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Compressive creep of Si_3N_4/MgO alloys

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The activation energy of two Si_3N_4/MgO materials, fabricated in the Si_3N_4–Si_2N_2O–Mg_2SiO_4 compatibility triangle of the Si–Mg–O–N system, was determined between 1300 and 1400° C under a compressive stress of 275 MPa. The activation energy of the material previously shown to exhibit pure diffusional creep was determined to be 660 kJ mol^{-1}, whereas the material shown to exhibit extensive cavitational creep had an activation energy of 1080 kJ mol^{-1}. These results are compared with results obtained by others for densification and slow crack growth.

1. Introduction

Previous articles [1–3] have reported the compressive creep behaviour of the Si_3N_4 materials fabricated in the Si_3N_4–Si_2N_2O–Mg_2SiO_2 compatibility triangle of the Si–Mg–O–N system. Two pertinent results were:

(1) cavitation and diffusion are the two phenomena that concurrently contribute to creep strain. The creep behaviour of compositions closer to the ternary eutectic (which are expected to contain a larger volume fraction of the continuous glassy phase) was dominated by cavitational creep, as determined by precise density measurements. Diffusional creep was dominant in those compositions closer to the Si_3N_4–Si_2N_2O tie line and furthest from the ternary eutectic; strain-rate/stress-exponents for these compositions were $n \simeq 1$;

(2) a pre-oxidation treatment significantly improves the creep resistance. Within the temperature and stress-range examined, pre-oxidized materials exhibit diffusional creep (as determined by their stress exponent $n \simeq 1$) despite their behaviour prior to the prolonged oxidation treatment. Other work [4] has shown that oxidation shifts the polyphase composition of Si_3N_4 toward the Si_3N_4–Si_2N_2O tie line and away from the ternary-eutectic composition, thus decreasing the volume fraction of the detrimental glassy phase.

The purpose of the present article is to report the activation energies associated with materials that exhibit one of the two dominant mechanisms, namely, either cavitational creep or diffusional creep.

Creep activation energies (Q) have previously been reported for Si_3N_4 materials fabricated in the Si–Mg–O–N systems with the assumption that the creep strain rate ($\dot{\epsilon}$) has a stress (σ) and temperature dependency as expressed by the empirical relation:

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

Values of Q for commercial materials have been reported by Kossowsky *et al.* [5] (535 kJ mol^{-1}, tension), Seltzer [6] (703 kJ mol^{-1}, tension and compression), Din and Nicholson [7] (585 kJ mol^{-1}, bending) and Arons and Tien [8] (850 kJ mol^{-1}, tension). Birch and Wilshire [9] have reported a value of 650 kJ mol^{-1} for a variety of experimental Si_3N_4/MgO materials. The stress exponents (n) reported by these same investigators lie between 1.5 and 2.4, indicative of a cavitational dominated creep regime [1]. It should also be noted that the effect of oxidation on creep resistance was not a known phenomena in the experimental schemes mentioned above.

2. Experimental details

Compressive creep experiments were performed on two materials in air as reported previously [1]. The specific composition of the two materials (denoted as A and B in Part 1 [1]), fabricated by hot-pressing, were (in mole fraction): A; 0.755 Si_3N_4, 0.225 SiO_2, 0.020 MgO; B; 0.755 Si_3N_4,

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TABLE I Steady-state creep rates

	Temperature (° C)	Stress (MPa)	$\dot{\epsilon}$ (h^{-1})
Material A	1400	275	1.07×10^{-3}
	1350	275	2.82×10^{-4}
	1300	275	5.25×10^{-5}
Material B	1400	275	1.04×10^{-2}
	1350	275	8.04×10^{-4}
	1300	275	7.59×10^{-5}
	1300	450	1.56×10^{-4}

0.090 SiO_2, 0.155 MgO. Both compositions lie within the Si_3N_4–Si_2N_2O–Mg_2SiO_4 compatibility triangle of the Si–Mg–O–N system. Previous study [1] has shown that at 1400° C, the creep behaviour of material A was dominated by diffusional processes (no density change, $n \simeq 1$) and material B was dominated by cavitational phenomena (density decreasing with increasing creep strain, $n \simeq 2$).*

Creep experiments were performed on both materials in air at 1300, 1350, and 1400° C with a compressive stress of 275 MPa. An additional experiment was performed at 1300° C with material B at 450 MPa to determine if the material had the same creep behaviour over the temperature range of interest. To minimize the effect of "hardening" due to oxidation [3], single specimens were used for each temperature and stress, and test periods were held to $\leqslant$ 24 h. Apparent activation energies were calculated from the data collected by using Equation 1.

3. Results

For all cases, a short period of primary creep strain was followed by a longer period of apparent steady-state creep. Experiments were terminated prior to any development of tertiary creep. Table I reports the steady-state creep data for each of the two materials. An analysis of the creep behaviour of material B at 1300° C resulted in a stress exponent of 1.91, consistent with a value of 2.05 previously reported for data obtained at 1400° C. An Arrhenius plot of these data is shown in Fig. 1, from which an apparent activation energy of 660 kJ mol^{-1} is obtained for material A and 1080 kJ mol^{-1} is obtained for material B.

4. Discussion

Results presented above for two different Si_3N_4/MgO materials fabricated within the same compatibility triangle indicate that the activation energy for pure diffusion creep is ~ 660 kJ mol^{-1} and ~ 1080 kJ mol^{-1} for creep dominated by cavitation. Speculations concerning the rate-limiting processes that give rise to these results will not be discussed;† instead, these results will be compared to other high-temperature processes reported for Si_3N_4/MgO material.

The first comparison will be made with densification processes which are known to occur by a solution-reprecipitation, i.e., diffusion through a liquid phase. It is not unreasonable to suspect that the diffusion processes that occur during the liquid-phase densification of Si_3N_4/MgO compositions are the same as those responsible for pure diffusional creep. Based on this premise, similar activation energies might be expected, even though the densification rates and creep rates may not be comparable. Activation energies for densification of Si_3N_4/MgO compositions have been reported by Bowen *et al.* [11] as ~ 690 kJ mol^{-1} in the temperature range 1450 to 1550° C and by Terwilliger and Lange [12] as ~ 710 kJ mol^{-1} between 1500 and 1700° C. These values are very similar to ~ 660 kJ mol^{-1} determined here for diffusional creep, suggesting similar rate-limiting steps for the two phenomena.

The second comparison will be made between the activation energies determined for creep dominated by cavitation and for slow crack growth observed in Si_3N_4/MgO materials at high temperature. Observations have shown that slow crack growth in dense Si_3N_4 materials occurs by a process that involves cavitation. Since cavitational creep will dominate over diffusional creep in the high stress regime of a propagating crack, slow crack growth in these materials is expected to occur by accelerated, cavitational creep. Thus, one might expect similar activation energies for slow crack growth and cavitational creep. Evans and Wiederhorn [14] obtained an activation energy of 920 kJ mol^{-1} for slow crack growth in commercial Si_3N_4 in the temperature range 1300 to 1400° C. Although their value is in fair agreement

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*As previously pointed out, $n = 2$ is not necessarily unique for cavitational processes. Theory indicates [1, 10] that creep due to cavitation is not simply related to strain through a power law, i.e., if a power law is assumed, n will depend on the stress range of experiments.

†The author is in agreement with the view point taken by Raj and Morgan, i.e., the large values of the measured, apparent activation energies strongly suggest that they are a sum of more than one activated process [13].

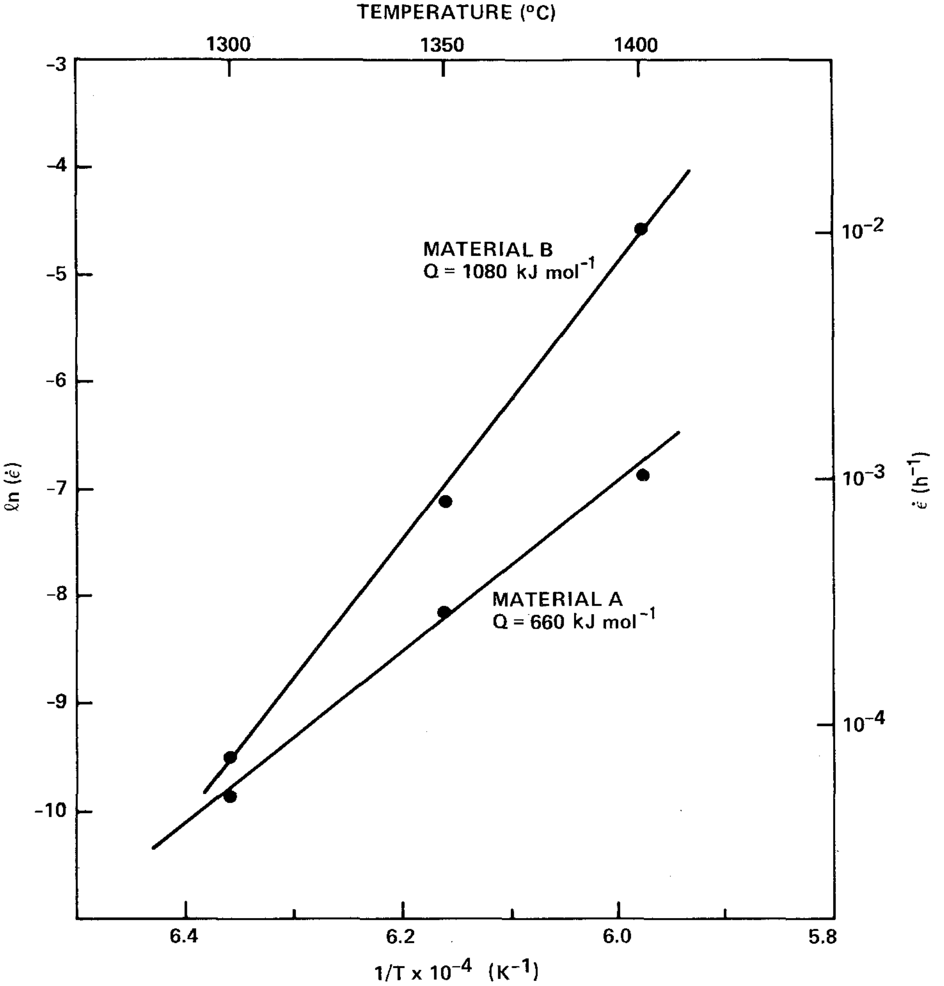

Figure 1 Arrhenius plot of steady-state creep rates for materials A and B.

with that reported here for cavitational creep (1080 kJ mol^{-1}), it should be noted that in a subsequent paper Evans *et al.* [15] reported a lower value (710 kcal mol^{-1}) obtained in the range 1150 to 1350° C by a different method of analysis.

In conclusion, it should be noted in Fig. 1 that the creep rates for both materials examined here approach one another at 1300° C. It would be unreasonable to extrapolate these data to lower temperatures to predict that material B would have a better creep resistance than material A. It would be more reasonable to expect that at lower temperatures, both materials will have similar creep behaviour, i.e., diffusional creep will become more dominant at lower temperatures. This reasoning is consistent with the creep results of others. That is, when data are analysed over a much wider temperature range, one would expect that the higher stress exponents observed in the high temperature regime (i.e., $\geqslant 1300°$ C) would result in an average stress exponent > 1, but that the activation energy might be more indicative of the predominant data obtained at lower temperatures, i.e., an activation energy more similar to that of the diffusional processes.

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