

Surface Characterization of Rhodium-Copper Alloys

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This paper presents the results of a surface analysis of copper-rhodium alloys by Auger electron spectroscopy during heat treatments under vacuum. It is shown that copper segregation takes place in the first atomic layer at every rhodium concentration. Special attention is given to the influence of diffusion rate on the composition of the surface region. The results are compared with theoretical models. A segregation enthalpy is determined for a 1.5 at.% Rh alloy at 873 K.

INTRODUCTION

As with all the other metals of the platinum group, rhodium shows interesting properties in the field of catalysis and anticorrosion. Industrial applications need a better understanding of the mechanisms controlling rhodium activity and of the modifications of the properties obtained by alloying rhodium. The choice of the copper-rhodium system is justified by:

- (1) the diversity of reactions catalysed by rhodium in various industrial processes;
- (2) the non-activity of copper towards the reactions catalysed by rhodium;
- (3) the price and rarity of rhodium;
- (4) the experience of the laboratory in the study of copper and some of its alloys (CuNi, CuMn, CuAl).¹⁻⁵

From a fundamental point of view, the rhodium-copper system presents interesting properties for the study of the segregation phenomenon.

The present paper deals with the characterization of single-crystal massive rods and thin films of rhodium-copper solid solutions. The paper previously published by Sundaram and Landers⁶ on the segregation behaviour of this system concerns only rhodium-rich films.

THEORETICAL APPROACH TO THE SYSTEM

To study the segregation of a solute to the surface of an alloy, it is necessary to examine the intrinsic properties of the constituent elements and those of the solid solutions.⁷

Table 1 presents the main properties of pure copper and rhodium. The enthalpies of mixing (ΔH_m) of rhodium in copper and of copper in rhodium are positive and of the order of 15 and 25 kJ mol⁻¹, respectively. Indeed, the system presents a large miscibility gap between 20 and 90 at.% Rh.

According to well-known theoretical models,⁸⁻¹¹ two factors favour the segregation of rhodium in copper-rich

alloys: the limited solubility of rhodium in copper and the difference in the atomic size of the elements; but the smaller surface tension of copper favours the migration of copper atoms to the surface, with a simultaneous reduction in the energy of the system. The relative importance of these three factors will determine the segregation behaviour of these alloys. For solid solutions of copper in rhodium, the three factors tend to promote copper segregation.

Theoretical models based on electronic properties forecast either a copper segregation or no segregation in both series of solid solutions.^{12,13}

EXPERIMENTAL PROCEDURE

The massive single crystals were prepared by the vertical Bridgman method and cut to obtain (111) faces. The detailed preparation procedure will be published elsewhere.¹⁴

Thin films of alloys were deposited by simultaneous sputtering of the two elements on polished single crystals of magnesium oxide in a high-vacuum vessel. The conditions of epitaxy of the alloys on the (100) face of MgO and the structure of the films were determined and are the subjects of another paper.¹⁵

Surface analysis was performed by Auger electron spectroscopy. The ultrahigh vacuum vessel was equipped with a retarding field analyser (VG Instruments). An angle of incidence of 75° between the electron beam and the surface normal allows good surface sensitivity for our measurements. Spectra were

Table 1. Main properties of pure copper and rhodium

	Copper	Rhodium
Crystallographic structure	fcc	fcc
Atomic radius (nm)	0.128	0.134
Atomic volume (cm ³ mol ⁻¹)	7.09	8.27
Melting point (K)	1356	2239
Vaporization enthalpy (J mol ⁻¹)	338 000	556 000
Surface tension (J mol ⁻¹)	1.85	2.75

registered in the $dN(E)/N(E)$ mode with a modulation voltage of $1.75 V_{pp}$ and a sweep rate of $0.5 eV s^{-1}$ for the low-energy peaks ($E < 80 eV$), or with a modulation voltage of $4 V_{pp}$ and a sweep rate of $0.7 eV s^{-1}$ for the high-energy peaks.

It was possible in this apparatus to register spectra during heat treatment (pressure = 7×10^{-7} Pa) and so avoid modifications of the surface composition due to the cooling process.

Before any segregation measurement, the samples were cleaned *in situ* by cycles of ion bombardment and heating in a hydrogen atmosphere. This procedure reduced the level of surface impurities and decreased the impurity content of the bulk phase. The relative sensitivity factors of copper and rhodium were measured with our apparatus on a sample presenting, simultaneously, the two pure elements at its surface. Calculations showed the negligible effect of the matrix on the sensitivity factors in the alloys.

RESULTS AND DISCUSSION

Three massive single crystals of 1.5, 8.75 and 15 at.% Rh were examined and heated at various temperatures: 473, 573, 623, 673, 723, 773 and 873 K. Figure 1 illustrates the change in element concentrations during heat treatment under vacuum. Thin films of 8 at.% Rh and higher (between 85 and 90 at.% Rh) were also analysed. The reduced thickness of these samples (~ 30 nm) did not allow many experiments, as each erosion modified the thickness and the global composition of the films. For this type of sample we chose two temperatures (673 and 773 K) for analogy with the massive alloys.

For every concentration and at any temperature, a different behaviour for high and low-energy peaks was observed (Fig. 2). The origin of this difference depends on the type of sample. The mean concentration of the surface region is obtained from the peak-to-peak height (H_i) of the 303 eV rhodium peak and of the 920 eV copper peak, corrected by the sensitivity factor of rhodium towards copper ($S_{Rh} = 7.5$, $S_{Cu} = 1$), following

the well-known formula

$$X_i = \frac{H_i}{S_i} / \sum_{i=1}^n \frac{H_i}{S_i}$$

The application of the monolayer model of Pons *et al.*,¹⁶ considering that the segregation modifies only the composition of the first monolayer, does not explain the observations for massive alloys at 8.75 and 15 at.% Rh and for the 8 at.% Rh thin films. By studying the evolution of the low- and high-energy peaks at different temperatures, we propose a model with a first layer enriched in copper followed by a few layers enriched in rhodium (Fig. 3). The increase of the copper concentration in the surface region with temperature is not characteristic of the segregation phenomenon, but is explained by the higher efficiency of the diffusion. From our results, it is impossible to assert that the rhodium enrichment in the first six layers is only due to the cleaning procedure and to the slowness of the diffusion, or that it will be eliminated by a very long heat treatment. It is possible that the equilibrium profile of the samples is non-monotonous.

Examination of the results obtained on the 1.5 at.% Rh alloy shows that at low temperatures (450, 563 K) the diffusion is too slow to reduce the enrichment resulting from ionic erosion (the heterodiffusion coefficient of rhodium in copper at 450 K is of the order of $3.4 \times 10^{-28} cm^2 s^{-1}$). The results obtained at 873 K reflect the influence of diffusion: the rapid increase of the copper peak at 106 eV reveals the presence of a driving force for the segregation of copper; the slower evolution of the copper peak at 920 eV is controlled by diffusion of the elements from the bulk. Indeed, at this temperature the diffusion coefficient is high enough to compensate for the erosion effect and the migration of the copper atoms from layers adjacent to the surface. In these conditions, we estimate that equilibrium of the segregation process is reached. If the segregation entropy is neglected, the segregation enthalpy can be estimated from the formula

$$\frac{X^a}{1 - X^a} = \frac{X^b}{1 - X^b} \exp(-\Delta H/RT)$$

where X^a and X^b are the solute concentration in the surface and in the bulk, respectively.

For the 1.5 at.% Rh alloy at 873 K, the copper segregation enthalpy is of the order of $-8 \times 10^3 J mol^{-1}$. This low value, in comparison with those observed for other systems, could be explained by the competition between surface tension, atomic size and the limited solubility effects. Experiments realised at temperatures higher than 873 K showed the important part played by copper evaporation, which reduces the concentration of this element in the first atomic layer. Heat treatments applied to thin films with a high content of rhodium induced a rapid growth of the 58 and 61 eV peaks of copper and the disappearance of the low-energy peak of rhodium at 40 eV. Simultaneously, the 106 eV copper peak appeared in the spectrum. This copper segregation was so important that, after five or six heat treatments followed by erosion, the copper peaks were no longer

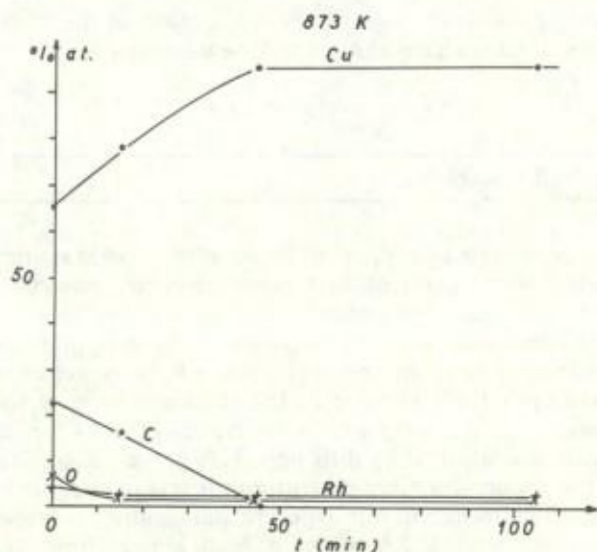


Figure 1. Change in the surface region composition of a 1.5 at.% Rh alloy during heat treatment at 873 K.

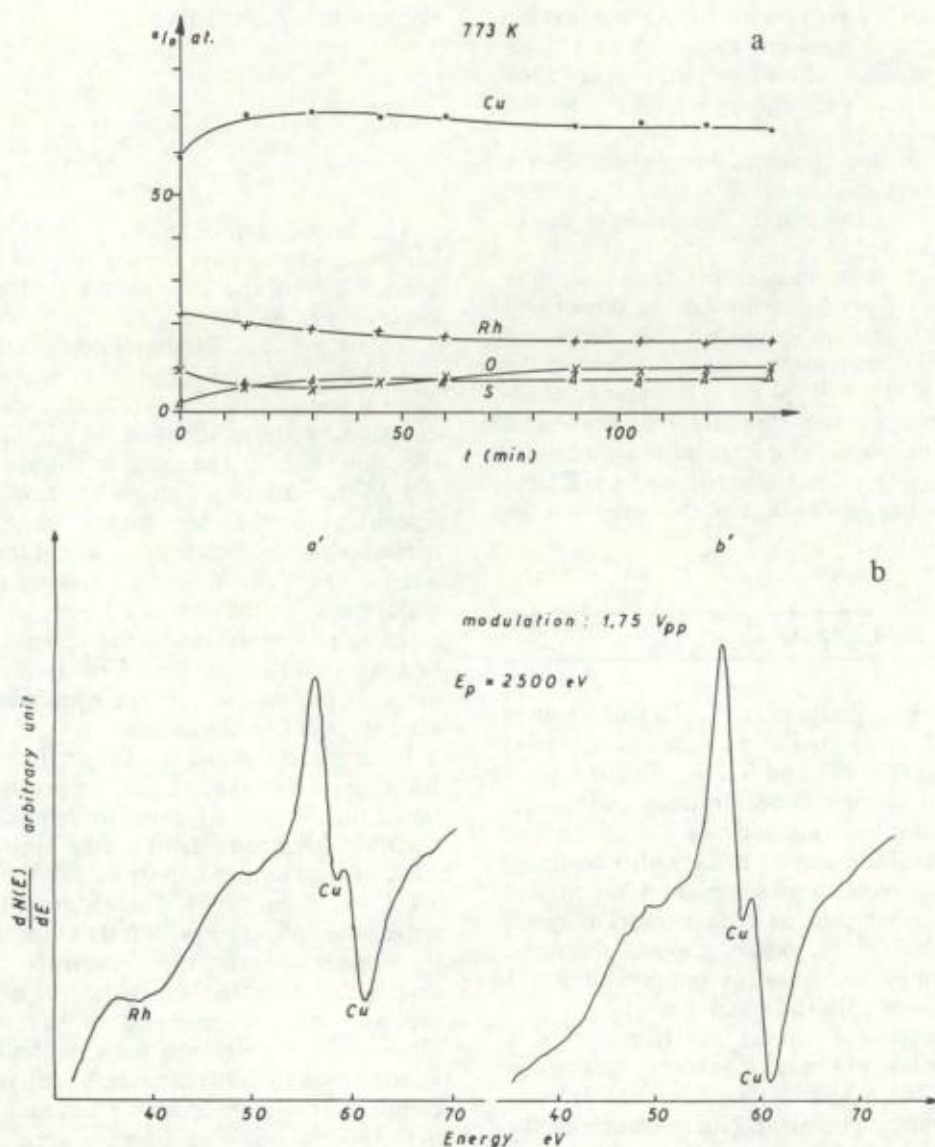


Figure 2. Change in the high-energy (a) and low-energy (b) peaks during heat treatment of an 8.75 at.% Rh sample (a' = after ion bombardment, b' = after 1 h at 773 K).

detected. These results, showing a marked copper segregation in the first atomic layer, are in agreement with the observations of Sundaram and Landers⁶ on a sample of 95 at.% Rh. In our experimental conditions, it

was impossible to quantify the segregation, as the 'bulk' concentration changed after each heat treatment.

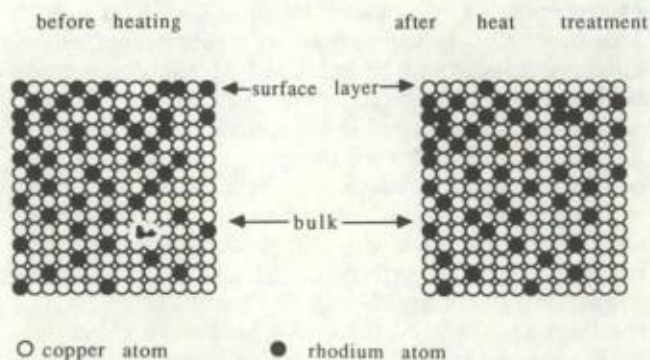


Figure 3. Model of the element distribution in the surface region of copper-rhodium alloys.

CONCLUSIONS

The behaviour of copper-rhodium alloys was examined during heat treatments. At every rhodium concentration, a surface segregation of copper was observed, in agreement with theoretical models. It seems that the dominating term in the expression of the segregation enthalpy is the difference in the surface tension of the elements. The composition variation of the surface region is controlled by diffusion. This process is so slow in the copper-rhodium system that it was impossible to reach equilibrium in our experimental conditions except for the 1.5 at.% Rh alloy at high temperature. We propose the following model for the other samples: the first layer is enriched in copper and the underlying

layers are impoverished in copper. The importance of the rhodium concentration in the layers adjacent to the surface is controlled by diffusion from the bulk. The behaviour of thin films and massive single crystals is similar.

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