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Viscoplastic Forming of Si_3N_4-Based Ceramic and Glass-Matrix Particulate Composites

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Abstract

Two different routes were explored to make ceramic parts by plastic deformation at high temperature. The first route consists of hot-forming at a temperature close to the sintering one. About 100% elongation was achieved above 1773 K in an α-phase rich silicon nitride, densified with Al_2O_3 and Y_2O_3, with an average grain size of 0·6 µm. The second route uses glass-rich materials (particulate composites) and offers the advantage of much lower forming temperatures, typically around 1273 K. In this latter case, post-forming strengthening can be achieved through a crystallization treatment of the glass. SiC particle reinforced oxynitride glass composites with up to 40 vol% SiC were successfully shaped and further strengthened this way. Published by Elsevier Science Limited.

Résumé

Deux voies ont été explorées pour mettre en forme des matériaux céramiques par déformation plastique à chaud. Une premiére voie consiste à porter le matériau à une température voisine de la température de frittage. Des allongements proches de 100% ont été atteints au-dessus de 1773 K sur une nuance de nitrure de silicium à phase majoritaire α-Si_3N_4, densifiée en présence d'Al_2O_3 et d'Y_2O_3, avec une taille de grains de 0·6 µm. Une deuxième possibilité réside dans la préparation de matériaux composites à matrice vitreuse, offrant l'avantage d'une mise en forme à relativement basse température, typiquement vers 1273 K. Dans ce dernier cas, un traitement post-formage de consolidation, par cristallisation de la phase vitreuse, peut être envisagé. Des composites particulaires verre oxyazoté-SiC contenant jusqu'à 40% vol. de SiC ont été mis en forme de cette façon.

1 Introduction

In materials such as sialon ceramics and silicon oxynitride glasses, the strength of the Si–N bond is the source of exceptional mechanical resistance and chemical stability. However, the highly covalent nature of this bond is a disadvantage for Si_3N_4 ceramics in that it makes the fabrication of structural components extremely costly. Consequently, although engineers have long recognized the remarkable intrinsic properties of this family of materials, the lack of reliable and affordable shaping techniques still prevents large-scale use. The recent discovery of superplasticity in Si_3N_4 at temperatures between 1773 and 1823 K, opens new perspectives for net-shaping of components[1-4]. An alternative route consists of starting from tough and resistant oxynitride glass-matrix particulate composites, which offer the possibility for viscoplastic forming at around 1273 K.[5]

2 Experimental Techniques

Compressive, tensile and plastic forming tests were performed at constant strain-rates in a gas-tight chamber under nitrogen atmosphere with the nitrogen gas being introduced into the chamber after a pressure of less than 0·1 Pa was reached. SiC fixtures, pipes and pistons were used. A differential measurement device, by means of an LVDT and mechanical contacts with the specimen, was designed to record the actual elongation during testing.[6] Rectangular bars, 4×4×7(height) mm^3,

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were tested in compression. Dog-bone shape specimens with 15 mm long and 3 mm diameter cylindrical gauges were used for the tensile tests. Young's moduli were measured in-situ at elevated temperatures by means of an ultrasonic technique.[7] Viscosity measurements were carried out in bending, on $3\times4\times30\,mm^3$ rectangular bars, in air, on a dead-weight creep machine.

3 Viscoplastic Forming of Si_3N_4-Based Ceramics

The strain-rate/temperature range for viscoplastic forming of silicon nitride is illustrated in Fig. 1. The higher the glass content is, the higher the strain-rate is at a given temperature. The apparent activation energy for flow in ceramics densified with Al_2O_3, Y_2O_3 (or MgO) additives, typically lies between 700 and 950 kJ mol^{-1}; that is above the value for the activation energy for flow in a β-Si_3N_4 polycrystalline ceramic sintered without additives (420 kJ mol^{-1}), and close to the values of 800 to 900 kJ mol^{-1} determined on oxynitride glasses. This suggests that the high temperature deformation in glass containing ceramics is controlled by the intergranular glassy phases, which act both as a lubricant and as an adhesive between Si_3N_4 grains. In most cases, large differences were noticed between compressive and tensile flow characteristics. Strain-rates are one to two orders of magnitude higher in compression than in tension. Furthermore, shear-thickening ($n<1$) is observed in compression for stresses between 20 and 200 MPa, whereas shear-thinning ($n>1$) occurs in tension. The possibility of achieving large elongations in an α-phase rich (70 vol%) material consisting of hard silicon nitride grains embedded in a vitreous YSiAlON phase,[4,6] led us to investigate the feasibility for net-shaping of components by viscoplastic-forming. Parabolic and conic shells were successfully produced at 1868 K within about 1 h (Fig. 2). The obtained parts have a remarkably smooth and regular surface, with no apparent damage.

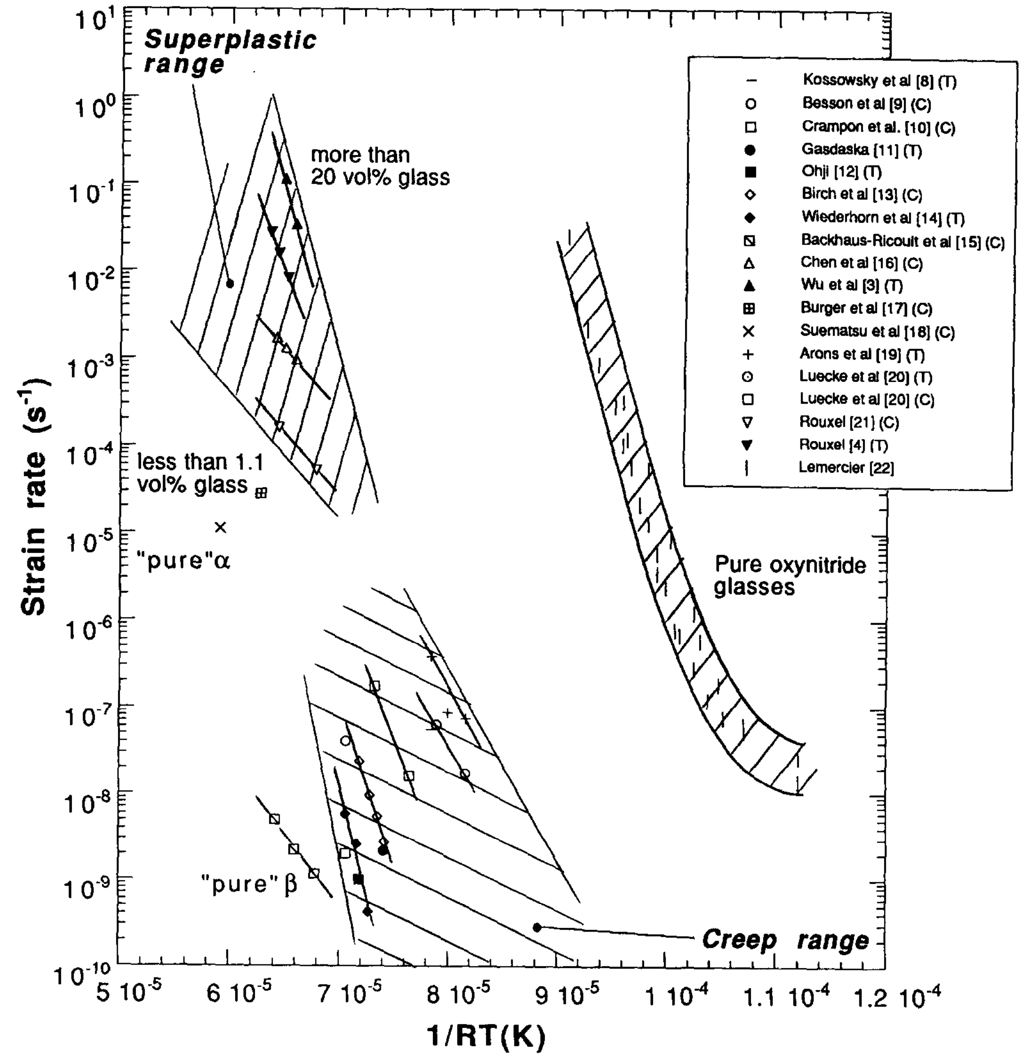

Fig. 1. Apparent activation energy for flow in silicon nitride-based ceramics and in oxynitride glasses. Data are normalized to a flow stress of 100 MPa to allow for comparison. Empty and solid marks refer to compressive and tensile tests respectively.

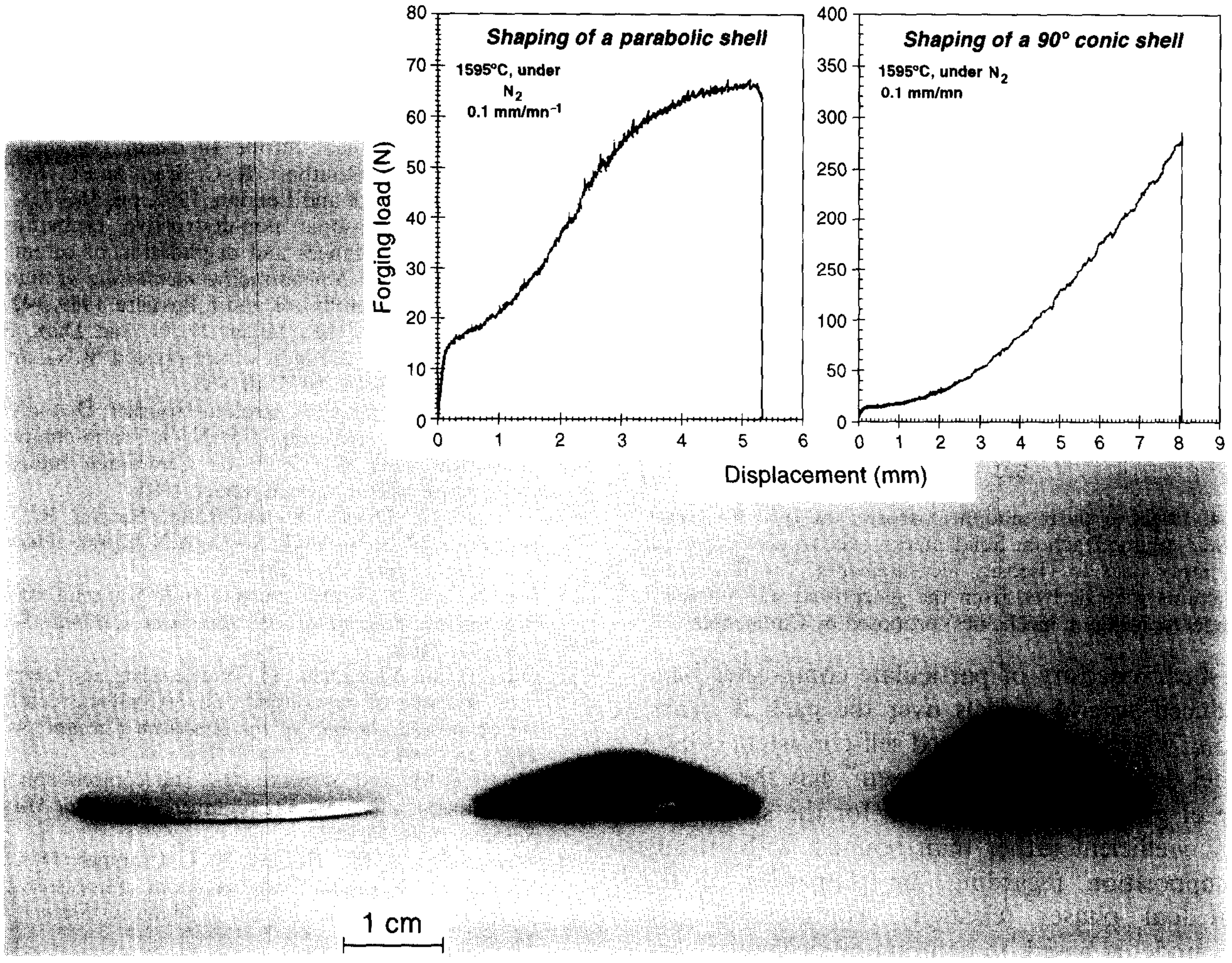

Fig. 2. Hot-forging of parabolic and conic shells, at 1868 K, using graphite moulds.

4 Viscoplastic Forming of SiC Particle Reinforced Oxynitride Glass

For a glass to be plastically deformed at a speed suitable for shaping techniques, the temperature must be higher than Tg but lower than the crystallization temperature. The viscoplastic forming range can be illustrated in a plot showing Young's modulus as a function of the temperature (Fig. 3). In the present case the glass belongs to the Y-Mg-Al-Si-O-N system. The glass, with stœchiometric composition $Y_{0\cdot124}Mg_{0\cdot16}Si_{0\cdot414}Al_{0\cdot302}O_{1\cdot4}N_{0\cdot515}$, has been prepared by heating up to 1973 K under nitrogen atmosphere a mixture of Y_2O_3, MgO, SiO_2, AlN and Al_2O_3 powders, and subsequent quenching.[23] The glass transition temperature is around 1112 K, and crystallization to form z-$Y_2Si_2O_7$ and $MgAl_2O_4$ starts at 1343 K. The hatched area corresponds to viscosity (η) between 10^{11} and 10^8 Pa.s. Particulate composites were fabricated from glass and SiC powders by mixing various amounts of each constituent and hot-pressing under a nitrogen atmosphere. Some physical and mechanical properties of the composites are given in a companion paper.[24] An apparent activation energy for flow of 870 kJ mol^{-1} was determined for the glass or for the glass–matrix composites as well. This value indicates a much larger temperature sensitivity for oxynitride glasses than for standard oxide glasses, for which values between 200 and 500 kJ mol^{-1} are typical. The flow kinetics of these composites is affected by the second phase particle size and volume fraction. Composites with more than 20 vol% SiC suffer from a large number of particle–particle contacts, with a percolation threshold, probably close to the rigidity threshold, at around 18 vol% SiC (for inclusions 1–10 μm in diameter). Above this value, η increases by several orders of magnitude (Fig. 4). Attempts to predict

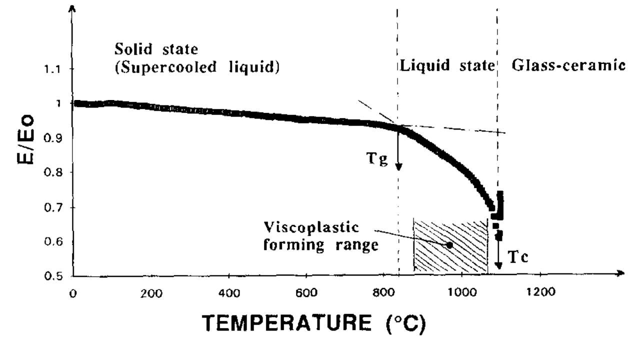

Fig. 3. Oxynitride glass matrix: in-situ changes in Young's modulus as a function of the temperature (E_o = 134 GPa).

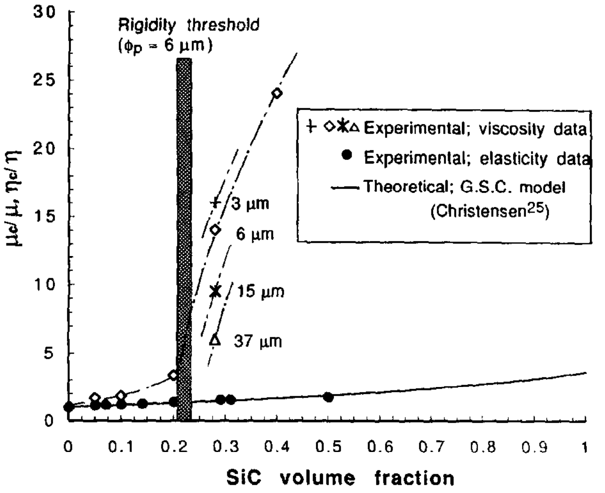

Fig. 4. Effective shear modulus-viscosity (at 1013 K) versus the SiC volume fraction. Solid marks refer to elastic moduli and empty ones to viscosity measurements. The theoretical predictions were derived from the generalized self-consistent model (continuum mechanics) proposed by Christensen.[25]

the shear viscosity of particulate composites have produced several models over the past 20 years, among which the generalized self-consistent (GSC) model developed by Christensen[25] has the advantage of giving an explicit form for the shear viscosity coefficient rather than bounds, without any presupposition regarding the properties of the individual phases (elasticity, compressibility...). The model is based on continuum mechanics elasticity solutions. The analogy between Hookean elasticity and Newtonian flow is then used to reinterpret displacements as velocities and the viscosity is then expressed by: $\eta_c/\eta = \mu_c/\mu$, where μ is the elastic shear modulus and subscript c refers to the composite. The model results in a good fitting of the elasticity data.[5] However, a poor fitting of the viscosity data is obtained. In this latter case, deviation from the theoretical model at large secondary phase volume fractions originates from the increasing number of particle–particle contacts. However, a 40 vol% SiC (6 μm) composite has been successfully used for the shaping of components at 1253 K, and the creep resistance was shown to be considerably improved by a crystallization treatment at 1373 K.[5]

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