Preparation of High-Strength Al–Mg–Si/Al₂O₃ Composites with Lamellar Structures Using Freeze Casting and Pressureless Infiltration Techniques

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Abstract Lamellar porous alumina scaffolds with the initial solid loadings of 20, 25, and 30 vol% were prepared by freeze casting using 5 µm alumina powders. With the addition of 3 wt% MgO–Al₂O₃–SiO₂ nanopowders in a eutectic composition as sintering aid, the maximum compressive strength of the sintered scaffolds reached (64 ± 2) MPa after sintering at 1,773 K for 2 h. The lamellar porous scaffolds were then filled with a molten Al–12Si–10 Mg alloy (in wt%) by pressureless infiltration at 1,223 K in a N₂ atmosphere, yielding the shell-like structure of the composites. The compressive strength of the upper part composite with the initial 30 vol% solid loading reached (1,190 ± 50) MPa, which was about 3.5 times as large as that of the matrix alloy.

KEY WORDS: Biomimetic; Metal-matrix composites; Porous materials

1 Introduction

Porous ceramics have attracted a great deal of attention due to their wide applications in industrial and biological fields. Recently, there has been great interest in the production of novel porous ceramics using freeze casting. Deville et al. reviewed the process and key factors for preparing lamellar ceramics by freeze casting, and suggested that shell-like biomimetic composites could be prepared by infiltrating alloys or polymers into porous ceramic scaffolds, in which the hard and ductile phases were alternately arranged and thus the strength and toughness of the composites could be substantially improved [1–3].

Based on this idea, Launey et al. [4] prepared the composites by infiltrating an Al–12.6 wt% Si alloy into a 36 vol%

porous Al₂O₃ body with lamellar structures at 1,173 K using gas pressure infiltration, which exhibited fracture toughness of 40 MPa m^{1/2} and tensile strength of 300 MPa. Similarly, Roy fabricated the composites by squeeze casting of an Al–12Si alloy into a 44 vol% alumina scaffold at 1,073 K. The average compressive strength of the composites was reported to be 688 MPa along the freezing direction [5]. Up to date, such work is still very limited and almost all the previous studies used sub-micron (300–700 nm) powders to prepare the porous alumina scaffolds by freeze casting, and employed pressure infiltration techniques to fabricate the shell-like biomimetic composites, making the fabrication cost high and processing complex.

In this work, we used micron-sized powders to prepare lamellar porous alumina scaffolds by freeze casting. The strength of the sintered scaffolds was improved by adding a small amount of MgO–Al₂O₃–SiO₂ nanopowders in a eutectic composition (hereafter abbreviated as MAS) into water-based slurries as sintering aid. Finally, the Al–Mg–Si/Al₂O₃ composites were fabricated by pressureless infiltration. The experimental procedure and equipment are very simple and the raw materials are cost-effective. Moreover, the composites exhibited much higher

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compressive strength as compared with that reported by Roy [5].

2 Experimental procedure

Lamellar porous alumina scaffolds in dimensions of ϕ 15 mm $\times$ 20 mm were fabricated by freeze casting using an apparatus similar to that reported in Ref. [6]. Commercially available alumina powders with a purity of 99.9 wt% and an average particle size of 5 μ m were used as raw material. Following the MgO–Al₂O₃–SiO₂ phase diagram, a mixture (3 wt% of all the powders) of the MAS nanopowders (30 nm) in a eutectic composition of 25:21:54 in weight ratio was added into water-based slurries as sintering aid. Alumina suspensions with 20, 25, and 30 vol% solid loadings were prepared using 1 wt% sodium polymethacrylate as dispersant. The slurries were ball-milled for 12 h using alumina balls and de-aired by stirring in a vacuum desiccator, then poured into Teflon molds and kept at 263 K for directional solidification by heat conduction through a Cu bar, whose end was immersed in liquid N₂. After demolding, the frozen samples were freeze-dried for 24 h under a 10 Pa vacuum at 223 K. The resulting bodies were then sintered in air at 1,773 K for 2 h with heating and cooling rates of 5 K/min.

The alumina scaffolds were subsequently infiltrated with a molten Al–12Si–10 Mg alloy using a pressureless infiltration technique [7, 8]. The furnace was first evacuated to a vacuum less than 100 Pa, purged with high-purity (99.999%) N₂, and then heated to 1,223 K at a rate of 5 K/min in a flowing N₂ atmosphere (flow rate 3 L/min). After holding at 1,223 K for 2 h, the furnace was cooled at 5 K/min. The resultant composites were sectioned from the middle part and finally cut into 5 mm $\times$ 5 mm $\times$ 10 mm specimens for compression test under the load paralleled to the freezing direction.

The viscosity of the slurry was investigated by using a viscometer (DV-79+PRO, NiRun Co. Ltd., Shanghai, China). The porosity of the samples was calculated by measuring their dimensions and weight. The microstructures of the sintered scaffolds and the composites were characterized by optical microscopy (Axio Imager A2m, Carl Zeiss, Germany) and scanning electron microscopy (SEM, Evo18, Carl Zeiss, Germany). The phases in the composites were identified by X-ray diffraction (XRD, D/Max 2500PC Rigaku, Japan). The compression property was tested using an Instron 5689 universal testing machine (Instron Corp., USA) under a strain rate of 3×10^{-4} s⁻¹.

3 Results and Discussion

Because the viscosity and rheological property of slurry play a significant role in controlling the growth of ice

Fig. 1 Variation in the viscosity of the alumina slurries with 20, 25 and 30 vol% initial solid loadings with shear rate

crystal, they were measured for the alumina slurries with the initial solid loadings of 20, 25, and 30 vol% and the results are shown in Fig. 1. The viscosities were 0.623, 1.053, and 1.319 Pa s, respectively, at a shear rate of 100 s⁻¹ and they decreased with increasing shear rate, showing shear-thinning behavior. Although the viscosity increased with the increase in the initial solid loading, it was much smaller than 5 Pa s, and thus the slurries were suitable for mold filling and subsequent freezing casting [9]. If the viscosity was too high, the alumina particles would be difficult to be rejected by the growing ice crystals to form an aligned lamellar structure. After the slurries were frozen, the samples were demolded, freeze-dried, and then sintered to produce the alumina scaffolds. It was found that all the scaffolds exhibited a certain degree of shrinkage after sintering at 1,773 K for 2 h. The porosities in the samples with the initial solid loadings of 20, 25, and 30 vol% were determined to be $(69 \pm 1)\%$, $(66 \pm 1)\%$, and $(59 \pm 1)\%$, respectively.

Figure 2a–e shows the microstructures of the horizontal and vertical sections of the sintered Al₂O₃ preform with the initial solid loading of 30 vol%. Lamellar structures are obvious, particularly in the regions from the middle to the top part. However, those in the lower part are less developed due to a larger freezing velocity, as explained in the following.

The microstructure in the vertical section of the Al–Mg–Si/Al₂O₃ composite is shown in Fig. 2f. Clearly, the resultant composite inherited the lamellar structure of the Al₂O₃ preform. In the presence of both Mg and N₂, the spontaneous infiltration of the Al–Mg–Si alloy into the alumina scaffold could readily occur. The mechanism could be summarized as follows. First, at elevated temperatures, the Mg in the Al alloy evaporated and reacted with nitrogen in the furnace to form Mg₃N₂, which coated the alumina particles in the lamellar scaffold. Then Mg₃N₂ reacted with Al in the liquid alloy, yielding AlN and Mg.

Fig. 2 Microstructures of the sintered Al₂O₃ preform with 30 vol% initial solid loading and the Al-Mg-Si/Al₂O₃ composite. **a–d** Horizontal sections at different locations away from the bottom rod; **e** Vertical section of the entire preform; **f** Vertical section of the Al-Mg-Si/Al₂O₃ composite (in the upper part); **g** XRD pattern of the Al-Mg-Si/Al₂O₃ composite

The formation of AlN greatly reduced the solid–liquid interfacial energy, improved the wettability between the molten alloy and the ceramic, and thus the spontaneous infiltration was initiated [8, 10]. On the other hand, the Mg in the alloy could be recycled, acting as a catalyst. The

presence of the AlN phase in the composites was demonstrated by the XRD examination, as shown in Fig. 2g, even though its formation could also result from the direct reaction between Al and the N atoms dissolved in the molten alloy at high temperatures [11].

Fig. 3 Influence of initial solid loading on the wavelength (λ) **a**, wall thickness (δ) **b** of the alumina scaffolds at different locations

Figure 3 shows the variations of the wavelength (λ) and wall thickness (δ) of the alumina scaffolds as a function of the distance away from the bottom rod along the freezing direction. Both λ and δ increase with increasing distance. This behavior can be explained by the fact that the evolved ice reduced the temperature gradient in the remaining unfrozen slurries since it was a poor conductor of heat, giving rise to the decrease in the freezing velocity and thus resulting in larger λ and δ from the bottom to the top. In addition, as indicated in Fig. 3, the wavelength decreased while the wall thickness increased with increasing initial solid loading at the same distance away from the cold finger (i.e., the bottom surface). For instance, the average wavelength at the top layer of the alumina scaffolds with the initial solid loadings of 20, 25, and 30 vol% was 105, 94, and 85 μm , while the corresponding wall thickness was 30, 57, and 71 μm , respectively. It can be attributed to the fact that the freezing velocity increased with the increase in the initial solid loading because of smaller amount of water, and the resistance to the growth of the ice crystal became stronger due to the larger viscosity of the slurry, leading to the smaller wavelength; likewise, during freezing, more amount of the alumina particles were pushed to the region between the ice crystals, yielding larger wall thickness.

Figure 4 shows the magnified images of the Al–Mg–Si/ Al_2O_3 composite with 25 vol% initial solid loading at an intermediate height as well as the elemental mapping graphs. The dark phase is alumina and the bright phase is the matrix alloy. The interfacial bonding between the Al_2O_3 skeleton and the Al matrix is fairly good. Some liquid even infiltrated into the alumina skeleton and filled small pores (see Fig. 4b), indicating good wettability. As seen from the mapping graphs, the concentration of Si in the lamellar metallic layer is much higher than that of Mg, suggesting that a considerable amount of Mg evaporated or

diffused outwards. The deposition of the Mg vapor inside the alumina skeleton may also trigger the liquid infiltration along the crevice between the alumina particles.

Figure 5 shows the compressive property of the sintered Al_2O_3 preforms and the Al–Mg–Si/ Al_2O_3 composites when they were compressed along the freezing direction. Both the porous preforms and the upper parts of the composites exhibit a remarkable increase in the strength with increasing initial Al_2O_3 loading. For the preforms with 30 vol% initial solid loading, the strength reached (64 ± 2) MPa. For the corresponding composites, it reached $(1,190 \pm 50)$ MPa with a strain of $(4.6 \pm 0.5)\%$. The strength is about 3.5 times as large as that of the matrix alloy and about 500 MPa higher than that reported by Roy [5], who used a squeeze casting technique to force the Al–12Si alloy into a 44 vol% alumina scaffold at 1,073 K.

The high strength obtained in our composites was presumed to result from the following reasons. First, the use of Mg-containing Al alloy improved the wettability and the formation of MgAl_2O_4 and MgO phases was likely to enhance the interfacial bonding between the Al alloy and the alumina particles (see Fig. 2g). Second, the formation of the AlN and Mg_2Si phases (Fig. 2g) strengthened the Al alloy. Third, the use of the pressureless infiltration technique reduced the damage to the lamellar structure of the alumina preforms, thereby benefiting to increase the strength of the resultant composites. By comparison, the high pressure employed in the squeeze casting damaged the lamellar structure of the preforms, as shown in Roy's work [5], decreasing the strength of the composites.

It is noted that the compressive strength of the composites in the upper part was much larger than that in the lower part, which is supposed to relate to the integrity of the lamellar structure and the amount of the defects in these two parts. As shown in Fig. 6, the alumina lamellae were

Fig. 4 SEM image of the Al-Mg-Si/Al₂O₃ composite with 25 vol% initial solid loading at the intermediate height **a**, the magnified image of the framed area in **a** **b**, and the elemental mapping graphs of elements Mg **c**, Al **d**, Si **e**, O **f** corresponding to **b**

Fig. 5 Variations in compressive stress with strain for the sintered Al₂O₃ preforms **a**, the Al-Mg-Si/Al₂O₃ composites **b** with different initial solid loadings

thicker and more continuous in the upper part than those in the lower part. Moreover, the defects such as pores or incompletely filled areas increased with the reduction in the distance to the bottom layer, which may significantly decrease the strength of the composite during the compression. If these defects were eliminated, superior properties could be also achieved in the lower part of the composites.

Despite the fact that the composites in a continuous lamellar structure could effectively support loads when they were compressed along the freezing direction, all the composites seemed to fail in a catastrophic brittle manner, without any plastic deformation (Fig. 5b). Figure 7 shows the fracture surfaces of the composites with different alumina loadings. Clearly, all the composites exhibit brittle fracture morphology. With the increase in the

Fig. 6 Optical micrographs showing the lamellar structures in the different regions of the Al–Mg–Si/Al₂O₃ composite with 25 vol% initial solid loading: **a** upper part; **b** middle part; **c** lower part

Fig. 7 Fractographs of the Al–Mg–Si/Al₂O₃ composites with different Al₂O₃ loadings: **a** 20 vol% (upper part); **b** 25 vol% (upper part); **c** 30 vol% (upper part); **d** 30 vol% (lower part)

alumina volume fraction, the relatively bright and flat fracture areas increase. The relatively dark metallic layers show cleavage fracture instead of dimple morphology (see inset a1 in Fig. 7a). Nevertheless, the metal–ceramic interface seems quite strong since there is no visible crack, as shown in the inset a2 in Fig. 7a. It was presumed that both the metallic and ceramic phases shared the load simultaneously at the beginning of the compression, but once the metallic phase started to deform plastically, the load was transferred to the ceramic phase,

and the latter acted as a main supporter until fracture occurred. The maximum strength of the composite is dependent not only on the alumina initial loading and the interfacial bonding, but also on the structural integrity of the lamellar layers as well as the defects in the composites. Because of more defects and discontinuous lamellae in the lower part of the composites, the strength was considerably lowered down even though the alumina volume fraction was larger, which consequently led to a more brittle fracture surface, as shown in Fig. 7d.

4 Conclusions

Lamellar porous alumina scaffolds with the initial solid loadings of 20, 25, and 30 vol% were prepared by freeze casting water-based slurries using 5 μm alumina powders and 3 wt% MAS nanopowders as sintering aid. The maximum compressive strength of the sintered scaffolds reached (64 ± 2) MPa. The porous scaffolds were then infiltrated with an Al–12Si–10Mg alloy using pressureless infiltration. The resultant composites exhibited high compressive strength up to 1,200 MPa in the upper part but much smaller values in the lower part, and they all failed in a catastrophic brittle manner during compression.

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