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High-temperature deformation of amorphous $AlPO_4$-based nano-composites

F. Gutiérrez-Mora[a], K.C. Goretta[b], D. Singh[b,*], J.L. Routbort[b], S. Sambasivan[c], K.A. Steiner[c], J. Adabie[c], K.K. Rangan[c]

[a] *Departmento de Fisica de la Materia Condensada, Universidad de Sevilla, Sevilla 41080, Spain*
[b] *Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA*
[c] *Applied Thin Films, Inc., Evanston, IL 60201, USA*

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Abstract

High-temperature compressive deformation of an amorphous aluminum phosphate nano-composite was investigated at 1200–1300 °C. Microstructural and X-ray diffraction investigations of sol–gel-derived material revealed an amorphous structure with relatively high fraction of closed porosity of ≈15 vol.%. Transmission electron microscopy revealed nanocrystallites, predominantly of carbon, dispersed in the amorphous matrix. Steady-state flow stresses were 10–50 MPa and 50–70 MPa for test temperatures of 1200 and 1300 °C, respectively, as the strain rates were varied from 5×10^{-6} to $2 \times 10^{-5}\ s^{-1}$. Flow stresses increased with strain rates at a fixed temperature: stress exponents were 2.2–2.8 for various test temperatures, indicative of non-Newtonian flow. The non-Newtonian flow was attributed to the presence of the nanocrystalline phases. The creep resistance was found to be on a par with those of conventional oxide ceramics.

Keywords: Creep; Nanocomposites; Deformation; $AlPO_4$

1. Introduction

Aluminum phosphate ($AlPO_4$) is a well-known inorganic material used in a wide variety of applications, such as catalysts,[1] refractories, and hermetic seals.[2] Aluminum phosphate has a low density ($\rho = 2.56\ g/cm^3$), is resistant to chemical attack, and is stable at high temperatures. Its chemical compatibility with many metals and with the most widely used ceramics (silicon carbide, alumina, and silica) over a wide range of temperatures makes it an excellent material for applications where bonding or sealing is required.

Conventional $AlPO_4$ ceramics are, however, unsuitable for high-temperature applications because they undergo polymorphic transformations (berlinite, tridymite, and cristobalite), with corresponding large changes in volume.[3] Thus, it is desirable to have a synthetic form of $AlPO_4$ that is meta-stable by remaining substantially amorphous at increasing temperatures or during heating and cooling cycles. An amorphous $AlPO_4$ based nano-composite that remains stable at elevated temperatures, has been developed recently.[4] This ceramic has low oxygen diffusivity and good corrosion resistance at elevated temperatures,[5] which may provide oxidation protection to substrates when deposited as a coating.

Because this material has many potential applications at elevated temperatures, it is useful to characterize its high-temperature deformation stress versus strain behavior. It is amorphous, and classical deformation mechanisms observed for crystalline solids are not expected to operate. Failure in an amorphous material generally occurs by brittle fracture at low temperatures and viscous deformation at temperatures close to its glass transition temperatures (T_g).[6] In this paper, high-temperature mechanical characterization data and microstructural information are presented, and a possible mechanism for the high-temperature deformation of this amorphous $AlPO_4$ based nano-composite is proposed.

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[*] Corresponding author. Tel.: +1 630 252 5009; fax: +1 630 252 4798.
E-mail address: dsingh@anl.gov (D. Singh).

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2. Experimental details

Amorphous $AlPO_4$ based nano-composite, available commercially as Cerablak^{TM}, is produced and supplied by Applied Thin Films, Inc., based in Evanston, IL, USA. It is derived from a chemical precursor system composed of an ethanolic solution of P_2O_5 and $Al(NO_3)_3\cdot 9H_2O$ in molar ratios that yield pyrolyzed products of "glassy" $Al_{1+x}PO_{4+3x/2}$, where x represents excess aluminum content over the stoichiometric $AlPO_4$ in the precursor formulation. The chemical reaction can be expressed by the following equation:

$$\frac{1}{4}P_4O_{10} + (1+x)Al(NO_3)_3 \cdot 9H_2O \xrightarrow{\Delta} AlPO_4 \cdot \frac{x}{2}Al_2O_3 \qquad (1)$$

The material can be fabricated in various forms, including powders, coatings, fibers, and bulk.[4] For the present study, 408.9 g of $Al(NO_3)_3\cdot 9H_2O$ and 25.23 g of P_2O_5 (molar ratio 1.75:1 Al:P), both from Aldrich Chemicals, Milwaukee, WI, USA, were dissolved in ≈300 ml ethanol separately and the solutions were mixed together. A clear solution was obtained after stirring. The solvent was evaporated by heating at 150 °C to obtain a powder, which was annealed in air at 1100 °C for 1 h to form amorphous aluminum phosphate. The annealed amorphous aluminum phosphate was finely ground (20 μm) and mixed with a binder and then pressed into a pellet. This pellet was then electroconsolidated at 1300 °C for 30 min.

Samples for high-temperature mechanical testing were cut, ground, and polished to 1.5 mm × 1.5 mm × 3 mm parallelepipeds. Additional samples were prepared for an annealing study in argon at various temperatures for various times. Constant crosshead-displacement-rate experiments were carried out in an Instron machine (Model 1125, Canton, MA) equipped with an atmosphere-controlled high-temperature furnace.[7] The samples were compressed between two alumina platens, with platinum foil used as a diffusion barrier. Temperatures of 1200–1300 °C were used, with initial strain rates ranging between 2×10^{-6} and $2\times10^{-5}\,s^{-1}$. All experiments were conducted in an argon atmosphere. At a specific test temperature, for each specimen, crosshead speeds were changed (with and without unloading the sample) to obtain various strain rates.

Microstructural analyses of pre- and post-deformed samples were conducted by X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). XRD patterns were acquired on a Scintag 2000 (Sunnyvale, CA, USA) with Cu Kα radiation at 40 kV. Powder samples were prepared by crushing in methanol to obtain fresh, thin regions for examination. The scan rates were between 0.10 and 0.15°/min and a step size of 0.01°. A Hitachi HF-2000 cold field-emission transmission electron microscope, operating at 200 kV, was used for TEM analyses. A Hitachi S-4700-II microscope (Tokyo, Japan) was used for the SEM analyses.

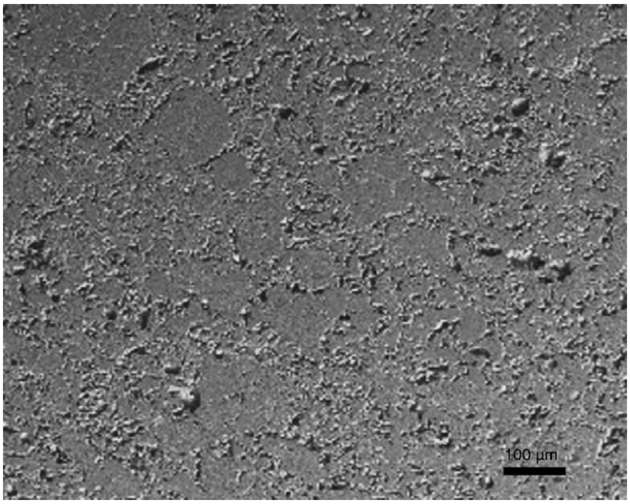

Fig. 1. Surface of electro-consolidated amorphous $AlPO_4$ based nano-composite.

3. Results

Fig. 1 shows the dense exterior surface of an as-electro-consolidated amorphous $AlPO_4$ based nano-composite sample. All samples contained isolated internal porosity, as shown in an SEM photomicrograph of a fracture surface (Fig. 2). Spherical pores (as indicated by arrow) were distributed throughout the samples, consistent with the ≈15 vol.% porosity levels measured for the bulk material.

Fig. 3a, a high-magnification TEM photomicrograph of as-fabricated sample, shows the presence of nanocrystals of $AlPO_4$ in an amorphous aluminum phosphate matrix. These nanocrystals were typically ≈20 nm in diameter. In addition, nanocrystalline glassy carbon, a residue of the fabrication process, was also observed (Fig. 3b).

The predominantly amorphous matrix structure of as-fabricated sample is retained during the high-temperature deformation tests. This was confirmed by the annealing

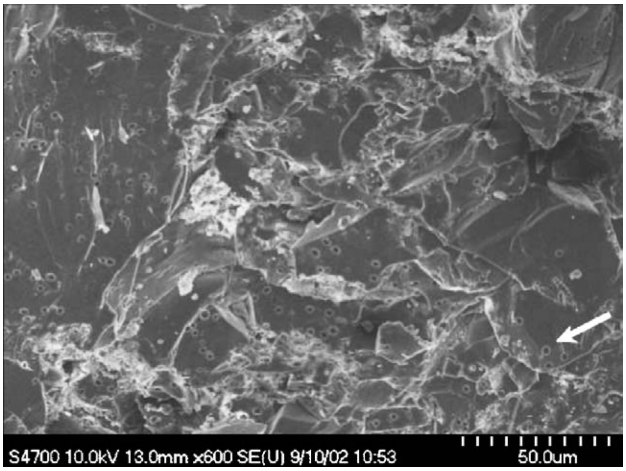

Fig. 2. Fracture surface of as-fabricated amorphous $AlPO_4$ based nano-composite.

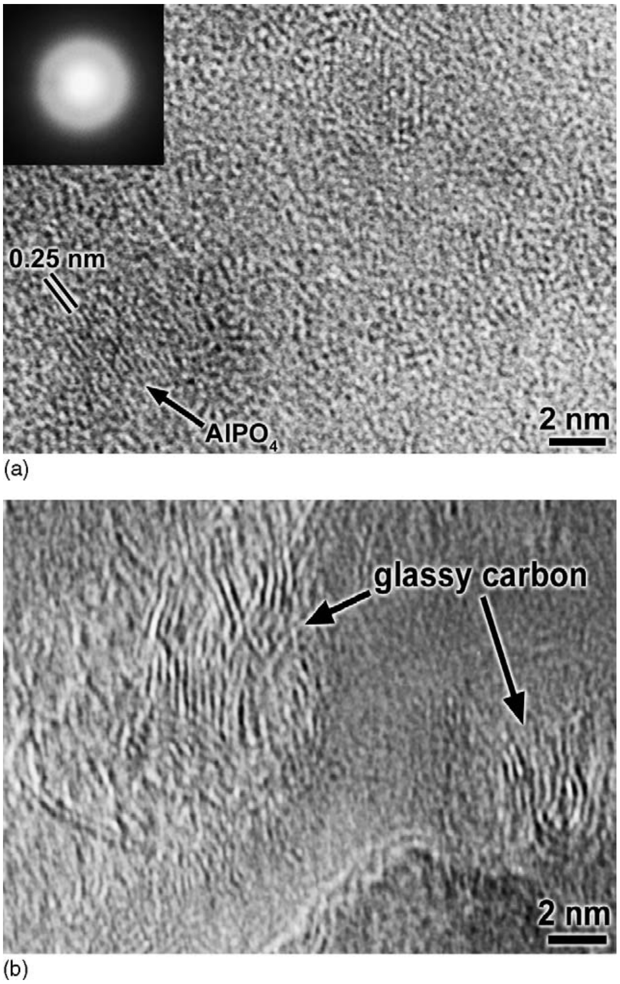

Fig. 3. TEM photomicrographs of as-fabricated amorphous $AlPO_4$ based nano-composite showing (a) nanocrystal of $AlPO_4$; (b) carbon nanocrystallites in amorphous $AlPO_4$, as indicated by arrows.

studies. XRD data from these studies are shown in Fig. 4. After 1 h at 1100 °C, the structure was primarily amorphous. However, presence of small amount of crystalline phase was observed corresponding to the presence of nanocrystals in the matrix (as shown in Fig. 3). It is believed that the tridymite peak arose from the formation of $AlPO_4$ nanocrystals (Fig. 3a). With further increase in temperature and annealing times, there were no significant changes in the XRD patterns. However, after exposure to 1400–1600 °C for extended periods, there are clear signs of the presence of the cristobalite form of $AlPO_4$ plus α-Al_2O_3. Thus, it is expected that during the test conditions used for deformation, the samples were primarily amorphous with nanocrystals of carbon and $AlPO_4$ dispersed in the matrix.

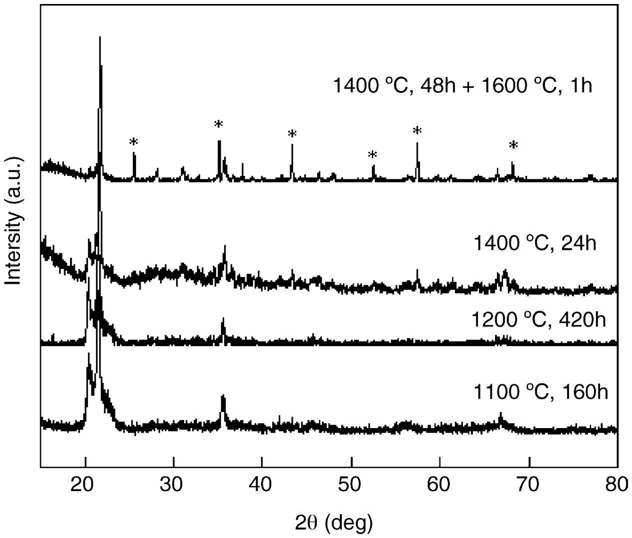

Fig. 4. XRD patterns of amorphous $AlPO_4$ based nano-composite as a function of annealing temperatures and times (* corresponds to α-Al_2O_3 peaks).

A typical stress–strain profile obtained in compression at 1300 °C is presented in Fig. 5. For each imposed strain rate, the stress reached a nearly constant value. At this plateau value, the steady-state flow stress, the material continued to deform without hardening or softening. Similar responses were obtained in deformation tests conducted at 1200 and 1250 °C. Final strains in all tests were ≈10%.

Fig. 6 represents the strain-rate dependence of the flow stress on a log–log basis for the three temperatures investigated. Assuming no substantive changes occurred in the microstructures during testing, a steady-state creep equation is used to define the dependence of strain rate on the flow stress:

$$\dot{\varepsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right) \tag{2}$$

where $\dot{\varepsilon}$ is the strain rate, σ the flow stress, n the stress exponent, A a constant, Q the activation energy, R the gas constant, and T the absolute test temperature. Values of n, estimated from best fits of the experimental data to Eq. (2), were (2.2–2.3) ± 0.2 for the specimens tested at 1250 and 1300 °C, and 2.8 ± 0.3 for samples deformed at 1200 °C. No work hardening or softening was observed in any of the tests.

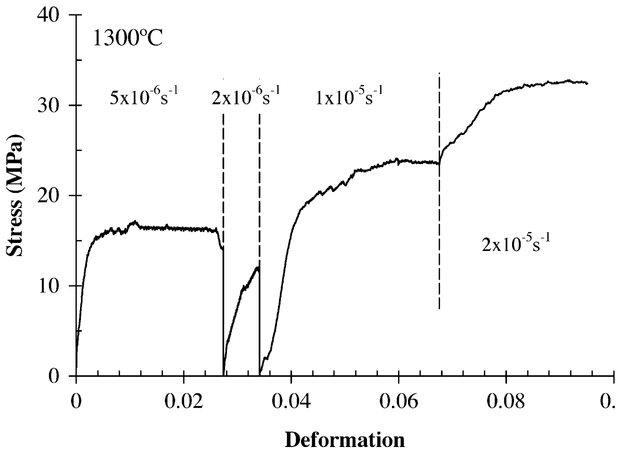

Fig. 5. Stress-strain profile for amorphous $AlPO_4$ based nano-composite obtained during compression testing at 1300 °C.

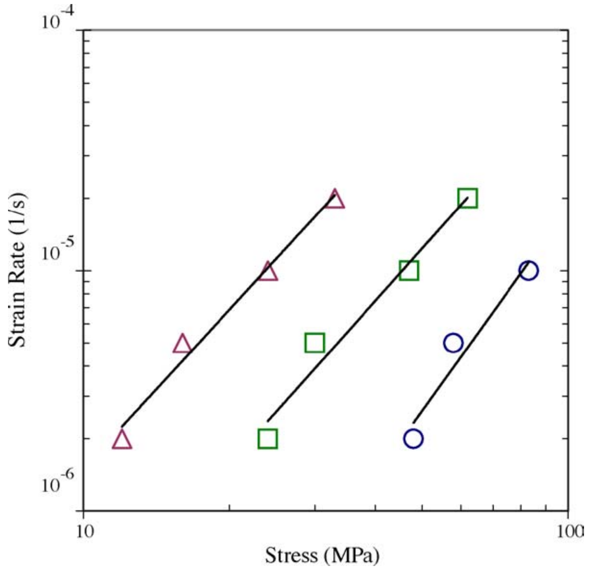

Fig. 6. Strain-rate dependency on flow stress for amorphous $AlPO_4$ based nano-composite ((○) 1200 °C ($n = 2.8 \pm 0.3$), (□) 1250 °C ($n = 2.3 \pm 0.2$), (△) 1300 °C ($n = 2.2 \pm 0.2$)).

4. Discussion

Deformation of amorphous brittle materials, in which nanocrystalline phases are present, is quite complex. A characteristic associated with the deformation of amorphous materials is the yield drop or the stress overshoot.[8,9] Nieh et al.[8] have shown that, in bulk metallic glasses, a significant yield drop is observed at lower temperatures and higher strain rates, but that this drop is virtually absent for samples tested at higher temperatures. This phenomenon has been attributed to redistribution of the excessive free volume by local atomic rearrangement during deformation. As a kinetic process, it is dependent on test temperature and strain rate.[10]

Another observation associated with mechanical deformation of amorphous materials is shear bands. The mechanical response of a glass at temperatures $<0.7T_g$ is generally characterized by the formation of localized shear bands, rapid propagation of these bands, and subsequent failure of the material.[6,8,11–14] Limited plasticity (only a few percent) is associated with the deformation process. However, in a recent work with amorphous ZrO_2–Y_2O_3, Gandhi and Jayaram[9] observed formation of shear bands on the sample surface, although their samples did not fail at strains up to 15%.

Results reported here were quite different from those in the literature for glassy materials and amorphous ceramics. First, stress overshoot was not observed in amorphous $AlPO_4$ based nano-composite. This absence may perhaps be because the temperature and/or strain-rate regimes used in the present study were not conducive to a yield drop because of redistribution of excessive free volume during deformation.[10] Moreover, only the sample tested at the lowest temperature failed, after 4% deformation; the samples deformed at higher temperatures did not exhibit any signs of deterioration up to 10% strain.

Second, as shown in Fig. 6, flow stresses for amorphous $AlPO_4$ based nano-composite were strongly dependent on the strain rate ($n = 2.2$–2.8), contrary to expectations for Newtonian flow ($n = 1$) observed in metallic glasses[8,10] or the observations of Gandhi and Jayaram in amorphous ZrO_2–Y_2O_3, for which flow stress showed no variance with strain rate ($n = 0$).[9] In metallic glasses[1,2,8,11,15] and amorphous ceramics,[12] at elevated temperatures ($T > 0.7T_g$), homogeneous deformation or Newtonian flow takes place, characterized by $n = 1$. However, at lower temperatures ($T < 0.7T_g$), non-Newtonian flow is observed.[8] Thus, non-Newtonian deformation behavior observed in amorphous $AlPO_4$ based nano-composite is indicative of flow characteristic of amorphous materials below $\approx 0.7T_g$.[8] For amorphous $AlPO_4$ based nano-composite, the n values of 2.2–2.8 are similar to the values found for metallic glasses by Nieh et al.[8] below $0.7T_g$. Nieh et al.[8] attributed the deviation from Newtonian flow to the presence of nanocrystalline phases in the amorphous matrix. These phases caused the vitreous matrix to respond as a dispersion-strengthened solid. Application of a mechanistic model yielded values of $n = 2$ and higher for non-Newtonian flow in amorphous materials.[8] Detailed TEM observations of the as-prepared amorphous $AlPO_4$ based nano-composite revealed the presence of carbon and $AlPO_4$ nanocrystalline phases (Fig. 3), which possibly explain the higher values obtained for the stress exponent.

Third, shear bands were not observed. This absence is most likely related to structural differences between amorphous $AlPO_4$ based nano-composite and typical glassy materials. For instance, unlike conventional glasses, sol–gel-derived amorphous $AlPO_4$ based nano-composite does not exhibit a distinct peak corresponding to its T_g during a differential scanning calorimetry analysis,[4] indicative of underlying differences in the structure between amorphous aluminum phosphate and glasses.

It is interesting to compare the creep resistance of amorphous $AlPO_4$ based nano-composite to those of commercial polycrystalline ceramics.[16–19] Fig. 7 shows the creep rates are in the same range as those of conventional oxides at 1200 °C. The experimental points correspond to the raw data and thus should be corrected because of the presence of significant porosity in the amorphous $AlPO_4$ based nano-composite samples. This correction will shift the experimental points to the right, corresponding to a level of creep resistance between those of mullite and coarse-grained alumina ceramics and those of ceramics that creep more readily, such as zirconia and fine-grained alumina. The relatively high creep resistance may be attributed to low oxygen diffusivity in the amorphous aluminum phosphate matrix (assuming creep is controlled by oxygen diffusivity) as evidenced by corrosion resistance properties of amorphous aluminum phosphates in oxidizing atmospheres.[5] Further, the creep properties were probably affected by the presence of the nanocrystalline second phases. To establish this, future deformation experiments

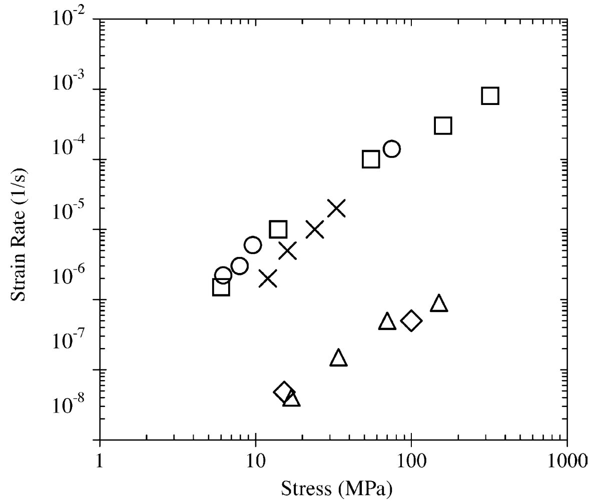

Fig. 7. Creep resistance of amorphous $AlPO_4$ based nano-composite compared with other high-temperature ceramics at 1200 °C ((×) $AlPO_4$ nano-composite, (□) Al_2O_3 (1 μm),[16] (△) Al_2O_3 (10 μm),[17] (◇) mullite (1.5 μm),[18] (○) Zirconia (0.3 μm)[19]).

are planned in which the density and size of nanocrystallites will be varied by modifying the processing conditions.

5. Conclusions

High-temperature compressive deformation of a sol–gel-derived amorphous $AlPO_4$ based nano-composite was investigated at 1200–1300 °C. Microstructural analyses revealed relatively high porosity of ≈15 vol.%. The majority of the pores were isolated and within the otherwise dense aluminum phosphate structure. TEM revealed carbon and $AlPO_4$ nanocrystallites dispersed in the amorphous matrix. Steady-state flow stresses ranged from 10 to 30 MPa and 50 to 70 MPa for test temperatures 1200 and 1300 °C, respectively. Steady-state flow stress was found to be dependent on the strain rate for strain rates of 5×10^{-6} to $2 \times 10^{-5}\,s^{-1}$. However, no strain hardening or softening was observed. Stress exponents were 2.2–2.8 for various test temperatures, indicative of a non-Newtonian flow. This non-Newtonian response was attributed to the presence of nanocrystalline phases. Deformation behavior exhibited distinct differences from typical amorphous materials reported in literature. These differences were possibly due to the structural in-homogeneities. The creep resistance of amorphous aluminum phosphate ceramic was similar to those of conventional high-temperature oxide ceramics.

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