobium.

3. Composition d'alliage selon l'une quelconque des revendications précédentes, ladite composition comprenant entre 0,19 % de carbone et 0,21 % de carbone et pouvant comprendre 0,2 % de carbone.

4. Composition d'alliage selon l'une quelconque des revendications précédentes, comprenant entre 0,7 % et 0,9 % de hafnium et pouvant comprendre 0,8 % de hafnium.

5. Composition d'alliage selon l'une quelconque des revendications précédentes, comprenant en outre et pouvant comprendre entre 1,3 % et 1,5 % de titane et pouvant comprendre 1,42 % de titane.

6. Alliage selon l'une quelconque des revendications précédentes, ledit alliage comprenant et pouvant comprendre entre 2,7 % et 2,9 % de tungstène et pouvant comprendre 2,8 % de tungstène.

7. Alliage selon l'une quelconque des revendications précédentes, possédant une résistance à la traction ultime comprise entre 380 MPa et 460 MPa à une température de 1000°C.

8. Article comprenant une composition d'alliage selon l'une quelconque des revendications précédentes.

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 1

	wt.%	
	Max	**Min**
Mo	bal.	bal.
Nb	17	16
Ti	1.5	1.3
C	0.15	0.25
Zr	-	-
Hf	0.9	0.7
W	2.9	2.7

Table 2

	wt.%
Mo	bal.
Nb	16.3
Ti	1.42
C	0.2
Zr	-
Hf	0.8
W	2.8

Table 3

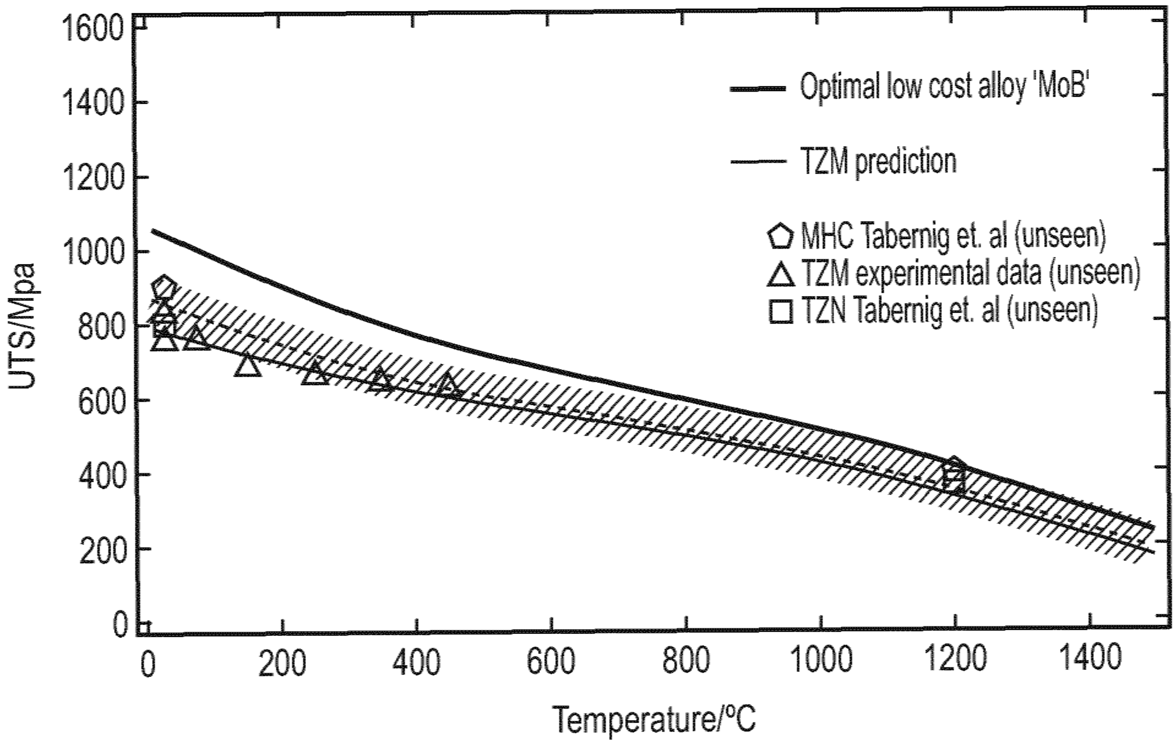
1600
1400
1200
1000
800
600
400
200
0
UTS/Mpa
0
200
400
600
800
1000
1200
1400
Temperature/°C
Optimal low cost alloy 'MoB'
TZM prediction
MHC Tabernig et. al (unseen)
TZM experimental data (unseen)
TZN Tabernig et. al (unseen)

FIG. 1

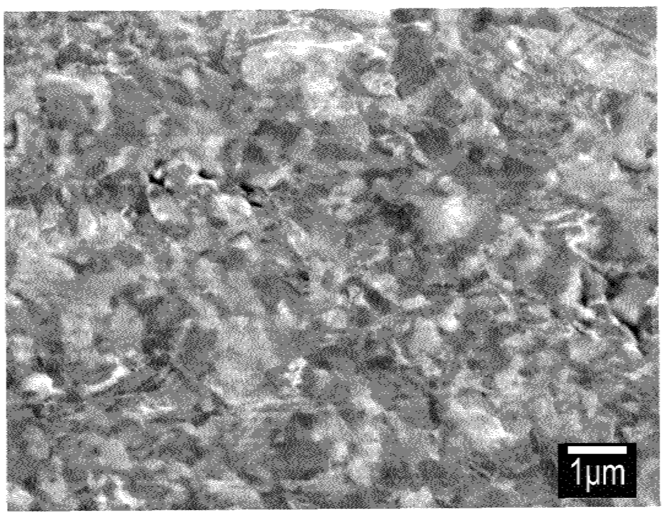
1μm

FIG. 2

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 3275434 A **[0003]**
- EP 2065479 A **[0004]**
- DE 3530837 **[0005]**
- US 5316723 A **[0005]**