

Compressive Creep Behavior of TiC/AZ91D Magnesium-matrix Composites with Interpenetrating Networks

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[Manuscript received April 18, 2006, in revised form October 8, 2006]

The 42.1 vol. pct TiC/AZ91D magnesium-matrix composites with interpenetrating networks were fabricated by *in-situ* reactive infiltration process. The compressive creep behavior of as-synthesized composites was investigated at temperature ranging from 673 to 723 K under loads of 95-108 MPa. For a comparative purpose, the creep behavior of the monolithic matrix alloy AZ91D was also conducted under loads of 15-55 MPa at 548-598 K. The creep mechanisms were theoretically analyzed based on the power-law relation. The results showed that the creep rates of both TiC/AZ91D composites and AZ91D alloy increase with increasing the temperature and load. The TiC/AZ91D composites possess superior creep resistance as compared with the AZ91D alloy. At deformation temperature below 573 K, the stress exponent n of AZ91D alloy approaches theoretical value of 5, which suggests that the creep process is controlled by dislocation climb. At 598 K, the stress exponent of AZ91D is close to 3, in which viscous non-basal slip deformation plays a key role in the process of creep deformation. However, the case differs from that of AZ91D alloy when the stress exponent n of TiC/AZ91D composites exceeds 9, which shows that there exists threshold stress in the creep process of the composites, similar to other types of composites. The average activation energies for the creep of the AZ91D alloy and TiC/AZ91D composites were calculated to be 144 and 152 kJ/mol, respectively. The existence of threshold stress in the creep process of the composites leads to an increase in activation energy for creep.

KEY WORDS: Magnesium-matrix composites; TiC/AZ91D; Interpenetrating networks; *In-situ* reactive infiltration; Creep

1. Introduction

Traditionally the microstructures of ceramic-metal composites consist of discrete, dispersed and isolated ceramic reinforcement phases embedded in matrix metals. The reinforcement can be ceramic particulate, long/short fiber or whisker. The properties of the composites depend largely on the matrix metal, while the effect of reinforcement phase is limited. In recent years, the composites with interpenetrating networks or co-continuous composites where both the ceramic and matrix metal are interpenetrated each other in the composite microstructure have attained great attention, since they offer some distinctive mechanical and physical behaviors relative to the traditional MMCs (metal matrix composites), such as high modulus, low coefficient of thermal expansion, good thermal and electrical conductivities, advanced damage tolerance and wear resistance^[1-3]. Till now, several processing routes, *e.g.* gas pressure infiltration of molten metal into porous preform^[4], directed metal oxidation (DIMOXTM) process^[5], and self-propagating high-temperature synthesis (SHS) combined with vacuum pressure infiltration^[6], have been used to fabricate Al₂O₃-containing co-continuous composites. More recently, *in-situ* reactive infiltration process was also utilized to synthesize co-continuous magnesium-matrix composites^[7].

In-situ reactive infiltration process is a rapid and cost-effective processing route for producing co-continuous ceramic-metal composites. In fabricating TiC/AZ91D magnesium-matrix composites, the

interpenetrated TiC phase is obtained *via in-situ* reaction between elemental powders of Ti and C, while the molten Mg infiltrates the ceramic preform to form the co-continuous matrix by capillarity^[8,9]. Usually the volume fraction of the ceramic phase in interpenetrated network composites is high, so the stiffness, resistances to wear and creep of the composites are greatly improved. Unfortunately, the properties of co-continuous composites are rarely reported.

In this paper, a 42.1 vol. pct TiC/AZ91D composite with interpenetrating networks was firstly synthesized by *in-situ* reactive infiltration process, and a comparative study was made on the compressive creep behavior at elevated temperatures with that of AZ91D magnesium alloy. The creep mechanisms were finally analyzed for these two materials on the basis of the calculated stress exponent and apparent activation energy for creep.

2. Experimental

The raw materials used in synthesizing co-continuous composites are pure Ti powder ($\sim 38 \mu\text{m}$, $>99.5\%$ purity), C powder ($\sim 1.5 \mu\text{m}$, $>98.5\%$ purity) and AZ91D alloy ingot (chemical compositions: Mg-9.0Al-0.6Zn-0.2Mn, in wt pct). At first, the Ti and C powders (molar ratio of Ti/C=1:1) were fully mechanically blended and cold compacted into a preform ($\phi=16.5 \text{ mm}$ in diameter) in a steel mould with a relative density of 56.6%. It is supposed that all Ti and C powders will transform into TiC phase in the pre-designed molar ratio during *in-situ* reactive infiltration process, and 42.1 vol. pct TiC/AZ91D magnesium-matrix composites could be obtained according to the product of TiC phase formed *in-situ*

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in the magnesium matrix and by considering the intrinsic shrinkage of the reactants due to the *in-situ* reaction^[7]. The preform together with a magnesium alloy ingot on it was then put into an alumina crucible. Several small holes were drilled at the bottom of alumina crucible in order to release the air during fabricating TiC/Mg composites. *In-situ* reactive infiltration experiments were finally carried out in an electric resistance furnace under a flowing Ar (99.999% purity) atmosphere. The reaction chamber was degassed prior to heating and then backfilled with Ar. The heating temperature was set as 1073 K with holding time 1.5 h, and the heating rate was 10 K/min. Following these, the samples were cooled down to room temperature together with the furnace.

Cylindrical samples ($\phi 5$ mm \times 8 mm) for compressive creep test were obtained by machining T6 heat-treated AZ91D alloy and TiC/AZ91D composites with an electrospark cutting machine. The compressive creep test was conducted with a constant-load creep machine in Dalian University of Technology, China. After several trials, the test condition for AZ91D alloy was determined at temperature of 548, 573 and 598 K with loads of 15-55 MPa, while the composites at 673-723 K under loads of 95, 100 and 108 MPa. The temperature was controlled within ± 1 K and the load-displacement curves were obtained by X-Y recorder. The samples were unloaded and rapidly cooled down to room temperature after they were compressed to the steady state.

After crept in compression, the specimens of 0.3 mm in thickness were cut and then mechanically grinded to 50 μ m thick, and finally thinned in an ion thinner (Gatan-691, USA). The microstructures after creep were observed in a transmission electron microscope (TEM, Tecnai G²20 S-Twin, USA).

3. Results and Discussion

3.1 Creep behaviors of TiC/AZ91D composites and AZ91D alloy

The microstructures of as-synthesized 42.1 vol. pct TiC/AZ91D composites can be found in literature [7]. Figure 1 shows the creep curves of the TiC/AZ91D composites and AZ91D alloy under the predetermined conditions. It is obvious that there exists long-time creep for TiC/AZ91D composites at stage of steady state at various temperatures and stresses. For AZ91D alloy, we can observe the steady state creep only at lower temperatures and lower stresses. At higher temperature and stress, a shorter steady stage occurred and at the same time the third stage of the creep appeared. This means that the creep of AZ91D alloy under such conditions becomes fast and is more sensitive to deformation temperature. The steady-state creep rates for TiC/AZ91D magnesium-matrix composites and AZ91D magnesium alloy are listed in Tables 1 and 2. We can see that the creep rates for both materials increase with increasing temperature and stress. It is interesting that the temperature and stress exerted on TiC/AZ91D composites are much higher than those on AZ91D alloy, while the creep rate of TiC/AZ91D composites is much lower than that of AZ91D alloy. Considering this, we may deduce that the resistance to creep of TiC/AZ91D composites with interpenetrating networks is superior to

that of matrix magnesium alloy.

3.2 Creep mechanism

The creep in magnesium alloys can be interpreted on the basis of dislocation movement. Mg has *hcp* crystal structure and only 3 slip systems at room temperature. When the deformation temperature is lower than 573 K, deformation occurs mainly by slipping along close-packed $\langle 11\bar{2}0 \rangle$ direction on the basal plane $\{0001\}$ and by twinning on pyramid plane $\{10\bar{1}2\}$. On the other hand, the creep is usually controlled by two interacting processes, *i.e.* work-hardening resulted from creep deformation and softening due to recovery at elevated temperatures. The steady state creep is dynamic and achieved by these two processes. So, the steady state creep rate is largely governed by recovery rate. More specifically, dislocations will multiply during slip deformation and be piled up, which lead to the increase in dislocation density and work-hardening. The piled-up dislocations will be annihilated with other ones by climbing, which lead to the decrease in dislocation density. It is well known that dislocation climbing is achieved by diffusion of atoms and has much lower moving rate at relatively low temperature as compared with slip. If the slip is hindered, dislocation will pass the obstacles by climbing. Hence, the creep rate is controlled by dislocation climbing.

When the temperature is relatively higher, slip deformation occurs not only on $\{0001\}$ basal plane, but on non-basal or additional plane $\{10\bar{1}1\}$ as well. In this process, slip deformation of dislocation behaves viscous and is dragged by solute atoms^[10]. As we know, slip rate is related and proportional to the stress to be applied, and this is a slow process as compared to the dislocation climbing over the obstacle. So, dislocation slip becomes the controlling step and the creep rate is controlled by the viscous slip deformation.

Figure 2(a) shows the configuration of dislocations in AZ91D alloy after compressive creep at 598 K/45 MPa. It indicates that there is a lower dislocation density within grains and the dislocation was impeded at grain boundaries during creep deformation and gradually piled up, which lead to a higher dislocation density at grain boundaries. Figure 2(b) shows the reinforcement surrounded by the matrix alloy, where a large number of dislocations exist in the matrix. For a better view, the dense dislocation configuration in composite matrix after creep deformation is presented in Fig.2(c). For the creep of composites at 698 K/108 MPa, with increasing the deformation, the driving force for recrystallization becomes large. The dynamic recrystallization occurred in steady-state creep and this is shown in Fig.2(d), which indicated the dynamic equilibrium between work-hardening and softening resulting from dynamic recovery and recrystallization.

According to the power-law relation for the creep^[11], the steady state creep rate-stress curve can be plotted, as shown in Fig.3.

$$\dot{\epsilon} = A\sigma^n \exp(-Q/RT) \quad (1)$$

where $\dot{\epsilon}$ is steady-state creep rate, σ the stress, n the stress exponent, Q the activation energy for creep and R gas constant. A is a constant and T the absolute

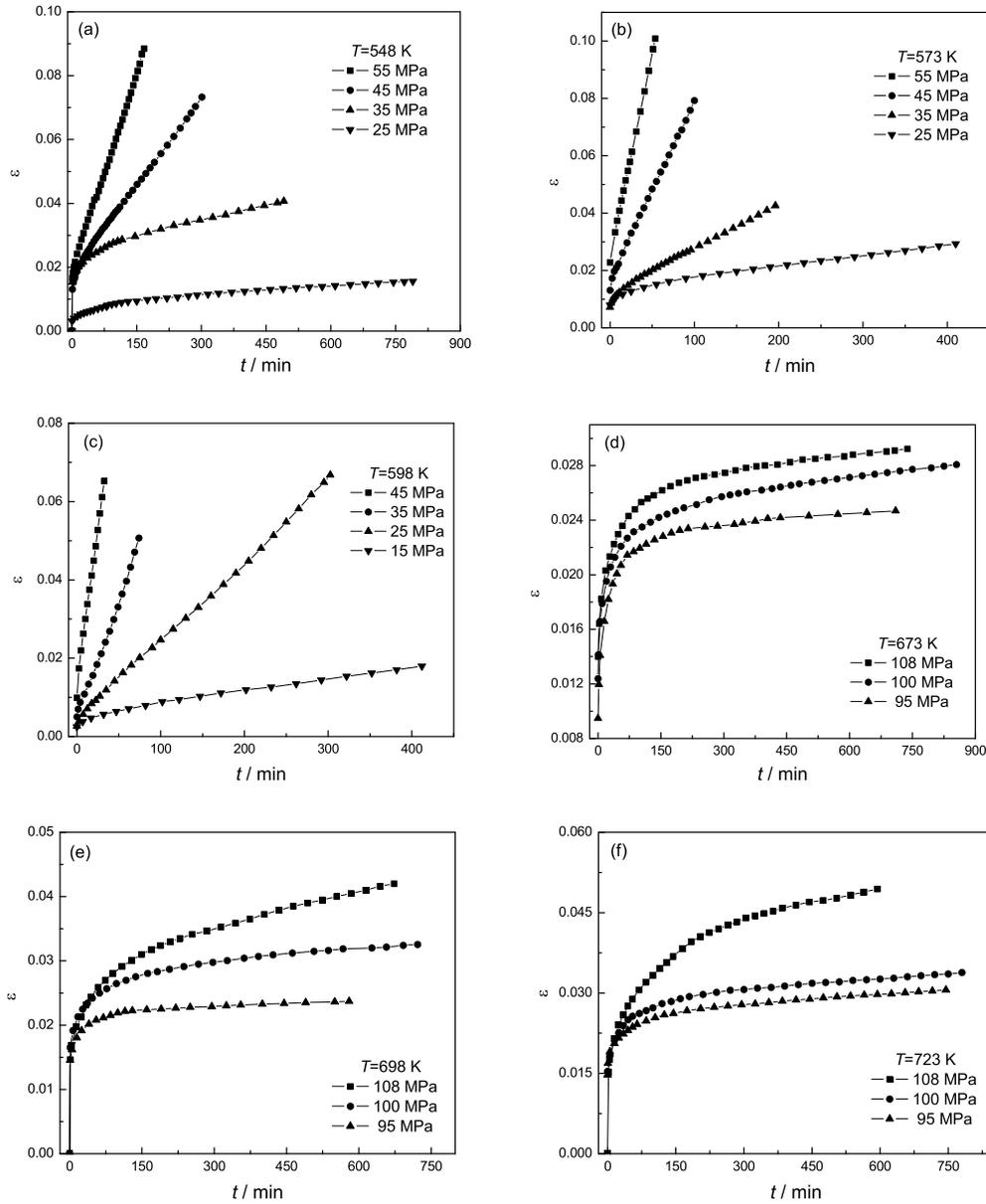


Fig.1 Compressive creep curves of AZ91D alloy (a-c) and TiC/AZ91D composites (d-f)

Table 1 Minimum creep rates of TiC/AZ91D composites at various stresses and temperatures

Temperature/K	Minimum creep rates/s ⁻¹		
	95 MPa	100 MPa	108 MPa
673	3.01×10 ⁻⁸	4.80×10 ⁻⁸	1.01×10 ⁻⁷
698	4.61×10 ⁻⁸	7.35×10 ⁻⁸	2.08×10 ⁻⁷
723	9.92×10 ⁻⁸	1.10×10 ⁻⁷	3.18×10 ⁻⁷

Table 2 Minimum creep rates of AZ91D alloy at various stresses and temperatures

Temperature/K	Minimum creep rates/s ⁻¹				
	15 MPa	25 MPa	35 MPa	45 MPa	55 MPa
548	–	1.53×10 ⁻⁷	4.95×10 ⁻⁷	2.91×10 ⁻⁶	6.61×10 ⁻⁶
573	–	6.13×10 ⁻⁷	2.62×10 ⁻⁶	1.15×10 ⁻⁵	2.33×10 ⁻⁵
598	4.60×10 ⁻⁷	3.20×10 ⁻⁶	9.30×10 ⁻⁶	2.52×10 ⁻⁵	–

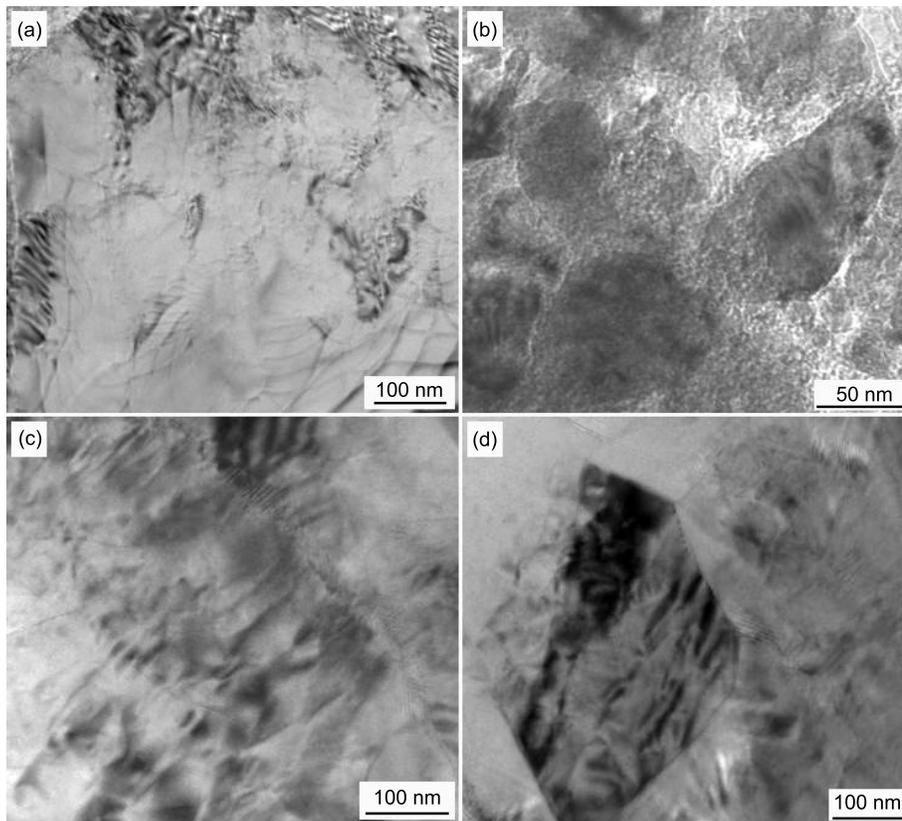


Fig.2 TEM microstructures after compressive creep deformation at 598 K/45 MPa in AZ91D alloy (a) and at 698 K/108 MPa in TiC/AZ91D composites (b-d)

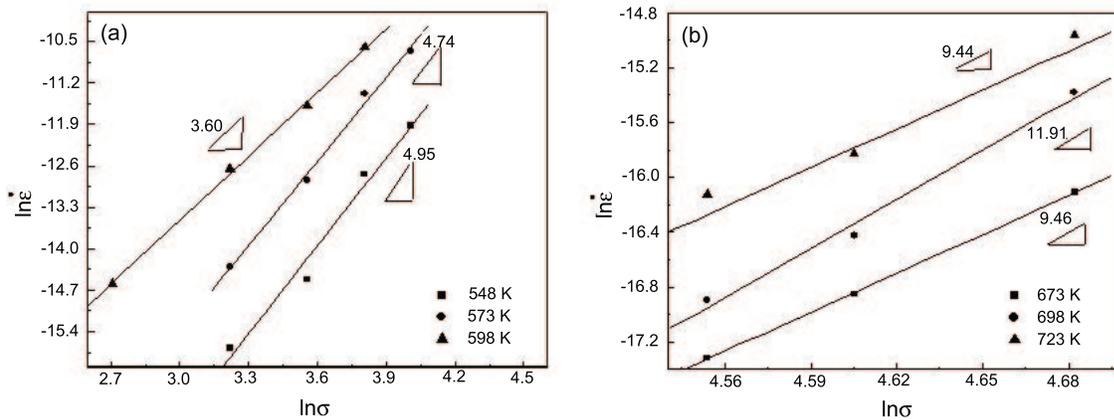


Fig.3 Dependence of the minimum creep rates of AZ91D alloy (a) and TiC/AZ91D composites (b) on the applied stress at different temperatures

Table 3 Calculated activation energy for creep of AZ91D alloy and TiC/AZ91D composites

Materials	Stress applied, σ /MPa	Activation energy, Q /(kJ/mol)
AZ91D	25	171
	35	163
	45	121
TiC/AZ91D	95	160
	100	155
	108	118

temperature. If we take logarithmic form for above equation at both sides, the expression can be written in the following form:

$$\ln \dot{\epsilon} = n \ln \sigma + A' \quad (2)$$

where $A' = \ln A - Q/RT$. The slope of the straight line $\ln \dot{\epsilon}$ vs $\ln \sigma$ is stress exponent n .

From Fig.3(a), the stress exponents n of AZ91D alloy can be determined as 4.95 and 4.74 at 548 and 573 K, respectively, which are close to the theoretical value of 5 for creep of dislocation climbing^[10,12]. It indicates that at deformation temperature lower than 573 K, the creep is controlled by dislocation climbing. At 598 K, the stress exponent n of AZ91D alloy equals 3.6, close to theoretical value of 3^[10,12], which indicates that the creep can be attributed to the non-basal viscous slip deformation. For TiC/AZ91D composites, we can also calculate the stress exponent n by power-law creep equation, which is equal to 9–12, much higher than the theoretical value of 3–5. It means that the power-law does not hold valid for ceramic reinforced MMCs, and it is obvious that the existence of second phase increases the resistance to creep in matrix alloy. It is generally believed that there exists a threshold stress for creep in composites and the creep is unlikely to occur when the stress applied is lower than the threshold stress. This is also confirmed in this experiment since the stress exerted on the composites is so much higher that the creep can take place. The threshold stress is usually determined by experiment and associated with the deformation temperature^[11].

The following two equations are usually adopted to describe the creep behavior of MMCs^[12].

$$\dot{\epsilon} = A_1 (\sinh \alpha \sigma)^n \exp(-Q/RT) \quad (3)$$

$$\dot{\epsilon} = A_2 \left(\frac{\sigma - \sigma_0}{G} \right)^n \exp(-Q/RT) \quad (4)$$

where A_1 , A_2 and α are constants. σ_0 is the threshold stress for creep and G the shear modulus of the composites. The threshold stress σ_0 for creep in composites can be determined by extrapolation. Since the stress exponent n in composites is normally greater than 5, we may take several values of n to try to plot the curve of $\dot{\epsilon}^{1/n}$ vs stress σ . It was found that the $\dot{\epsilon}^{1/n}$ vs σ can be linearly regressed when n is 8. Thus, when $\dot{\epsilon}$ is set to be zero, the threshold stress can be obtained. It was calculated that the threshold stresses is 32, 24 and 2 MPa when the TiC/AZ91D composites was compressively deformed at 673, 698 and 723 K, respectively, which shows that the higher the deformation temperature, the lower the threshold stress.

Till now, there is no reasonable interpretation for the higher stress exponent n in composites. For the present magnesium-matrix composites with high volume percentage of ceramics, there exists large amount of TiC phase that plays a key role in creep process. The fact that the increase in n and decrease in creep rate can be related to the mechanism of dislocation by-passing the second phase particles.

The creep deformation can be regarded as a thermal activation process if it does not occur at absolute temperature 0 K. Thus, the creep rate $\dot{\epsilon}$ follows

Arrhenius-type equation.

$$\dot{\epsilon} = A \exp(-Q_c/RT) \quad (5)$$

where A is a constant relating to temperature, stress and materials microstructural factors. Q_c is activation energy for creep and can be determined by creep test, *e.g.* transient temperature change^[13]. If the sample is creep-deformed under constant load at temperature T_1 with a strain rate of $\dot{\epsilon}_1$, the microstructures can be regarded as unchanged when deformation temperature is quickly changed to T_2 by ΔT resulting to a strain rate of $\dot{\epsilon}_2$. In such a case, the change of strain rate can be totally viewed as the temperature change such that

$$\dot{\epsilon}_1 \exp(Q_c/RT_1) = \dot{\epsilon}_2 \exp(Q_c/RT_2) \quad (6)$$

From Eq.(6), we can obtain:

$$Q_c = R \ln(\dot{\epsilon}_2/\dot{\epsilon}_1) / (1/T_2 - 1/T_1) \quad (7)$$

The activation energy for creep is calculated according to Eq.(8), an other form of Eq.(7), and the results are listed in Table 3.

$$Q = \left. \frac{\partial \ln \dot{\epsilon}}{\partial (-1/RT)} \right|_{\sigma=\text{const}} \quad (8)$$

We know that the self-diffusion activation energy of pure Mg is 135 kJ/mol^[14] and that of Al in magnesium alloy is 143 kJ/mol. If the creep process is controlled by dislocation climbing, the stress exponent is close to 5 and the activation energy Q for creep approaches 135 kJ/mol, *i.e.* the self-diffusion activation energy. On the other hand, if the creep process is controlled by viscous slip deformation, the stress exponent is close to 3 and the activation energy Q for creep 143 kJ/mol, *i.e.* the self-diffusion activation energy. From Table 3, it can be found that the average activation energy of AZ91D magnesium alloy is 144 kJ/mol, which is close to the self-diffusion activation energy of Al (143 kJ/mol) and demonstrates the viscous slip deformation that controlled the creep process of Mg alloy in this experiment. In NiAl-25Cr alloy, there was a similar result^[15]. The average activation energy of TiC/AZ91D composites is 152 kJ/mol, higher than that for self-diffusion in Mg. This case is similar to those during creep deformation in other composites, *e.g.* SiC/6061Al^[11] and TiC/Ti-6Al-4V^[16], that is, the activation energy for creep deformation in composites is always higher than that for self-diffusion in pure matrix metal. Obviously, there indeed exists a threshold stress in composite materials above which creep can take place. It is the existence of threshold stress that results in the enhancement of activation energy for creep in composite materials.

4. Conclusions

(1) TiC/Mg composites with interpenetrating networks have very high resistance to creep as compared with matrix AZ91D alloy, both of which showed that the creep rates increase with deformation temperature or applied stress.

(2) When the deformation temperature is lower than 573 K, the stress exponent n in AZ91D alloy is close to the theoretical value 5, which shows that the creep deformation is controlled by dislocation climbing. At 598 K, the stress exponent n in AZ91D alloy approaches the theoretical value 3, which shows that the creep deformation is controlled by viscous slip deformation on non-basal planes. The case in TiC/AZ91D composites differs in that there exists higher stress exponent, usually $n > 9$. Similar to other kinds of composites, there is a threshold stress in magnesium-matrix composites during its creep deformation process.

(3) The average activation energy for creep in AZ91D alloy is 144 kJ/mol, while that in TiC/AZ91D composites is 152 kJ/mol, higher than that for self-diffusion in pure magnesium. The reason for the enhancement of activation energy for creep in composites is due to the existence of threshold stress for creep.

Acknowledgements

Financial supports from Natural Science Foundation (Grant No. 20032012), Liaoning Province, China, the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, China and from the Starting for New Scientific Researchers of Institute of Metal Research (IMR), Chinese Academy of Sciences (CAS), are gratefully acknowledged. The authors would like to thank Profs. ZHANG Junshan and WANG Yinong, Department of Materials Engineering, Dalian University of Technology, China, for providing much assistance in creep test and TEM experiments.

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