

Monitoring The Internal Oxidation In Rapidly Solidified Copper

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Abstract. On the case of pure copper we present the special kind of internal oxidation phenomenon. That kind of process can take place in pure metals containing a high concentration of defects, particularly thermodynamically stabilized vacancy clusters. The process starts with dissolution of oxygen into the metal at the free surfaces. After that, process continues with diffusion of oxygen atoms into the volume of the metal matrix. Oxygen atoms are trapped at numerous defects in the crystal lattice. The increasing oxygen activity, at these places causes the local oxidation of the matrix and consequently precipitation of fine oxide particles. The experimental results confirmed the formation of microstructure consisting of continuous three-dimensional copper matrix and homogeneous fine dispersed Cu₂O particles of submicron size. The volume fraction of precipitated oxides depended on the started microstructure of the Cu matrix. Also, it depends of the temperature and time of the internal oxidation process. About 2 vol. % of oxide particles has been obtained with the proposed manufacturing technique.

Introduction

The ordinary internal oxidation processes [1,2] normally start with the dissolution of the oxidant atoms into the lattice of the base metal. Dissolved oxidant contain to diffusion in the interior matrix, and reaction with a less-noble solute element (N). Afterward, the solubility product of the compound is exceeded at this reaction front, critical super saturation for homogeneous precipitation from the solid solution. The layer, composed of precipitated particles is called "subsurface" or the internal oxidant zone (IOZ). The border of this zone is the oxidant front (OF). When the metallic solute is exhausted at OF, the oxidant diffuses further into the matrix, and increases the thickness of the IOZ. Theoretically, the oxidation of pure metal is possible when the partial pressure of oxygen in the atmosphere exceeds the equilibrium value for the reaction ($M+yO=MO_y$) at a related temperature. The possible form that this layer can take is numerous. The form may even alter as the reaction progress, and some Me-O system can form a multiple scale-layer. A lot of solute element, especially impurities, usually segregates at the defects in the crystal lattice [3]. It occurs at higher temperatures. Solute element diffuses through the metal matrix, encounters lattice defects and becomes trapped there. The driving forces for this process are size differences and chemical incompatibility between the segregated elements at these places. Because of increasing chemical activities of the segregate elements at these places, there are a number of various chemical reactions that can occur. For instance, in the case of oxygen atom segregation, the local oxidant and consequently, the precipitation of fine oxide particles, can be expected.

Experimental work

Rapidly solidified (RS) Cu ribbons (Cu-99.99%) previously had been prepared using the Chill-Block Melt Spinning Technique. The process was performed under Ar atmosphere using a quartz crucible 48mm in inner diameter, and a nozzle with an orifice diameter of 1.5mm. The melt was ejected by Argon overpressure of 0.02-0.03 MPa onto the surface of a copper-beryllium wheel,

rotating at speed of about 21m/s. Continuous ribbons were produced 3 to 5 mm in width and 60 to 80 mm in thickness.

The internal oxidation was performed at temperatures from 873 to 1173 K. Partial oxygen pressure equal to the decomposition pressure of the cuprous oxide. In order to accomplish this, short pieces of ribbon were packed in a mixture of equal parts cuprous oxide and copper metal powder, and enclosed in a quartz ampoule (Rhines packet). The heat treatments were carried out in a tube furnace over various periods of time.

Microstructural characterization of the internally oxidized samples was carried out using optical microscopy (OM), scanning electron microscopy (SEM-Jeol JSM 849 A), as well as EDX microanalysis (Link analytical AN 1000). In addition, Auger Electron Spectroscopy (AES-Microlab 310-F equipped) was used to determine the elemental compositions of the precipitated particles after internal oxidation. The surfaces of the particles were cleaned and etched with Ar^+ ions ($E=2\text{keV}$, $r=12\text{mAcm}^{-2}$; $Q=47^\circ$) to remove surface contaminants and to obtain compositional depth profiles. Specimens of internally-oxidized ribbons for optical and scanning electron microscopy were prepared using standard metallographic methods and etched in $\text{FeCl}_3\text{-H}_2\text{O-HCl-C}_2\text{H}_5\text{OH}$ solution.

The electrical resistance measurements of the initial and annealed rapidly solidified Cu ribbons were performed by four Ni probes for electrical resistance monitoring. The electrical resistance was measured by a four probe method with a bidirectional current of 1 A, with a resolution of $1\ \mu\Omega$ and accuracy of $\pm 3\ \mu\Omega$.

Results and discussions

The metallographic examination of the annealed revealed a microstructure consisting of copper grains and very fine submicron particles. The particles are homogeneously distributed throughout the volume matrix.

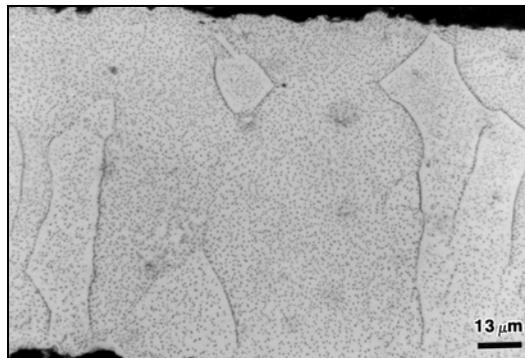


Fig. 1. Microstructure of a transverse cross-section of the annealed ribbon after 2 h at 1173 K

During heat treatment of pure Cu RS ribbons the particles have been identified the particles precipitated simultaneously throughout the entire volume of Cu matrix. Also, during the experiments no precipitation front appears in the microstructure. The number and mean size of the particles increased with the time of heat treatment. Also, the volume fraction of precipitated particles increases, too.

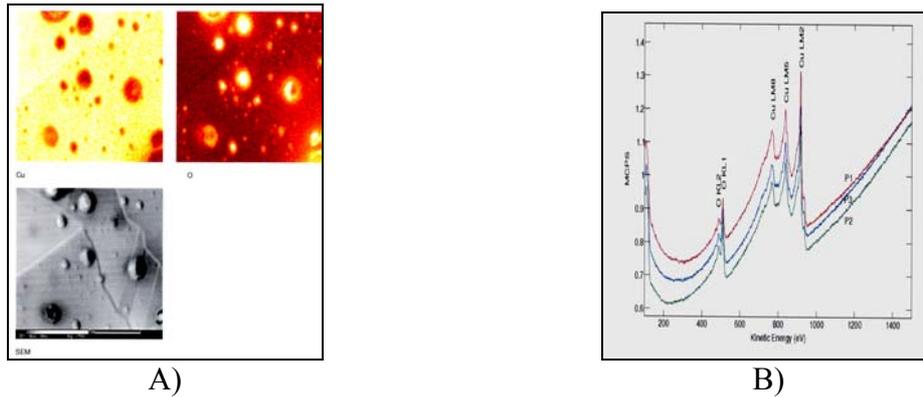


Fig. 2: The particles performed by Auger Electron Spectroscopy
 A) Auger chemical mapping of the Cu and O in the annealed microstructure
 B) Auger spectra from the precipitated particles

Figure 2A shows a typical Auger chemical mapping of the copper and oxygen in the annealed microstructure containing the particles. Particles are strongly enriched in oxygen. Figure 2B position and shape of the peak for the oxygen and copper in the direct energy spectrum clearly show that the surface layer, as well as the interior of the particles, contains oxygen atoms in the copper oxide.

The shape of the double peak in the case of oxygen indicates that the oxide particles are not stoichiometrically compound. A comparison of the position peak for the copper in the oxide particles with theoretical values for copper in the Cu_2O and CuO , shows that in smaller particles, the copper and oxygen atoms in these regions are bound into CuO . Contrary to this, the position of the energy peaks taken from surface layers of the coarser particles indicates that the atoms in these regions are bound into Cu_2O . The atoms of oxygen dissolve and migrate in metals as interstitials. In the ordinary internal oxidant of alloys the number, size and morphology of the precipitated particles are also dependent on oxygen diffusely.

Rapid oxidant diffusion favors the nucleation of new particles, whereas slower oxidant diffusion favors sidewise particle growth and formation of continuous film. The solubility of oxygen and other oxidants (C, S, N) is very limited in most solid metals and this is also valid for copper. The diffusion of oxidants in metals is quite rapid. Based on a size considerations ($R_o=61\text{pm}$, $R_c=77\text{pm}$, $R_n=70\text{pm}$) [4] it is expected that oxygen diffusion should be slightly higher than those of other oxidants. In the case of our rapidly solidified ribbons, the excess in the structure additionally increases the diffusion rate. During internal oxidation of the rapidly solidified pure copper ribbons in oxygen containing atmosphere, it is expected that the oxygen concentration in the solid solution attains maximum solubility, throughout the whole volumes of the ribbons in a short time.

Theoretical calculations show that at 1173K oxygen atoms react the centre of the copper ribbons with a thickness of about $100\mu\text{m}$ in few seconds. The low solubility and the rapid diffusion of oxygen in rapidly solidified metals, are very important for understanding the mechanism of oxide precipitation in pure copper.

In the first period the atoms of oxygen dissolve at the metal/gas interface into copper lattice and diffuse in the interior copper matrix. The atoms of oxygen are attracted at numerous defects in the crystal lattice and produce local segregation. In this period, oxide particles do not precipitate from the copper/matrix.

In the second period, fine particles of copper oxide start to precipitate. In this period a chemical activity of oxygen increases. This causes a chemical reaction between the trapped oxygen and the copper-matrix. The primary driving forces for this process is differences size atoms of solute and matrix. Increasing activity of the trapped oxygen atoms leads to local oxidation and probably, the oxide cluster formation. They will precipitate as finally dispersed oxide particles after the critical super saturation is attained for heterogeneous precipitation of the oxide [5].

Table 1: The results of electrical resistance

The type of Cu ribbon	[m Ω]
RS pure Cu	6.88
Internally oxidized RS pure Cu	6.26
Annealed RS pure Cu	5,42

We compare also the electrical resistance of the oxidized RS pure Cu, which were *annealed* on temperature 1173K in duration of 1h.

The comparison of the measured results for electrical resistance confirms that the formation of non-sharable Cu₂O dispersions has practically no influence on their electrical conductivity.

Conclusions

In this paper we present some results of our experimental studies and monitoring of oxygen behaviour in pure copper.

The results show that, during the annealing process of rapidly solidified pure copper in Rhines packet, the Cu₂O particles precipitate simultaneously throughout the entire volume of Cu matrix and no precipitation front appears in the microstructure. In this novel processing approach, rapid solidification is used for obtaining a high concentration of defects in the copper crystal lattice, which act as segregation sites for oxygen. The increasing chemical activity of oxygen at these places causes a chemical reaction between the trapped oxygen atoms and the copper matrix, and the formation of copper oxide. Vacancy clusters are probably the most important defects where the oxygen atoms are trapped.

The mean size of the precipitated particles is smaller at lower temperature but at all temperatures it increases with the annealing time. The volume fraction of precipitated particles depends on the started microstructure of the Cu matrix, and on the temperature and time of internal oxidation (it increases with temperature and longer time of annealing).

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