

Surface and sub-surface oxidation of α -Cu-(17 at.%)Al(100) studied by X-ray photo-electron spectroscopy and low energy He⁺ scattering spectroscopy

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Abstract

In this study the initial stages of oxidation of the α -Cu-(17 at.%)Al(100) single crystal oriented alloy surface was investigated by X-ray photo-electron spectroscopy and low energy He⁺ scattering spectroscopy. It was found that oxygen adsorption can be divided in two sequential stages: (i) a fast process, up to 15–20 L exposure, in which oxygen adsorbs on the alloy's surface resulting mostly in the formation of Al–O chemisorbed bonds; and (ii) a slower process during which oxygen adsorbs forming Cu–O and Al–O chemisorbed bonds concurrent with diffusion of O to the sub-surface and Al segregation to the surface region. The surface oxidation rate is much higher than the sub-surface one. The rate of Al segregation increases with oxygen exposure and involves both surface and sub-surface regions. Annealing of the oxidized alloy surface results in a pronounced segregation of Al and formation of an aluminum oxide layer.
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1. Introduction

The α -phase of the Cu–Al alloy system possesses a number of properties which make it attractive as a prototype for the study of the electronic structure of the alloy. A surface related important property of this system is segregation. It is respon-

sible for reactivity, corrosion resistance and adhesion properties. The alpha phase of the Cu–Al alloys exists over a composition range from 0 to 19.6 at.% Al. For concentrations larger than ~16%, a short range order is established between aluminum atoms [1,2]. It was found that for some Al concentrations no pronounced Al segregation occurs onto the clean α -Cu–Al (100) surface [3,4]. However oxygen adsorption results in Al segregation and formation of a stable surface oxide [3,5]. The oxidation of α -Cu–Al(100) for various

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Al concentrations (1.5, 5, 12, 17 and 18 at.%) were studied by Auger and X-ray photo-electron spectroscopies (AES and XPS) by Hoffman et al. [3,6], Shen et al. [5] and Zhu et al. [4,7,8]. Based on these studies the interaction of oxygen with these surfaces may be divided in two main stages: a fast one, during which oxygen adsorption takes place mostly on top of the alloy surface, followed by a slower one, which involves oxidation-induced aluminum enrichment.

The aim of this study was to investigate oxygen adsorption phenomena at the initial stages of oxidation of α -Cu-(17 at.%)Al(100) oriented single crystal surface by XPS and low energy ion scattering (LEIS) using He^+ ions at 350 and 1000 eV incident ion energies. For comparison, similar oxidation measurements were carried out on the Cu(100) surface. Surface versus sub-surface processes as a function of oxygen exposure were resolved.

2. Experimental

The samples (2 mm thick and 8 mm in diameter) were cut from single crystal grown by the Bridgman method and oriented within 1° of the (100) plane. The samples surface were prepared by polishing followed by several cycles of Ar^+ bombardment and annealing to 400 °C [6]. The adsorption experiments were carried out in an ultra high vacuum (UHV) system with a background pressure of 7×10^{-10} Torr. XPS experiments were carried out using a SPECS spectrometer, using non-monochromatic Al $K\alpha$ (1486.6 eV) radiation at normal emission. LEIS experiments were performed using a differentially pumped ion source with He^+ beam (99.999% He of purity) at a fixed scattering angle of 135° with chamber He partial pressure at 1×10^{-7} Torr. The LEIS spectra were recorded using primary He^+ energies of 350 and 1000 eV. It is estimated that during such LEIS experiments less than 1% of a monolayer was removed [9]. All spectroscopic measurements were recorded using a hemispherical electron analyzer operated at a pass-energy of 97 eV. The positive ions spectra were detected by operating the spectrometer in an inverse polarity mode.

3. Results and discussion

3.1. XPS measurements

In Figs. 1(a) and (b) XPS spectra in the O(1s) peak range as a function of oxygen exposure up to ~ 160 L of Cu(100) and α -Cu-Al(17 at.%) (100), respectively, are shown. For Cu(100) the O(1s) binding energy (BE) obtains a value of 530.1 ± 0.1 eV and it remains constant with oxygen coverage, however upon annealing the oxidized surface to 400 °C it shifts by -0.55 ± 0.1 eV. For the alloy's surface up to ~ 15 L of oxygen exposure the O(1s) BE was measured at 532.5 ± 0.1 eV, for larger exposures a shift of -1.7 ± 0.1 eV was observed. Upon annealing the oxidized alloy surfaces to 400 °C, the O(1s) BE peaks shifts by $+1.7 \pm 0.1$ eV, a value, similar to the one recorded for low oxygen exposures. Based on a comparison with oxidation experiments carried out on the Al(100) [12] and Cu(100) surfaces (Fig. 1(a)) it can be concluded that as a function of oxygen exposure of the α -Cu-(17 at.%)Al(100)/O₂ system, Al–O chemisorbed bonds are formed first following by Cu–O chemisorbed bonds. Annealing the oxidised alloy surface induces segregation of Al atoms from bulk to surface, oxygen bonded to Cu sites exchanges with Al atoms thus resulting in the formation of an aluminium oxide rich surface region.

3.2. LEIS measurements

Assignment of the LEIS spectral features was done using a simple classical elastic scattering model where ion trajectories are described by a two-body collision [10,11]. In Table 1 the calculated energy values of scattered ions are compared to the experimental results. There exists reasonable agreement between the corresponding entries of this table [10]. The LEIS spectra show additional peaks at 273 and 646 eV. It is envisaged that these peaks could be associated with secondary scattering phenomena or low level surface impurities. According to XPS surveys these peaks could not be associated to any surface impurities. However, considering the limited sensitivity of XPS to the upper atomic layer the possibility that these peaks

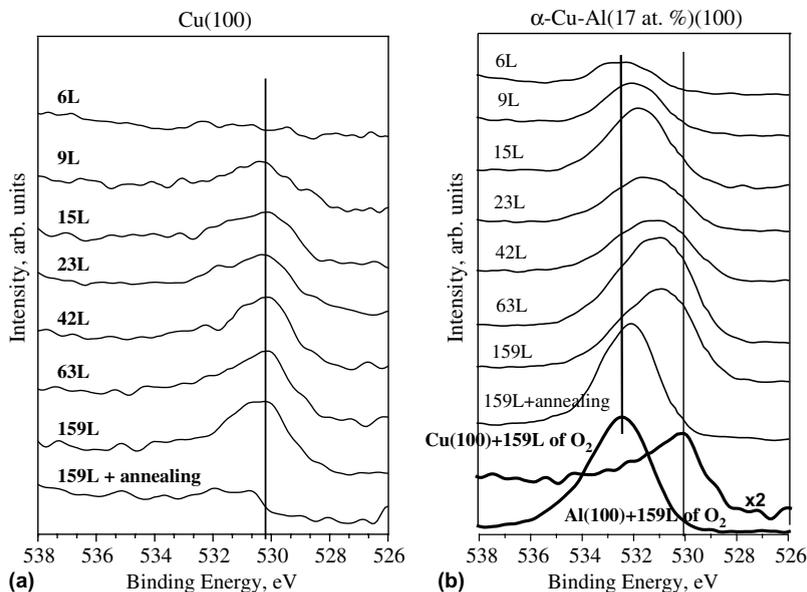


Fig. 1. XPS-O(1s) peak measurement as a function of oxygen exposure on (a) Cu(100) and (b) α -Cu-(17 at.%)Al(100).

Table 1

Calculation of scattered ion energies and comparison with experimental values, using a simple kinematic two-body model

Element	$E_0(\text{He}^+) = 350 \text{ eV}$		$E_0(\text{He}^+) = 1000 \text{ eV}$	
	Calculated (eV)	Measured (eV)	Calculated (eV)	Measured (eV)
O	146	147	417	426
Al	210	211	600	590
Cu	282	303	806	805

could be associated with a low concentration surface impurity cannot be completely discarded. Therefore at present time we are not able to determine the origin of these two LEIS peaks.

In Figs. 2(a) and (b) LEIS spectra measured using a 1000 eV He^+ incident beam as a function of oxygen exposure, are shown for Cu(100)/ O_2 and α -Cu-(17 at.%)Al(100)/ O_2 , respectively. As seen from these figures the oxygen peak increases in intensity with oxygen exposure whereas those of copper and aluminum decrease. Also the total intensity of the LEIS spectra decreases with oxygen exposure. A similar effect was observed in LEIS measurements of the Al(100)/ O_2 system recently published by us [12]. In Figs. 3(a) and (b)

LEIS spectra measured using 350 eV He^+ as a function of oxygen exposure is shown for the two samples studied. The general tendency of these spectra is similar to those obtained using 1000 eV He^+ .

The LEIS results suggest, similarly to XPS, that as a function of oxygen exposure of the α -Cu-(17 at.%)Al(100) surface Al–O chemisorbed bonds are formed first, followed by Cu–O bonds. This may be concluded from the fact that with oxygen exposure, the Al LEIS peak decreases in intensity followed by a decrease of the Cu peak. This is most likely an effect in which oxygen adatoms “shadow” the adsorption sites.

3.3. Surface versus sub-surface adsorption processes

The interaction of oxygen with the α -Cu–Al(17 at.%) (100) surface includes the competition of three surface phenomena: oxygen adsorption and bonding, oxygen diffusion and aluminum segregation. The oxygen surface concentration as a function of exposures (up to ~ 160 L) calculated from the XPS and LEIS (Figs. 1–3) are shown in Fig. 4. As seen from it, up to 15–20 L the oxygen concentration calculated by LEIS at both ion

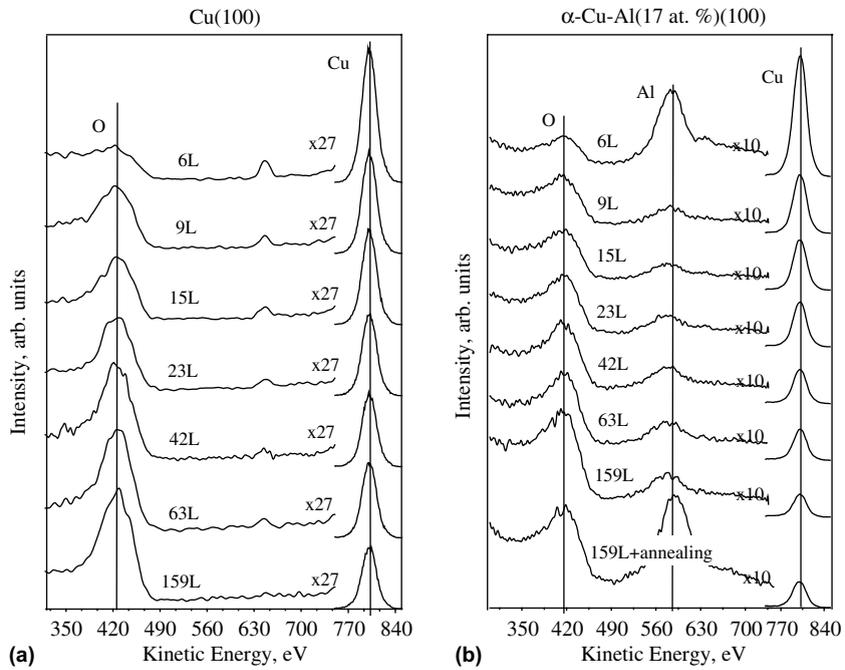


Fig. 2. LEIS ($E_0(\text{He}^+) = 1000 \text{ eV}$) spectra as a function of O₂ exposures, from (a) Cu(100) and (b) α -Cu-(17 at.%)Al(100).

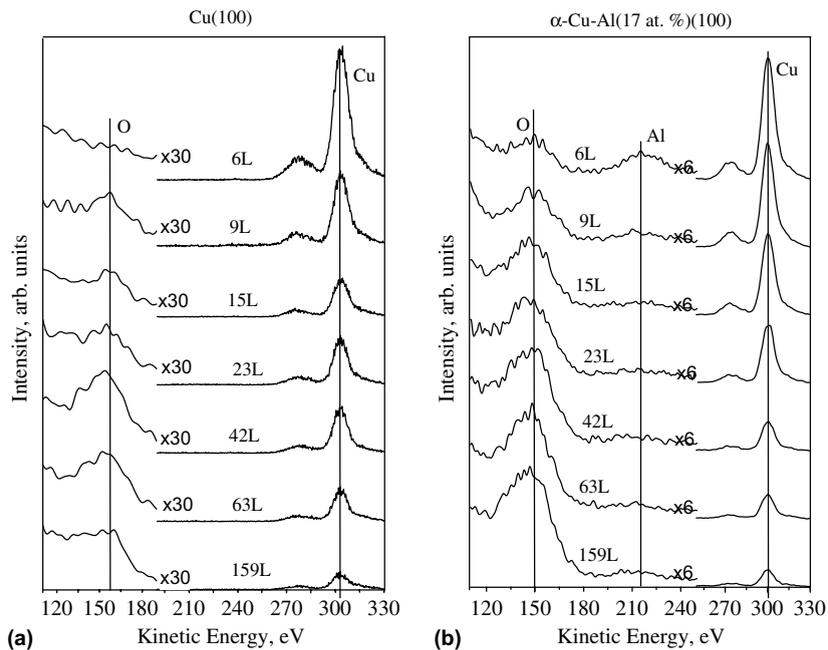


Fig. 3. LEIS ($E_0(\text{He}^+) = 350 \text{ eV}$) spectra as a function of O₂ exposures, from (a) Cu(100) and (b) α -Cu-(17 at.%)Al(100).

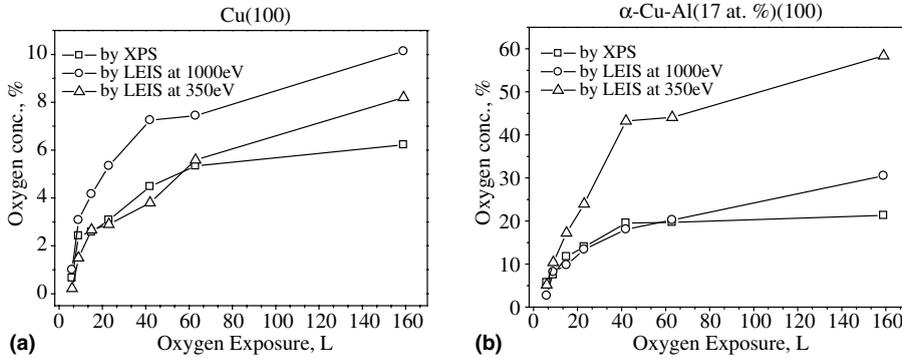


Fig. 4. Oxygen relative concentration as a function of exposure measured by different methods on (a) Cu(100) and (b) α -Cu-Al(17 at.%)Al(100).

energies and XPS increases at a similar rate with oxygen exposure. For exposures larger than 15–20 L the oxygen concentration calculated by LEIS at 350 eV He^+ increases continuously and monotonically, whereas the oxygen concentration measured with 1000 eV He^+ and XPS displays a much slower increase rate.

Considering that the LEIS measured at 350 eV He^+ incident energies is extremely sensitive to the upper atomic layer whereas the XPS and LEIS measured at 1000 eV He^+ are also sensitive to deeper layers it can be concluded that the oxidation process of the alloy's surface consists of two stages: (i) the first one, up to 15–20 L, is fast and oxygen adsorbs most predominantly with aluminum sites; (ii) the second one, for exposures larger than 15–20 L, is slower and both Al–O and Cu–O chemisorbed bonds are formed, at this stage surface and sub-surface oxidation processes occur simultaneously.

During the second step of oxidation, aluminum induced segregation begins to be more visible as can be concluded from Fig. 5 in which the Al to Cu peak area ratio calculated from LEIS increases with oxygen exposure. This result is similar for both energies used in LEIS measurements, therefore it is suggested that both surface and sub-surface regions, as probed by LEIS at 350 and 1000 eV He^+ , are enriched by aluminum segregation induced oxygen adsorption. Annealing to 400 °C of the oxidized alloy surface (Fig. 2(b)) results in a pronounced aluminum induced segregation.

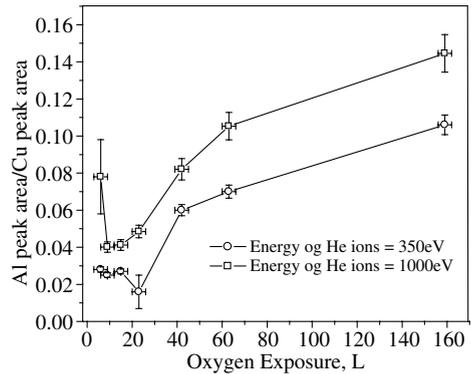


Fig. 5. Ratio of Al to Cu LEIS peaks integral intensity as a function of oxygen exposure measured with 1000 and 350 eV incident He^+ energies.

In summary, based on the different surface sensitivity of the spectroscopic methods applied in this work surface versus sub-surface oxidation processes of the α -Cu-(17 at.%)Al(100) surface were studied. It was established that oxidation proceeds via two sequential stages: a fast one and a slower one. During the first process, up to 15–20 L exposure, oxygen adsorbs on the alloy's surface resulting mostly in the formation of Al–O chemisorbed bonds. During the second process, for larger exposures, oxygen adsorbs on less reactive sites concurrent with diffusion of O to the subsurface and Al segregation to the surface region. The surface oxidation rate is faster than the subsurface one. The rate of Al segregation increases with oxygen

exposure and involves both surface and sub-surface regions. Annealing of the oxidized alloy surface results in enrichment of the upper surface with aluminum and formation of a stable aluminum oxide upper layer.

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