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Segregation-Induced Reconstruction of the $Co_{50}Ni_{50}(100)$ Surface

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The surface crystallographic structure and layer-by-layer composition of single-crystal $Co_{50}Ni_{50}(100)$ alloy were studied in a wider temperature range than in previous studies. Using the Low Energy Electron Diffraction (LEED) and Ionization Spectroscopy (IS), a strong temperature dependence of surface enrichment in Co and the possibility of the segregation-induced surface martensitic-type reconstruction were shown to occur.

1. Introduction

The surface of Co-Ni alloys is the subject of much current interest because of its catalytic (for example, CO+NO and $CO+H_2$ reactions) and magnetic (magnetic storage) properties. The alloys with ferromagnetic components are also of great interest for theoretical studies of surface segregations [1–4], in particular, in the case of alloy components having similar values of parameters such as heat of formation, binding energies, atomic mass, atomic radius, etc. According to the theories based on broken bond models and the lattice-strain theory, the surface segregation in Co-Ni alloys should be vanishingly small. The other point of interest to this system is connected with using the Co-Ni alloys as a new reference material for quantitative surface analysis, because the correction of matrix effects of those alloys, such as the atomic density, the back-scattering factor and inelastic mean free path correction, as well as the effect of preferential sputtering and ion irradiation-induced surface segregation were found to be negligibly small [5].

The Co-Ni system has been the object of a number of studies in view of its unique surface segregation behaviour [6–11]. However, their results on the surface composition both at room temperatures and also at high temperatures are controversial. Cherepin *et al* [6] have used the Auger electron spectra, corresponding to the high-energy transitions, for the analysis of surface content, and they have found for the first time a slight enrichment (a few percent above the polycrystalline $Co_{50}Ni_{50}$ bulk composition) in Ni on the surface of sample after the heating at 773 K for 1 h, bombardment with Ar^+ ions, and cooling down to the room temperature. Tanaka *et al* [7] have suggested that no surface segregation occurs in the polycrystalline sample of the Co-Ni system. They applied various preheating procedures (770 K 1 h, 850 K 1 h, and 1200 K 1 s) and registered the high-energy AES spectra after cooling the samples down to the room temperature. No differences in Auger spectra were observed. Godowski and Rundny [8] have investigated using AES both the surface composition of the polycrystalline $Co_{50}Ni_{50}$ alloy as a function of temperature, and the influence of sulphur on this composition. They have used for the first time the qualitative method of AES based on the low-energy $M_{23}VV$ transition and recorded the Auger signals during the stepwise increase of temperature. Cleaning of the sample surface was performed by the bombardment with potassium ions (500 eV) at 500 K. It was found that a clean surface contains 52 % Ni in the temperature range 600 to 800 K, while at higher temperatures up to 1100 K the surface is enriched in cobalt (66.1 % Co at 1100 K). The presence of sulphur does not disturb the trend for the Co segregation on the surface of $Co_{50}Ni_{50}$ alloy, but changes the proportion of the concentration of both alloy constituents. The first attempt to study both the temperature and crystallographic dependences of surface composition for Co-Ni alloys has been performed by Hajcsar *et al* [9]. They have studied the polycrystalline $Co_{56}Ni_{44}$ sample, but it was possible to study separately two large grains (1 mm in diameter) with surfaces oriented along the (111) and (210) faces. In subsequent experiments [10] this group has investigated the (100), (110), and (111) faces of the $Co_{50}Ni_{50}$ single crystal. The authors [9,10] have performed the measurements of relative low-energy Auger yield at various temperatures. The Ni segregation was found in these studies on all faces over the temperature range from 879 to 1100 K (73.5, 75.1, and 74.4 at.% Ni for (111), (110), (100) faces at 909 K, respectively). These experimental data [9,10] were confirmed by the studies of Underhill [11] with the use of Embedded Atom Method (EAM).

The aim of the present work is the study of the temperature dependence of the surface composition and crystallographic structure of monocrystalline $Co_{50}Ni_{50}$ (100) alloy in a wider (in comparison with previous studies) temperature range above the room temperature. This is the first study where both the surface structure and surface multilayer composition of the Co-Ni system alloys were observed. Using the IS and LEED methods we have found a strong temperature dependent Co enrichment of a few surfaces layers and the possibility for segregation-induced surface reconstruction in this alloy.

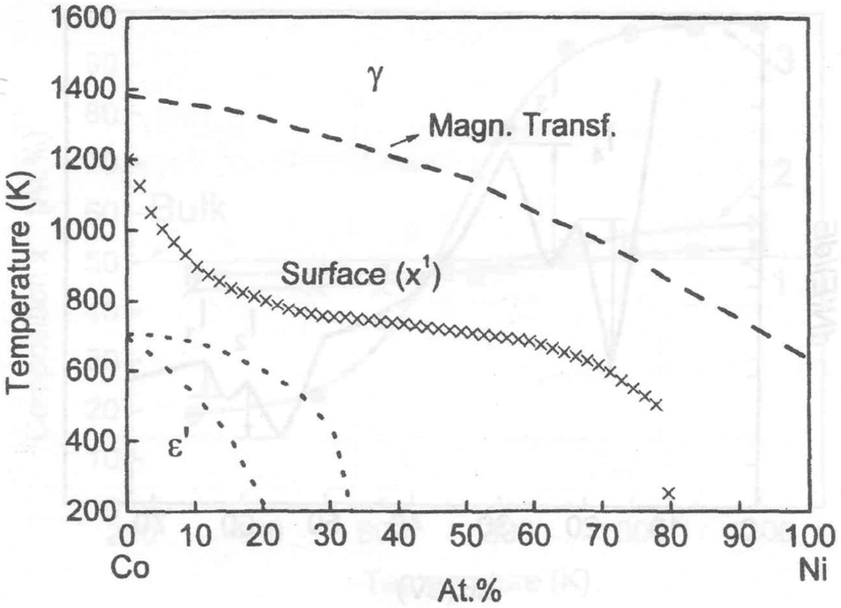

Figure 1. Phase diagram of the Co-Ni alloys [12]. The symbols × were plotted on the basis of the present work.

2. Experimental Procedures

According to the phase diagram of the Co-Ni alloys system [12] (Fig.1), the $Co_{50}Ni_{50}$ alloy has the fcc γ phase in the whole temperature range. This system is known to form a continuous series of random substitutional solid solutions across the whole composition range at all temperatures. The temperature interval between liquidus and solidus is very small, which indicates that the solid solution may be described as nearly thermodynamically ideal. At room temperature, the ε'(hcp) phase exists in the range of Ni content from 0 at.% to 35 at.%. According to the results of X-ray diffraction studies of the bulk monocrystalline sample of $Co_{50}Ni_{50}$ alloy, it forms a homogeneous solid solution with fcc structure at room temperature.

A sample of the $Co_{50}Ni_{50}$ single crystal with a (100) oriented face was mounted, after the electropolishing, at a manipulator in the vacuum system [13] with base pressure of $5 \cdot 10^{-8}$ Pa. On the surface of the sample a Pt-PtRh thermocouple was attached by spot welding. The accuracy of the temperature measurement was of the order of 1 %. *In situ* cleaning of the sample surface was achieved by means of cycles of Ar^+ ion bombardment (600 eV, 3 mA/cm^2) at 870 K for several hours. The AES measurements were carried out using the four-grid quasi-spherical LEED optics as retarding field electron analyser (RFA)

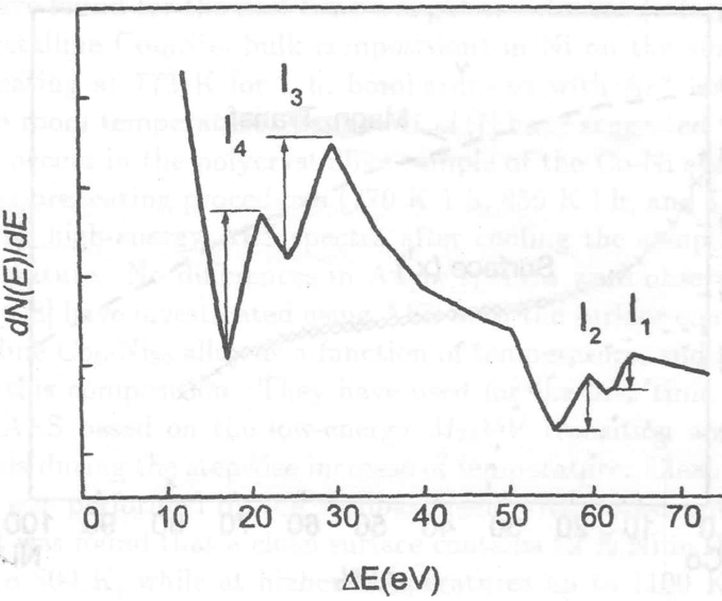

Figure 2. Ionization loss peaks spectra.

to detect the surface contamination composition. The absence of C and O peaks in the AES spectra was a criterion of accomplishment of the cleaning process. In this case the peak of sulphur at 150 eV was about 50 times smaller than the peak of Ni at 102 eV. At room temperature, after slow cooling from 1000 K, the clean surface exhibited a LEED pattern corresponding to the fcc bulk-like termination (1 × 1)-(100) structure without additional reflexes.

It is known that the determination of the quantitative composition of Co-Ni alloys by AES is very difficult because of the strong effects of peaks overlapping [8–10]. Besides, strong temperature dependence of the intensity of low-energy Auger peaks for L_3VV and M_3VV transitions in ferromagnetic pure Ni and Co was found by Vasiliev *et al* [14]. This is related to the changes in the valence electron band structure caused by an increase of interlayer spaces during the sample heating (thermal expansion and magnetostriction effects). On the other hand, the high-energy Auger peaks be independent of these effects but have not sufficient surface sensitivity for layer-by-layer analysis with monolayer resolution. For this reason we have used the IS method to study the thermostimulated surface segregation in Co-Ni alloy. It was described for the first time by Gerlach [15] for the surface contaminations analysis on metals. He has demonstrated that IS gives narrower less complex features, which simplify analysis.

In order to measure the changes of Co and Ni compositions, we have moni-

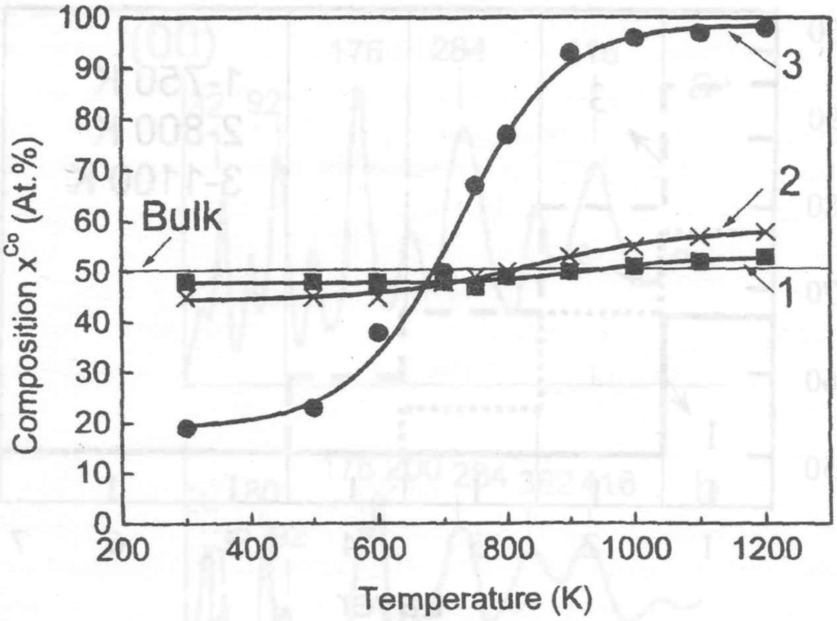

Figure 3. Temperature dependence of the Co surface content observed by XPS (curve 1), AES (curve 2), and IS (curve 3).

tored the ionization loss peaks from Co3p-and Ni3p-states, corresponding to the core level peaks $E(\mathrm{Ni}) = 68$ eV and $E(\mathrm{Co}) = 62$ eV (Fig.2). Recording of the $dN(E)/dE$ IS peaks was done using the LEED optics in the RFA mode. IS spectra were recorded without switching off the sample heater. Since the energy of the IS electrons is generally lower in comparison with Auger electrons, IS is a more surface sensitive method. Moreover, the surface sensitivity can be varied by varying the energy of the primary electron beam. Vasiliev *et al* [16] were the first to propose a novel approach for non-destructive layer-by-layer analysis of the composition in the near-surface region. The essence of this approach is in the experimental measurement of the element concentrations, determined by IS, on the basis of the change of the primary electrons energy with subsequent recovery from these data of a layer-by-layer information using the mathematical processing methods. In addition, for qualitative comparison, we also used the high energy AES peaks measurement in a standard way and the XPS with X-ray MgK$_\alpha$ radiation excited the photoelectrons, using ESCALAB-type system.

3. Results and Discussion

Fig.3 shows the temperature dependence of Co composition calculated after XPS (curve 1), after AES for Co $L_3M_{4.5}M_{4.5}$ and Ni $L_3M_{4.5}M_{4.5}$ Auger peaks

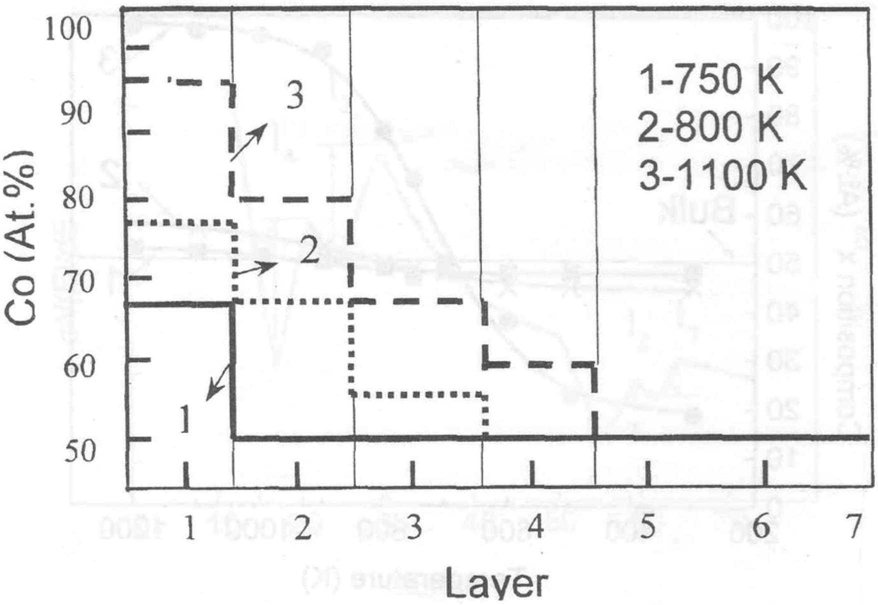

Figure 4. Co content x^{Co} in ten surface layers at different temperatures.

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(curve 2), and IS data for the first layer (curve 3). Three curves shown in Fig. 3 behave in the same manner, i.e. there is Ni enrichment of the surface in the range 300–700 K and the increase of Co content in the temperature range from 700 to 1200 K. However, the values of x^{Co} are different for XPS, AES, and IS at each fixed temperature. According to the XPS and AES data, Co segregates slowly (about 5–10 %), while IS yields a very strong Co enrichment at the same temperatures. The matter is that the noncoincident data shown in curves 1–2 correspond to the depth-averaged composition (curves 1 and 2 correspond to approximately 4–5 and 6–7 layers, respectively), while curve 3 corresponds to the composition of the first (topmost) layer. So we can conclude that XPS and AES with high-energy transition give only rough data and the concentration profile of Co and Ni atoms distribution in the near surface region cannot be deduced. Using the non-destructive IS layer-by-layer analysis [16] we calculated the Co content for ten surface layers at several temperatures (Fig.4).

One can see from Fig.3 that the Co content in the first layer varies monotonously and has a maximum at ∼ 1150 K. A composition crossover with Co bulk value was found at approximately 700 K. For lower temperatures the surface enrichment in Ni is observed, whereas for higher temperatures the enrichment in Co occurs, and the Co concentration can reach up to 98–99 at.% at high temperatures. Fig.4 shows the complete results of the IS layer-by-layer depth profiling. The surface enrichment in Co is seen for the first few layers at high

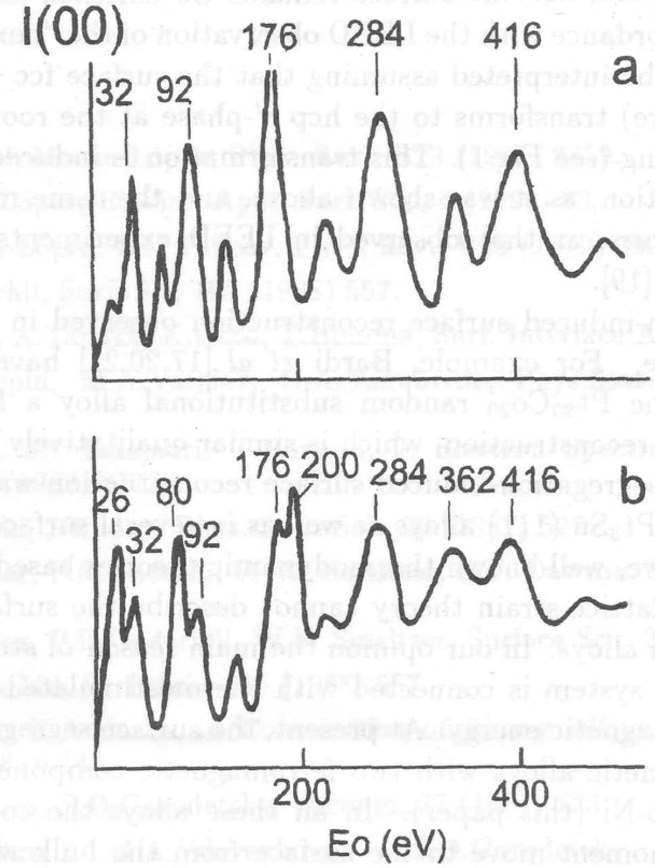

Figure 5. $I_{(00)}(E_0)$ LEED spectra. a) for the initial state and b) after annealing at 1100 K and quenching.

temperature and, conversely, in Ni – for the temperatures lower than 700 K. A monotonous decrease in the composition as a function of the surface atomic layer is typical of non-ordering alloys [17,18].

At all temperatures investigated the LEED patterns corresponded to the bulk-like fcc (1 × 1)-(100) structure. However, the quenching of the sample (the cooling rate being 0.6 K/s) after annealing at 1150 K to room temperature led to the appearance of additional reflexes. In the first approximation these reflexes form two regular hexagons. These new surface-layer diffraction reflexes coexist with the bulk (100) reflexes in the energy range $20 \leq E_0 \geq 200$ eV and vanish at $E_0 > 400$ eV. We suggest that the new structure exists only in the outermost 1–2 layers. An example of the LEED $I_{00}(E)$-curves from the annealed sample and from the one after quenching are shown in Fig.5. Quenching results in the changes in the numbers and energy of the Bragg reflections. Using IS analysis we also found a "freezing" of the high Co content after the sample quenching from high temperature; i.e. the surface remains Co enriched also at the room temperature in accordance with the LEED observation of the "hexagonal" phase. These results may be interpreted assuming that the surface fcc γ-phase (stable at high temperature) transforms to the hcp ε'-phase at the room temperature during the quenching (see Fig.1). This transformation is induced by the strong surface Co segregation, as it was shown above, and the same martensitic-type transformation occurs, as that observed in LEED experiments at the (1000) surface of pure Co [19].

The segregation-induced surface reconstruction observed in $Co_{50}Ni_{50}$ (100) alloy is not unique. For example, Bardi *et al* [17,20,21] have found on the (100) surface of the $Pt_{80}Co_{20}$ random substitutional alloy a Pt segregation-induced hexagonal reconstruction, which is similar qualitatively to that of pure Pt(100) [20]. The segregation-induced surface reconstruction was also found in $Pt_{50}Ni_{50}$(100) and Pt_3Sn (111) alloys as well as in several surface alloys [17,18].

As pointed above, well-known thermodynamic theories based on the broken bond models and lattice-strain theory cannot describe the surface segregation behaviour in Co-Ni alloys. In our opinion the main reason of strong Co surface segregation in this system is connected with thermostimulated changes of the bulk and surface magnetic energy. At present, the surface segregation is studied for three ferromagnetic alloys with two ferromagnetic components: Co-Fe [1], Fe-Ni [22], and Co-Ni (this paper). In all these alloys the components with higher magnetic moment move to the surface from the bulk with the growth of temperature. This was predicted for the first time by Morán-López [1,2] for $Co_{50}Fe_{50}$ alloy. In this connection, entropy is the most important term in the free surface energy.

4. Conclusions

A surface structure and composition of the $Co_{50}Ni_{50}$(100) alloy were studied by Low Energy Electron Diffraction (LEED) and non-destructive quantitative depth profiling Ionization Spectroscopy (IS) over the temperature range from 300 to 1100 K. At the room temperature the cleaned surface shows a LEED pattern of the bulk-like (1 × 1)-(100) face, suggesting a bulk termination of fcc structure. The data of IS-experiments reveal a monotonous surface enrichment (in the first few layers) in Co, observed above 700 K, and in Ni, below this temperature. We also observed by LEED a hexagonal reconstruction of the surface layer resulting from rapid quenching after annealing the sample at 1100–1200 K. This reconstruction can be interpreted as a result of surface phase transition from high-temperature Co-rich fcc phase to the surface hcp ε' phase at room temperature. The possible driving forces of surface enrichment in Co are discussed.

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