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Compressive creep of Si_3N_4/MgO alloys

Part 2 *Source of viscoelastic effect*

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Highly localized strain fields are observed at grain boundaries in crept specimens of Si_3N_4/MgO alloys which were frozen under stress. These fields disappear upon annealing. Unresolved asperities between the grain pairs appear to give rise to the strain field during deformation. Viscoelastic effects responsible for primary creep and strain recovery are explained in terms of grain-boundary sliding on the glassy interphase which is accommodated by the elastic strain arising at the asperities. Each boundary containing an asperity can be modelled as a simple Kelvin element. The spectrum of these boundaries within the bulk gives rise to a spectrum of relaxation times that is observed for the strain recovery effect. The highly stressed region at the asperity also gives rise to the higher chemical potential required to drive diffusional creep. Although the source of the asperities was not observed, the possibility of opposing ledges of either single or multiple interplanar height is discussed.

1. Introduction

Time-dependent creep strain recovery has been reported by Clews *et al.* [1] for porcelain and refractories, Morrell and Ashbee [2] for glass-ceramics, and, during the course of the present work, by Arons [3] for commercial grade, hot-pressed Si_3N_4. Each of these investigators has shown that the recoverable strain is linearly proportional to the stress imposed on the specimen prior to unloading, indicating that the recovery process is viscoelastic, a phenomenon commonly observed for glasses.

Viscoelasticity can be modelled with a Kelvin element, i.e. a spring in parallel with a dashpot, or an arrangement of such elements. The strain produced by stressing this element is exponentially dependent on time divided by a characteristic relaxation time. Upon unloading, the viscoelastic strain decays inversely to that observed upon loading. The process is analogous to the charging and discharging of a capacitor. Thus, if a viscoelastic recovery is observed upon unloading, a corresponding viscoelastic effect is produced upon initial loading. Within this frame of reference, Morrell and Ashbee [2] and Arons [3] each conducted an analysis based on the Boltzman superposition principle and both concluded that the primary creep observed in their respective materials was inversely related to the viscoelastic recovery phenomenon.

In the course of examining the creep behaviour of the Si_3N_4 alloys, detailed in Part 1 [4], a time-dependent strain recovery phenomenon was discovered independently of Arons [3]. This discovery was manifested by the following observations. First, during initial compressive creep experiments conducted with a load cell in a testing frame, unloaded, creep specimens were observed to produce a back stress that would build up as a function of time. This observation showed that the crept specimens contained residual stresses, which arose during creep, that produced a strain recovery upon unloading. Second, during initial tests in which a single specimen was examined at successive stresses, it was observed that when the stress was reduced, the initial strain rate at the lower load was negative for a period before increasing, after an extended period, to the strain rate expected for the applied stress. Third, direct observation of the complete strain behaviour after unloading showed a time-dependent strain recovery phenomenon. This strain recovery phenomenon was observed for

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all the materials examined in Part 1 [4]. Analysis of these recovery phenomena with respect to the viscoelastic model (plots involving log (recoverable strain) versus time) did not produce a single characteristic time, but indicated a spectrum of relaxation times. Similar results were obtained by Clews *et al.* [1] for porcelain and refractories, Morrell and Ashbee [2] for glass-ceramic, and Arons [3] for hot-pressed Si_3N_4.

With the discovery in Arons [3] careful investigation, further work was concentrated on unusual features observed with TEM in crept specimens; as was uncovered, these were directly related to the viscoelastic phenomena.

2. Experimental details

Part 1 [4] described in more detail the two Si_3N_4 alloy compositions labelled (C and D) fabricated in the same compatibility triangle of the Si–Mg–O–N system, that were used in this study. In summary, composition C exhibited diffusional creep behaviour and did not cavitate, whereas cavitational creep appeared to dominate the behaviour of composition D. Although a continuous glassy grain-boundary phase was observed in both materials (Part 1, Fig. 2), composition C was furthest away from the ternary eutectic and thus was assumed to contain a smaller volume fraction of the glass. Both materials were observed to exhibit primary creep in which the strain rate decreased over a period to an apparent steady-state value, and both exhibited an apparent viscoelastic strain recovery.

Specimen foils were prepared for TEM studies from both materials in their as-fabricated, crept plus cooled under stress (1400° C, 350 MPa compression, 4% strain) and crept plus annealed* (1400° C, 1 h) states. Most strain is recovered after a 1 h anneal at 1400° C. Density measurements (Section 2.3, Part 1) were made for both the crept plus cooled under stress and crept plus annealed specimens.

3. Observations

The transmission electron micrograph in Fig. 1 illustrates the features, termed strain whorls, that were observed at the majority of grain pairs in foils prepared from the crept and cooled under load specimens. As indicated in Table I, the strain whorls were only seen in samples that had been cooled under load. The strain whorls were located only along grain boundaries and, in general, appeared to be asymmetrical with respect to the boundary normal. In addition, the contours of the whorls appeared to originate from a single point, suggesting that the source might be one of a point contact between the grains. From both high-resolution bright- and dark-field imaging, it was determined that no inclusions or particles were present at the centre of the whorls. In addition, strain whorls were not seen at those locations (principally three grain junctions) where small inclusions could be found. Attempts to investigate the centres of the whorls by lattice fringe imaging were unsuccessful because of the abrupt changes in the deviation parameter (s) from the

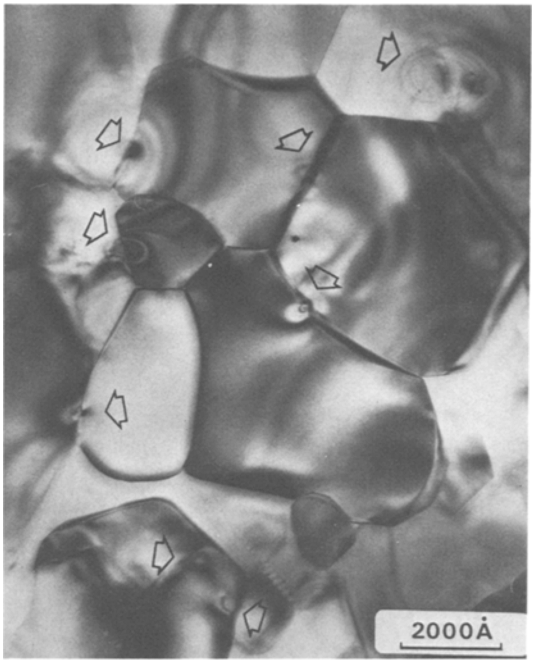

Figure 1 Examples of strain whorls observed at a majority of grain boundaries in crept specimens cooled under stress.

TABLE I Occurrence of strain whorls

Material	C	D
As-fabricated	Absent	Absent
Crept and cooled under load	Present	Present
Crept, cooled under load and annealed (1 h, 1400° C)	Absent	Absent

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* The crept specimens used for this study were diamond cut into several pieces for annealing and density measurements.

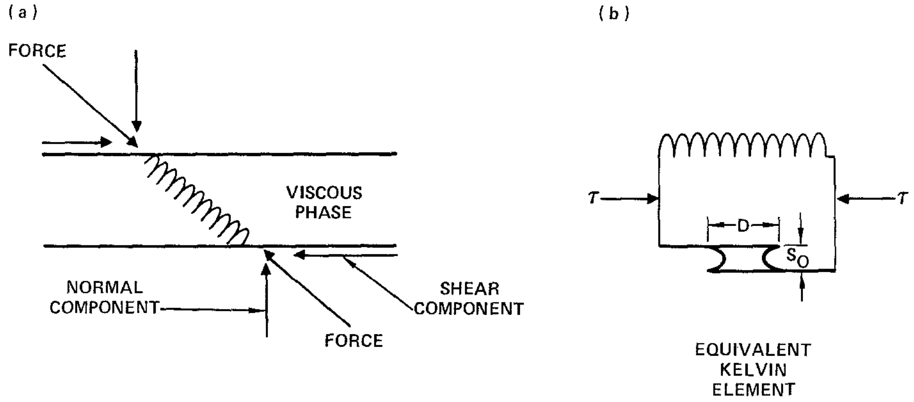

Figure 2 (a) Model of sliding grains separated by a glassy interphase and hindered from sliding by an asperity represented as a spring. (b) The Kelvin element representing (a).

exact Bragg condition in the vicinity of the whorls. That the whorls were, in effect, extinction contours resulting from a localized out-of-plane buckling of the electron microscope foil was determined from three experiments: (1) tilting the foil in the microscope caused the whorls to change shape and orientation; (2) at any foil orientation, each fringe or contour of the whorl could be made to appear bright in dark-field imaging by tilting the illumination, (equivalently, the diffraction pattern of the grains in the vicinity of the whorls was tilted with respect to that obtained from the same grains away from the whorls); (3) no two-beam diffraction conditions could be found for which a line of no contrast was formed, as is characteristic of strain centres produced by, for instance, misfitting precipitates [5].

These observations, when taken with the fact that the whorls were only seen to occur in those samples that have been cooled under load, confirm that the whorls are manifestations of a localized residual stress and are not artifacts produced in sample preparation.

An interesting observation on the occurrence of the whorls is illustrated by the micrograph of Fig. 8a in Part 1: the whorls are seen only on those grain boundaries whose plane lie approximately parallel to the direction of grain separation at L. This implies that the whorls form on those boundaries where the relative grain displacement includes a component of grain-boundary sliding.

Both density measurements and TEM observations of samples C and D indicated that the volume fraction of cavities remained unchanged after annealing.

4. Discussion

4.1. Viscoelastic effect

The presence of strain whorls in crept specimens cooled under load and their relaxation upon annealing illustrates that they depict (at least, in part) the stress fields responsible for the strain recovery. Their existence at grain boundaries and their general asymmetrical orientation* with respect to the grain boundary suggest that they arise and relax by grain-boundary sliding. Since a viscous phase separates each grain pair (Part 1, Fig. 2), the rate of grain-boundary sliding will be governed by the viscosity of the fluid between the grains and its thickness. Fig. 2a models this situation in terms of a spring fixed between two parallel plates which contain a viscous glass. The spring represents the asperity that gives rise to the strain whorl when the asymmetric force is applied across the plates.

Derivation of the time-dependent strain (ϵ_v) in relation to the areas of the asperity (A), the grain-boundary area (D^2), the thickness of the glassy interphase (S_0), the elastic modulus of the asperity (E), and the viscosity of the glass (η) is accomplished by summing the shear stress (τ) across the model:

$$\tau = E\frac{A}{D^2}\epsilon_v + \eta\frac{D}{S_0}\frac{d\epsilon_v}{dt}.$$

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* The asymmetrical strain pattern indicates that the force couple at the origin is asymmetrical with respect to the grain boundary and that a shear component of this couple lie in the grain boundary. If their asymmetry were due to strongly anisotropic elastic properties in the two respective grains, one would not expect to see the commonly observed axis of symmetry within the strain whorls.

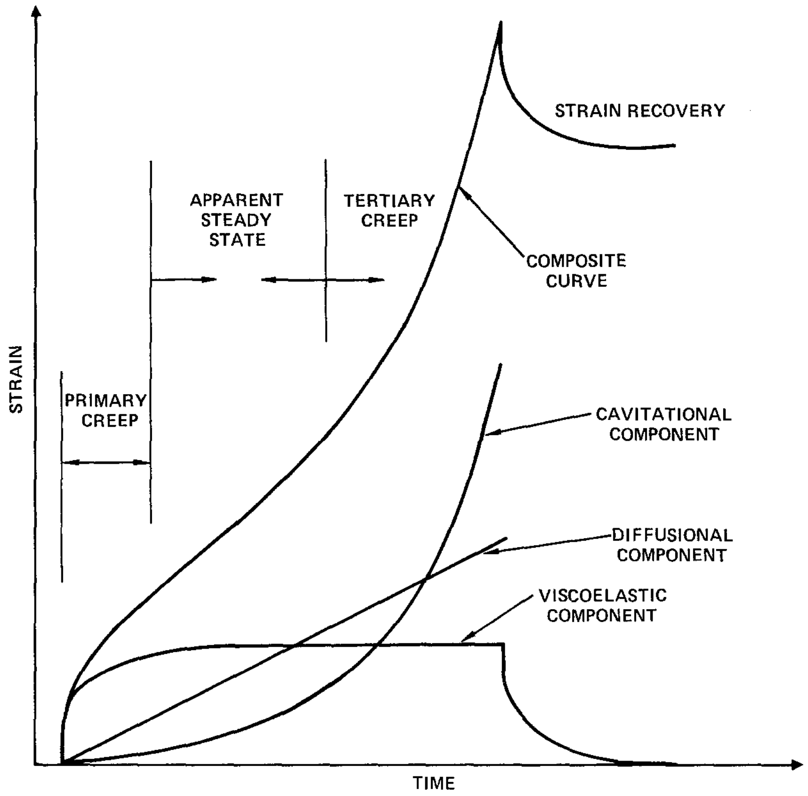

Figure 3 Functional forms of the three concurrent strain mechanisms that occur in Si_3N_2 alloys. The composite curve illustrates the experimental behaviour.

Upon integrating by parts:

$$\epsilon_v = \frac{\tau}{ER} 1 - \exp\left(-\frac{tER V_1}{3\eta}\right),$$

where R is the ratio of the asperity area to the grain-boundary area $(R \equiv A/D^2)$, and $(V_1 = 3S_0/D)$. The relaxation time constant for the single element is thus $3\eta/ER V_1$.

This model is equivalent to a single Kelvin element shown in Fig. 2b, where the dashpot is represented by two sliding plates containing the viscous glass. Since the bulk of the material contains many of these Kelvin elements, each with its own characteristic relaxation time, the summation of these elements will produce a viscoelastic response with a spectrum of relaxation times. This view is consistent with our own observations and those of Arons [3] for Si_3N_4 alloys. It can thus be concluded that the viscoelastic response of Si_3N_4 alloys, which appears to be responsible for both the primary creep and strain relaxation transients, arises from both the viscoelastic response of the glassy grain-boundary phase itself and the sliding of grain boundaries which is accommodated by the elastic deformation of material adjacent to asperities between the grains.

It should be noted that the stress fields that arise at the asperities would also give rise to the differential chemical potentials required as the driving force from diffusional creep (Part 1, Section 4).

Combining the observations of Part 1 [4] with those of this study, three concurrent mechanisms may be cited as responsible for the general creep behaviour of polyphase Si_3N_4 alloys: viscoelastic, diffusional and cavitational creep mechanisms. The latter two are the persistent creep modes which account for the unrecoverable creep strain. The functional forms of these three mechanisms are shown in Fig. 3. When all three mechanisms contribute, the general creep behaviour will be equal to their sum. Thus, the three recognized stages of creep can be matched with a dominant mechanism as follows: (1) primary creep is dominated by viscoeleastic deformation due to grain-boundary sliding accommodated by elastic deformation at grain-boundary asperities and/or adjacent grains; this deformation is recoverable; (2) secondary creep

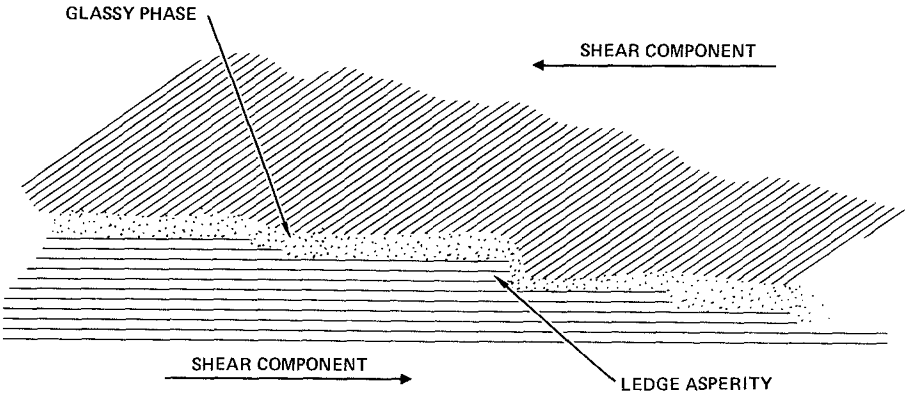

Figure 4 Model of ledge interference to form an asperity which give rise to strain whorls upon boundary sliding.

may, for materials with a small amount of glass, be dominated by diffusional creep; (3) tertiary creep is dominated by cavitation and will be accentuated by the subcritical growth of pre-existing cracks. As will be shown in Part 3 [6], a fourth mechanism also exists which is related to oxidation-induced composition changes.

4.2. Asperities at grain boundaries

It is evident from the localization of the strain whorls, that some sort of asperity which hinders sliding, exists at the grain boundary. Within the resolution of current TEM studies, the source of the asperity was not evident. It is evident that the size of these asperities must be approximately equal to the thickness of the glassy phase between the grains (i.e. < 50 Å). Likely sources are thus crystalline second phases and ledges composed of one or more lattice planes.

Although secondary crystalline phases have not been observed within the glass phase between the grains, they are commonly observed at triple points. For the Si_3N_4 alloys studied here, tungsten-containing particles are commonly observed, but no strain whorls were seen in the Si_3N_4 grains adjacent to these particles. In addition, crystalline magnesium silicate phases were not observed in the present materials; if they were the asperities, they would be expected to quickly dissolve under stress.

Ledges of single and multiple interplanar height at grain boundaries have been observed in a number of different Si_3N_4 alloys [7–9]. It is likely that ledges of opposing sign which lock together as shown in Fig. 4 can act as asperities and give rise to the observed strain whorls. This is a possibility since the height of the grain-boundary ledges that have been observed is commensurate with the measured thickness (< 20 Å) of the intergranular phase. Because ledges are also expected to be present on all boundaries, except those formed by low index, crystalline planes, a sufficient number would exist to act as sources of strain. Dissolution of the grains during diffusional creep might also be expected to be more energetically favourable at grain-boundary ledges, particularly those that form stressed asperities. Dissolution would not eliminate the asperity since ledge contact would be maintained by grain-boundary sliding. Material at the opposing ledge interface would diffuse to other ledges of lower chemical potential. Thus, the hypothesis that opposing ledges can act to impede grain-boundary sliding opens up many interesting questions for further work.

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