Acta Materialia 126 (2017) 202–209

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Small-volume aluminum alloys with native oxide shell deliver unprecedented strength and toughness

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A R T I C L E I N F O

Article history:
Received 23 June 2016
Received in revised form
2 October 2016
Accepted 20 December 2016
Available online 3 January 2017

Keywords:
Aluminum
Native oxide shell
Small-volume metals
Strength
Toughness

A B S T R A C T

Mechanically robust nanoscale metallic materials are highly desirable in many miniaturized devices. However, the lack of strain hardening and controllable plasticity plagues such small-volume metals. Using Al-4Cu alloy as an example, here we show that a submicron-sized metallic material with ultrathin native oxide shell exhibits a high degree of deformation controllability, unprecedented strain hardening, size strengthening and toughness, in uniaxial tensile deformation. The metal/native oxide "composite" is easy to make, and the emergent properties extend well beyond the benchmark range known for metals in a normalized (i.e., dimensionless) strength-toughness plot. The origin of the combination of strengthening and plastic stability is that an intact ultrathin native oxide shell exerts a strong confinement on dislocation movement and annihilation, thereby breaking the envelope on dislocation storage and strain hardening achievable in small-volume metals.

1. Introduction

Mechanical properties of small volume metals have attracted tremendous interests in the past decade due to potential microscale and nanoscale applications [1,2]. A variety of metals and alloys were fabricated into micro- and nanoscale samples, and tested under micro-compression or tension, in order to explore their size-strength relationship [1–12]. A strong sample size-dependent strength behavior has been reported for small-volume metals, hence the phrase "smaller is stronger". "Dislocation starvation" [6,7] and "truncation of dislocation sources" [8–10] theories have been proposed to explain the dislocation-avalanche-controlled jerky flow and the size-dependent strengthening. However, some unfavorable deformation characters, such as strain bursts, lack of strain hardening and near-zero uniform elongation, are often displayed by the small volume metals [1–12]. Therefore, how to overcome the deformation instability, lack of strain hardening and strength-ductility tradeoff still remains as a bottleneck for the utilization of microscale and nanoscale metals.

Recently, interfaces [13–19], precipitates [20–25] and artificially deposited thin film cover [26,27] have been introduced into small volume metals to amend the deformation instability. These attempts show improved deformation stability, but strain bursts are still frequently observed, and meanwhile the strain hardening is still very limited due to the inefficiency of dislocation storage [17–25]. In this regard, new strategies need to be developed. Here we report that the naturally formed ultrathin native oxide shell could promote efficient storage of dislocations in a small-volume Al-4Cu alloy, thus effectively suppressing strain bursts and enhancing strain hardening. As a result, the nanoscale Al-4Cu alloys demonstrate high degree of deformation controllability, unprecedented strain hardening, size strengthening, and extraordinary combination of strength and toughness, showing a broad spectrum of mechanical performances that are superior to other small-volume metals [1–12] (as well as their bulk counterparts).

2. Experimental design

We choose Al-4Cu alloy aged at 200 °C for 1.5 h (peak aged) as the model material. It contains a high density of shear-resistant precipitates, θ' (Al_2Cu) [28,29]. The plate-shaped shear-resistant precipitates form on $\{001\}_\alpha$ planes of the Al matrix. As shown in

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http://dx.doi.org/10.1016/j.actamat.2016.12.055
1359-6454/

Fig. 1a and 1b, two edge-on variants of precipitates and one face-on variant precipitate can be observed with the electron beam along the $<001>_\alpha$ in transmission electron microscope (TEM). The interface structure of θ' and Al matrix can be found elsewhere [30]. The average grain sizes of the peak aged Al-4Cu are ~80 μm, hence it is easy to cut out nanoscale single crystal samples, away from grain boundaries for nano-mechanical testing. Micro-tensile samples with size, $D(D\equiv\sqrt{A}$, where A is the cross-section area of tensile samples), ranging from 100 nm to 800 nm were fabricated by focused ion beam (FIB) micromachining. The final polishing was done using a low ion beam current to minimize possible Ga^+ damage. Quantitative *in situ* mechanical tests were conducted using a Hysitron PicoIndentor (PI95) inside a FEG JEOL 2100F TEM (200 kV) under displacement control. The displacement rate was programmed to be 5 nm/s in tension, which corresponds to a strain rate of $\sim 5\times10^{-3}\ s^{-1}$. In order for easy comparison, all of the tensile tests were performed using the fixed strain rate of $5\times10^{-3}\ s^{-1}$ in current study. Tensile samples with various sizes were loaded along four different orientations ([100], $[\bar{3}11]$, $[\bar{7}40]$ and $[\bar{1}10]$). Real-time observation of the tensile deformation was recorded by a charge-coupled device camera. All tensile samples were examined in SEM and TEM to determine the sample sizes and loading axis before *in situ* tensile tests.

3. Results

3.1. Size-dependent tensile properties

Fig. 1a shows a typical Al-4Cu single crystal micro-tensile sample. Profuse plate-shaped θ' precipitates can be found in the small volume inside the single crystal. These precipitates have habit planes along $\{001\}_{Al}$, as highlighted in Fig. 1b. The average precipitates length and thickness are 56 ± 20 nm and 2.3 nm, respectively [28]. The total volume fraction of θ' is ~2.6%. Besides, a layer of ultrathin and fully dense native amorphous Al oxide shell, with a homogeneous thickness of $<t> = 4.3$ nm, covers the whole micro-tensile sample, as displayed in Fig. 1c. Such a native Al oxide film is typical for Al alloys once exposed to air [31–33]. The thickness of the native Al oxide film is roughly the same for all the tensile sample dimensions.

Fig. 1d (red curve) demonstrates the tensile true stress-strain curve of an Al-4Cu single crystal with $D = 245$ nm and loading along $[\bar{3}11]$. With increasing stress, the nanoscale Al-4Cu single crystal shows linear elastic behavior, and yields at ~0.68 GPa, following a steep, stable and continuous strain hardening up to the ultimate tensile strength (UTS) of ~1 GPa, then fractured with a total strain of ~13%. No strain burst or jerky flow was displayed during tension, significantly different from the unstable deformation of other small-volume metals [1–12]. For comparison, we also tested a pure Al single crystal sample with native Al oxide shell. The sample had a similar size ($D = 255$ nm) but was loaded along $[\bar{1}10]$, as shown in Fig. 1d (blue curve) and Movie S1. The nanoscale Al single crystal shows a similar yield strength as the nanoscale Al-4Cu. However, there is only a very short stable deformation and strain hardening stage after yielding, showing a serrated stress-strain response, although the strain burst is much smaller than previously reported [1–12]. As revealed by Movie S1, the jerky flow in the nanoscale Al case mainly results from the dislocation-native

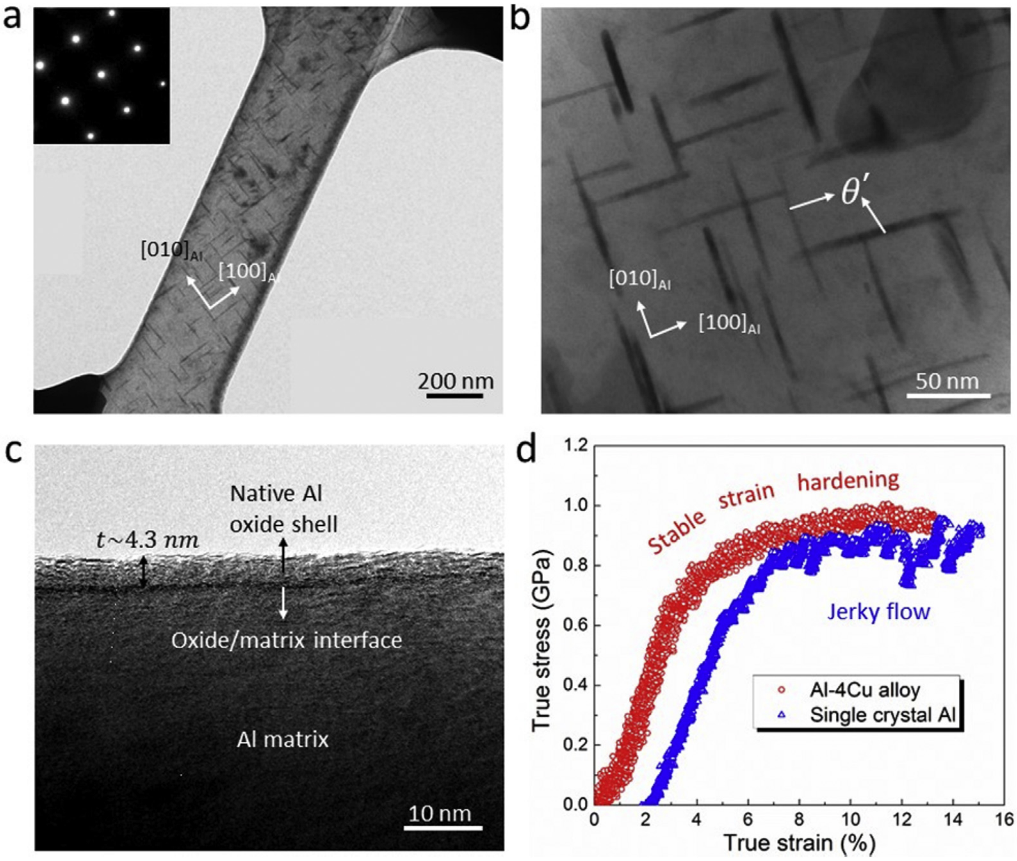

Fig. 1. Microstructure and tensile deformation of nanoscale Al and Al-4Cu. **(a)** TEM image of Al-4Cu single crystal tensile sample. The inserted is the selected area diffraction pattern of $[001]_{Al}$; **(b)** Highlight of the shear-resistant precipitates (θ') in Al matrix; **(c)** A layer of fully dense and ultrathin native Al oxide shell with thickness of 4.3 nm is formed on the Al and Al-4Cu sample; **(d)** True stress-strain curves of a nanoscale Al-4Cu single crystal (red curve, $D = 245$ nm) and an Al single crystal (blue curve, $D = 255$ nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)