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Creep and Microstructure of TiC Particulate Si_3N_4-based Composites

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Abstract

The compressive creep properties of Si_3N_4/TiC composite, in comparison with those of Si_3N_4 matrix and Si_3N_4/TiN, were studied in temperature range 1260–1340°C at stresses between 100 and 300 MPa. The creep curves and the stress dependence of the creep rate showed that a diffusional creep, with a stress exponent $n = 1$*, was dominant up to 1340°C and 300 MPa. Although the creep rate was greater than that of the matrix, a significant increase of creep ductility was obtained. Furthermore, the microstructural development under applied processing conditions was examined. The TiC dispersoid, added to improve the toughness and strength of Si_3N_4, was found to be 'chemically' reactive with the Si_3N_4 matrix. The reaction products, composed of $TiC_{0.5}N_{0.5}$ and SiC crystals, were observed in the vicinity of TiC/Si_3N_4 interfaces. The matrix grain refinement, desirable interfaces and a modification of the glassy film were suggested to affect both the creep rate and creep ductility.*

Das Kriechverhalten von Si_3N_4-Verbundwerkstoffen wurde im Temperaturbereich von 1260 bis 1340°C bei Drücken von 100 bis 300 MPa untersucht und mit dem von reinem Si_3N_4 und Si_3N_4/TiN verglichen. Bis 1340°C und 300 MPa zeigten die Kriechkurven und die Spannungsabhängigkeit der Kriechgeschwindigkeit diffusionsgesteuertes Kriechen mit einem Spannungsexponent von $n = 1$*. Obwohl die Kriechgeschwindigkeit größer war als die der Matrix, zeigte sich eine beträchtliche Zunahme der Kriechverformung. Desweiteren wurde die Gefügeentwicklung unter den angewandten Prozeßbedingungen untersucht. Es zeigte sich, daß die zur Erhöhung der Zähigkeit und der Festigkeit des Si_3N_4 zugegebenen TiC-Teilchen mit der Si_3N_4-Matrix reagierten. Die Reaktionsprodukte, bestehend aus $TiC_{0.5}N_{0.5}$ und SiC Kristallen, konnten in der Umgebung der TiC/Si_3N_4 Grenzflächen nachgewiesen werden. Auf den Einfluß einer reduzierten Korngröße des Matrixmaterials, der Bindungsverhältnisse an den Korngrenzen und einer Veränderung der Zusammensetzung der vorhandenen Glasphase auf die Kriechgeschwindigkeit wie auch auf die Verformung während des Kriechens wird eingegangen.*

Les propriétés du fluage en compression du composite Si_3N_4/TiC, comparativement à celles de la matrice Si_3N_4 et du Si_3N_4/TiN, ont été étudiées dans une plage de température 1260–1340°C, sous des contraintes allant de 100 à 300 MPa. L'étude de la déformation et de sa vitesse pour différentes contraintes montre qu'un fluage diffusion, avec un exposant de contrainte $n = 1$*, est dominant jusqu'à 1340°C et sous 300 MPa. Bien que la vitesse de fluage soit plus grande que celle de la matrice, la ductilité augmente de façon significative. En outre, le développement de la microstructure dans les conditions appliquées au cours du processus d'élaboration a été examiné. Les particules de TiC, ajoutées pour améliorer la résistance mécanique et la ténacité, sont 'chimiquement' réactives avec la matrice de Si_3N_4. Des produits de réaction, composés par des cristaux de $TiC_{0.5}N_{0.5}$ et de SiC, ont été observés prés de l'interface TiC/Si_3N_4. La réduction de taille de* *grain de la matrice, la cohésion des interfaces et le changement de composition du film vitreux sont considérés affecter la vitesse et la ductilité de fluage.*

1 Introduction

Silicon nitride-based ceramics are materials with high strength, low thermal shock sensitivity, good oxidation resistance and relatively high fracture toughness, and as such represent an appealing base for the development of particulate modified microstructures. Indeed, for some time, increasing attention has been devoted to additives containing Si_3N_4 for some specific elevated temperature applications and dense intricate components, stimulating the development of reinforced Si_3N_4-based ceramics with electrical conductive particles (TiN, TiC, TiB_2, etc.).[1–4] Among these electroconductive composites, TiC particles/silicon nitride composites form a new class of wear-resistant materials, combining the outstanding properties of the silicon nitride matrix with the high hardness of TiC, successfully utilized in metal cutting tool and wear applications.[5–8] Intended applications have generally directed mechanical studies on rupture strength and fracture toughness of composites at room and elevated temperature.[7–12] However, a recent work was undertaken to study the creep and microstructure of electroconductive TiN particles/Si_3N_4 matrix composites.[13] Considering the influence of chemically 'inert' TiN particles on the creep behaviour of pressureless sintered Si_3N_4, a decrease of the creep strength with increasing volume fraction and decreasing particle size of TiN was shown. In the microstructure microcracks along weakly bonded particle/matrix interfaces were characteristic of a cavitational creep mechanism.

Since chemically 'active' additives as TiC particles are known to modify the Si_3N_4 matrix microstructure development during processing,[7–9] it is expected that these dispersoids can prevent the formation of weakly bonded dispersoid/Si_3N_4 matrix interfaces. This study was then undertaken to consider the creep behaviour and the microstructural features of Si_3N_4/TiC composites compared with Si_3N_4 matrix and Si_3N_4/TiN composites.

2 Experimental

Silicon nitride-based composites were obtained by mixing commercial Si_3N_4 powder and 40 wt% TiC (2·5 μm) or 40 wt% TiN (2·5 and 1 μm) particles with high purity Y_2O_3 and Al_2O_3 used as sintering aids in the weight ratio of unity. The different powders were ball milled in liquid medium. Green parts, obtained by slip casting, were sintered under a nitrogen atmosphere at about 1750°C and densities higher than 99% d_{th} were achieved. In the case of TiC particles/Si_3N_4-based composites a hot uniaxial pressure (HPSN) was used. Billets were prepared and supplied by C. T. Desmarquest (CTD, Evreux, France), and the Si_3N_4 matrix had the same composition as the Kersit 601 grade from CTD.

Crystalline phase identification by X-ray diffraction showed that the matrix consists only of β-Si_3N_4 with no detectable α-phase.

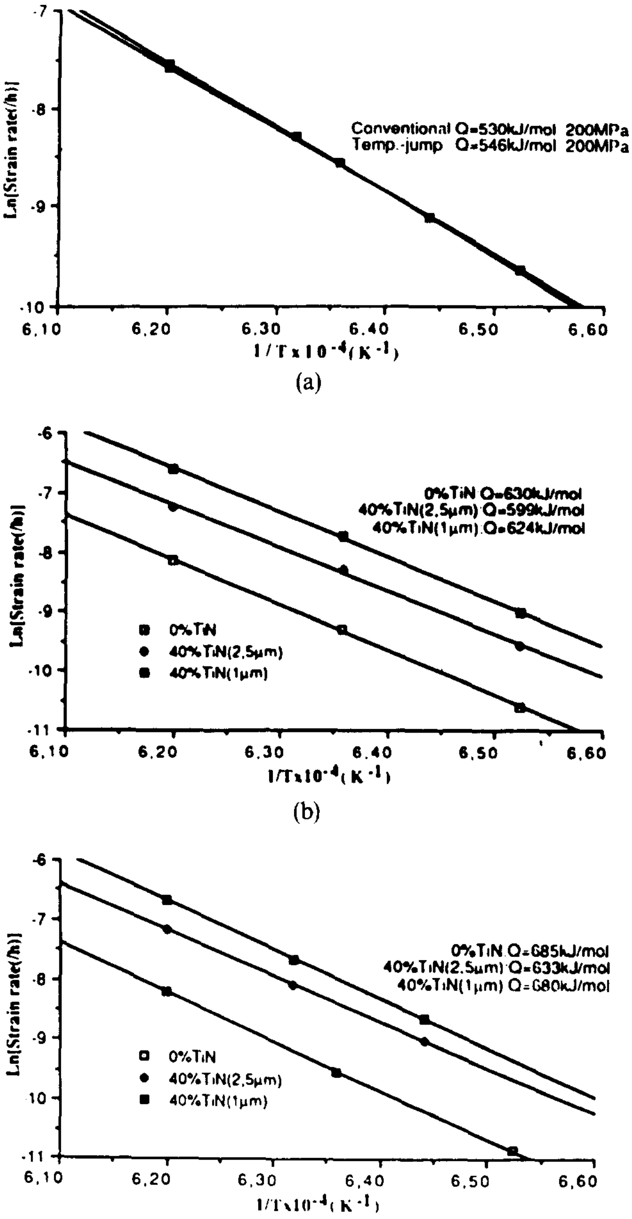
Specimens of approximately $3 \times 3 \times 8\,mm^3$ were utilized for compressive creep tests using a constant load machine built in the laboratory.[14] All the experiments were performed in air between 1260 and 1340°C. The final dimensions of samples were measured to determine their strain from dimensional variation recorded during test. The deformed samples were cooled under load. Thin foils were taken from crept samples and ion-thinned for transmission electron microscopy (TEM) observations and energy dispersive spectroscopy (EDS) X-ray microanalysis.

3 Results and Discussion

The results of the compressive creep experiments performed on the composite containing 40 wt% TiC particles showed a normal transient and steady-state creep behaviour in the temperature range 1260–1340°C. The stress exponent n was found to be of the order of 1 for stress jumps 150–200–250–300 MPa (Table 1). The value of activation energy, determined both by conventional and temperature jump methods, was about 540 kJ/mol for a stress of 200 MPa (Fig. 1(a)).

Table 1. Determination of the stress exponent, n

TiN/TiC (wt%)	*T (°C)*	*100→150*	*150→200*	*200→250*	*250→300*
0	1 260	1	1	1·1	1·5
	1 300	0·9	1	1·4	2·4
	1 340	0·9	1·2	2·6	Rupture
40% TiN	1 260	1	1	1·4	2·6
	1 300	1	1	2	3·5
	1 340	0·8	1·1	2·5	Rupture
40% TiC	1 260				
	1 300		1	1	1
	1 340		1	1	1

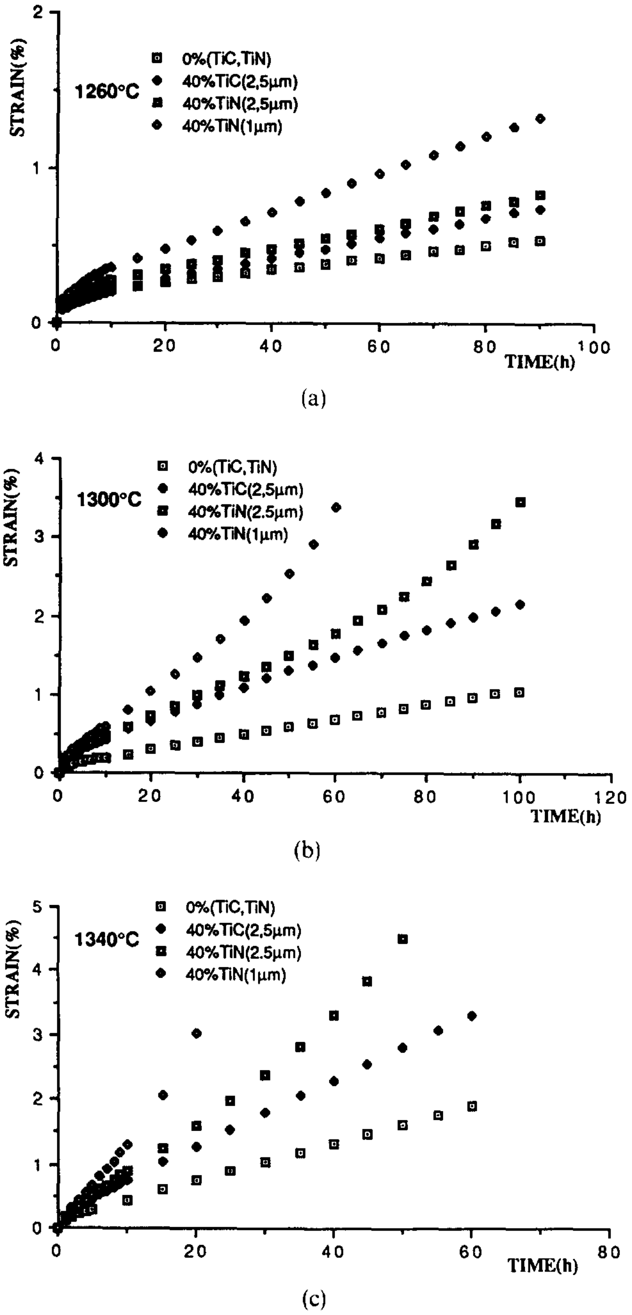


(c)

Fig. 1. Arrhenius plots of steady-state creep rates for (a) 40 wt% TiC–Si_3N_4 composite by both the conventional and the temperature-jump method, and for 0 and 40 wt% TiN–Si_3N_4 composites by (b) the conventional methods and (c) the temperature-jump method.

The preceding results are compared in Figs 1 and 2 with results for the matrix alone and for composites containing 40 wt% TiN particles. The activation energies determined by both methods in the present work for the Si_3N_4 matrix and for the Si_3N_4/TiN composites are higher than the previous values (Fig. 1(b) and (c)). For the Si_3N_4/TiC composite the creep rate increased with respect to the matrix but was lower than in the Si_3N_4/TiN composites. In addition, the creep ductility significantly improved, the deformation remaining in the steady state up to 15% without acceleration at 1340°C for a stress of 300 MPa. In other words, the strain to the onset of tertiary creep was about twice and five times as large as those of the Si_3N_4 matrix and Si_3N_4/TiN composites respectively. In the case of TiN particles/Si_3N_4-based composites the tertiary period was observed with an acceleration of creep strain in the temperature range 1300–1340°C for a stress of 200 MPa and a maximum deformation of 5% was achieved. The limit stress for which the secondary creep of the Si_3N_4/TiN composites exhibited nearly viscous creep ($n = 1$) was 200 MPa.

The addition of hard TiN particles did not improve the creep properties of the composite as



(c)

Fig. 2. Compressive creep curves at (a) 1260°C, (b) 1300°C and (c) 1340°C for a stress $\sigma = 200$ MPa of composites with 0 and 40 wt% TiC, and 40 wt% TiN particles. ▣, 0% (TiC, TiN); ◆, 40% TiC (2·5 μm); ■, 40% TiN (2·5 μm); ◇, 40% TiN (1 μm).


(a)

(b)

(c)

Fig. 3. TEM images of (a) the dispersoid-free, (b) 40 wt% TiN–Si_3N_4 and (c) 40 wt% TiC–Si_3N_4 matrices. Scale bar = 1 μm.

expected from models treating the matrix material as a homogeneous continuum and the dispersoids as mechanically or chemically inert particles.[15] On the one hand the creep rates increased and on the other hand the creep ductilities significantly decreased, with respect to the matrix, as the volume fraction to particle size ratio of the particles increased.[13] In the case of TiC particles/Si_3N_4-based composites the effect of particle size should not be so important, since it was reported that TiC presents a brittle to ductile transition in the range 800–1000°C.[16,17] As TiC particles are known to modify the Si_3N_4 matrix microstructure development during hot pressing,[7–9] the change of chemical composition in the vicinity to the Si_3N_4/TiC interfaces and the resulting new microstructure, in addition to the TiC high-temperature ductility, could determine the creep behaviour of the composite. Thus a careful observation of samples in TEM has been necessary throughout this study.

In TEM the Si_3N_4 microstructure of the dispersoid-free material appeared perfectly dense and the grain size varied from 0·25 to 1 μm (Fig. 3(a)). It was the same for both TiN-dispersed particle composites (Fig. 3(b)). The micrograph in Fig. 4

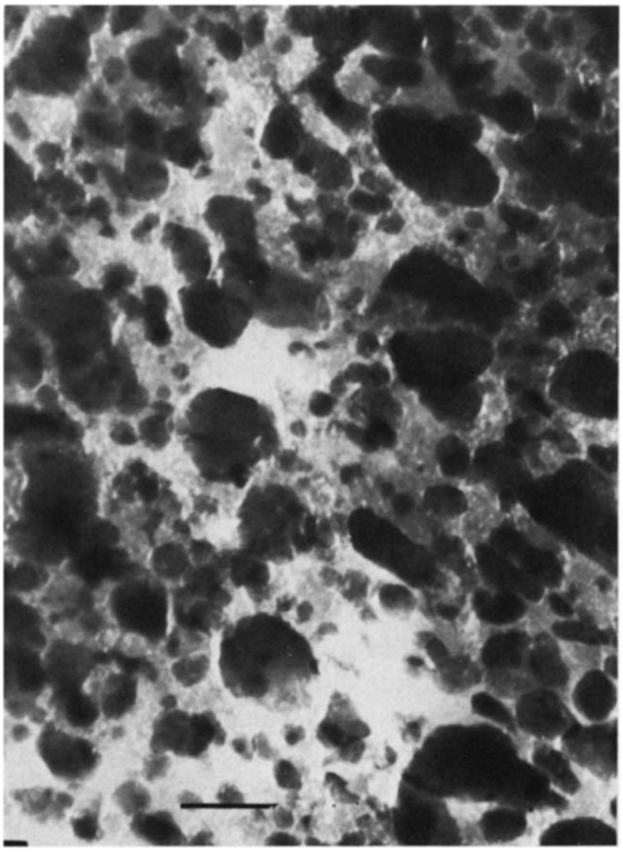


Fig. 4. TEM micrograph showing the distribution of TiN 'inert' particles in a Si_3N_4/TiN composite crept at 1340°C for a stress of 200 MPa. Scale bar = 5 μm.

Fig. 5. TEM micrograph of the Si_3N_4/TiC composite showing the matrix polluted by SiC precipitates. Scale bar = 0·5 μm.

Fig. 6. TEM micrograph of a Si_3N_4/TiC composite showing the reaction zone. Scale bar = 0·2 μm.

revealed the homogeneous distribution of TiN particles in the Si_3N_4 matrix. In contrast, the TiC particles/Si_3N_4-based composites showed a refinement in the matrix grain size (Fig. 3(c)). The larger ones were absent and SiC precipitates could be detected in the Si_3N_4 matrix (Fig. 5). This is in agreement with previous work,[9] where it has been shown that the presence of a TiC dispersoid, chemically reactive with the Si_3N_4 matrix, leads to substantial matrix grain refinement as compared to the Si_3N_4 monolith.

The microstructure of the TiC particles/Si_3N_4-based composites revealed the presence of reaction product zones around TiC grains (Fig. 6). It seemed that the reaction products were arranged in distinct and separate layers in the vicinity of Si_3N_4/TiC interfaces (Fig. 7), but sometimes small SiC precipitates of the order of 0·05 μm, embedded in the Si_3N_4 grains, were observed (Fig. 8). Previous work[7,8] suggested that this reaction zone was composed of SiC and $TiC_{0.5}N_{0.5}$ crystals, which formed under applied hot-pressing conditions according to the reaction

$$Si_3N_4 + 6TiC \rightarrow 3SiC + 6TiC_{0.5}N_{0.5} + 0.5N_2$$

EDS X-ray microanalytical data of the reaction zones showed the presence of titanium and carbon according to the previous reaction (Fig. 9). In TEM the SiC grains were apparent and their particle size in the examined zones varied between 0·1 and 0·2 μm, while the larger $TiC_{0.5}N_{0.5}$ grains were generally juxtaposed to the TiC ones. In contrast to previous observations in TiN particles/Si_3N_4 composites, cavities and microcracks were not observed in the material up to 15% strain (Fig. 10), but numerous strain whorls located along grain boundaries of Si_3N_4 were also present (Fig. 11), their density depending on the sample deformation.

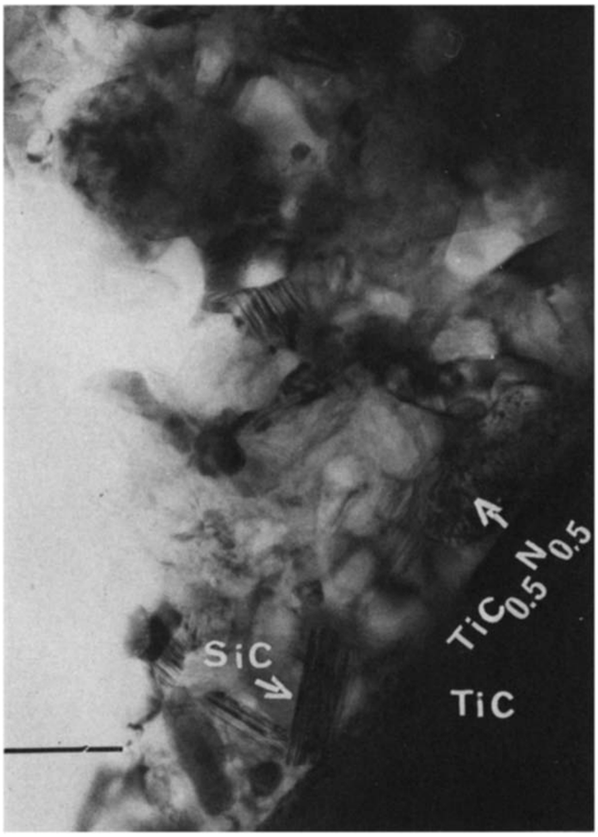


Fig. 7. TEM micrograph showing the distribution of $TiC_{0.5}N_{0.5}$ and SiC crystals in the vicinity of the TiC/Si_3N_4 interface. Scale bar = 0·2 μm.

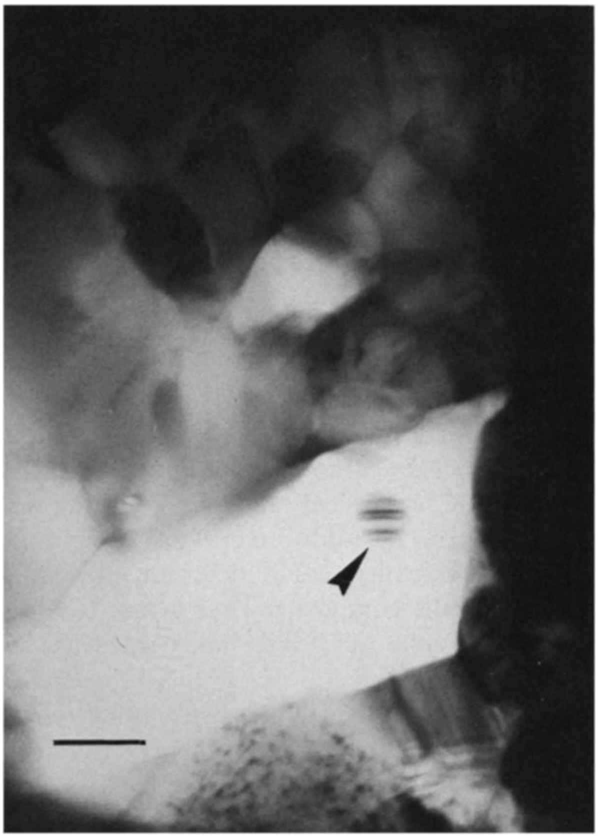
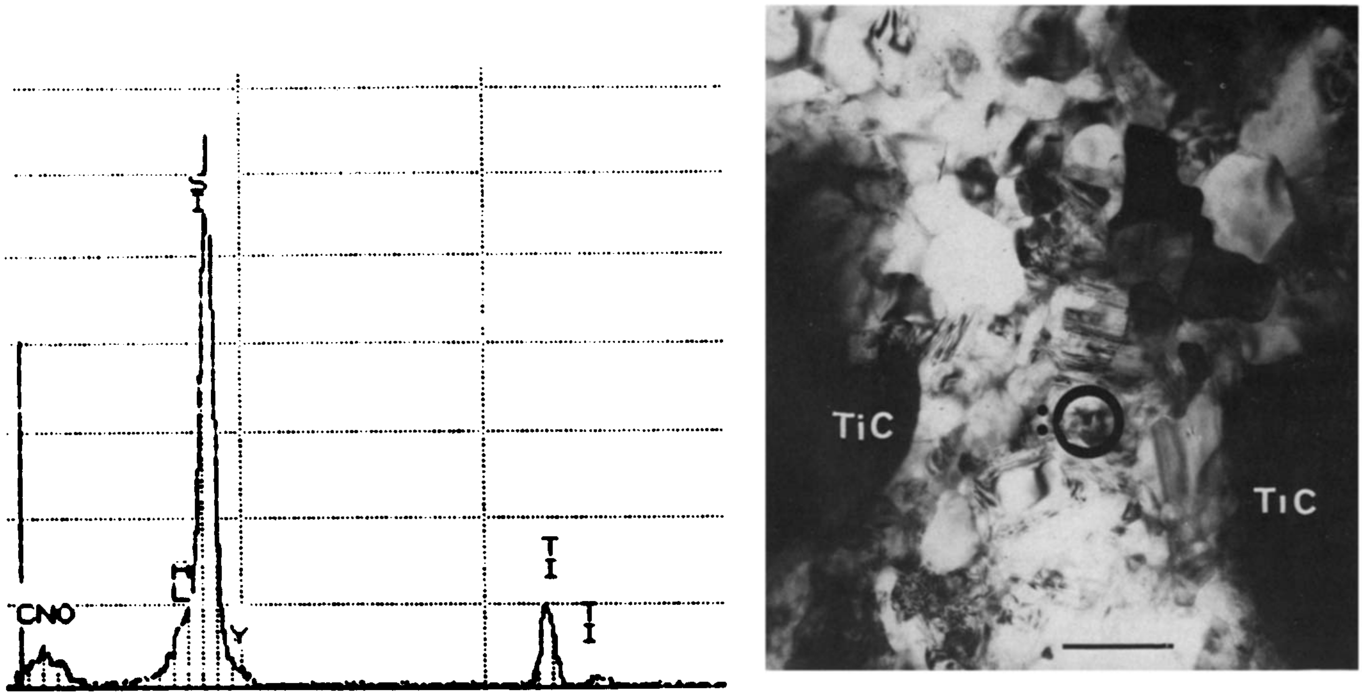


Fig. 8. TEM micrograph of a Si_3N_4/TiC composite showing a small SiC precipitate of the order of 0·05 μm embedded in the Si_3N_4 grain. Scale bar = 0·1 μm.

The deformation of the matrix has been determined to be controlled by solution–diffusion–precipitation accommodated grain-boundary sliding.[18] In the TiC particles/Si_3N_4-based composites the absence of cavities and microcracks at the Si_3N_4/TiC interfaces indicated that the diffusional creep of the Si_3N_4 matrix was well accommodated by the TiC particles. In addition to the properties of dispersoid, creep behaviour of the Si_3N_4/TiC composite is strongly dependent on the composition of the intergranular liquid phase and on the coherency of the Si_3N_4/dispersoid interfaces. Based on TEM observations, the SiC crystals were separated from



(a) (b)

Fig. 9. (a) EDS X-ray spectrum corresponding to the reaction zone (b) of a Si_3N_4/TiC composite. Scale bar = 0·1 μm.

Fig. 10. TEM micrograph of a Si_3N_4/TiC composite crept at 1340°C for a stress of 200 MPa up to 15% deformation showing the absence of microcracks and cavities. Scale bar = 0·5 μm.

Fig. 11. TEM micrograph showing strain whorls in a Si_3N_4/TiC composite crept at 1340°C for a stress of 200 MPa. Scale bar = 0·5 μm.

the $TiC_{0.5}N_{0.5}$ crystals and their size diminished moving away from the TiC grains, suggesting that their formation occurs by combining Si with C, diffused from the TiC surface. Elsewhere $TiC_{0.5}N_{0.5}$ crystals were found to be crystallographically coherent with the parent TiC grains, while the SiC crystals were usually set in glassy intergranular films near TiC.[8] However, it has been shown[19] that the dispersion of SiC nano particles, having desirable interfaces with the Si_3N_4 matrix, improved both toughness and strength at high temperatures. It is likely that such a dispersion could have favourable effects on the creep properties of the Si_3N_4/TiC composite, especially on the creep ductility. On the other hand, presumed inclusions of SiC, C and Ti in the glassy film, diffused during processing, have changed its composition and viscosity, thus affecting the matrix microstructure development. Fine grain matrix microstructure developed in the Si_3N_4/TiC composite was suggested to be responsible for increasing the creep rate as compared to the Si_3N_4 monolith.

4 Conclusion

The creep and microstructure of a Si_3N_4/TiC composite, compared with the Si_3N_4 matrix and with Si_3N_4/TiN materials, were studied in the temperature range 1260–1340°C. In contrast to the addition of 'inert' TiN dispersoid, which resulted in decreased creep resistance with respect to the matrix, the ductile and 'active' TiC had a better influence, particularly on the creep ductility. It was shown that the development of microstructure was influenced by the presence of the TiC dispersoid, chemically reactive with the Si_3N_4 matrix under applied processing conditions. A gradient of reaction products, composed of $TiC_{0.5}N_{0.5}$ and SiC crystals, and a substantial matrix grain refinement as compared to the Si_3N_4 monolith, were detected. TiC properties, fine grain matrix microstructure, desirable interfaces and a modification of the glassy film were suggested to be responsible for the creep properties of the Si_3N_4/TiC composite as compared to those of the matrix and of the Si_3N_4/TiN composites.

References

1. Martin, C., Cales, B., Vivier, P. & Mathieu, P., Electrical discharge machinable ceramic composites. *Mater. Sci. Eng.*, **A109** (1989) 351–6.
2. Kamijo, E., Honda, M., Higushi, M., Takeushi, H. & Tanimura, T., *Sumitomo Electr. Tech. Rev.*, **24** (1985) 183–90.
3. Bellosi, A., Fiegna, A. & Babini, G. N., Electroconductive Si_3N_4-based composites. In *Euro-Ceramics*, Vol. 3, *Eng. Ceramics*, ed. G. de With, R. A. Terpstra & R. Metselaar. Elsevier Science Publishers, London, 1989, pp. 389–93.
4. Yasutomi, Y., Nakamura, K., Sobue, M. & Kubo, Y., Development and characterization of electroconductive Si_3N_4-bonded TiN ceramics. *J. Ceram. Jpn Inter.*, **97** (1989) 145–51.
5. Buljan, S. T. & Sarin, V. K., Machining performance of ceramic tools. Cutting of materials. In *Proc. Int. Conf. on Cutting Tool Materials*, ASM, 1980, pp. 335–47.
6. Page, R. A., Blanchard-Ardid, C. R. & Wei, W., Effect of particulate additions on the contact damage resistance of hot-pressed Si_3N_4. *J. Mat. Sci.*, **23** (1988) 946–57.
7. Zilberstein, G. & Buljan, S. T., Characterization of matrix-dispersoid reactions in Si_3N_4–TiC composites. In *Advances in Material Characterization. II: Material Science Research*, Vol. 19, ed. R. L. Snyder, R. A. Condrate & P. F. Johnson. Plenum Press, New York, 1985, pp. 389–402.
8. Buljan, S. T. & Zilberstein, G., Effect of impurities on microstructure and mechanical properties of Si_3N_4–TiC composites. Tailoring of multiphase and composite ceramics. *Mat. Sci. Res.*, Vol. 20. Plenum Press, New York, 1985, pp. 305–16.
9. Buljan, S. T. & Zilberstein, G., Microstructure development in Si_3N_4-based composites. *Mat. Res. Soc. Symp. Proc.*, **78** (1987) 273–81.
10. Buljan, S. T. & Baldoni, J. G., Silicon nitride-based composites. *Mat. Sci. Forum*, **47** (1989) 249–66.
11. Buljan, S. T., Baldoni, J. G. & Huckabee, M. L., Si_3N_4–SiC composites. *Amer. Ceram. Soc. Bull.*, **66** (1987) 347–52.
12. Baldoni, J. G., Buljan, S. T. & Sarin, V. K., Particulate titanium carbide–ceramic matrix composites. In *Science of Hard Materials*. Adam Hilger Ltd, 1986, pp. 427–38.
13. Crampon, J. & Duclos, R., Creep and microstructure of electrical discharge machinable Si_3N_4 composites. *Acta Metall. Mater.*, **38** (1990) 805–10.
14. Duclos, R., Doctoral thesis, USTLFA, 59655 Villeneuve d'Ascq, France, 1980.
15. Chong K. Yoon & I. Wei Chen, Superplastic flow of two-phase ceramics containing rigid inclusions–zirconia/mullite composites. *J. Amer. Ceram. Soc.*, **73** (1990) 1555–65.
16. Williams, W. S. & Schaal, R. D., Elastic deformation, plastic flow, and dislocations in single crystals of titanium carbide. *J. Appl. Phys.*, **33** (1962) 955–62.
17. Das, G., Mazdiyasni, K. S. & Lipsitt, H. A., Mechanical properties of polycrystalline TiC. *J. Amer. Ceram. Soc.*, **65** (1982) 104–10.
18. Rakotoharisoa, N. S., Doctoral thesis, USTLFA, 59655 Villeneuve d'Ascq, France, 1988.
19. Niihara, K., Suganuma, K., Nakahira, A. & Izaki, K., Interfaces in Si_3N_4–SiC composite. *J. Mat. Sci. Lett.*, **9** (1990) 598–9.