Research Article

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Solidification pathways and phase equilibria in the Mo–Ti–C ternary system

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Abstract: The liquidus surface projection and isothermal section at 1,800°C in the Mo–Ti–C ternary system are examined using arc-melted alloys. A ternary transition peritectic reaction ($L + \text{Mo}_2\text{C} \rightarrow \text{Mo} + \text{TiC}$) takes place during solidification, which is apparently different from the ternary eutectic reaction ($L \rightarrow \text{Mo} + \text{TiC} + \text{Mo}_2\text{C}$) observed in a previous report. Since the composition of the eutectic reaction ($L \rightarrow \text{Mo} + \text{TiC}$) shifts toward the Mo–Ti binary line with increasing Ti concentration, the volume fraction of the Mo phase and the interlamellar spacing of the Mo and TiC phases increase in the eutectic microstructure. At 1,800°C, the TiC phase in equilibrium with the Mo phase can contain more than 28 at% Mo and a Mo/TiC/Mo₂C three-phase region exists at around Mo–15Ti–10C.

Keywords: Mo–Ti–C ternary system, phase equilibria, solidification

1 Introduction

The efficiency and performance of jet engines and gas turbines have steadily improved as their operating temperature has increased [1]. While Ni-based superalloys are commonly used in such engines, the engine operating temperatures often exceed the superalloy melting points [2]. Consequently, high-pressure turbine blades made of superalloys usually need to be protected by ceramic thermal barrier coatings and by the passage of cooling air, which reduces efficiency. To overcome this problem, new refractory-metal-based materials

with higher melting points, such as molybdenum- and niobium-based alloys reinforced with silicides and/or ceramics, have been widely studied [1,3–7].

Cermets are a type of composites composed of ceramic and metal phases that are generally fabricated by sintering. Ceramics such as TiC, ZrC and HfC are reinforcement phases and have the property of being hard but brittle ($K_{IC} = 2\text{--}5 \text{ MPa}(m)^{1/2}$) [8]. The metal phases are, in contrast, ductile and tough. Therefore, cermets exhibit high hardness, stiffness and wear resistance, and their fracture toughness is better than that of ceramics [9,10]. Among them, TiC-based cermets are attractive for high-temperature applications because of their relatively good oxidation resistance in addition to their low density (4.93 g/cm³) and high melting point (3,067°C) of TiC [10]. However, the melting point of the metal phases in TiC-based cermets, which include Ni (1,455°C) and Co (1,495°C) phases, limits their high-temperature applications [11]. Additionally, cermets have small grain sizes because of their sintering production process, which may degrade creep strength [12].

In this study, molybdenum, which has a high melting point (2,623°C), is focused on as a metal phase and the microstructure formed during solidification is carefully investigated [13]. It has been well known that molybdenum has an eutectic reaction during solidification with group IV element carbides such as TiC, ZrC and HfC [14–16]. Kurisita et al. reported the eutectic microstructure and the high-temperature strength of Mo–TiC alloys produced by arc-melting [17,18]. The volume fractions of Mo and TiC in the eutectic areas of the literature look similar though the eutectic point in the pseudo binary phase diagram is closer to the Mo solid solution than to TiC [19]. Suzuki et al. systematically studied the mechanical properties of Mo–TiC, ZrC and HfC [20–23].

On the other hand, the material properties of the TiC phase should be varied due to off-stoichiometry. In the fractography of an MoSiBTiC alloy, river patterns can be observed in both the Mo solid solution and TiC phases, suggesting that the TiC phase may be toughened by off-stoichiometry and solid solute Mo [24]; however, the fracture toughness of stoichiometric TiC is only $3 \text{ MPa}(m)^{1/2}$ [25].

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The TiC phase in the MoSiBTiC alloy is in equilibrium with Mo solid solution and contains more than 20 at% of Mo, which might also affect the properties of the TiC phase, such as its elastic modulus and deformability [26]. Considering this background, the Mo–Ti–C ternary system was investigated in this study.

To understand the solidification pathways and off-stoichiometry of the TiC phase in equilibrium with Mo solid solution, knowledge about phase equilibria in the Mo–Ti–C ternary system is necessary. According to the literature on the liquidus surface projection of the Mo–Ti–C system, a ternary eutectic reaction [$L \rightarrow \text{Mo} + \text{TiC} + \text{Mo}_2\text{C}$] occurs at around Mo–18Ti–20C [14]. However, the microstructural observations in the previous study [14] were only conducted by optical microscopy, and thus a more detailed microstructural analysis is required. In fact, the results obtained in our preliminary research do not show any ternary eutectic reaction. Eremenco and Ya Velikanova investigated the isothermal section of Mo–Ti–C at 1,400, 1,700, 2,000 and 2,200°C [19]. Rudy investigated the isothermal section at 1,500, 1,750, 2,500 and 2,750°C [14]. However, the changes in the Mo/TiC two-phase regions with temperature did not agree with each other, as the shape of the phase boundary and the gradient of the tie line were completely different.

Therefore, the objective of this study was to reconsider and understand the details of the microstructural evolution of Mo solid solution and TiC phases during solidification, and the off-stoichiometry of the TiC phase in equilibrium with the Mo phase. In this paper, we determine the liquidus surface projection and isothermal section at 1,800°C in the Mo–Ti–C ternary system.

2 Experimental

The composition of the alloys used in this study ranged from Mo–(5 to 90)Ti–(10 to 20)C in atomic percent. These alloys were prepared as 9–10 cm³ ingots by an arc-melting technique from pure Mo (99.99 wt%), Ti (99.9 wt%), Mo₂C (99 wt%) and TiC (99 wt%) in an argon (Ar) atmosphere. In the rest of this paper, all compositions are expressed in atomic percentages unless otherwise noted. Each ingot was melted five times and was turned over each time to avoid segregation. Heat treatment was carried out at 1,800°C for 72 h in an Ar atmosphere to ensure phase equilibria. The microstructure was examined by field-emission (FE) scanning electron microscopy. Constituent phases were identified by X-ray diffractometry (XRD). Phase compositions were analyzed using a FE electron-probe

microanalyzer (EPMA) equipped with a wavelength-dispersive X-ray spectroscope operated at 10 kV and 5.0×10^{-8} A. The composition results were obtained from more than five sets of data, calibrated by the ZAF correction method. The standard samples for each element were as follows: pure Mo for Mo in the Mo solid solution and the TiC phase; pure Ti for Ti in the Mo solid solution; pure TiC fabricated by spark plasma sintering (SPS) at 1,650°C and 65 MPa for 10 min for Ti and C in the TiC phase, C in Mo solid solution and Ti in the Mo₂C phase; and Mo₂C fabricated by SPS at 1,650°C and 65 MPa for 10 min for Mo and C in the Mo₂C phase.

3 Results and discussion

3.1 Microstructure

Figure 1 shows backscatter electron images (BEIs) of the as-cast Mo–Ti–C alloys. Mo–5Ti–15C is composed of a primary phase with bright contrast and a eutectic phase with bright and medium contrast (Figure 1(a)). In Mo–10Ti–20C, the primary phase changes to a medium-contrast phase, and a eutectic phase with bright and medium contrast is also observed. Besides, a finer eutectic phase is also observed in the finally solidified areas, especially around the medium-contrast phase (Figure 1(b)). In Mo–10Ti–15C, the primary phase is a bright-contrast phase and it is apparent that there are two types of eutectic phases, as observed in Mo–10Ti–20C (Figure 1(c)). The finer eutectic phase shows a lamellar microstructure of bright- and dark-contrast phases, and the eutectic lamellae have interfaces with the bright- and medium-contrast phases (Figure 1(d)). These suggest that the finer eutectic microstructure in the finally solidified areas is formed by a ternary transition peritectic reaction. In Mo–15Ti–15C, the primary phase is a bright-contrast phase, and a eutectic phase composed of bright- and dark-contrast phases is observed (Figure 1(e)). The finer eutectic phase is not observed in the alloy. In Mo–30Ti–15C, the primary phase changes to a dark-contrast phase (Figure 1(f)). The volume fraction of the bright-contrast phase and the interlamellar spacing of the bright- and dark-contrast phases increase with increasing Ti concentration in the eutectic microstructure.

Figure 2 shows the BEIs of the microstructures after heat treatment at 1,800°C. For Mo–5Ti–15C, it is observed that the coarse primary phase with bright contrast contains an amount of small precipitates, and coarsened lamellae with bright- and medium-contrast

Figure 1: BEIs of as-cast alloys: (a) Mo-5Ti-15C, (b) Mo-10Ti-20C, (c and d) Mo-10Ti-15C, (e) Mo-15Ti-15C and (f) Mo-30Ti-15C.

Figure 2: BEIs of microstructures after heat treatment at 1,800°C: (a) Mo-5Ti-15C, (b) Mo-10Ti-20C, (c) Mo-10Ti-15C and (d) Mo-15Ti-15C.

phases are also evident (Figure 2(a)). The interlamellar spacing has changed to approximately $5\ \mu\text{m}$, which is much larger than that in the as-cast microstructure shown in Figure 1(a). In Mo–10Ti–20C, three phases are observed with bright, medium and dark contrast (Figure 2(b)). Volume fraction is the highest for the medium-contrast phase and the lowest for the dark-contrast phase. In Mo–10Ti–15C also, three phases are observed, which are similar to those in Mo–10Ti–20Ti (Figure 2(c)). In this alloy, the bright-contrast phase has the highest volume fraction among the three phases. Only bright- and dark-contrast phases are observed in Mo–15Ti–15C even after heat treatment (Figure 2(d)).

Figure 3 shows the results of phase identification by XRD for the as-cast alloys and the heat-treated alloys at $1,800^\circ\text{C}$. Simulated patterns for pure Mo, TiC and Mo_2C phases are also shown in Figure 3 [27–29]. For Mo–5Ti–15C, since the peaks of the Mo and Mo_2C phases are detected in both the as-cast and heat-treated alloys (Figure 3(a) and (b)), the constituent phases with bright

and medium contrasts are determined to be Mo solid solution (Mo_{ss}) and Mo_2C phases, respectively. Mo–10Ti–15C shows peaks of the TiC phase as well as Mo_{ss} and Mo_2C phases on both the as-cast and heat-treated alloys (Figure 3(c) and (d)) and, thus, the dark-contrast phase is determined to be the TiC phase. On the other hand, the peaks of the Mo and TiC phases are detected on the XRD profiles in both the as-cast and heat-treated alloys of Mo–15Ti–15C (Figure 3(e) and (f)), indicating that the bright- and dark-contrast phases are Mo_{ss} and TiC phases. It should be noted that the experimental peaks of the TiC phase are slightly shifted to the high-angle side, indicating that the TiC phase with the NaCl structure is slightly contracted by the solute atom of Mo.

Mo solute atoms would have a small effect on the lattice parameter of TiC near the stoichiometric composition, but Tsurekawa et al. [30] pointed out that the size misfit between Ti and Mo is too small to consider the decrease in the lattice parameter. On the other hand, off-stoichiometry in TiC rather than the effect of Mo solute atom is likely to cause the decrease in the lattice parameter [31]. To consider both the effect of off-stoichiometry and Mo solute atom, the lattice parameter of the TiC phase was compared at almost the same $\text{C}/(\text{Mo} + \text{Ti})$ (0.72–0.75) ratios but with different $\text{Ti}/(\text{Ti} + \text{Mo})$ ratios. Figure 4 shows the change in the lattice parameter of the TiC phase as a function of $\text{Ti}/(\text{Ti} + \text{Mo})$ atomic ratio at the $\text{C}/(\text{Mo} + \text{Ti})$ ratio of 0.72–0.75 for the heat-treated alloys at $1,800^\circ\text{C}$. It is clarified that the lattice parameter increases continuously with the increase in the $\text{Ti}/(\text{Ti} + \text{Mo})$ atomic ratio. This strongly suggests that the lattice parameter of the C-poor off-stoichiometric TiC phase with the NaCl structure is slightly contracted by solute elements such as Mo.

Figure 3: XRD patterns of samples used in this work and comparison with simulated ones: (a) Mo–5Ti–15C, as-cast; (b) Mo–5Ti–15C, $1,800^\circ\text{C}/72\ \text{h}$; (c) Mo–10Ti–15C, as-cast; (d) Mo–10Ti–15C, $1,800^\circ\text{C}/72\ \text{h}$; (e) Mo–15Ti–15C, as-cast; (f) Mo–15Ti–15C, $1,800^\circ\text{C}/72\ \text{h}$; (g) Mo ($Im\bar{3}m$) [27]; (h) TiC ($Fm\bar{3}m$) [28]; and (i) Mo_2C ($P6_3/mmc$) [29].

Figure 4: Lattice parameter of TiC as a function of $\text{Ti}/(\text{Ti} + \text{Mo})$ atomic ratio in Mo–(10, 15, 30)Ti–15C and Mo–10Ti–20C heat-treated at $1,800^\circ\text{C}/72\ \text{h}$.

3.2 Liquidus projection and isothermal section at 1,800°C

Figure 5 shows the liquidus surface projection for the Mo–Ti–C ternary system. The lines are drawn based on the micro-structural observations and phase identifications performed in this study with the binary data [14,32,33]. As mentioned before, it is found that a ternary transition peritectic reaction of $L + \text{Mo}_2\text{C} \rightarrow \text{Mo} + \text{TiC}$ takes place in the Mo-rich region, which was not shown in the ternary liquidus projection previously reported [14]. Furthermore, the mono-variant eutectic reaction composition of $L \rightarrow \text{Mo} + \text{TiC}$ shifts toward the Mo–Ti binary line with increasing Ti concentration.

Figure 5: Liquidus surface projection of the Mo–Ti–C ternary system [14,30,31].

The isothermal section of the Mo–Ti–C ternary system shown in Figure 6 is also drawn based on the microstructural observations, phase identifications and compositional analyses of the constituent phases. The compositions of the constituent phases analyzed by EPMA are shown in Table 1. The broken line is drawn based on the results reported in the literature [14,30,31]. It is realized that the TiC phase in equilibrium with Mo_{ss} contains more than 28 at% Mo. A Mo/TiC/ Mo_2C three-phase region should exist around Mo–15Ti–10C.

3.3 Comparison with previous reports

This study clarifies that there is a ternary transition peritectic reaction of $L + \text{Mo}_2\text{C} \rightarrow \text{Mo} + \text{TiC}$ in the

Figure 6: Isothermal section of the Mo–Ti–C ternary system at 1,800°C [14,32,33].

Table 1: Analyzed compositions of the constituent phases present in the alloys of the Mo–Ti–C ternary system at 1,800°C

Bulk alloy composition			Constituent phase	Composition (at%)		
Mo	Ti	C		Mo	Ti	C
Bal.	5	15	Mo	97.4	1.6	0.9
			Mo_2C	59.6	10.8	29.5
Bal.	10	15	Mo	96.5	2.7	0.7
			Mo_2C	52.3	14.3	33.4
			TiC	28.4	29.6	42.1
Bal.	10	20	Mo	96.5	2.6	0.9
			Mo_2C	52.7	14.3	32.9
			TiC	28.1	30.1	41.8
Bal.	15	15	Mo	94.5	4.8	0.6
			TiC	20.2	37.0	42.7
Bal.	30	15	Mo	78.7	20.3	1.1
			TiC	6.2	50.9	42.8
Bal.	50	15	Mo	53.6	45.6	0.8
			TiC	2.3	57.8	39.8

Mo–Ti–C ternary system. Therefore, even if the bulk composition is close to the Mo_2C primary region, for example, in Mo–15Ti–15C, the Mo_2C phase cannot remain during solidification and the lamellar microstructure of the Mo_{ss} and TiC phases develops around the Mo_2C phase, as shown in Figure 1(b) and (d). This microstructural development apparently differs from that reported by Eremenco and Velikanova [19] and Rudy [14], who suggested that a ternary eutectic reaction of $L \rightarrow \text{Mo} + \text{TiC} + \text{Mo}_2\text{C}$ takes place.

At 1,800°C, the TiC phase in equilibrium with the Mo_{ss} phase contains more than 28 at% Mo, as shown in Table 1. This value is close to the value previously reported.

However, the compositional region of Mo₂C shown in Figure 6 is much larger than that reported previously [14,19], which makes the Mo/TiC/Mo₂C three-phase region slightly small.

4 Conclusions

The liquidus surface projection and isothermal section at 1,800°C for the Mo–Ti–C ternary system were examined using arc-melted ternary alloys. The conclusions can be summarized as follows.

1. A ternary transition peritectic reaction ($L + \text{Mo}_2\text{C} \rightarrow \text{Mo} + \text{TiC}$) takes place, which is apparently different from the ternary eutectic reaction ($L \rightarrow \text{Mo} + \text{TiC} + \text{Mo}_2\text{C}$) previously reported.
2. Since the composition of the eutectic reaction ($L \rightarrow \text{Mo} + \text{TiC}$) shifts toward the Mo–Ti binary line with increasing Ti concentration, the volume fraction of the Mo phase and the interlamellar spacing of the Mo and TiC phases increase in the eutectic microstructure.
3. At 1,800°C, the TiC phase in equilibrium with the Mo phase can contain more than 28 at% Mo, and a Mo/TiC/Mo₂C three-phase region exists at around Mo–10Ti–15C.
4. The lattice parameter of the C-poor off-stoichiometric TiC phase is slightly contracted by the solute atom of Mo.

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