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SciVerse ScienceDirect
Scripta Materialia 68 (2013) 91–94
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Atomic-scale characterization of the nucleation and growth of SnO_2 particles in oxidized CuSn alloys

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Received 16 July 2012; revised 6 September 2012; accepted 10 September 2012
Available online 14 September 2012

The internal oxidation of Sn was investigated to understand the oxidation kinetics of monophase CuSn alloys. SnO_2 particles were characterized by analytical transmission electron microscopy. The orientation relationship between SnO_2 and Cu was determined with a special emphasis on the atomic-scale structure of Cu/SnO_2 interfaces (misfit dislocations and chemical structure). Habit planes with a pure oxygen plane terminating the SnO_2 phase are greatly favored and large misfits promote the growth of plate-shaped precipitates.

Keywords: Internal oxidation; Copper alloy; SnO_2; Orientation relationship (OR); TEM

At elevated temperatures (i.e. 500–800 °C), the oxidation of pure copper is characterized by the formation of a double oxide layer of Cu_2O and CuO [1–4], in a ratio that depends on the temperature [5] and pressure [6]. As Cu_2O is a metal-deficient oxide in which the lattice diffusion of copper ions is several orders of magnitude faster than oxygen diffusion, the rate of growth of the cuprous oxide sublayer is controlled by outward diffusion of copper cations via metal vacancies [7,8]. In the top CuO layer, there are no vacancies available for fast diffusion of reacting species and hence the growth rate remains very low as compared to Cu_2O [9,10]. The presence of impurities in copper plays a very important role on the oxidation mechanisms and kinetics. Zhu et al. suggested that impurities could explain the discrepancies in the literature data reported for the copper oxidation kinetics [11]. Impurities impede the lateral growth of both Cu_2O [11] and CuO grains [2,9]: this favors grain boundary diffusion of Cu, faster than lattice diffusion, and consequently leads to an increased oxidation rate. Alloying element in solid solution in the face-centered cubic (fcc)-Cu phase can also strongly affect the oxidation kinetics. Depending on the alloying element diffusivity in both the alloy and metal oxides, various scenarios are reported. For example, in the case of oxidized Cu–Si alloys, a continuous SiO_2 layer appears at the Cu/Cu_2O interface. This layer significantly reduces the oxidation rate which is explained by the lower diffusion rate of copper ions in SiO_2 than in Cu_2O [12,13]. For other alloys, such as Cu–Ti [14] or Cu–Ni [15], internal oxidation of the alloying element was reported. The nucleation of oxide particles inside the matrix is promoted by the oxygen diffusion [14,16] and these particles can exhibit various shapes and sizes depending on misfits and interfacial energies [17,18]. Their influence on the overall oxidation rate of the alloys is, however, not fully understood and could be rather complex. The case of CuSn alloys is of particular interest because a small amount of Sn slows down the oxidation kinetic, thus this element has a protective effect against oxidation. Internal oxidation of Sn was reported in 3–13 wt.% Sn alloys oxidized in 1 atm O_2 [19] and in 8.2 wt.% alloy oxidized in 1 atm laboratory air [20]. This phenomenon is attributed to the relatively low mobility of Sn. However, depending on the concentration and oxidation temperature, SnO_2 particles are detected in an inner mixed oxide layer of Cu_2O and SnO_2 or accumulated close to the alloy/scale interface [19–22]. The aim of the present work was to clarify the exact role of tin in the oxidation kinetics of CuSn alloys with a special emphasis on the nucleation and growth of SnO_2 nanoparticles precipitated internally in the fcc-Cu matrix.

Two model monophase CuSn alloys were prepared by cast melting (provided by KME Corporation), containing 4.2 and 8.2 wt.% Sn, respectively (Cu balance). In the following, they are referred as CuSn4 and CuSn8, respectively. Samples for oxidation experiments were cut

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1359-6462/$ - see front matter © 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.scriptamat.2012.09.005

in coupons approximately 15 mm × 10 mm × 0.8 mm in size and homogenized under vacuum ($\sim 5 \times 10^{-5}$ mbar) at 600 °C for 4 h. Then, they were mechanically polished and finally cleaned with isopropanol and dried before oxidation. Oxidations were performed under laboratory static air in a muffle furnace maintained at 600 °C (±2%) for 4 h. After such a treatment, samples typically exhibit external multilayered oxide scales on the surface and an internal oxidation zone as discussed in Ref. [20]. To characterize the internally oxidized area, Transmission electron microscopy (TEM) samples were prepared from the specimen cross-section by the site-specific focused ion beam (FIB) lift-out technique [23] in a cross-beam NVISION-40 Zeiss®. Samples were then observed in a probe corrected JEOL® ARM200F transmission electron microscope operated at 200 kV. Energy-filtered images were recorded using a Gatan® Imaging Filter (GIF Quantum). High-angle annular dark-field (HAADF) images were recorded in scanning mode (STEM) with a 0.1 nm probe having a convergence angle of 30 mrad. The collection angle on the HAADF detector was in the range of 50–180 mrad.

In the internal oxidation zone, the Sn in solid solution is oxidized, giving rise to a two-phase mixture formed from fcc-Cu matrix and a significant volume fraction of SnO_2. The number density of SnO_2 particle is rather low, and these particles are plate shaped as observed in the internal oxidation zone of the CuSn8 alloy (Fig. 1a). The thickness of these platelets is in the range of 10–50 nm, the length up to few micrometers and the width in the range of 50–100 nm (not shown here). There is a large distribution in the inter-plate spacing, from 100 to 500 nm. Energy-filtered (EF) TEM confirms that these platelets are embedded in the Cu matrix and are rich in Sn and O (Fig. 1a, inset). Furthermore, using electron diffraction, the crystallographic structure of the internal oxide platelets was identified; it matches the expected rutile structure of SnO_2 [24]. A diffraction pattern was recorded in the [1 1 0] zone axis of the fcc-Cu (Fig. 1b), and it is interesting to note that it also fits the [1-10] zone axis of SnO_2. Obviously, platelets are elongated along the Cu [-1 1 0] and the SnO_2 [0 0 1] directions. Internal oxide particles were also characterized in STEM. Since the average atomic number in the SnO_2 structure is lower than that of Cu, oxide platelets appear dark on HAADF images as shown in Figure 2a. The internal oxidation front is clearly exhibited on this image where platelets are growing from the top left corner

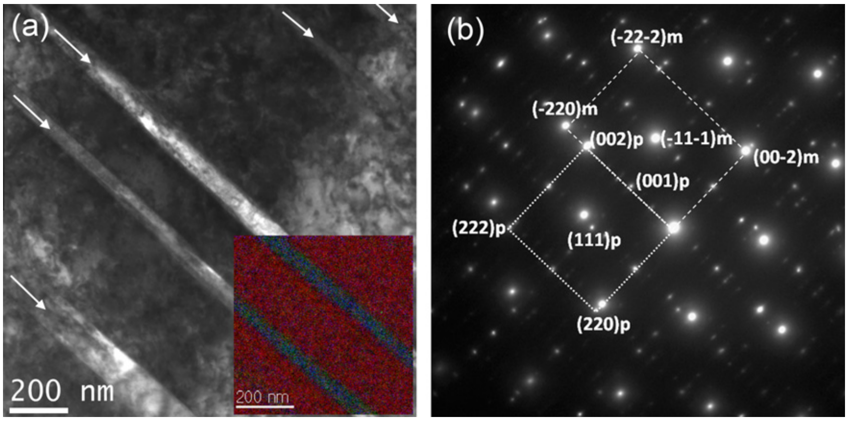

Figure 1. CuSn8 oxidized at 600 °C for 4 h. (a) BF-TEM image showing SnO_2 platelets (arrowed) within the Cu matrix; inset: EFTEM image (Cu, red; Sn, blue; O, green), confirming that the platelets are Sn and O rich (tin oxide). (b) Corresponding SAED pattern, spots are indexed: subscript **m** refers to the fcc-Cu matrix in the [1 1 0] zone axis and subscript **p** refers to the tetragonal SnO_2 oxide platelets in the [1-10] zone axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

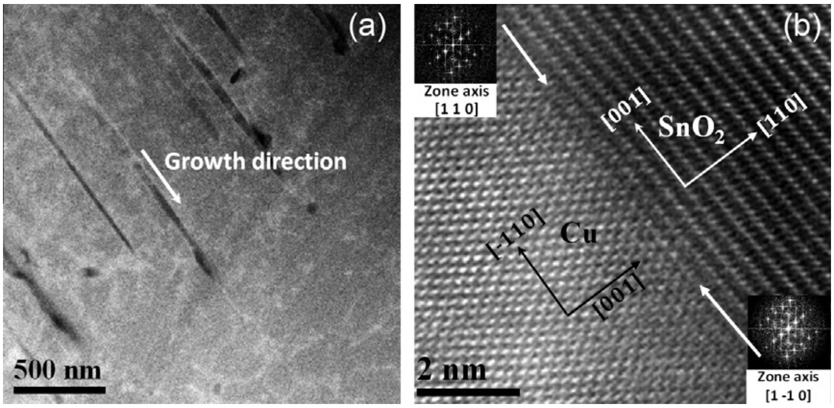

Figure 2. CuSn8 oxidized at 600 °C for 4 h. (a) Low-magnification HAADF-STEM images showing several parallel SnO_2 plates growing in the fcc-Cu matrix. (b) High-magnification HAADF-STEM filtered image showing the atomic structure of the Cu/SnO_2 interface in [1 1 0] fcc-Cu and [1-1 0] SnO_2 zone axes.