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Kinetic processes in the growth and decomposition of a two-dimensional binary alloy

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Abstract

The growth and decomposition of a two-dimensional cobalt–chromium binary alloy on the W(110) surface were studied with scanning tunneling microscopy. At room temperature, co-deposited cobalt and chromium were found to grow in a homogeneous nucleation scheme. At the annealing temperature of 150°C, the co-deposited films decompose into two phases, cobalt-rich and chromium-rich phases, showing good agreement with the reported phase diagram. In the decomposed film with 0.9 monolayer of cobalt and 0.2 monolayer of chromium, the second-layer islands are cobalt-rich phases. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Alloys; Cobalt; Chromium; Decomposition; Growth

1. Introduction

In metal alloys, technologically important properties such as mechanical strength, toughness, creep, corrosion resistance, magnetism and superconductivity are determined by the bulk phase diagrams, which are functions of formation energy, entropy, size difference, composition, impurity, etc. [1]. Alloys formed near the melting temperatures of metals often decompose into two or more phases as they are cooled down, showing variation of concentration at room temperature. Knowing the thermodynamic and kinetic mechanisms for the decomposition of alloys, one can optimize the properties of alloys as well as design new materials with novel properties by controlling the growth of precipitates.

Thin films of Co–Cr magnetic alloy have been a promising candidate for longitudinal high-density recording media [2,3]. But films grown by sputtering the target sources of cobalt and chromium at room temperature reveal relatively low coercive field and substantial media noise [4]. It was suggested that paramagnetic chromium precipitates, provided they were grown inside and at the interface of the ferromagnetic single domains, could enhance magnetic anisotropy, resulting in a higher coercive field [5]. Experimentally, the film grown at the substrate temperature of >200°C reveals higher coercive field with lower media noise than that grown at room temperature [4,6,7].

Experimental efforts have been made to visualize the chromium precipitates in the films grown

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at substrate temperature of >200°C. The growth of chromium precipitates was indirectly confirmed by the observation of a flower-like pattern in transmission electron microscopy (TEM) images of chemically etched Co–Cr thin films [8,9]. In atom-probe field ion microscopy (APFIM) studies [10,11], concentration modulation was reported in the sputter-grown Co–Cr thin films. In a recent scanning tunneling microscopy (STM) study, the decomposition of Co–Cr alloy into cobalt-rich and chromium-rich phases was observed on W(110) [12]. In this paper, we report the kinetic processes for the growth and decomposition of a two-dimensional (2D) Co–Cr binary alloy on a W(110) surface.

2. Experimental

The detailed design of the scanning tunneling microscope used in this study can be found elsewhere [13]. The W(110) substrate was cleaned by repeated cycles of Ar^+-ion sputtering and annealing. Carbon impurity was removed by repeated annealing at 2200°C in an O_2 pressure of 1×10^{-7} Torr and 1×10^{-10} Torr. The STM images were taken within 30 min at room temperature after annealing the substrate. The cobalt was deposited by directly heating a 5N cobalt wire and the chromium was deposited from a Knudsen cell. The deposition rates could be controlled within 0.1–1.1 ML min^{-1} (ML = monolayers) for both

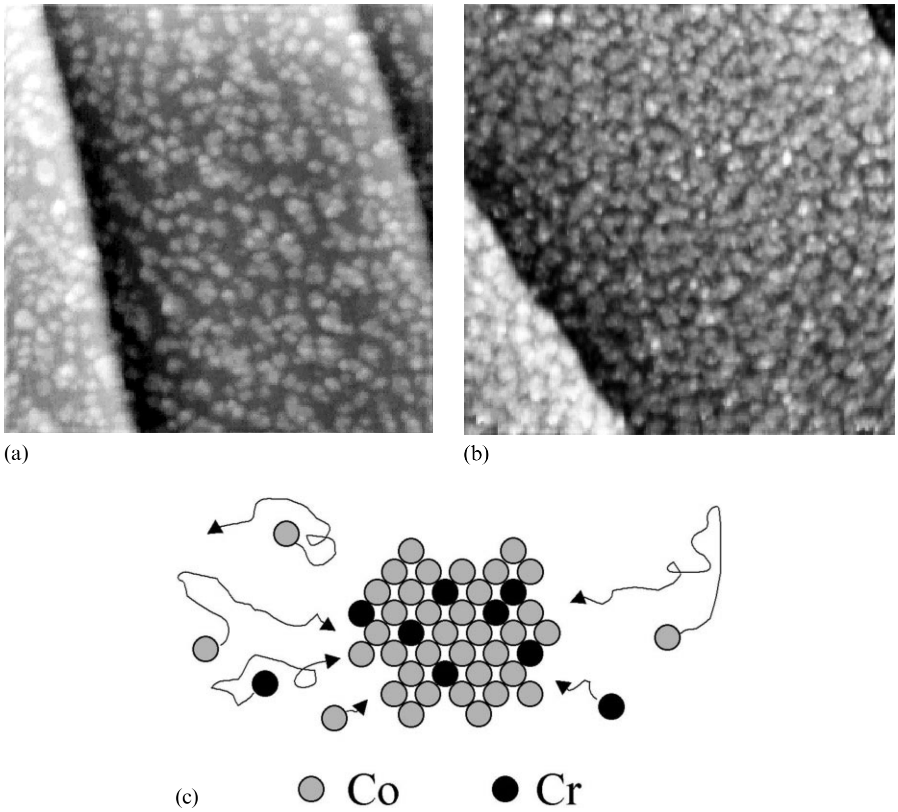

Fig. 1. STM images obtained after co-depositing cobalt and chromium on the W(110) surface at room temperature: (a) 0.3 ML of cobalt and 0.1 ML of chromium; (b) 1.1 ML of cobalt and 0.1 ML of chromium. Both images are 400 Å × 400 Å and were taken with a sample bias voltage of 2 V. (c) Schematic illustration of the growth process.

cobalt and chromium, and were cross-checked with STM images and by Auger electron spectroscopy (AES). During the deposition, the pressure of the chamber did not exceed 6×10^{-10} Torr. All images were taken at room temperature as-deposited or cooled after annealing.

3. Results and discussion

A bare W(110) surface was chosen as a substrate to study the alloying behaviors of cobalt and chromium. It is well known that neither cobalt nor chromium forms a surface alloy on the close-packed W(110) surface at <1000°C [14,15]. At the same time, both cobalt and chromium are grown pseudomorphically on the W(110) surface up to ~1 ML. In order to understand the kinetically limited alloying process, cobalt and chromium were co-deposited at room temperature. Fig. 1 shows typical STM images at the initial stages. It is well known that cobalt and chromium atoms are mobile on the W(110) surface at room temperature [14,15]. The observed growth behavior mainly depends on the total coverage of cobalt and chromium, regardless of the detailed compositional ratio. At the total coverage of <0.5 ML, 2D islands are uniformly distributed over the surface as shown in Fig. 1a. Most of the islands do not form percolation paths with some exceptions. The grown films maintain their structure for several hours at room temperature. The growth process can be explained as homogeneous nucleation. As newly deposited adatoms diffuse to meet another mobile adatoms or pre-existing 2D islands, they eventually attach to 2D islands as depicted in Fig. 1c. At high temperature with large enough diffusivity, the island shape is determined by minimizing the free energy of the system. At low temperature, the island shape depends on kinetic parameters such as the deposition flux, the island size and the edge diffusivity [16]. With the island shape given in Fig. 1a, cobalt and chromium adatoms diffuse along the edges of the islands until they reach a kink to lower the configuration energy of the island. At the total coverage of >1 ML, in Fig. 1b, 2D islands with one or two atomic layers height coalesce to form a complex structure with percolation paths among the islands, as the growth of co-deposited cobalt and chromium is kinetically limited. Regular and smooth structure cannot be formed with the low edge diffusivity. Since the deposition fluxes have a random nature, cobalt and chromium adatoms arrive at the 2D islands in random sequence. Therefore, the co-deposited thin film is a homogeneously disordered alloy.

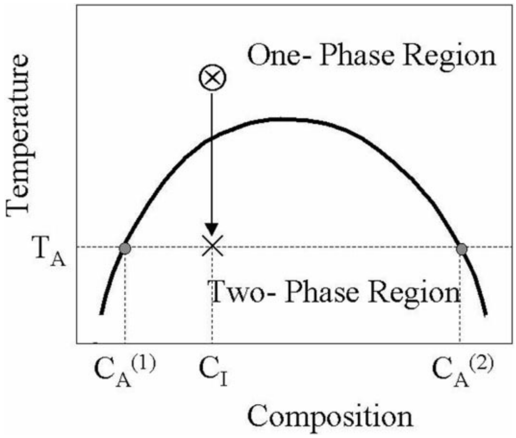

Fig. 2. A schematic phase diagram for cobalt and chromium at ~100°C with a miscibility gap which separates the one-phase region at high temperature and the two-phase region at low temperature.

It was reported that the Co–Cr system has a miscibility gap at low temperature (~100°C) [11,17]. Fig. 2 shows a schematic phase diagram with a miscibility gap which separates the one-phase region at high temperature and the two-phase region at low temperature. In view of the phase diagram, once an initial state with composition C_I in the one-phase region is cooled down to the two-phase region, it results in two decomposed phases with the compositions $C_A^{(1)}$ and $C_A^{(2)}$ at temperature T_A. But we took a slightly different experimental scheme to solve the practical problem of the Co–Cr system [12]. By co-depositing cobalt and chromium at room temperature, we initially made the homogeneously disordered alloy and annealed at T_A to decompose it into the two stable phases [12], which is determined by the miscibility gap in the phase diagram.

Fig. 3 shows an STM image of the film with 0.9 ML of cobalt and 0.2 ML of chromium co-deposited and annealed at 150°C for 1 min. As

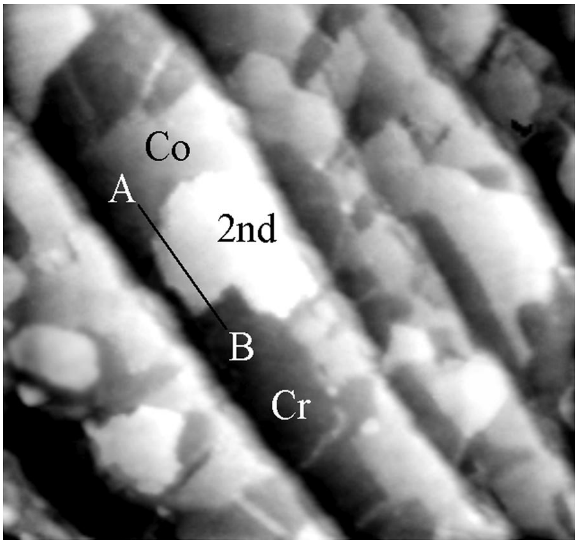

Fig. 3. STM image of the surface with 0.9 ML of cobalt and 0.2 ML of chromium co-deposited at room temperature and subsequently annealed at 150°C for 1 min. Cobalt-rich, chromium-rich and second-layer islands are labeled as Co, Cr and 2nd, respectively. Image size: 1300 Å × 1300 Å. Sample bias voltage of 2 V. Labels 'A' and 'B' are for Fig. 4.

reported earlier [12], three regions are clearly discernible due to their apparent height differences. These are cobalt-rich, chromium-rich and second-layer islands, labeled Co, Cr and 2nd, respectively, in Fig. 3. The kinetic processes for the decomposition can be described as follows. With abundant vacancies among the first-layer islands in the co-deposited film, (i) at 150°C, the adatoms at the first-layer islands can detach from the islands and diffuse until they reach stable sites. Cobalt adatoms find cobalt-rich neighbors, while chromium adatoms find chromium-rich ones. In the meantime, (ii) some adatoms at the second-layer islands can diffuse down to completely wet the W(110) surface and follow the first process. Since the total coverage is larger than 1 ML, (iii) some adatoms should remain at the second layer while decomposition takes place there. The decomposition process slows down with time since the number of vacancies at the first layer is decreased with process (ii).

As can be seen in Fig. 3, single second-layer islands always share a boundary with both the first-layer cobalt-rich phase and the chromium-rich phase. Fig. 4 shows atomic ball models for the cross-sectional view across the second-layer islands. In the first model, a second-layer island consists of two decomposed phases, which then share a phase boundary with the underlying layer (Fig. 4a). The two phases in the second layer should show a height difference between them, presumably twice that in the first layer. But we observed that, within the second-layer islands, the height is uniform without any noticeable regional variation. The second possibility is that second layer is cobalt (chromium)-rich, while first layer is chromium (cobalt)-rich, as shown in Fig. 4b. This may not have an appreciable height difference, but is less likely in view of the phase diagram with a miscibility gap. The next possibilities are that the second-layer islands have the same phases as those of their underlying layers (Fig. 4c and d). The single phase can be either cobalt-rich or chromium-rich. In a previous low-energy electron diffraction (LEED) experiment [15] and our STM experiment [18], it was found that second-layer chromium forms a (2×2) reconstruction, while unreconstructed cobalt is grown up to 2 ML. But the second-layer islands in the decomposed surface do not have any high-order reconstruction. Furthermore, the bias-dependent images observed on second-layer islands are similar to those on cobalt-rich phase [12]. Therefore the second-layer islands consist of cobalt-rich phase.

What is the origin of the preferential growth in the second-layer islands? First, let us assume that the system is in its equilibrium state after annealing, and explain with energetic terms. The binding energy for chromium atoms on the W(110) surface can be higher than that for cobalt atoms. Accordingly, chromium preferentially occupies the first layer. On the basis of density-functional calculations it was reported that the surface segregation energy of cobalt is lower than that of chromium on W(110) [19]. Since segregation energy can roughly be interpreted as binding energy, it may not be only reason for the preferential growth. Second, the origin can be in kinetics. In step (ii) of the decomposition process, chromium atoms may diffuse down more easily than cobalt atoms, resulting in pure cobalt islands at the second layer. It was reported that the Ehrlich–Schwoebel barrier for one element can be higher than that for the

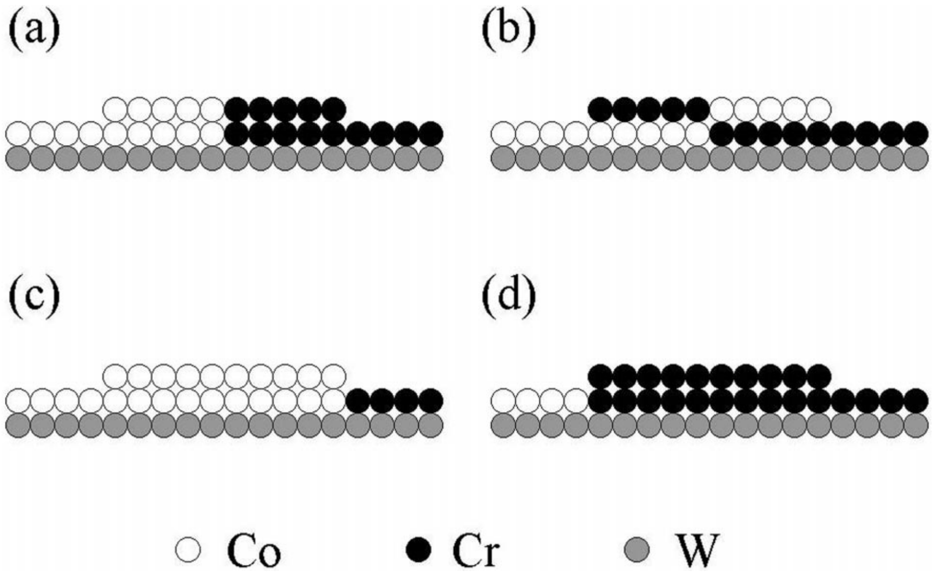

Fig. 4. Atomic ball models of the cross-sectional view across the second-layer islands, for example from point 'A' to point 'B' in Fig. 3.

other element even on the same substrate, reflecting the delicate strain-relieving atomic structures of the two elements [20]. The third scenario is related to the site exchange of cobalt and chromium adatoms. Recently, it was found that the 2D alloying reaction occurs through hopping diffusion of adatoms followed by site exchange between a second-layer cobalt (silver) adatom and a silver (cobalt) adatom [21]. In analogy with the alloying process, a similar mechanism can take place in decomposition. In particular, at the end of process (ii), it can be the dominant process with reduced number of vacancies. In the exchange process, a cobalt (chromium) atom may sit temporarily on the first-layer chromium (cobalt) atom as an intermediate state. It was reported that the configura-

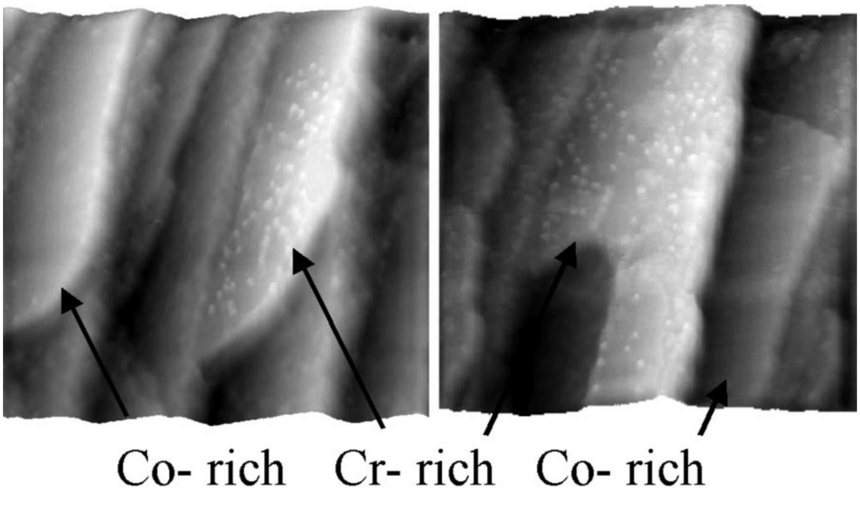

Fig. 5. STM images of the decomposed surface with (a) 0.3 ML of cobalt and 0.3 ML of chromium, and (b) 0.2 ML of cobalt and 0.5 ML of chromium. Image size: 500 Å × 500 Å. Sample bias voltage of 3 V.

tion of cobalt on chromium can be stable, while that of chromium on cobalt cannot [19]. Therefore, second-layer chromium adatoms may prefer exchange sites with first-layer cobalt adatoms, segregating cobalt adatoms on the top surface, while first-layer chromium adatoms would not prefer exchange sites with second-layer cobalt adatoms.

We confirmed that the decomposition occurs at various compositions and coverages, showing good agreement with the phase diagram. Fig. 5 shows two examples for $Co_{0.5}Cr_{0.5}$ and $Co_{0.3}Cr_{0.7}$ with a total coverage of ~0.7 ML in both cases. At these submonolayer coverages, the patches of the two phases frequently do not share a phase boundary, which makes it difficult to compare the height difference directly. However, as marked with arrows, the two phases are easily distinguished at a sample bias voltage of ~3 V. In the chromium-rich phase, a distribution of bright protrusions is observed due to the compositional inhomogenity [12], while a clear and flat topography is observed in the cobalt-rich phase without any noticeable variation.

4. Conclusion

In conclusion, we were able to grow a homogeneously disordered alloy by co-depositing cobalt and chromium at room temperature on a W(110) surface and decompose it into two phases, cobalt-rich and chromium-rich, by annealing at 150°C. We found that the second-layer islands are preferentially made of cobalt-rich phase, which can be explained by possible asymmetric diffusion behaviors.

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