Introduction

The seeking after more-efficient energy-related technologies necessitates the development of lightweight, high-performance structural materials with exceptional strength and ductility [1]. Nanostructured metal matrix composites (MMCs) are being considered for a range of structural and non-structural applications because of their high specific strength and high fatigue resistance [2]. However, for nanostructured metal-matrix composites (MMCs), reduced ductility and lower energy-absorbing capabilities [2] are often obtained in comparison with monolithic materials, which is an obvious drawback to their practical applications. One approach in the quest for the design of strong and ductile materials is to heed the examples of Nature that creates hierarchical hybrid composite such as nacre or bone. Nacre is a remarkable biological composite that has gained tremendous interest as model system for materials science, in which ordering nanolaminated structures with alternating the protein collagen layers (10-50 nm thick) and aragonite tablets (200-900 nm thick) forming in a self-assembled manner [3]. Gao et al. had found that a key factor for the excellent properties of the natural materials is the nanometer-thickness laminated structures, which failure at the theoretical strength, irregardless of the presence of any flaws[4]. For this reason, there is an increasing effort to artificially create bio-mimetic similar nano-laminated structures. Our prospect is extending natural biological design to develop new synthetic metal matrix composites (MMCs). This is a challenge that requires the development of fabrication procedures to implement these designs.

A recent breakthrough was due to Deville et al. [1, 5] who developed a freeze-casting process to fabricate porous, layered bulk ceramic-matrix composites. This process offers a large number of material combinations and a wide range of dimension control. However, the product is intrinsically porous and needs to be filled with a second phase to make a composite material, and more importantly the thickness ceramic layer still much coarser than the scale of the mineral plates in the nacre (about 500nm)[5]. Accumulative Roll bonding (ARB) [6] and nanostructured multilayer techniques such as physical or chemical deposition [7] are feasible methods to obtain submicron lamellar thicknesses in MMCs, but these methods are inherently laborious and time-consuming, thus are restricted to the fabrication of miniature sized sheets and films [8].

Herein, we report a simple, quick, and mass-producing approach called “Flake Powder Metallurgy” (Flake PM), in which Al flake powders with native Al₂O₃ skins are used as building blocks to self-assemble into nanolaminted composites, giving rise to strong and ductile composite with tensile strength of 262 MPa and plasticity of 22.9%.

Keywords: Metal matrix composites; Nanostructure; Layered structures; Flake powder.
be forced to order into astonishingly well-aligned macroscopic assemblies even under common and time-efficiency processes, such as hot-pressing and extrusion. The primary result shows that using the Flake PM route, Al$_2$O$_3$/Al nanolaminated composites with enhanced tensile plasticity of 22.9% at strength of 262 MPa can be achieved.

2 Experimental

In a typical Flake PM process, three steps were involved: (i) Flake powders' preparation. The flake Al powders can be easily obtained by micro-rolling (ball-milling) the spherical powder. (ii) In-situ introduced Al$_2$O$_3$. The as-prepared flake powder was heated in flowing Ar atmosphere at 400°C for 1 h to remove all stearic acid from the powder and then kept in air atmosphere at room temperature for several days to grow a native Al$_2$O$_3$ membrane. (iii) Flake powder alignment and consolidation. Compacting was used to align the flake powders into column (Φ40 mm×30 mm) under 500 MPa pressure. As illustrated in Fig.1, the flake powders with a native Al$_2$O$_3$ membrane tend to lie flat on each other in an irregular manner with the reason that potential energy is minimized under self-gravitational force and/or the applied force fields, as the leaves fall and spread flatly on the ground due to the gravity. Sintering in flowing Ar atmosphere at 630°C for 2 h and hot extrusion at 400°C with an extrusion ratio of 20:1 at a ram speed of 0.5 mm/min were conducted to consolidate the flake powders. The details of these steps can be obtained in our previous work [9].

The nanolaminated structure was characterized by field emission scanning electron microscopy (FESEM) using a LEO Supra 55 FESEM and high-resolution transmission electron microscopy (HRTEM) in a Philips CM200 microscope operated at 200 kV. The phase of Al$_2$O$_3$ in composite was analyzed by X-ray diffraction (XRD, Rigaku, and CN2301) with a Cu Ka radiation source. The chemical compositions of the flake powders and extrusion rods were analyzed using inductively-coupled plasma-optical emission spectroscopy (ICP) to determine the amount of oxide layers. To evaluate the tensile strength, specimens were machined from the extruded rods with the tensile axis parallel to the extrusion direction. The gauge length of the specimens was 25 mm, and the diameter was 5 mm. The tensile strength was measured by a universal testing machine at an initial strain rate of 5×10$^{-4}$ s$^{-1}$ at room temperature (AUTOGRAPH AG-I 50 KN, Shimadzu Co. Ltd., Japan).

3 Results and Discussions

As seen from Fig.2a, the as-received spherical Al powders have a 3-D spherical morphology which has a random stacking mode. While, the as-prepared flake Al powder has a 2-D planar morphology with an average diameter of 70μm, thus giving a large aspect ratio of 140 (diameter to thickness) as shown in Fig.2b. Additionally, due to the using of stearic acid during ball milling, the flake powders tend to be individual platelets after ball milling, as seen in Fig.2b, which is helpful for the alignment and consolidation of flake powder. By zooming in such a flake powder, we can see that there exists a very thin outer Al$_2$O$_3$ layer in a quite different contrast with the Al core as shown in the inset of Fig.2b. As seen in Fig.2c-d, the compacting column of flake powders exhibit structure with a strikingly strong alignment of flake powders, and the high-resolution SEM image (Fig.2d) reveals well defined and highly aligned self-assemblies with a periodicity of 500-600 nm.

A typical optical microscopy (OM) of the extrusion composite shows the overall microstructures in the vertical (extrusion) directions. As can be seen in Fig.3a, the vertical section shows that all the platelets are organized with their faces parallel to extrusion direction. So, the highly-ordered nanolaminated structure was well maintained after consolidation. The Al$_2$O$_3$ layers were so thin that it is hard to be observed at SEM or OM images. However, from TEM image (Fig.3b), the extruded multilayer structures with alternating Al (300-500nm) and Al$_2$O$_3$ (about 10nm) layers can be successfully observed from the vertical section of extrusion samples.

The tensile stress-strain curve of the Al$_2$O$_3$/Al nanolaminated composites is shown in Fig.4, which displays a plasticity of 22.9% at tensile strength of 262 MPa. What’s more important, the Al$_2$O$_3$/Al nanolaminated composites have a uniform elongation of 16.5%, much higher than the critical ductility (5%) that required for many structural applications. It is supposed that such a remarkable
uniform elongation should come from the nanoscaled Al$_2$O$_3$ layers that characterize the laminated structure. The nanoscaled Al$_2$O$_3$ layers may act to hinder the recovery and recrystallization processes of Al matrix, thus significantly increase the strain hardening capacity. The ductile failure of the Al$_2$O$_3$/Al nanolaminated composites can also be seen from the fracture surface shown in the inset of Fig.4, the elongated dimples exhibited a size about 300-500nm, which is similar to the thickness of laminated Al layers.

A better appreciation of the unique mechanical properties of the Al$_2$O$_3$/Al biomimetic nanolaminated composites can be gained by comparing with those fabricated by severe plastic deformation (SPD), such as equal channel angular pressing (ECAP) [10] and friction stir process (FSP) [11]. The room temperature tensile properties of Al$_2$O$_3$/Al composites by different process are summarized in Tab.1. It is interesting to observe that ultrafine grained Al fabricated by ECAP (Ref. [10]) has a very low uniform elongation (strain before necking), less than 1%. The low uniform elongation of ultrafine grained and nanocrystalline metals has been argued to be a result of diminishing strain hardening capacity and insufficient strain rate hardening due to the intrinsic difficulty in keeping dislocations inside the tiny grains [11]. Strengthening metallic materials without a substantial degradation of strain hardening capacity can also be achieved by FSP or HPT. For example, Ref. [11] inserted 1.5 vol% α-Al$_2$O$_3$ dispersoids (~30nm) homogeneously into pure Al by FSP to significantly increase work hardening, and thus tensile elongation was enhanced. Although remarkable success has been achieved to enhance tensile elongation in laboratory-scale models by HPT or FSP, it remains difficult to foresee the potential industry applications due to time-consuming or energy-intensive processes. Compared with the reported SPD methods, the novel approach of the Flake PM described in this research is simple, feasible and applicable for mass-production.

4 Conclusions

In summary, utilizing nature’s solution for strong and ductile design, we developed an upgraded Flake PM technique route to fabricate bulk metal matrix composites with a refined nanolaminated structure over large-scale dimensions. The resulted Al$_2$O$_3$/Al biomimetic composites exhibited excellent combinations of strength and ductility, which indicates that the proposed flake powder metallurgy is very effective for fabricating biomimetic nanolaminated metal matrix composite with well balanced mechanical properties. At present, our materials contain too little of the hard phase, and our metal layer thicknesses are still somewhat coarse. Indeed, an increase in the hard phase content and refinement of the metal layers should improve strength and provide additional nanoscale toughening mechanisms similar to those acting in natural materials. In this regard, our current studies are focused on the development of bio-mimetic structures with much higher hard phase content, the manipulation of the properties of the soft metal phase, and extending this concept to other alloy composites.

Acknowledgment

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References


Table captions

**Table 1.** Room temperature tensile properties of Al₂O₃/Al composites.

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Figure captions

**Figure 1.** Self-assembly strategy toward the preparation of Al₂O₃/Al biomimetic nanolaminated composites by Flake PM.

**Figure 2.** FESEM of: (a) spherical Al powder; (b) flake Al powder, inset shows the native Al₂O₃ skin on the Al surface; (c) self-assembled nanolaminated structure; (d) magnification image of (c).

**Figure 3.** The microstructure of Al₂O₃/Al nanolaminated composites: (a) optical microscopy images for the vertical direction of the extrusion rod (b) TEM images to show laminate structure.

**Figure 4.** Tensile properties of Al/Al₂O₃ nanolaminated composites, inset shows the fracture surface after tensile testing.
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