Microstructure and Creep of Mo–ZrC *In-situ* Composite^{*1}

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Microstructure and creep of arc-melted and annealed Mo–40 mol%ZrC *in-situ* composite were investigated in this study. Microstructure after annealing is found to consist of primary ZrC particles and fine Mo/ZrC eutectic structure, *i.e.* hyper-eutectic structure. Compressive creep tests in the temperature range from 1673 to 1873 K indicate that the stress exponent, n , is approximately 5 in the stress range from 100 to 500 MPa, and the apparent activation energy for the creep deformation is estimated to be about 500 kJ/mol at 200 MPa and 300 MPa. TEM observation for crept specimens shows that the creep deformation is accompanied with sub-boundary formation in Mo solid solution phase. It is suggested that the creep deformation of the composite in the temperature range examined is interpreted in terms of the dislocation creep of Mo solid solution phase controlled by the lattice diffusion of either Mo or Zr.

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1. Introduction

Molybdenum-base alloys, *e.g.*, TZM, TZC, MHC and so on, have been extensively developed as structural materials at high temperatures.^{1–3)} Most of these alloys are precipitation-strengthened with carbides, nitrides and oxides, which are formed by the addition of a small amount of active elements such as titanium, zirconium and hafnium.^{2,3)} In recent years, for the high temperature structural applications such as turbine blades, Mo–TiC *in-situ* composites with a high volume fraction of TiC have been studied by some researchers.^{4–6)} One of the merits of this composite is that the depression of the melting point due to Mo/TiC eutectic reaction facilitates the synthesis by a casting process.⁴⁾ In addition, this composite has characteristic microstructure containing relatively coarse particles of Mo or TiC primarily solidified and very fine structure produced by the Mo/TiC eutectic reaction.^{5,6)} Nomura *et al.*⁶⁾ mentioned that Mo–40 mol%TiC with hyper-eutectic structure possesses high strength over 1473 K and acceptable fracture toughness at ambient temperature.

In order to further improve the heat resistance of the above Mo/carbide *in-situ* composites, *in-situ* mixture of Mo and ZrC has been investigated.⁷⁾ ZrC is a IVa group transition metal carbide like TiC and has a higher melting point. A previous study displayed that Mo–40 mol%ZrC *in-situ* composite has higher strength at high temperatures in comparison with Mo–40 mol%TiC.⁷⁾ Furthermore, fracture toughness of this composite estimated at room temperature is also better than that of Mo–40 mol%TiC, which is probably due to the contribution of Mo as a ductile phase.⁷⁾

There have never been any reports, however, on creep and its deformation mechanism of the Mo–ZrC *in-situ* composites. The purpose of this study is to examine the creep properties and deformation microstructure of a Mo–ZrC *in-situ* com-

posite. Based on the result obtained, the deformation mechanism of the composite will be discussed.

2. Experimental

The raw material powders of molybdenum (99.98 mass%Mo) and zirconium carbide (99.4 mass%ZrC_{0.94}) were weighed and mixed in a cross-rotary blending machine for 18 ks. The nominal composition was Mo–40 mol%ZrC (compositions are given in mol% in this paper unless otherwise stated and abbreviated as Mo–40ZrC). The mixed powder was cold-pressed at room temperature, and then arc-melted in an Ar gas atmosphere. The ingot was annealed at 1873 K for 252 ks in a vacuum of better than 3×10^{-3} Pa. Microstructure was observed by scanning electron microscopy (SEM), and phase identification was performed by X-ray diffractometry (XRD) and electron probe micro analysis (EPMA). Metallographical investigation was also done by transmission electron microscopy (TEM). TEM specimens were prepared by an ion-milling machine.

Test specimens with $2 \times 2 \times 5$ mm³ were cut by an electro-discharge machine (EDM) from the annealed ingot, and then the surfaces were mechanically polished. Compressive creep tests under various constant loads were conducted using an Instron-8562 test machine in an Ar-gas atmosphere in the temperature range from 1673 to 1873 K and in the stress range from 100 to 500 MPa. Deformation substructure was observed for the crept specimens by TEM.

3. Results

3.1 Microstructure

Table 1 shows the alloy composition of Mo–40ZrC. Figure 1 indicates a secondary electron (SE) image of the composite after annealing. As seen in the figure, two regions are seen in the microstructure. One is the dark region of relatively coarse particles and the other is the bright region containing very fine particles. The result of XRD indicates that the composite is composed of Mo solid solution (Mo_{ss}) phase with A2 structure and ZrC phase with B1 structure. It is

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Table 1 Chemical composition of Mo–40ZrC after annealing.

Sample	Mo	Zr	C	(mol%)
Mo–40ZrC	42.1	30.0	27.9

Fig. 1 Microstructure of Mo–40ZrC annealed at 1873 K for 252 K.

Fig. 2 TEM micrograph of eutectic structure in Mo–40ZrC.

found from the results of XRD and EPMA that the coarse particles seen in Fig. 1 are primarily solidified ZrC and the two phase structure is Mo/ZrC eutectic. Therefore, it is obvious that Mo–40ZrC possesses hyper-eutectic structure.

Figure 2 shows a TEM bright field image of the eutectic in Mo–40ZrC. In the eutectic area, fine ZrC particles with different sizes and irregular shapes, which are formed through the eutectic reaction, are dispersed intergranularly and transgranularly in Mo_{ss} matrix. The observation at a high resolution condition suggested that there is no apparent orientation relationship between Mo and ZrC. The figure also indicates that Mo_{ss} phase has fine grain size as small as several microns. Additionally, dislocations are observed in Mo_{ss} phase,

which would be introduced by thermal stress because of different thermal expansion coefficients between two phases. In contrast, no dislocation is observed in ZrC phase.

3.2 Creep properties

Figure 3 shows creep curves obtained by compressive creep tests at 1773 K. Steady state deformation at a constant strain rate appears after a several percent strain at any condition examined. Figure 4 shows the relation between minimum creep rate and applied stress. The minimum creep rate for Mo–40ZrC is found to be of the order of 10^{-8} to 10^{-3} s^{-1} in the stress range between 100 and 500 MPa at 1773 K. The creep deformation of Mo–40ZrC obeys the power law, and the values of stress exponent, n , estimated from the gradients of the curves in Fig. 4 are approximately 5.2, 4.8 and 4.3 at 1673 K, 1773 K and 1873 K, respectively. The minimum creep rate of Mo–40TiC reported by Nomura *et al.*⁽⁶⁾ is also inserted into the figure for comparison. It is obvious that the creep strength of Mo–40ZrC is higher than that of Mo–40TiC at 1773 K.

Fig. 3 Creep curves of Mo–40ZrC at 1773 K in the stress range from 100 to 500 MPa.

Fig. 4 Relation between minimum creep rate and applied stress for Mo–40ZrC. The minimum creep rate of Mo–40TiC is also inserted.⁽⁶⁾

Fig. 5 Temperature dependence of minimum creep rate for Mo-40ZrC at 200 and 300 MPa.

Figure 5 indicates the relation between minimum creep rate and inverse test temperature in the range from 1673 to 1873 K. For the applied stresses of 200 and 300 MPa, the apparent activation energy for creep deformation is estimated to be 484 and 508 kJ/mol, respectively.

3.3 TEM observation of deformation substructure

Deformation substructure was observed in TEM for a specimen crept to a strain of approximately 9.8% at 1773 K with 300 MPa. As shown in Fig. 6, dislocation density in Mo_{ss} phase is remarkably increased, and dislocation rearrangement and sub-boundary formation are occurring frequently in contrast to Fig. 2. Although no dislocation was observed in ZrC

Fig. 6 Deformation substructure of Mo-40ZrC crept to 9.8% at 1773 K and 252 ks. Arrowheads indicate sub-boundaries formed in Mo_{ss} phase.

phase before deformation, a small number of dislocations were occasionally observed even in primary ZrC particles after deformation, suggesting that ZrC deforms plastically at 1773 K.

4. Discussion

As shown in Fig. 4, the stress exponent of Mo-40ZrC is estimated to be approximately 5 in the temperature range from 1673 to 1873 K. This value generally corresponds to dislocation creep in metals and alloys.

TEM observation revealed that the dislocation density in Mo_{ss} phase is remarkably increased, and that dislocations are also introduced in ZrC phase. It is unlikely that the deformation of ZrC phase is the dominant process for the creep of Mo-40ZrC, since the dislocation density in ZrC phase is too low to give the strain of 9.8%. Therefore, it seems that the creep deformation of Mo-40ZrC at 1773 K proceeds by dislocation creep in Mo_{ss} phase.

As shown in Fig. 5, the values of the apparent activation energy for creep deformation are about 500 kJ/mol at 200 and 300 MPa. These values are very similar to those of the lattice diffusion of Mo (488 kJ/mol) and Zr (503 kJ/mol) in Mo.⁸⁾ Thus, it is suggested that the rate controlling process of the creep deformation of Mo-40ZrC at 1773 K is either the recovery of substructure controlled by self-diffusion of Mo, often seen in pure metals, or the viscous glide of dislocation controlled by diffusion of Zr seen in solid solution alloys. Unfortunately, it is difficult to conclude which process is dominant from the dislocation structure at present.

Mo-40ZrC exhibits higher creep strength than that of Mo-40TiC at 1773 K, as seen in Fig. 4. It was reported that the yield strength of monolithic ZrC is higher than that of monolithic TiC at 1773 K.^{9,10)} The present TEM observation shows that a small number of dislocations is introduced into primary ZrC phase, indicating that ZrC phase in Mo-40ZrC can deform at this temperature. In other words, it is also suggested that larger strain can be introduced in TiC phase of Mo-40TiC than in ZrC phase of Mo-40ZrC. This implies that the predominant dislocation mechanism for deformation would be different between both the composites in spite of analogous material system. In addition, we may need to consider the interaction process of dislocations with carbides. Further studies using TEM are in progress.

5. Conclusion

Microstructure and high temperature creep behavior of Mo-40 mol%ZrC *in-situ* composite were investigated in this study. Microstructure after annealing consists of primary ZrC particles and fine Mo/ZrC eutectic structure. The high temperature creep deformation of the composite obeys the power law in the temperature range from 1673 to 1873 K. The stress exponent, n , is estimated to be approximately 5. The apparent activation energies of the creep deformation are approximately 500 kJ/mol at 200 MPa and 300 MPa. They correspond to the activation energy for the lattice diffusion of Mo or Zr in Mo. Moreover, the TEM observation of deformation substructure revealed that dislocation density in Mo_{ss} phase is

remarkably increased. Consequently, it is considered that the creep deformation of Mo–40 mol%ZrC at 1773 K proceeds by dislocation creep in Mo_{ss} phase. The recovery process rate-controlled by the self-diffusion of Mo or the viscous glide of dislocations by the diffusion of Zr will be dominant.

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REFERENCES

- 1) N. E. Ryan, W. A. Soffa and R. C. Crawford: *Metallography*, **1** (1968), 165–220.
- 2) C. T. Liu and H. Inouye: *Metal. Trans.*, **5** (1974), 2515–2525.
- 3) J. R. Davis: *Heat-Resistant Materials*, ASM Specialty Handbook, ASM, (1997), pp. 361–365.
- 4) H. Kurishita, H. Yoshinaga, F. Takao and S. Goto: *J. Japan Inst. Metals*, **44** (1980), 395–403.
- 5) H. Kurishita, J. Shiraishi, R. Matsubara and H. Yoshinaga: *J. Japan Inst. Metals*, **49** (1985), 963–971.
- 6) N. Nomura: *Doctoral Thesis*, (1999), Tohoku University.
- 7) T. Suzuki, N. Nomura, K. Yoshimi and S. Hanada: to be published in *J. Japan Inst. Metals*, **64** (2000).
- 8) In *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology New Series*, Group III/26, Springer-Verlag, Berlin, (1990), pp. 48 and pp. 176.
- 9) G. Das, K. S. Mazdhyasni and H. A. Lipsitt: *J. Am. Ceram. Soc.*, **65** (1982), 104–110.
- 10) R. Darolia and T. F. Archbold: *J. Mater. Sci.*, **11** (1976), 283–290.