Characterization of Mo/Mo₂C interface in MoSiBTiC alloy

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Abstract (100–200 words)

TiC-added Mo-Si-B alloys are stably composed of Mo_{ss} , Mo_5SiB_2 , $(\text{Ti},\text{Mo})\text{C}$, and $(\text{Mo},\text{Ti})_2\text{C}$ phases. In the alloys, interfacial cracking mainly occurred at the interface between Mo_{ss} and Mo_5SiB_2 (T_2). Thus, other interfaces such as between Mo_{ss} , $(\text{Ti},\text{Mo})\text{C}$ and $(\text{Mo},\text{Ti})_2\text{C}$ were investigated for understanding the mechanical properties. The above three kinds of the interfaces have special atomistic structures probably favorable to the mechanical properties. At the interface of $\text{Mo}_{\text{ss}}/(\text{Mo},\text{Ti})_2\text{C}$, $(\text{Mo},\text{Ti})_2\text{C}$ decomposes into Mo_{ss} and $(\text{Ti},\text{Mo})\text{C}$, and then serrated, blade-shaped interfaces are formed. The $\text{Mo}_{\text{ss}}/(\text{Ti},\text{Mo})\text{C}$ interface has an orientation relationship of $(110)_{\text{Mo}}// (111)_{(\text{Ti},\text{Mo})\text{C}}$. The $(\text{Ti},\text{Mo})\text{C}/(\text{Mo},\text{Ti})_2\text{C}$ interface forms a ledge and terrace semi-coherent structure, and its orientation relationship is $(111)_{(\text{Ti},\text{Mo})\text{C}}// (100)_{(\text{Mo},\text{Ti})_2\text{C}}$ and $[0\bar{1}1]_{(\text{Ti},\text{Mo})\text{C}}// [010]_{(\text{Mo},\text{Ti})_2\text{C}}$. Therefore, Mo_{ss} , $(\text{Ti},\text{Mo})\text{C}$ and $(\text{Mo},\text{Ti})_2\text{C}$ have good coherency in the MoSiBTiC alloy. (119 words)

Keywords: Interfaces; Intermetallic alloys and compounds; Microstructure; borides; carbides; interface structure

1. Introduction

Mo-Si-B-based alloys have good material performance as an ultrahigh temperature material such as a high melting point and good high-temperature strength.

However, they also have some drawbacks such as a high density and low room-temperature fracture toughness [1–7]. To overcome these disadvantages for ultrahigh temperature applications, alloy design with 4th and 5th element additions has been investigated to improve the properties of Mo-Si-B alloys [8–13]. Quite recently, we have challenged to develop new Mo-Si-B-based alloys with TiC addition [14–16]. The MoSiBTiC alloys have excellent properties such as a low density, superior high-temperature strength [14, 15], and good room-temperature toughness [16]. For understanding the mechanical properties, we should pay great attention to the interfaces between Mo solid solution (Mo_{ss}) and $(\text{Ti}, \text{Mo})\text{C}$, Mo_{ss} and $(\text{Mo}, \text{Ti})_2\text{C}$, and $(\text{Ti}, \text{Mo})\text{C}$ and $(\text{Mo}, \text{Ti})_2\text{C}$ because interfacial cracking mainly occurred at the interface between Mo_{ss} and Mo_5SiB_2 (T_2). The above three kinds of the interfaces may have special atomistic structures favorable to the mechanical properties. Therefore, the purpose of this study is to observe and analyze the interfaces in the MoSiBTiC alloys by high-angle annular-dark-field (HAADF) scanning transmission electron microscopy (STEM) and high-resolution transmission electron microscopy (HRTEM).

2. Experimental procedure

Samples were prepared with pure Mo (99.99 wt.%), Si (99.9999 wt.%), B (99.95 wt.%), and cold-pressed TiC powder (99 wt.%; 2 to 5 μm in diameter) using a conventional arc-melting technique in an Ar atmosphere. The nominal sample composition was Mo-5.0%Si-10.0%B-7.5%Ti-7.5%C (at.%). The cast ingots were then subjected to heat-treatment at 1800 °C for 24 h in an Ar atmosphere and subsequently furnace-cooled to room temperature. The temperature rapidly decreased to 1450 °C for 2 min and then reached room temperature for about 3 h. X-ray diffractometry (XRD) using a Bruker AXS D8 Advance with Cu-K α radiation was carried out to identify constituent phases and measure lattice parameters. Microstructure observation and phase identification were performed using a scanning electron microscope (SEM; JEOL JSM-7800F). HAADF images were obtained using a field-emission-gun STEM (JEOL ARM200F) equipped with an energy dispersive X-ray spectroscopy (EDS) operated at 200 keV.

3. Results and discussion

Figure 1 shows XRD spectrum of powder samples with the diameter of less

than 46 μm . This indicates that the constituent phases, whose crystal structure and lattice parameter estimated from the spectrum are given in following brackets, were Mo_{ss} (cubic, $a = 3.14 \text{ \AA}$), Mo_5SiB_2 (T_2 ; tetragonal, $a = 6.01 \text{ \AA}$, $c = 11.06 \text{ \AA}$), $(\text{Ti},\text{Mo})\text{C}$ (cubic, $a = 4.29 \text{ \AA}$), and $(\text{Mo},\text{Ti})_2\text{C}$ (orthorhombic, $a = 4.76 \text{ \AA}$, $b = 6.10 \text{ \AA}$, $c = 5.22 \text{ \AA}$). Figure 2 shows back-scattered electron (BSE) images of the microstructures of the MoSiBTiC alloy after the heat treatment. An overview of the microstructure is shown in Figure 2a. Coarse Mo_{ss} developed from the primary Mo_{ss} phase through solidification and a fine $\text{Mo}_{\text{ss}} + T_2 + (\text{Ti},\text{Mo})\text{C} + (\text{Mo},\text{Ti})_2\text{C}$ four-phase area developed from the four-phase peritecto-eutectic also through solidification were observed. Figure 2b shows a high-magnification image of the four-phase area in the square marker in Figure 2a. In the image, T_2 phase is shown by a grey contrast, while $(\text{Mo},\text{Ti})_2\text{C}$ is shown by a darker contrast. Furthermore, bright contrast indicates the Mo_{ss} phase, and there are small $(\text{Ti},\text{Mo})\text{C}$ dispersions (marked by white triangles) shown by black contrast. Figure 2c shows a part of a $\text{Mo}_{\text{ss}}/(\text{Mo},\text{Ti})_2\text{C}$ interface. Interestingly, the $\text{Mo}_{\text{ss}}/(\text{Mo},\text{Ti})_2\text{C}$ interface marked by white arrows in Figure 2b has a characteristic serrated shape.

Figure 3 shows STEM-BF images of a Mo_{ss} , T_2 and $(\text{Mo},\text{Ti})_2\text{C}$ area. The serrated, blade-shaped interface was observed in parts of the Mo_{ss} and $(\text{Mo},\text{Ti})_2\text{C}$ interface as shown in Figure 3b. Figure 3c and d show the EDS Ti-K α and Mo-L α maps,

respectively, obtained with STEM. The Mo map shows that Mo distributed in both the Mo_{ss} and $(\text{Mo,Ti})_2\text{C}$ phases. In the Ti map, it can be seen that Ti has a lower concentration on the Mo_{ss} side and a higher concentration on the $(\text{Mo,Ti})_2\text{C}$ side. Furthermore, along the $\text{Mo}_{\text{ss}}/(\text{Mo,Ti})_2\text{C}$ interface, a high Ti-concentration phase was observed as shown by white triangles. The Mo concentration was low in the corresponding phase in the Mo map. From the analysis of obtained electron diffraction patterns, it was confirmed that a thin $(\text{Ti,Mo})\text{C}$ layer formed between Mo_{ss} and $(\text{Mo,Ti})_2\text{C}$ at the interface. The results of the EDS maps obtained in the present study were in accordance with the EDS analysis of each phase of the MoSiBTiC alloy reported previously [15].

Figure 4a shows a HAADF-STEM image of a part of a blade-shaped $\text{Mo}_{\text{ss}}/(\text{Ti,Mo})\text{C}/(\text{Mo,Ti})_2\text{C}$ interfacial area. And figure 4b shows SAED patterns of the blade-shaped $\text{Mo}_{\text{ss}}/(\text{Ti,Mo})\text{C}/(\text{Mo,Ti})_2\text{C}$ interfacial area. The image was taken from $[0\bar{1}1]_{(\text{Ti,Mo})\text{C}}//[010]_{(\text{Mo,Ti})_2\text{C}}/\text{near-}[1\bar{1}\bar{1}]_{\text{Mo}_{\text{ss}}}$. The zone axis of Mo_{ss} was slightly rotated from the $[1\bar{1}\bar{1}]_{\text{Mo}_{\text{ss}}}$ direction around the $[110]_{\text{Mo}_{\text{ss}}}$ axis. The $\text{Mo}_{\text{ss}}/(\text{Ti,Mo})\text{C}$ interface shows an orientation relationship of $(110)_{\text{Mo}_{\text{ss}}}/(111)_{(\text{Ti,Mo})\text{C}}$. It is considered that the incident beam direction tilt is approximately 5.2° away from the $[111]_{\text{Mo}_{\text{ss}}}$ direction according to the orientation relationship and habit plane of Mo/MoC, Mo/TiC reported in the literature

[17–21]. The $\text{Mo}_{\text{ss}}/(\text{Ti},\text{Mo})\text{C}$ interface was slightly tilted with respect to the observation direction, while the $(\text{Ti},\text{Mo})\text{C}/(\text{Mo},\text{Ti})_2\text{C}$ interface was parallel to the observation direction. The $(\text{Ti},\text{Mo})\text{C}/(\text{Mo},\text{Ti})_2\text{C}$ interface formed a ledge and terrace semi-coherent structure. The orientation relationship is given as;

$$(111)_{(\text{Ti},\text{Mo})\text{C}} // (100)_{(\text{Mo},\text{Ti})_2\text{C}}$$

$$[\bar{0}11]_{(\text{Ti},\text{Mo})\text{C}} // [010]_{(\text{Mo},\text{Ti})_2\text{C}}$$

These habit planes and orientation relationships are schematically shown in Figure 4c.

Figure 4d shows an enlarged image of the $(\text{Ti},\text{Mo})\text{C}/(\text{Mo},\text{Ti})_2\text{C}$ interface area in the white square in Figure 4a, and Figure 4e shows a model of the atomic arrangement in the ledge area marked by the black rectangle in the direction along the white arrow in Figure 4d. The arrangement of Mo atoms in the $(\text{Ti},\text{Mo})\text{C}/(\text{Mo},\text{Ti})_2\text{C}$ interface hardly changes between $(\text{Ti},\text{Mo})\text{C}$ and $(\text{Mo},\text{Ti})_2\text{C}$, meaning that the interface is kept good coherency by the introduction of the ledges.

Figure 5a and b show the $\text{Mo}_{\text{ss}}/(\text{Mo},\text{Ti})_2\text{C}$ interface at the tip of a blade-shaped interface. The zone axis was parallel to $[111]_{\text{Mo}_{\text{ss}}}$. In the image, $(110)_{\text{Mo}_{\text{ss}}}$ planes appear to form a ledge. The habit plane of the $\text{Mo}/\text{Mo}_2\text{C}$ (hexagonal) interface was reported to be $\{110\}_{\text{Mo}} // \{00 \cdot 1\}_{\text{Mo}_2\text{C}}$ [18]. It was reported that the first-order transformation takes place in the Mo_2C phase from the hexagonal $\varepsilon\text{-Fe}_2\text{N}$ -type superstructure to the

orthorhombic ζ -Fe₂N-type superstructure in a mid-temperature range (1100–1400 °C) [22, 23]. These two kinds of structures correspond to the relations of $a \simeq c_{hcp}$, $b \simeq 2a_{hcp}$, and $c \simeq \sqrt{3}a_{hcp}$. In this case, the elongated direction of the blades is parallel to this habit plane. Figures 5c to f show schematic diagrams of the formation mechanism of the serrated, blade-shaped interface. At first, the sympathetic nucleation [24, 25] of Mo_{ss} in (Mo,Ti)₂C appears at the Mo_{ss}/(Mo,Ti)₂C interface (Figure 5d), and (Ti,Mo)C is successively precipitated at the newly created Mo_{ss}/(Mo,Ti)₂C interface (Figure 5e). The Mo_{ss}/(Ti,Mo)C and (Ti,Mo)C/(Mo,Ti)₂C interfaces serve as habit planes during the growth of Mo_{ss} in (Mo,Ti)₂C. Finally, the Mo/(Mo,Ti)₂C interface forms a blade-stacked structure as shown in Figure 5f. If these characteristic interfaces are able to be controlled, it may lead to further improvement of the mechanical properties of the MoSiBTiC alloys.

4. Conclusions

The atomic arrangement and orientation relationships of Mo_{ss}/(Ti,Mo)C/(Mo,Ti)₂C characteristic serrated shape interface has been studied by HAADF-STEM. The following conclusions were obtained:

(1) Thin (Ti,Mo)C layer formed in parts of the Mo_{ss}/(Mo,Ti)₂C interface. Around the

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3 interface, $(\text{Mo,Ti})_2\text{C}$ decomposes into Mo_{ss} and $(\text{Ti,Mo})\text{C}$, and then serrated,
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6 blade-shaped interfaces formed.
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10 (2) The arrangement of Mo atoms in the $(\text{Ti,Mo})\text{C}/(\text{Mo,Ti})_2\text{C}$ interface hardly changes
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12 between $(\text{Ti,Mo})\text{C}$ and $(\text{Mo,Ti})_2\text{C}$. And the $(\text{Ti,Mo})\text{C}/(\text{Mo,Ti})_2\text{C}$ interface is kept good
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41 **References**

- 42
43
44 [1] Sakidja R, Myers J, Kim S, Perepezko JH. The effect of refractory metal
45
46 substitution on the stability of $\text{Mo}(\text{ss}) + \text{T}_2$ two-phase field in the Mo–Si–B
47
48 system. Int J Refract Met Hard Mater 2000;18:193–204.
49
50
51
52
53 [2] Choe H, Chen D, Schneibel JH, Ritchie RO. Ambient to high temperature fracture
54
55 toughness and fatigue–crack propagation behavior in a Mo–12Si–8.5B (at.%)
56
57
58
59
60
61
62
63
64
65

1
2
3 intermetallic. Intermetallics 2001;9:319–29.
4
5

- 6 [3] Schneibel JH, Kramer MJ, Ünal Ö, Wright RN. Processing and mechanical
7
8 properties of a molybdenum silicide with the composition Mo–12Si–8.5B (at.%).
9
10 Intermetallics 2001;9:25–31.
11
12
13

- 14
15 [4] Dimiduk DM and Perepezko JH. Mo-Si-B Alloys: Developing a revolutionary
16
17 turbine-engine material. MRS Bulletin 2003;28:639–45.
18
19
20
21

- 22 [5] Schneibel JH. High temperature strength of Mo–Mo₃Si–Mo₅SiB₂ molybdenum
23
24 silicides. Intermetallics 2003;11:625–32.
25
26
27

- 28 [6] Alur AP, Chollacoop N, Kumar KS. High-temperature compression behavior of
29
30 Mo–Si–B alloys. Acta Mater 2004;52:5571–87.
31
32
33

- 34 [7] Alur AP, Chollacoop N, Kumar KS. Creep effects on crack growth in a Mo–Si–B
35
36 alloy. Acta Mater 2007;55:961–74.
37
38
39
40

- 41 [8] Yang Y, Chang YA, Tan L, Cao W. Multiphase equilibria in the metal-rich region
42
43 of the Mo–Ti–Si–B system: thermodynamic prediction and experimental
44
45 validation. Acta Mater 2005;53:1711–20.
46
47
48
49

- 50 [9] Krüger M, Schliephake D, Jain P, Kumar S, Schumacher G, Heilmaier M. Effects
51
52 of Zr additions on the microstructure and the mechanical behavior of PM Mo-Si-B
53
54 alloys. JOM 2013;65:301–6.
55
56
57
58
59
60
61
62
63
64
65

- [10] Yang Y, Bei H, Tiley J, George EP. Re effects on phase stability and mechanical properties of $\text{Mo}_{55}\text{Si}+\text{Mo}_3\text{Si}+\text{Mo}_5\text{SiB}_2$ alloys. *J Alloys Compd* 2013;556:32–8.
- [11] Majumdar S, Kumar A, Schliephake D, Christ H-J, Jiang X, Heilmaier M, Microstructural and micro-mechanical properties of Mo–Si–B alloyed with Y and La. *Mater. Sci. Eng. A* 2013;573:257–63.
- [12] Hochmuth C, Schliephake D, Völkl R, Heilmaier M, Glatzel U. Influence of zirconium content on microstructure and creep properties of Mo–9Si–8B alloys. *Intermetallics* 2014;48:3–9.
- [13] Nakamura J, Kaneko T, Hara T, Yoshimi K, Maruyama K, Katsui H, et al. Site-occupation behavior and solid-solution hardening effect of rhenium in Mo_5SiB_2 . *Intermetallics* 2014;53:85–91.
- [14] Miyamoto S, Yoshimi K, Ha SH, Kaneko T, Nakamura J, Sato T, et al. Phase equilibria, microstructure, and high-temperature strength of TiC-added Mo-Si-B alloys. *Metall Mater Trans A* 2014;45:1112–23.
- [15] Yoshimi K, Nakamura J, Kanekon D, Yamamoto S, Maruyama K, Katsui H, et al. High-temperature compressive properties of TiC-added Mo–Si–B alloys. *JOM* 2014;66:1930–8.
- [16] Moriyama T, Yoshimi K, Yokoyama T, Masnou T, Zhao M, Nakamura J, Katsui H,

Goto T. Intermetallics (to be submitted).

- [17] Ryan NE, Soffa WA, Crawford RC. Orientation and habit plane relationships for carbide and nitride precipitates in molybdenum. *Metallography* 1968;1:195–220.
- [18] Igarashi T. Strengthening and toughening of molybdenum by carbide particles. *J. Jpn. Soc. Powder Powder Metall* 2002;49:163–71.
- [19] Morita K, Uehara M, Tsunekawa S, Nakashima H. Structures and impurity effect on symmetric tilt boundaries of molybdenum. *J. Jpn. Inst. Metals* 1997;61:251–60.
- [20] Hoshika T, Hiraoka Y, Nagase M, Takada J. Hardness distribution of molybdenum alloys which performed carbonization treatment. *J. Jpn. Soc. Powder Powder Metall* 2002;49: 32–6.
- [21] Kumar A, Eyre BL. An electron microscope study of Mo_2C precipitates in molybdenum—I. crystallographic relationships. *Acta Metall* 1978;26:569–77.
- [22] Epicier T, Dubois J, Esnouf C, Fantozzi G. Neutron powder diffraction studies of transition metal hemiacarbides $\text{Mo}_2\text{C}_{1-x}$ —II. in situ high temperature study on W_2C_{1-x} and $\text{Mo}_2\text{C}_{1-x}$. *Acta Metall* 1988;36:1903–21.
- [23] Kikuchi M, Nagakura S, Oketani S. Crystal structures of transition metal carbides. *Tetsu to Hagane* 1971;57:1009–53.

- 1
2
3 [24] Aaronson HI, Spanos G, Masamura RA, Vardiman RG, Moon DW, Menon ESK, et
4
5
6 al. Sympathetic nucleation: an overview. Mater. Sci. Eng. B 1995;32:107–23.
7
8
9 [25] Oku N, Asakura K, Inoue J, Koseki T. In-situ observation of ferrite plate formation
10
11
12 in low carbon steel during continuous cooling process. Tetsu to Hagane
13
14
15 2008;94:363–8.
16
17
18
19
20
21
22
23
24
25
26
27
28
29
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Figure Captions

Figure 1. XRD pattern of the MoSiBTiC alloy.

Figure 2. SEM-BSE micrographs of MoSiBTiC alloy. (a) An overview of microstructure. (b) Part of a fine $\text{Mo}_{\text{ss}} + (\text{Ti},\text{Mo})\text{C} + (\text{Mo},\text{Ti})_2\text{C}$ four phase area. (c) $\text{Mo}_{\text{ss}}/(\text{Mo},\text{Ti})_2\text{C}$ interface.

Figure 3. STEM bright field images and EDS maps of $\text{Mo}_{\text{ss}}/(\text{Mo},\text{Ti})_2\text{C}$ interface. (a) Lower-magnification STEM image. (b) Higher-magnification STEM image. (c) Ti-K α map. (d) Mo-L α map.

Figure 4. (a) HAADF-STEM image of $\text{Mo}_{\text{ss}}/(\text{Ti},\text{Mo})\text{C}/(\text{Mo},\text{Ti})_2\text{C}$ interface. (b) SAED pattern of $\text{Mo}_{\text{ss}}/(\text{Ti},\text{Mo})\text{C}/(\text{Mo},\text{Ti})_2\text{C}$ interface. (c) Schematic illustration of $\text{Mo}_{\text{ss}}/(\text{Ti},\text{Mo})\text{C}/(\text{Mo},\text{Ti})_2\text{C}$ interface. (d) HAADF-STEM image of $(\text{Ti},\text{Mo})\text{C}/(\text{Mo},\text{Ti})_2\text{C}$ interface. (e) Atomic model of Mo atom arrangement at tip of ledge.

Figure 5. (a) and (b) HAADF-STEM images around the tip of a blade-shaped $\text{Mo}_{\text{ss}}/(\text{Mo},\text{Ti})_2\text{C}$ interface. (c), (d), (e), and (f) Schematic illustrations of the formation mechanism of the blade-shaped interface.

Figure 1 Nakamura et al.

Figure 2 Nakamura et al.

Figure 3 Nakamura et al.

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Figure 5 Nakamura et al.

At the interface of $\text{Mo}_{ss}/(\text{Mo,Ti})_2\text{C}$, $(\text{Mo,Ti})_2\text{C}$ decomposes into Mo_{ss} and $(\text{Ti,Mo})\text{C}$, and serrated, blade-shaped interfaces are formed.