

Site specific effects in alloy surface reactivity probed by Li ions

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Abstract

We investigated site specific reactivity of the α -Cu–Al(17 at.%(100)) alloy surface versus that of Al and Cu by measuring neutralisation of Li^+ ions. Experiments show that Li^+ neutralisation on the α -CuAl(100) alloy surface does not occur efficiently on Al and is somewhat more efficient on Cu as compared to a pure Cu sample, indicating depletion of electron density on Al and transfer to neighboring Cu. It can thus be concluded that Cu sites in presence of Al are more reactive in the sense that processes involving electron capture from the surface would proceed more efficiently on these.

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Bimetallic surfaces are extensively used in many industrial processes in the areas of heterogeneous catalysis, corrosion protection, electrochemistry, microelectronics fabrication etc. These mixed metallic systems display enhanced catalytic activity and selectivity as compared to their constituent metals. A substantial effort both experimentally and theoretically has been made over past years to investigate the structural, electronic, and chemical properties of bimetallic systems in terms of their reactivity [1–4]. A number of recent studies have focussed on well defined model systems formed by deposition of metals on single-crystal substrates, which offered a unique possibility to correlate surface chemical reactivity with atomic-level surface structure. The activity of bimetallic systems has been discussed in terms of “ensemble” effects related to the number of surface atoms needed for a catalytic process to occur on the one hand and on the other hand to binding or “ligand” effects related to changes in reactivity following changes in electronic structure as a result of the interaction between

the two metal components. The electronic effects are related to some degree of electron transfer from one metal to the other [3,5]. Modifications in electron density on specific surface sites may be expected to lead to local changes in reactivity involving electron transfer between the surface and gas phase atoms and molecules. In this work we strived to get direct evidence of these changes for the case of the α -Cu–Al system and shed some light on initial steps in reactivity.

The α -Cu–Al alloys have been a prototype for alloys where the incorporation of a small amount of sp metals results in significant changes in surface properties. A number of experimental [3,6–10] and theoretical [3–5] studies of the reactivity and electronic structure of Cu–Al and similar alloys were published. Gas–surface interactions are found to be very different from that observed on the pure elemental surfaces. The interaction of α -Cu–Al(100) alloy surfaces with oxygen was studied in the past by several authors [6–10]. It was found, that the reactivity of the alloy is different from that on the pure elemental surfaces and depends on aluminum concentration. These experimental results would suggest [7,10], that at the very initial stage

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oxygen is bonded to aluminium sites and subsequently bonds to both Al and Cu. However, the picture of the initial oxidation process is still unclear. It is interesting to note in this context that in general although oxidation of metals has been the subject of extensive study the initial steps of this process are still under extensive investigation for rather simple systems [11]. This complex problem motivated us to study the site specific characteristics of the electronic properties and reactivity of the α -Cu–Al(17 at.%(100)).

Our approach involves the back scattering of Li ions off the alloy surface and simultaneous monitoring of the final energy and charge state of the projectile. This allows us to obtain site specific information about Li neutralisation on Al and Cu. These results can be compared to data on neutralisation of Li on Al and Cu single crystal surfaces. We are thus able to show that in this system Li neutralisation does not occur efficiently on Al and is somewhat more efficient on Cu as compared to a pure Cu sample, indicating depletion of electron density on Al and transfer to neighboring Cu. In the following we describe the experimental procedure and results and then discuss these aspects.

The Cu and CuAl alloy samples were cut from single crystals grown at the Technion by the Bridgman method and oriented within 1° of the (100) plane. Prior to insertion into the UHV chamber polishing and cleaning procedures were undertaken [6]. The experiments were performed on the Orsay setup described elsewhere [12]. The setup allows for ion scattering (ISS) and time of flight (TOF) spectroscopy, Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). Li^+ ions were produced using a Li getter source. Ions scattered through 114° were energy analysed with an electrostatic analyser. TOF experiments were performed using a channel-plate detector set at the end of a 113 cm long tube. In this case also the scattering angle is 114° . The multinode channel-plate detector allows simultaneous, separate detection of ions and neutrals in

continuous or pulsed beam modes. *In situ* sample preparation consisted of repeated cycles of Ar^+ sputtering (using a 1 keV Ar^+ beam incident at about 15° with respect to the surface plane) and annealing to about 400°C . Surface quality was ascertained by LEED. Note that the exact order of the Al atoms on the Cu–Al surface is not exactly known. Low energy ion scattering (LEIS) with 1 keV He^+ ions was used to monitor surface cleanliness. The scattering of Li ions was performed along a “random” direction not corresponding to a channelling direction.

Energy losses of scattered Li^+ ions were investigated for different incident energies. Typical spectra of Cu(100) and α -Cu–Al(17 at.%(100) alloy for 0.5 keV Li^+ ions are presented on Fig. 1a when scattered particles leave normal to the surface (incident angle with respect to the surface plane is 24° ; total scattering angle is 114°). The final “exit” energy of the backscattered Li projectile can be estimated simply from classical mechanics considering scattering of Li mass M_1 off a target atom of mass M_2 , through the 114° scattering angle. An inspection of the spectra shows that on Cu(100) they present a peak related to surface scattered Li on Cu. In case of the CuAl alloys however one observes also a small structure attributable to scattering off Al. There is also a “background” component, due to multiple scattering events but the two “surface” peaks are clearly identifiable.

Time-of-flight measurements were performed for a number of initial Li^+ energies for two incident angles. Fig. 1b present TOF spectra for 0.5 keV Li^+ ions scattered from the α -Cu–Al(17%)(100) alloy surfaces, for the indicated exit angles with respect to the surface plane. Every graph presents simultaneously detected ions and neutrals as a function of arrival time. The fastest particles (at $2\ \mu\text{s}$) are related to double collision scattering of Li^+ from surface copper atoms (Cu–Cu). The broad energy loss distribution is similar to the one detected by LEIS. On the spectra for

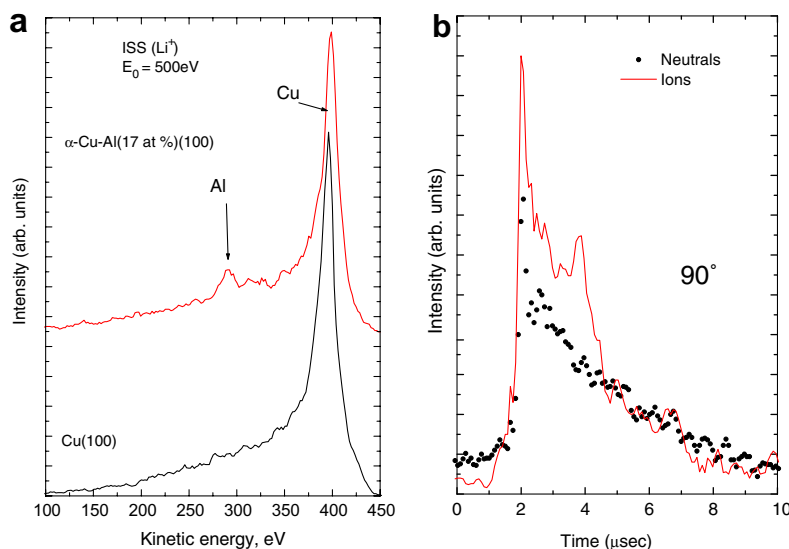


Fig. 1. (a) Typical LEIS spectra of the Cu(100) and the α -Cu–Al(17 at.%(100) alloy for 0.5 keV Li^+ ions. (b) TOF spectrum for 0.5 keV Li^+ ions scattered from the α -Cu–Al(17 at.%(100) alloy surface.

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