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Interface Reactions in Bilayers of Aluminum and Nickel-Chromium Alloy

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ABSTRACT

Glancing angle EXAFS and x-ray reflectivity are used to study the interface reaction between nickel-chromium alloys and aluminum. The two metals are found to react independently with Al, with the first reactions taking place at temperatures similar to those found for the pure metals. This means that Ni reacts first with Al to form $NiAl_3$, leaving behind a Cr-rich region at the interface. In this Cr-rich region some of the Cr transforms to the bcc structure from the fcc form of the alloy. At higher temperatures Cr reacts to form $CrAl_7$, and there is no evidence for ternary compound formation. Samples were also prepared with a controlled O contamination at the interface, and it inhibits the reaction much the same as for the pure metal cases. The Ni reaction is not identical to the pure sample case, since the presence of Cr slows down the reaction, and inhibits the initial reaction in the as-prepared bilayers.

INTRODUCTION

Nickel-chromium alloys have many applications such as for thin film resistors. In this paper glancing angle x-ray reflectivity and extended x-ray absorption fine structure (EXAFS) are used to look at the early stage of reaction of these alloys with Al. The reflectivity provides the overall density profile of the films as a function of depth, and the EXAFS is sensitive to small amounts of reaction at the interface. These results are compared to those obtained previously on Ni-Al and Cr-Al bilayers[1,2]. In the alloy both Ni and Cr react with Al at temperatures similar to the pure metal cases. This means that at lower temperatures Ni reacts but Cr does not. The diffusion of Ni into the Al layer leaves behind a Cr-rich layer in which bcc Cr particles nucleate. These results differ somewhat from earlier work[3], in that we observe lower reaction temperatures for $NiAl_3$ formation, and $CrAl_7$ formation below 400 °C. This may be due to the greater sensitivity of our methods, and cleaner sample preparation conditions.

A film with deliberate O contamination at the interface was also studied to compare with past results for the pure metals. Again the O had a similar effect by increasing the reaction temperature for both Ni and Cr. In many respects the Ni and Cr are found to react individually with the Al.

EXPERIMENTAL

The samples were prepared using e-beam evaporation in a UHV chamber with base pressure of 10^{-9} torr. The Ni-Cr alloy was deposited first from a single source of composition 80 at. % Ni and 20% Cr, and covered with a 50 nm pure Al layer. Since the Cr has a higher vapor pressure the deposited films were enriched in Cr and had compositions near 1:1 as

determined from the reflectivity and an Auger measurement. The gradual depletion of the Cr also caused a small composition gradient with the Cr concentration becoming smaller near the top of the Ni-Cr layer. The substrates were either float glass or Si with the float glass used for the glancing angle x-ray measurements because of its superior flatness. Two types of samples were prepared. The first had a clean interface, and for the second the Ni-Cr surface was exposed to 600 L of O_2 prior to the Al deposition.

The x-ray measurements were made at beamline X-11A at the National Synchrotron Light Source (NSLS). Reflectivity measurements were made at energies of 6289 eV (+300eV from Cr K-edge), and at 8033 and 8633 eV (±300eV from the Ni K-edge). Fig. 1 shows some examples of the reflectivity measured on the clean sample. The EXAFS measurements were made using Si (111) monochromator crystals, and a 100μm slit which gives an energy resolution of about 1.5 eV. The crystals were detuned 20-30% to reduce harmonics. Both the reflectivity and fluorescence signals were recorded using ion chambers, but only the fluorescence signal will be considered here. Fig. 2 shows examples of the Ni and Cr EXAFS from the clean sample. Fig. 3 shows similar spectra for the O_2 exposed sample. These spectra were recorded at the first reflectivity peak following the Al critical angle, and thus are probing approximately the first 5 nm of the Ni-Cr layer. For further quantitative analysis they were corrected for the anomalous dispersion distortions caused by the glancing angle method[4].

For the Ni data it is seen that major changes in the EXAFS for the clean sample begin at 255 °C with the spectra beginning to take on features similar to $NiAl_3$. For the O exposed sample, however, temperatures in excess of 300 °C are required for significant changes. This

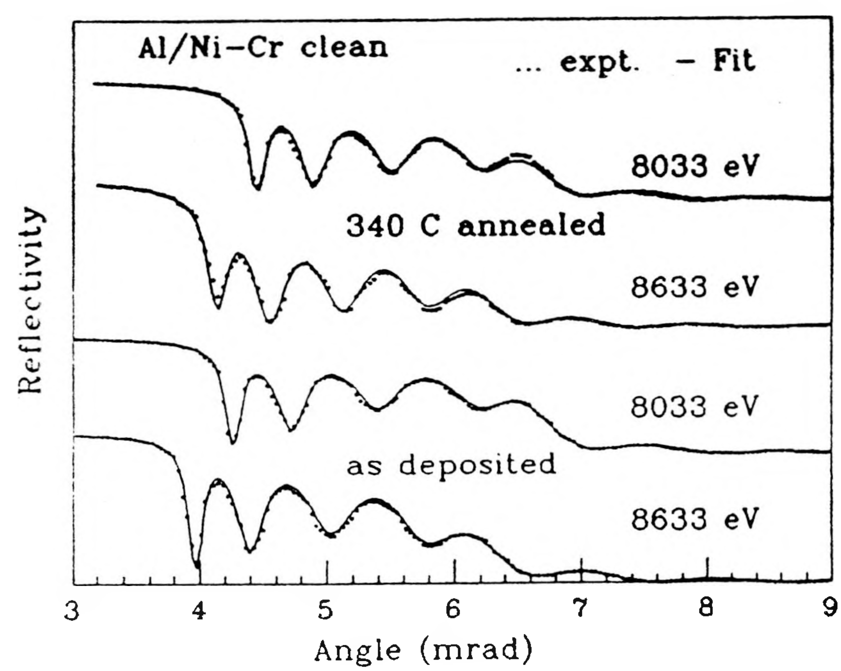

Fig. 1 Reflectivity data (points) obtained from the clean sample at two different annealing stages. The solid line is a fit to the data used to extract the density profiles as shown in fig. 4. The small breaks in the measured data are due to a minor stepping motor problem on the angle goniometer.

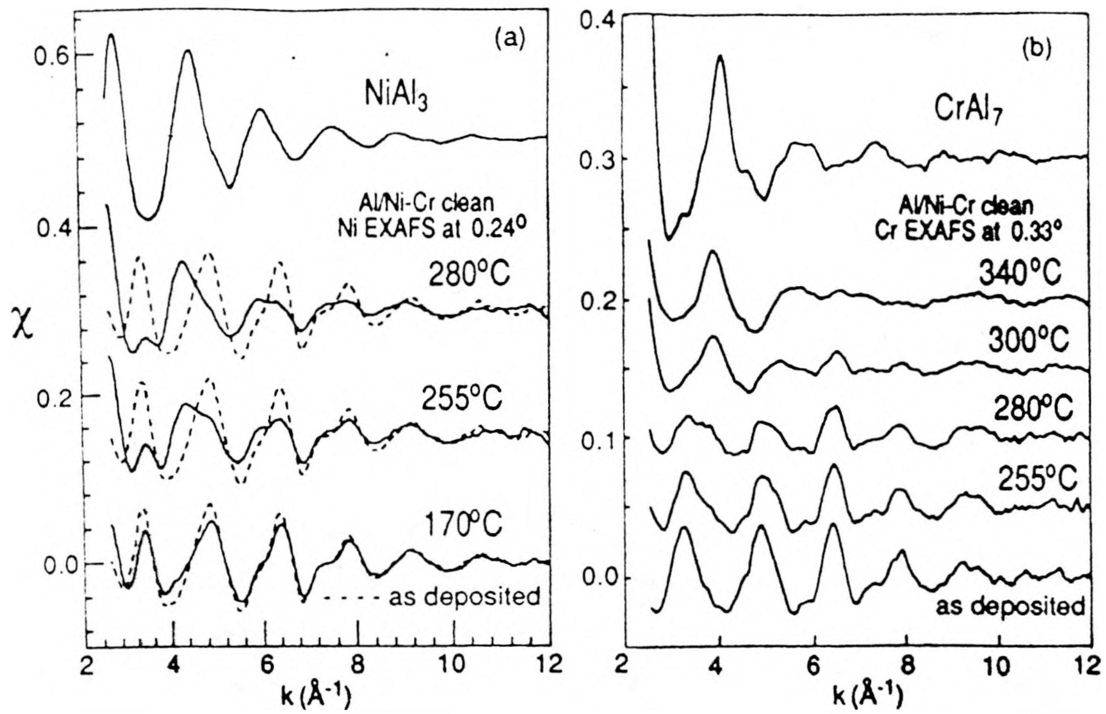

Fig. 2 EXAFS data for the clean sample measured at an angle corresponding to the first peak past the Al critical angle. (a) Ni edge data. (b) Cr edge data. The spectra for bulk $NiAl_3$ and $CrAl_7$ are included for comparison.

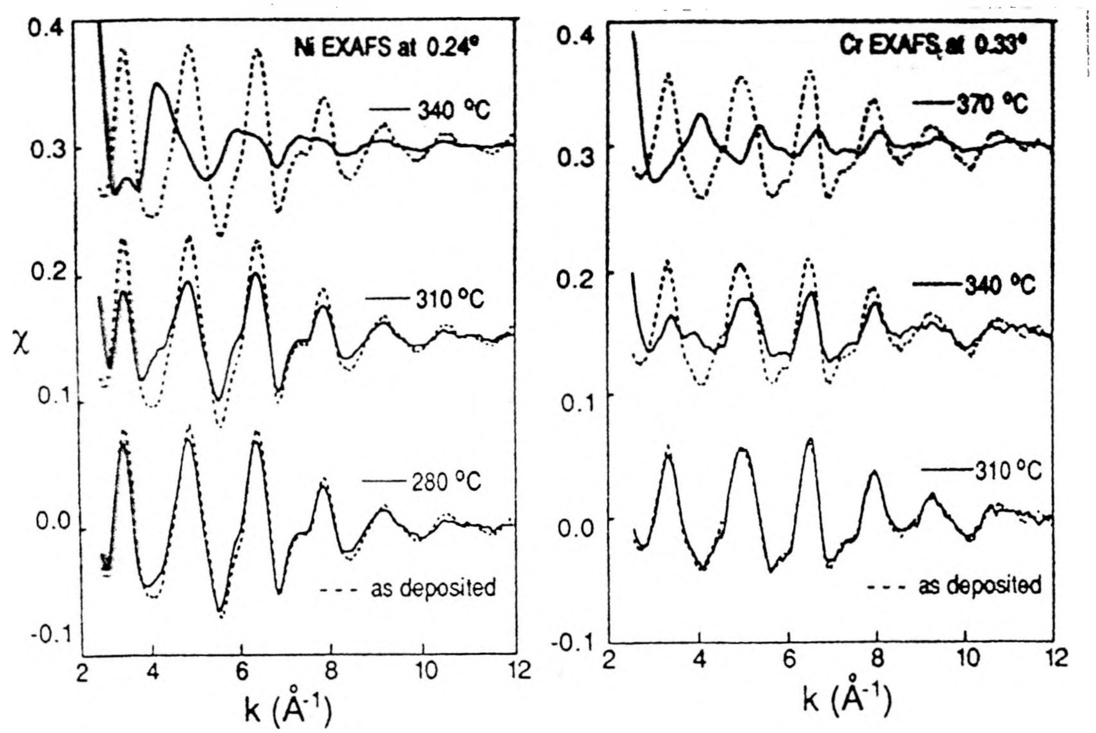

Fig. 3 EXAFS data for the 600 L O_2-exposed sample measured at an angle corresponding to the first peak past the Al critical angle. (a) Ni edge data. (b) Cr edge data.

is the same behavior and temperatures as found in pure Ni/Al bilayers, and indicates that the Ni-Al reaction occurs almost independently of the presence of Cr. The reaction between Cr and Al is delayed and requires temperatures in excess of 300 °C. Again the behavior is similar to pure Cr/Al bilayers.

ANALYSIS AND CONCLUSIONS

The reflectivity data were fit using procedures described elsewhere[5]. Basically the samples were modeled with a small number of layers of varying composition, density, and roughness. Having data at a number of energies greatly constrains the parameters, and makes the fitting simpler. Some examples of the fits are shown in fig. 1. The results of the fits are easiest to visualize by plotting the density profiles of the individual metals as shown in fig. 4. For the clean sample we see that at low temperatures the Ni-Al reaction proceeds in a planar fashion from the interface. This is in contrast to the behavior observed for pure Ni/Al bilayers where grain boundary diffusion of the Ni in the Al allowed the reaction to take place throughout the Al layer. Thus, the presence of the Cr seems to be hindering the Ni diffusion in the Al grain boundaries. The reaction is also observed to occur more slowly than for the pure Ni case. As seen in the profiles the Ni reaction results in a build up of Cr at the interface, since the Cr does not take part in the reaction with Al until higher temperatures. The high concentration of Cr at the interface may be hindering the movement of the Ni and causing the slower formation of $NiAl_3$.

In both samples the Cr is observed to build up at the interface as the Ni moves into the Al layer. The movement of the Ni probably results in the formation of voids at the interface, but these seem to be largely annealed out as the total Ni + Cr density is relatively constant. One consequence of the high Cr concentration is the formation of bcc Cr regions near the interface. This can be

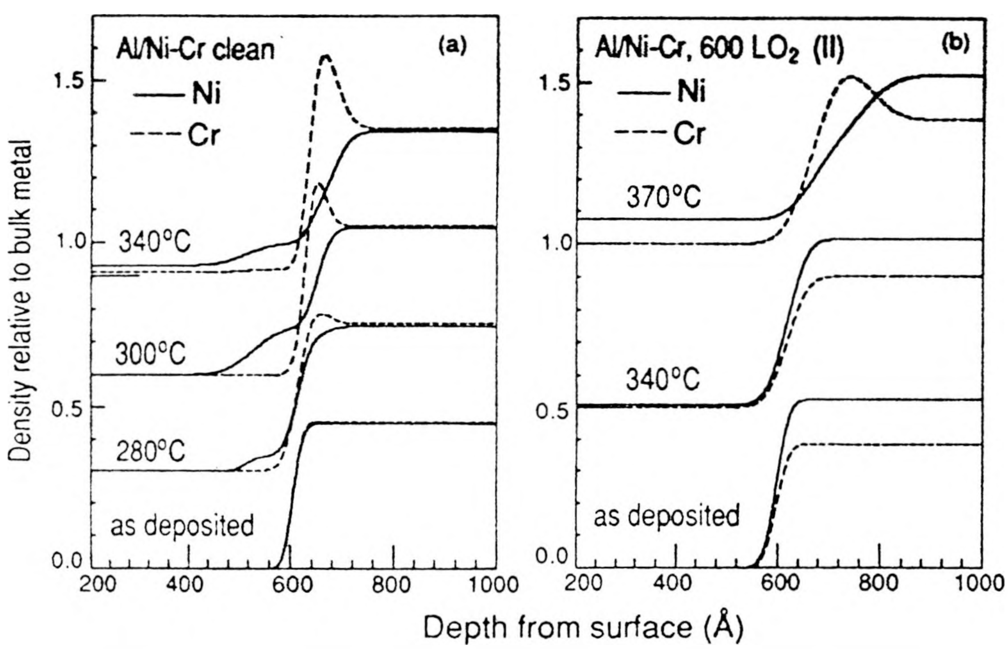

Fig. 4 Ni and Cr density profiles derived from the reflectivity fits: (a) clean interface sample, and (b) 600L O_2-exposed sample.

observed in the EXAFS spectra for the Cr edge. An example is shown in fig. 5. The spectra obtained at different angles probe different depths. At 5° the entire film is sampled, and the signal is still dominated by the fcc environment of the alloy. Clearly the Cr environment changes near the interface as measured at the smaller angles. For 0.476° the similarity to bcc Cr is evident. At smaller angles the spectra become increasingly different from bcc Cr. Detailed analysis indicated that this is due to the formation of $CrAl_7$. In the Ni EXAFS from this region Ni-Cr bonds characteristic of the fcc structure were still observed. Thus, the Cr rich region seems to be a mixture of nearly pure bcc Cr particles in a fcc Ni-Cr matrix.

To summarize the reflectivity and EXAFS results indicate that the Ni and Cr in the Ni-Cr alloys separately react with the Al overlayer. Both react at temperatures similar to the pure metal cases, and form the same compounds with Al ($NiAl_3$ and $CrAl_7$). No indication is found for ternary Ni-Cr-Al compounds. Since the Ni reacts at lower temperatures, a Cr rich layer is initially formed at the interface, and in this layer some of the Cr transforms to nearly pure bcc Cr. There are some differences from the pure metal bilayers. The Cr seems to be significantly changing the Ni diffusion. The reaction proceeds more slowly and the grain boundary diffusion of the Ni is suppressed. Also for the as prepared samples there is little indication of Ni-Al bonding as was observed in the pure metal bilayers.

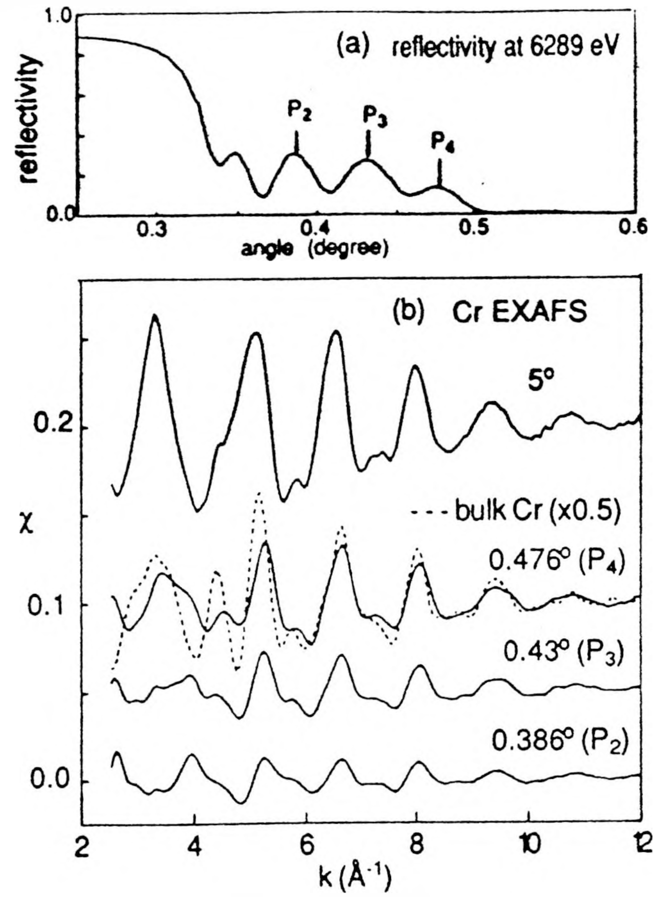

Fig. 5 Cr EXAFS from the 370 °C annealed O_2-exposed sample. The spectra were measured at different angles, as indicated in the reflectivity curve, to probe different depths. The 5° spectrum probes the entire film which is still mainly fcc. The dashed line is for pure bcc Cr, and the 0.476° spectra has strong similarities. At smaller angles the $CrAl_7$ contribution becomes significant.

ACKNOWLEDGEMENTS

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REFERENCES

1. S. M. Heald, E. V. Barrera, and H. Chen, Faraday Discuss. Chem. Soc. **89**, 21 (1990).

2. S. M. Heald, and E. V. Barrera, J. Mater. Res. **6**, 935 (1991).

3. A. E. Gershinskii, G. V. Timofeeva, and N. A. Shalygina, Thin Solid Films **162**, 171 (1988).

4. S. M. Heald, H. Chen, and J. M. Tranquada, Phys. Rev. B **38**, 1016 (1988).

5. H. Chen and S. M. Heald, J. Appl. Phys. **66**, 1793 (1989).