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Compressive creep of Si_3N_4/MgO alloys

Part 3 *Effects of oxidation induced compositional change*

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A comparison of "creep" resistance in as-fabricated and pre-oxidized specimens of different Si_3N_4/MgO alloys shows that pre-oxidation not only significantly reduces the apparent steady-state creep rate, but can also change the stress dependence from a non-linear to a linear behaviour. This phenomenon is discussed in terms of compositional changes induced by oxidation.

1. Introduction

During the course of this investigation of the compressive creep behaviour of four Si_3N_4/MgO alloys, it became apparent that oxidation was significantly affecting results (see Part 1, Section 3.1) [1], i.e. oxidation appeared to produce a form of strengthening. Results of an independent investigation of the oxidation behaviour of the same alloys showed that oxidation produces a compositional change because of the diffusion of oxygen into the bulk and of nitrogen, magnesium and impurities out of the bulk [2]. Since the creep behaviour of the Si_3N_4/MgO alloys was found to be significantly affected by composition [1], it was suspected that the apparent hardening effect was being produced by oxidation-induced compositional changes. Experiments were therefore planned to illustrate this effect.

2. Experimental details

Specimens (approximately 0.3 cm × 0.3 cm × 0.9 cm) were diamond cut from Si_3N_4/MgO alloy compositions A, B and D (see Part 1, Fig. 1). The series of specimens for this investigation were pre-oxidized at 1400° C for 100 h prior to the creep experiments. For comparative purposes, one specimen was diamond ground after oxidation so that material was removed to a depth of 0.1 cm from all surfaces. The oxide surface layer was not removed from the other specimens. Sectioning after testing showed that the thickness of the oxide surface scale was dependent on composition, but was never $> 50\,\mu m$. Because the oxide scale is partially liquid at 1400° C [2], it is not expected to support load. Inclusion of the oxide scale thickness in the specimen dimensions used in calculating the applied stress, thus resulted in a small error (~ 3%) for the assumed applied, compressive stress.

Compressive creep testing was performed at 1400° C in air as outlined in Part 1, Section 2. After testing, representative specimens were sectioned so their gross compositional change could be determined by using X-ray diffraction.

Unlike the unoxidized specimens (Part 1, Section 3), the pre-oxidized specimens exhibited an extensive period of steady-state creep. Within the time frame of each experiment (~ 25 h at each stress)* the strain rate was constant over the last ~ 80% of the period before the specimen was unloaded. Periods of primary creep and strain recovery were also observed for each composition. Tertiary creep was not observed.

The empirical equation relating the steady-state creep rate ($\dot{\epsilon}$) to the applied compressive stress (σ)

$$\dot{\epsilon} = A\sigma^n.$$

was used in analysing the data. The log–log plots of these data are shown in Fig. 1 along with the data for the unoxidized specimens previously presented in Part 1 of this series [1]. As shown, the pre-oxidation treatment significantly improved

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* The test period was designed to be shorter than the pre-oxidation period so that significant changes in the material, due to an added period of oxidation during testing, could be prevented.

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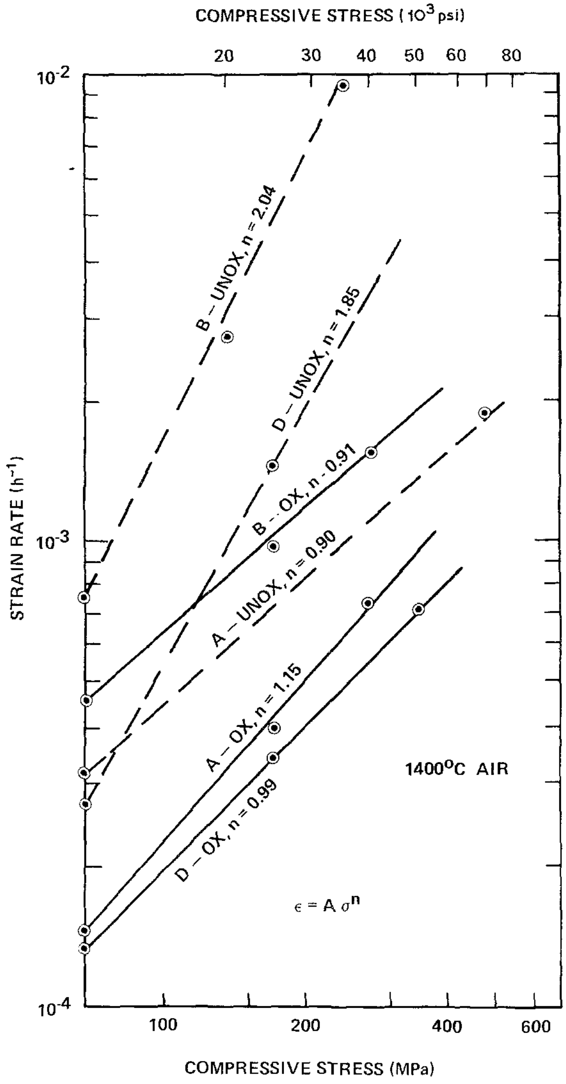

Figure 1 Log–log plot of apparent steady-state creep rate versus compressive stress for Si_3N_4/MgO alloy compositions A, B and D in the as-fabricated states (broken lines) and their pre-oxidized states (1400° C, 100 h); *n* is the stress exponent for creep rate.

the creep resistance of all alloys. Greatest improvement was achieved for compositions B and D. The strain rate for all the pre-oxidized compositions was linearly related to stress, indicating the dominance of diffusional creep as the persistent mode of deformation [1]. Data for the pre-oxidized specimen which was surface ground to remove the oxide scale was similar to the data for specimens in which the scale was not removed. This observation indicated, as expected, that the surface scale was not responsible for the improved creep resistance.

X-ray diffraction data of sectioned, pre-oxidized specimens revealed the presence of Si_2N_2O in materials B and D that was not present in the as-fabricated compositions (Part 1, Table I). This observation showed that the pre-oxidation treatment shifted the bulk composition toward the Si_2N_2O end member of the Si_3N_4–Si_2N_2O–Mg_2SiO_4 compatibility triangle in which the initial materials were fabricated.

4. Discussion

Conclusive evidence is presented which shows that a pre-oxidation treatment can significantly improve the creep resistance of Si_3N_4/MgO alloys as suspected by earlier work in this investigation [1]. The effect of oxidation on composition changes and the effect of compositional change on creep behaviour will be the subject of discussion.

An independent study of the oxidation behaviour of the complete compositional series from which the materials reported here were taken, has resulted in the following conclusions [2] with respect to the current study:

(1) oxidation not only results in the formation of a relatively thin, friable surface scale, but also results in a compositional gradient that can penetrate deep into the bulk;

(2) the compositional gradient is a result of the diffusion of oxygen into the bulk and of nitrogen, magnesium, and impurities out of the bulk; diffusion is presumed to occur within the glassy interphase. The Mg and impurities (Ca and Fe) concentrate in the surface scale; the bulk is depleted of these same impurities;

(3) for materials studied here, Si_2N_2O is the major phase at the scale/bulk interface and its concentration decreases as the centre of the bulk is approached.

These results show that oxidation causes compositions initially on the Si_3N_4–Mg_2SiO_4 side of the compatibility triangle to shift toward the Si_3N_4–Si_2N_2O side; the shift is greatest as the scale/bulk interface. Depending on the specimen thickness and the oxidation kinetics (time and temperature) the compositional shift can be significant at the specimen centre. Interpreted in another manner, oxidation causes the initial composition to shift away from the ternary eutectic, i.e. the glass interphase acts as a fugitive phase during oxidation.

When these results are applied to the present study, it is evident that a pre-oxidation treatment of 100 h at 1400° C for the specimen size used in the study was sufficient to cause a significant shift to compositions that exhibit predominantly diffusional creep. This is demonstrated by materials B and D. In their as-fabricated state, cavitational creep was dominant [1]; in their pre-oxidized state, diffusional creep was dominant. This shift in creep behaviour is consistent with the shift in their integrated composition and the observed compositional effect on creep behaviour as detailed in Part 1 [1]. The unchanged deformation behaviour (with regard to mechanism and not creep resistance) of composition A is also consistent with this view. Details of the effect of the compositional gradient produced by oxidation on the mechanics of creep deformation have not been explored in the present study. Study of this effect will be important not only for defining the explicit creep hardening function, but also for using this phenomenon to improve the creep resistance of poorer quality materials.

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References

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