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Abstract

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Comments

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Paraffin-Based Process for Producing Layered Composites with Cellular Microstructures

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A paraffin-based process that results in high-strength bimaterial ceramic layered composites is reported. The process facilitates rolling, folding, and shape retention at room temperature and allows the transition from a laminar to a cellular microstructure during deformation. The strength of sintered alumina/zirconia/alumina composites reached 700 MPa, higher than that of conventional zirconia-toughened alumina composites containing dispersed particles.

I. Introduction

CERAMIC powder suspensions containing paraffins are suitable for plastic forming and shaping. Paraffins (waxes) are hydrocarbons with low molecular weights and melting points. Therefore, their ceramic powder mixtures can be deformed at, e.g., 60°C, and solidified at room temperature. Debinding of these polymers is also relatively easy; it is typically conducted at no higher than 200°C.¹ For these reasons, industrial processes such as low-pressure injection molding have been using paraffin suspensions to produce ceramic parts. In fact, using paraffin oils can further reduce the deformation temperature, since paraffin oils belong to the same hydrocarbon series but have even lower molecular weights. The ceramic suspension thus obtained is both plastic and shape-retaining at room temperature. In this paper, we report on a paraffin-oil-based process that produces high-strength laminated composites of alumina and zirconia.

Our method incorporates deformation processing by the repeated folding and rolling of ceramic slurries. As reported by Chen and co-workers,^{2–4} a large variety of microstructures, from flat to wavy laminates to cellular composites, are obtainable in this way. This is because the relative viscosity of suspensions can affect the deformation stability of the interface, which leads to the entrapment of the rheologically harder phase in the softer matrix. The suspensions used in the previous work,^{2,5} however, cannot be deformed and solidified at the same temperature. Paraffin-based suspensions thus offer an attractive alternative solution.

II. Experimental Procedure

The starting powders in this work were high-purity alumina (A16, Alcoa, Pittsburgh, PA) and yttria-stabilized zirconia (TZ-3YS, Tosoh, Japan). The average particle size was 0.6 μm for the

alumina and 0.3 μm for the zirconia. They were first milled in an acetone solution of stearic acid (0.6–1.0 wt% with respect to powders) to condition the powder surfaces into hydrophobic ones. The powders were then dried at 120°C for 4 h.

Powder suspensions were prepared using a paraffin oil (Kemika, Zagreb, Croatia) as the main component of the liquid phase. Various amounts (20 wt% for alumina and 5 wt% for zirconia) of a low-melting-point (58°C) paraffin (INA 58/62, INA, Zagreb, Croatia) were added to the suspension to adjust the viscosity. In addition, a small amount (0.4 wt% with respect to the powders) of poly(ethylene glycol) (PEG 400, Merck, Germany) was used as a plasticizer. The initial suspensions were mixed at 80°C through a (water-heated) three-roller mill. After typically three to four passes, the suspensions acquired a stable viscosity because they became sufficiently homogeneous. Tapes of 1-mm thickness were then prepared from cooled suspensions using a twin-roller mill operated at room temperature. Laminates were obtained by rolling an initial stack of alumina/zirconia/alumina (AZA) composite tapes from 3 to 1 mm (66% reduction), followed by repeated folding and rolling at 50% reduction to maintain a constant thickness of 1 mm. For comparison, laminates of alumina/alumina/alumina (AAA) and zirconia/alumina/zirconia (ZAZ) were also prepared in an identical way. To facilitate handling during rolling, the laminate was placed between plastic carrier foils (PET 75, Richard E. Mistier, Inc., USA). Specimens of dimensions 25 mm × 4 mm × 1 mm were cut from the laminate tapes, which were subjected to debinding at 200°C for 2 h (heating rate = 0.5°C/min). Final sintering was performed at 1520°C in air for 4 h.

The viscosity of the suspension was measured with a rotational viscometer (HAAKE VT 500, Germany) at room temperature using the sensor Mode MV-1. Microstructural studies were performed using light microscopy. Strengths were measured in the four-point bending configuration using a servo-hydraulic testing machine (Instron 1362, USA). The reported strengths were taken from an average of five measurements.

III. Results and Discussion

Steady-state viscosity measurements at all strain rates shown in Fig. 1 verified that the paraffin-oil mixture containing a higher weight percent of paraffin is more viscous. Since the alumina slurry was prepared using a higher weight percent of paraffin, it should be harder than the zirconia slurry. Previous work on laminates found that, after a large deformation, the rheologically harder phase is preferentially trapped in a matrix of the softer phase. However, a complication arises if the volume fractions of the two phases are not equal, since there is a tendency for the minority phase to appear entrapped, which may or may not reflect the underlying mechanical stability. Therefore, to compare the deformation stability of our suspensions we prepared AZA and ZAZ laminates of 4 foldings. In the former case (Fig. 2(a)) the

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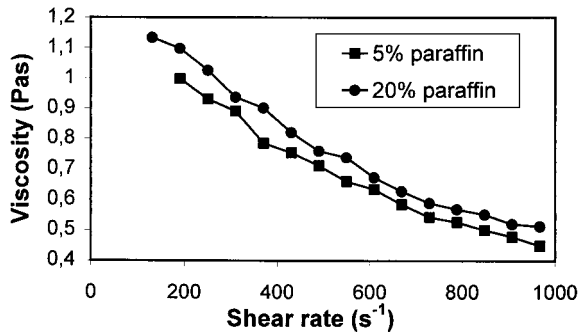


Fig. 1. Viscosity versus shear rate for liquid phases used for the preparation of alumina (20% paraffin + 80% oil) and zirconia (5% paraffin + 95% oil) suspensions.

minority (zirconia) layers remained contiguous, albeit some waviness developed along with shear banding, similar to that reported in the previous study.² In the latter case (Fig. 2(b)) the minority (alumina) layers are not contiguous. Instead, they have broken down in many places.

The above comparison suggests that the alumina suspension, which is harder, is less stable and tends to be entrapped. Such an effect is especially severe when alumina constitutes the minority phase. In contrast, when the softer zirconia phase is the minority phase, as in AZA composites, the layered structure is relatively stable. Examples of the latter are shown in Fig. 3(a) (after 6 foldings) and Fig. 3(b) (after 7 foldings). Note that in Fig. 3(a) the layer interfaces are highly corrugated but their long-range continuity remains intact, while in Fig. 3(b), discontinuities have appeared and isolated layers have become the main feature in this cellular microstructure.

The flexural strengths of the alumina/zirconia/alumina composites are significantly improved by repeated rolling and folding. As shown in Fig. 4, the initial strength is low. This is not surprising

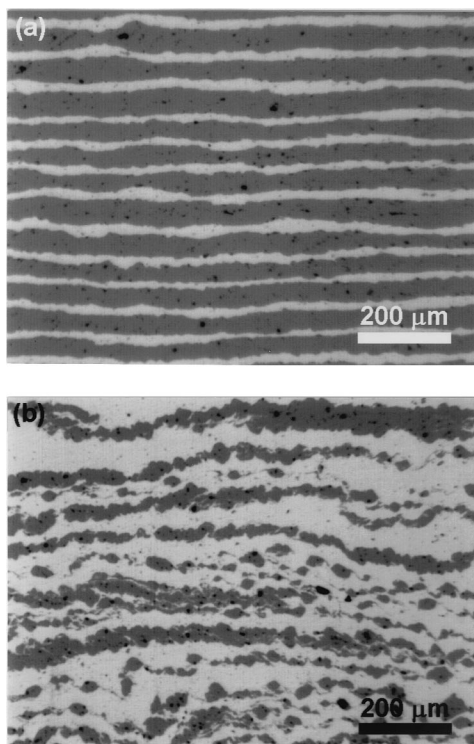


Fig. 2. Optical micrographs of sintered 4-times-folded AZA (a) and ZAZ (b) composites.

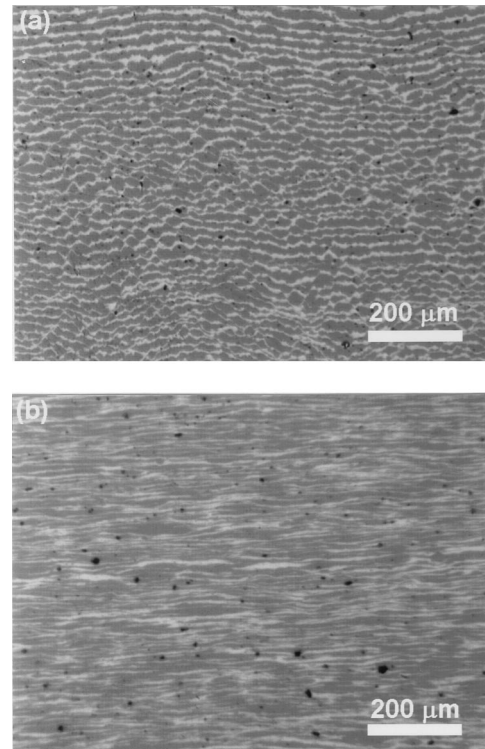


Fig. 3. Optical micrographs of sintered 6-times-folded (a) and 7-times-folded (b) AZA composites.

since sintering cracks are present for up to 3 foldings. The more dramatic improvement begins after 6 foldings, which coincides with the transition from corrugated, but still laminar, to a cellular microstructure, and the improvement continues with more folding and rolling. To determine whether this strength enhancement is unique to the composite, we compared it with the strength of AAA “laminates,” also shown in Fig. 4. In the latter materials, there is no sintering crack since only one phase is present, but there is no strength improvement either, despite repeated rolling and folding. (Air bubbles trapped in the suspension led to sintering pores and relatively low strengths.) Compared with AAA, the cellular composite at 8 foldings is more than 3 times stronger. This strengthening effect is much larger than what has been typically observed in conventional zirconia-toughened alumina composites containing a comparable amount of dispersed zirconia particles.⁶

Strength improvement due to rolling and folding of alumina/zirconia composites was also reported in the previous study of cellular composites.⁴ The most improvement was seen when the zirconia suspension was softer than the alumina suspension, which is consistent with the present result. The zirconia used in our work,

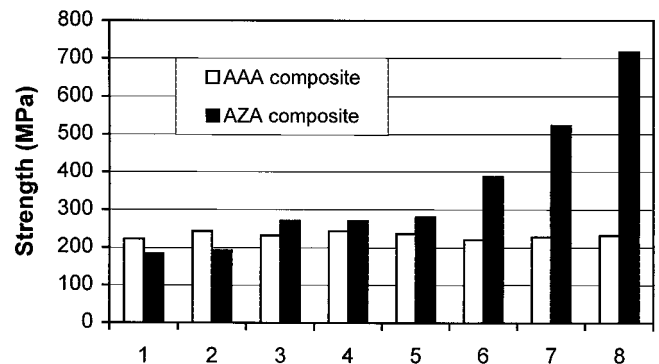


Fig. 4. Dependence of flexural strength of sintered specimens on number of foldings for AAA and AZA composites.

however, has a lower transformability than the one used in the previous study⁷ (CeO₂-stabilized zirconia), so the toughening effect of zirconia transformation is less pronounced (indentation toughness = 6.8 MPa·m^{1/2} at 8 foldings). A large strengthening effect may nevertheless arise because of grain size refinement. The largest alumina grains in the 8-times-rolled AZA composite is 2 μm in size, compared with 20 μm in the single-phase alumina, rolled or not. Large alumina grains are likely to be the controlling flaws in these ceramics. If so, a 10-fold decrease in the grain size could already cause a 3-fold increase in the strength, even with the same fracture toughness.

IV. Conclusions

- (1) A paraffin-oil-based process has been demonstrated for the preparation of alumina/zirconia laminates by rolling, folding, and shape forming at room temperature.
- (2) A transition from a laminar to a cellular microstructure, similar to the one previously reported in other slurry-based processes, has been confirmed after repeated deformation.
- (3) The strength of sintered alumina-rich composites reaches

700 MPa and is higher than that of conventional zirconia-toughened alumina composites containing dispersed particles of a similar composition.

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