Multi-phase Al-based ultrafine composite with multi-scale microstructure

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A new class of Al-base multi-phase ultrafine composites with multi-scale microstructure, which exhibits high strength and large compressive plasticity at ambient temperature, has been developed in the Al–Cu–Si ternary system. The formation of the favorable multi-phase multi-modal structure can be achieved by proper alloy selection and by controlling the solidification process. The developed hierarchical ultrafine composites exhibit high fracture strength of ~1 GPa and large compressive plasticity up to ~25%. The large macroscopic plastic strain is attributed to the combination of dislocation-based slip deformation in the ductile phase and extensive shear banding in the intermetallic phase.

1. Introduction

The mechanical properties of nanostructured materials and bulk metallic glasses are of considerable interest at present [1,2]. Such materials have revealed many attractive characteristics, such as high strength, high hardness and low elastic limit [3,4]. However, low ductility is also frequently reported for these materials [5,6]. For applications, it is imperative to design (nano)structures that deliver not only high strength, but also adequate plasticity. The available experimental and theoretical studies show that the low ductility of nanostructured materials is due to their defect in dislocation activity [7,8]. Recently, nanostructured Al alloys with a microstructure containing multiple length scales have demonstrated an excellent combination of strength and ductility [9,10]. However, in this case, complex and multiple manufacturing processes are required [11]. At the same time, monolithic Al-based metallic glasses with high strength and distinct plasticity have been developed [12]. Meanwhile, multi-phase alloys with multi-scale microstructures including nanometer length scale structural features have been sparsely studied as engineering materials. It is generally assumed that although such alloys may give very high strength, they exhibit very little ductility and poor fracture toughness at room temperature. In recent time interest in complex multi-phase materials has emerged due to the finding that it is possible to design microstructures through nonequilibrium processing routes to overcome some of these deficiencies [13–17]. Moreover, eutectics constitute an exciting multi-phase approach where self-evolution of the patterns occurs by arrangement of distinctly different phases during growth [18]. It is possible to modify both the length scales and the patterns themselves by tuning the growth conditions [19,20]. At nanometer length scale, the nano-eutectics exhibit very high strength and some current reports indicate also large ductility in special cases [21,22]. However, the understanding of the properties of multi-scale multi-phase composites with nanometer length scale structural features is still in its early stage [23].

The primary aim of this study was to synthesize high strength multi-phase alloys based on aluminum with adequate plasticity by producing a multi-scale microstructure including nanometer length scale eutectics and to evaluate their deformation behavior. The alloy design has been explored to obtain novel and enhanced properties for Al–Cu–Si ternary alloys. The aluminum-rich corner of the Al–Cu–Si phase diagram has a very simple constitution with no ternary compounds [24]. Also, the very low solubility of the constituents in aluminum allow for tailor-made material design by tuning the alloy chemistry and the solidification. Following these lines, we have been successfully developed novel hierarchical ultrafine Al-base composites with extraordinary strength of GPa level and plasticity up to ~25% in compression. The mechanical properties are correlated with the microstructural features of the Al–Cu–Si alloys and the deformation mechanisms will be discussed in detail.
2. Experimental

The Al–Cu–Si alloys (Al83Cu17, Al81Cu13Si6 and Al79Cu15Si6) were prepared by arc-melting of the high purity (99.99 wt.%) elemental constituents under an Ar atmosphere. Cast samples were produced by injection casting into a copper mould with a cylindrical cavity with 1 mm diameter and 50 mm length. Microstructural analyses of the as-cast and deformed samples were performed by scanning electron microscopy (SEM, Hitachi, S-2700). X-ray diffraction (XRD; Rigaku CN2301, monochromatic Cu Kα radiation) and transmission electron microscopy (TEM; JEM 2100F) coupled with energy-dispersive x-ray analysis (EDX, Oxford instrument INCA system) were used for structural characterization and phase identification. The TEM samples were prepared by conventional ion milling (PIPS, Gatan Model 600). The room temperature mechanical properties were evaluated by uniaxial compression tests using an Instron-type machine. Cylindrical specimens with a 2:1 aspect ratio were prepared and tested at a strain rate of $1 \times 10^{-4}$ s$^{-1}$.

3. Results and discussion

Fig. 1 shows the XRD patterns (a) and SEM secondary electron micrographs (b)–(d) of the as-cast Al–Cu–Si alloys. The XRD pattern of the binary Al83Cu17 alloy can be identified as a mixture of a face-centered cubic (f.c.c.) α-Al solid solution (Fm3m, $a = 0.4039$ nm) and a body-centered tetragonal (b.c.t.) θ phase (Al2Cu) ($I4/mcm$, $a = 0.6064$ nm and $c = 0.4873$ nm). The ternary alloys (Al83Cu12Si6 and Al85Cu9Si6) exhibit additional peaks corresponding to a diamond cubic (d.c.) Si phase ($Fd3m$, $a = 0.543$ nm) besides the reflections of the α-Al solid solution and θ phase (Al2Cu) phases [25]. The SEM micrograph of the Al83Cu17 alloy shown in Fig. 1(b) displays a typical regular lamellar eutectic structure, in which two phases are arranged in an alternating fashion with a lamellar spacing of 200–300 nm. The ternary alloys exhibit a significantly different morphology. As shown in Fig. 1(c), the overall microstructure of the Al81Cu13Si6 alloy clearly displays a bimodal eutectic structure with length scale heterogeneity. The micrometer-scale cellular eutectic phases are evenly distributed in a nanostructured matrix (anomalous ternary eutectic). For the cellular eutectic region with spherical morphology, the volume fraction, the average colony size and the lamellar spacing are 75–85 vol.%, 10–20 μm and 300–700 nm, respectively. Fig. 1(d) shows a hierarchical complex structure consisting of coarsened dendritic phases and bimodal eutectics with different length scale (Al85Cu9Si6). EDX analysis reveals similar compositions for both the overall lamellar eutectic region (Al83Cu17) and the ultrafine cellular eutectic region (Al83Cu12Si6 and Al85Cu9Si6), whereas the complex nanostructured matrix region (Al83Cu12Si6 and Al85Cu9Si6) is enriched in Si, indicating the presence of a Si-containing phase in the nanocrystalline matrix. Moreover, analyzing the individual alternating phases within the cellular eutectic region of the Al81Cu13Si6 and Al85Cu9Si6 alloys reveals that the bright phase is

![Fig. 1. XRD patterns (a) and SEM secondary electron micrographs (b)–(d) of the as-cast Al–Cu–Si ultrafine composites: (b) Al83Cu17, (c) Al83Cu12Si6, and (d) Al85Cu9Si6, respectively. The inset in (c) shows the BF TEM image of the nanostructured matrix region.](image-url)
enriched in Cu and the dark phase is enriched in Al, respectively. Similarly, the coarsened primary phases in Al85Cu9Si6 are enriched in Al. From the phase and microstructural analyses (XRD, SEM and EDX), one can conclude that the alternating dark and bright phases in the cellular-type eutectic of the ternary alloys are related to the α-Al solid solution and the θ phase (Al5Cu), respectively, whereas the nanostructured matrix contains very fine and complex multiple phases including the d.c. Si phase. The bright-field (BF) TEM image of the nanostructured matrix (inset in Fig. 1(c)) shows three interlocked phases [bright contrast: Si, gray contrast: α-Al, and dark contrast phase: θ]. In addition, EDX analysis reveals that the average compositions of the α-Al and θ phases of the cellular eutectic are Al97.6Cu2.4 and Al66.5Cu33.5, and the gray contrast (α-Al), dark contrast (θ) and bright contrast (Si) phases are Al96.8Cu2.7Si0.5, Al63.8Cu35.4Si0.8 and Al5.7Cu6.1Si88.2, respectively.

Fig. 2 displays the room temperature engineering stress-strain curves of the as-cast samples and the corresponding mechanical properties are summarized in Table 1. The Al83Cu17 alloy, which has a completely ultrafine-scale lamellar eutectic structure, exhibits ultrahigh yield (σy: ~1.0 GPa) and ultimate fracture (σf: ~1.2 GPa) strength with very limited plastic strain (εp: ~2%). On the contrary, the Al81Cu13Si6 and Al85Cu9Si6 alloys with multi-modal microstructure distribution present a lower yield strength (σy: ~0.8 GPa) and ultimate fracture strength (σf: ~1.1 GPa), but significantly increased plastic strain (εp: ~20 ± 5%). This reveals the crucial impact of the microstructural features on the mechanical properties of the Al–Cu–Si alloys.

In order to investigate the plastic deformation of the multi-phase ultrafine composites with multi-scale microstructure in more detail, interrupted compression tests were carried out at different levels of strains. The BF TEM micrograph shown in the inset of Fig. 3(a) clearly reveals the multi-phase microstructure with different length scale features, composed of micrometer-size α-Al dendrites, ultrafine-scale cellular eutectic (α-Al + θ) and nanometer-scale anomalous ternary eutectic, as marked by the squared region, (α-Al + θ + Si). This is in good agreement with

![Fig. 2. Room temperature compressive stress-strain curves obtained for the Al–Cu (–Si) ultrafine composites.](Image)

![Fig. 3. Stress-strain curves for each interruption during compression testing of the Al85Cu9Si6 hierarchical composite (a) and corresponding SEM secondary electron micrographs (b) and (c) obtained from the surface of the deformed Al85Cu9Si6 sample: (b) 8% deformed, (c) 25% deformed samples; The inset shows the BF image of the as-cast microstructure.](Image)

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>Microstructure</th>
<th>ρ (g/cm³)</th>
<th>σy (MPa)</th>
<th>σmax (MPa)</th>
<th>εp (%)</th>
<th>εf (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al83Cu17</td>
<td>Lamellar eutectic</td>
<td>3.43 ± 0.05</td>
<td>1024 ± 26</td>
<td>1200 ± 75</td>
<td>2.1 ± 0.1</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>Al81Cu13Si6</td>
<td>Bimodal eutectic</td>
<td>3.21 ± 0.05</td>
<td>890 ± 14</td>
<td>1149 ± 40</td>
<td>2.2 ± 0.1</td>
<td>11.4 ± 3</td>
</tr>
<tr>
<td>Al85Cu9Si6</td>
<td>Multimodal eutectic</td>
<td>3.02 ± 0.06</td>
<td>800 ± 9</td>
<td>1047 ± 25</td>
<td>2.2 ± 0.05</td>
<td>19.7 ± 6</td>
</tr>
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</table>
In order to understand the deformation behavior and to develop a criterion for the imparting plasticity in such materials, further TEM investigations were performed. The TEM studies on the deformed samples provide further insight into the deformation mechanisms of the complex multi-phase composite (Al85Cu9Si6). Fig. 4 shows bright-field TEM images (a), (b) and (d), and a dark-field TEM image (c) of the deformed sample. Fig. 4(a) shows dislocation networks at the interface between the ductile phases and the nano-scale eutectic matrix, as indicated by arrows, implying that the plastic deformation in the dendrites is governed by a dislocation slip mechanism. Large differences in contrast and band-contours in the ductile \( \alpha \)-Al phase are provoked by the high amount of dislocation created during deformation and the high residual stresses accumulated in the ductile phases. As marked by the dashed squared region in Fig. 4(a), Fig. 4(b) and (c) indicate the high density of dislocations (dislocation tangle) found even in the \( \alpha \)-Al layers within the nano-scale eutectic. On the other hand, the deformation of the hard intermetallic phase \( \text{Al}_2\text{Cu} \) occurs through shear banding. Shear bands are initiated in the hard intermetallic phase and their propagation is arrested in the surrounding ductile phase regions (Fig. 4(d)). The inter-phase boundaries between the \( \alpha \)-Al and \( \text{Al}_2\text{Cu} \) phases show a step-like morphology formed by the propagation and interaction of shear bands. The nano-scale \( \alpha \)-Al layers do not exhibit sharp shear bands or nanocracks, even when the compressive strain reaches as high as \( \sim 25\% \), indicative of homogeneous flow in the \( \alpha \)-Al layers. This further suggests that the observed work hardening-like behavior is due to the strong interaction between dislocations and the complex microstructure (Figs. 2 and 3(a)). Based on the macroscopic and microscopic investigations, multiple shear bands and dense dislocation networks can be recognized, suggesting that the large plastic deformation is accompanied by simultaneous formation of a large number of shear and slip bands. These observations provide the origin for the plastic deformation of the investigated multi-phase composite materials with multi-scale microstructure.

The significant improvement in the plastic deformation properties of multi-modal ultrafine composites \((\text{Al}_8\text{Cu}_{17})\) compared to the ultrafine lamellar eutectic alloy \((\text{Al}_8\text{Cu}_{13})\) is attributed to the occurrence of special microstructure features in the composites, in particular the high volume fraction of bimodal eutectics combined with a ductile dendritic phase. Probably the bimodal and multi-modal microstructural distribution is helpful to maintain a high strength at the dendrite—matrix interface and facilitates better slip transfer from the matrix to the dendrites. Obviously, the ductile solid solution phase is beneficial since it restricts catastrophic failure by preventing the propagation of shear bands. Therefore, the deformation and fracture behavior is to more uniform, and the stress state may become quite complex, thus leading to an overall homogeneous plastic deformation throughout the whole sample volume. Accordingly, a very good combination of strength and ductility can be obtained in these hierarchical multi-modal composites. These high strength Al-based alloys are of great interest for possible use as advanced engineering materials. Moreover, complex alloys and eutectics are perpetually candidate materials for higher temperature application. Thus, high strength eutectics with nanometer length scale and the prospect of imparting plasticity is of potential interest to advanced metallic material applications in aerospace, air-force and aeronautics industries. These in-situ multi-phase hierarchical ultrafine composites make it possible to create a new generation of aluminum alloys with superior strength.

4. Summary

Multi-modal ultrafine composites with dendrites and different length scale eutectic phases containing a nanometer-scale eutectic have been developed via a simple single-step solidification process. The excellent room temperature mechanical properties combining high specific strength and large compressive plasticity are ascribed to the generation of a favorable multi-phase microstructure with length scale heterogeneity. By combining different characteristic length scales, extraordinary mechanical properties can be achieved that would give designers more “knobs to turn” to meet engineering needs.

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References