BRIEF
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Solid-Phase Reaction of Aluminum with the Hexagonal and Cubic Phases of Cobalt in Film Systems

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Abstract—Solid-phase reactions taking place in Al/β-Co/MgO(001) and Al/α-Co/MgO(001) film systems under conditions of self-propagating high-temperature synthesis (SHS) are investigated. In both systems, SHS products exhibit the single CoAl superstructure, which epitaxially grows on the MgO(001) surface in the Al/β-Co/MgO(001) structures and has a fine-dispersed disordered structure in the Al/α-Co/MgO(001) films. It appears that the difference in the reagent structure has an effect on the energy of activation but does not change the SHS initiation temperature and the temperature at which the initial phase involved in the reaction products nucleates. It is shown that the SHS initiation temperature in the Al/β-Co/MgO(001) and Al/α-Co/MgO(001) systems coincides with the temperature of CoAl superstructure ordering. © *2002 MAIK "Nauka/Interperiodica".*

Thin-film components are a building block of today's microelectronic devices. During fabrication and operation, these components are subjected to temperature effects, which cause solid-phase transformations and thus change the performance of the devices. That is why solid-phase reactions in thin films have been the subject of extensive investigation [1–3]. It has been repeatedly shown that upon heating bi- and multilayer films, the initial (first) phase of reaction products appears at some temperature. As the temperature is increased further, new phases form sequentially (so-called phase sequence) [1–3]. Grain-boundary diffusion is believed to be the basic mechanism of solid-phase reactions. Therefore, the energy of activation and the rate of a solid-phase reaction must depend on the film structure and crystallographic orientation. For example, early in $NiAl_2O_4$ spinel formation at the NiO–single-crystal Al_2O_3 interface, the orientation of the Al_2O_3 substrate specifies the energy of activation, rate, and even kinetic law of the process [4, 5].

At high heating rates, the initial stage of many solid-phase reactions in thin films has been shown [6, 7] to proceed under SHS conditions. In thin films, SHS may be considered as a surface combustion wave and is characterized by the initiation temperature T_0. The effect of reagents with different polymorphic modifications on the reaction product structure, the formation of the first phase, and the SHS initiation temperature is of great scientific and applied interest.

In this work, we study solid-phase reactions under the SHS conditions in Al/β-Co/MgO(001) and Al/α-Co/MgO(001) film systems. The total thickness of the films was no more than 100 nm. It is known that the low-temperature hexagonal structure of bulk α-Co is stable up to 420°C. Above this temperature, it transforms into the fcc phase of β-Co by the martensitic mechanism. However, in cobalt thin films and nanocrystals, the β-Co phase is also stable at room temperature under various process conditions [8]. The structure and modification of Co films on the MgO(001) surface depend strongly on the substrate temperature T_s. For $T_s = 220$–240°C, the high-temperature fcc cubic phase of β-Co grows epitaxially on the MgO(001) surface. The first constant of magnetic anisotropy was found to be $K_1 = -(6$–$7) \times 10^5$ erg/cm^3. Diffraction reflections (Fig. 1a) and the arrangement of the easy axes show that the β-Co film and the MgO substrate form an epitaxial system [100](001)β-Co‖[100](001)MgO. The situation changes radically when the substrate temperature rises to $T_s = 370$–400°C. As follows from diffraction reflections (Fig. 2), an α-Co layer grows in this case so that its (110) plane is parallel to the (001)MgO surface. The reflections (110)α-Co and (110)β-Co coincide. Electron microscopy studies [9] indicate, however, that Co films grown at high temperatures consist of α-Co grains with their *c* axis aligned with the [100] and [010] directions in MgO. The effective constant of bilayer magnetic anisotropy for these films is $K_{eff} = (1.1$–$1.3) \times 10^6$ erg/cm^3. The magnetic anisotropy energy per unit volume E_{an} of the hexagonal crystal (with the in-plane anisotropy neglected) is given by [10] $E_{an} = K_1\sin^2\varphi + K_2\sin^4\varphi + \dots$, where $K_1 = 4.3 \times 10^6$ erg/cm^3 and $K_2 = 1.2 \times 10^6$ erg/cm^3 for hexagonal cobalt (φ is the angle between the *c* axis and the magnetization vector).

I, arb. units
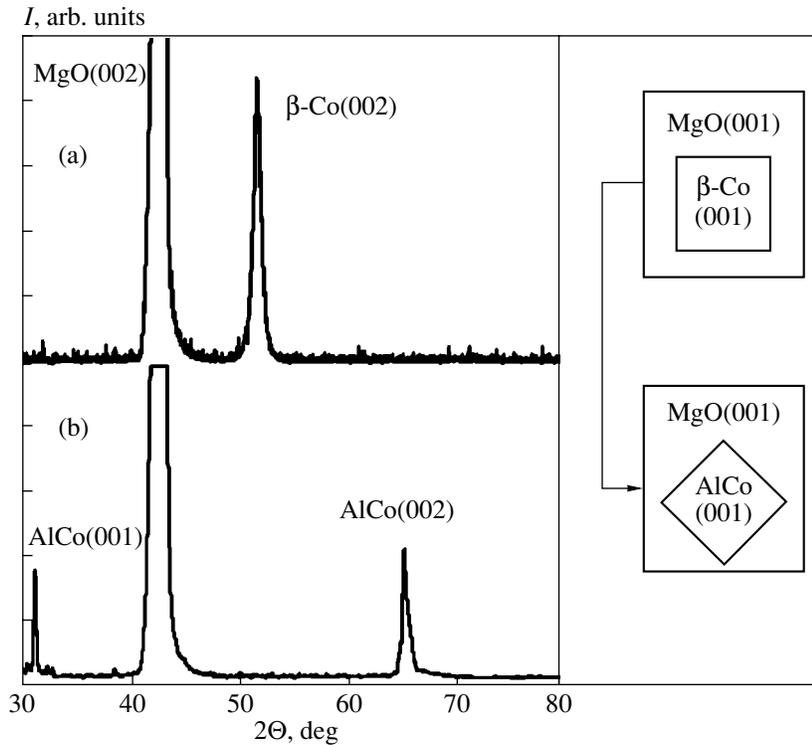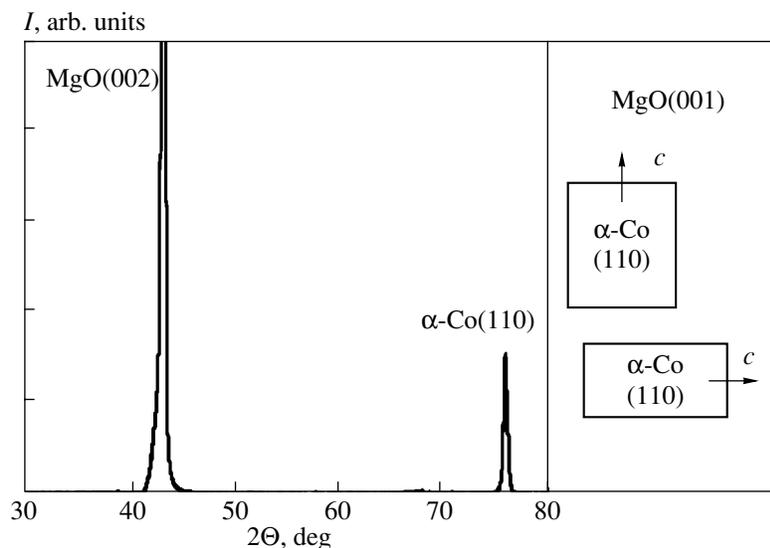

Fig. 1. Diffraction patterns from the Al/β-Co/MgO(001) film structure (a) before and (b) after the passage of the SHS front. Crystallographic epitaxial relations of the MgO(001) substrate and the initial β-Co phase and the CoAl phase of the reaction product are shown on the right of the figure.

Assuming that the α-Co grains whose *c* axes are aligned with the [100] and [010] directions of MgO experience exchange coupling and their volumes are the same, we calculated the effective bilayer magnetic anisotropy of such a film system and found that $K_{eff} = K_2$. The coincidence between K_{eff} and K_2 found experimentally also confirms the formation of the α-Co grains on the MgO(001) surface. An aluminum layer with a thickness equal to that of the Co film was deposited on the initial β-Co/MgO(001) and α-Co/MgO(001) film systems. The absence of aluminum reflections from the as-prepared Al/Co/MgO(001) structures (Figs. 1a, 2) implies that the aluminum film is amorphous or fine-grained. The Al/β-Co/MgO(001) and Al/α-Co/MgO(001) samples were heated to the SHS initiation temperature T_0 with a rate of 20 K/s at a pressure of 10^{-4} Pa. The appearance of the SHS front was observed visually. The initiation temperature T_0 lay in the 750–780 K interval. The discrepancy in the T_0 values is associated with heat removal into the substrate, which depends on the substrate thickness and heating rate. However, the values of T_0 for the Al/β-Co/MgO(001) and Al/α-Co/MgO(001) systems coincide within the experimental error. To exclude the Headwall effect, we experimentally checked that solid-phase transformations and $\alpha \rightleftarrows \beta$ transitions in the initial β-Co and α-Co films do not occur before the initiation temperature. The reaction products from the Al/β-Co/MgO(001) system contain the ordered AlCo

phase that grows epitaxially on the MgO(001) surface (Fig. 1b). This phase has a cubic lattice with spacing $a = 0.286$ nm. The lattice mismatch between MgO and AlCo is the smallest if the orientation relation is (001)[100]AlCo∥(001)[110]MgO (Fig. 1b). After SHS in the Al/β-Co/MgO(001) system, the AlCo phase may grow with its (110) plane parallel to the (001)MgO surface, although such cases are untypical. In the Al/α-Co/MgO(001) system, diffraction reflections after SHS are absent. However, phase analysis of bi- and multilayer polycrystalline Al/Co films indicates the presence of the AlCo phase alone in the reaction products. From the aforesaid and the equality of the initiation temperatures, it follows that the SHS products in the Al/α-Co/MgO(001) system also contain the AlCo phase that grows randomly on the (001)MgO surface and is amorphous or fine-grained. The different crystal structure of the SHS products in the Al/α-Co/MgO(001) and Al/β-Co/MgO(001) systems implies different reaction mechanisms, which are governed by the crystallographic planes containing the reagents.

The results obtained lead us to conclude that polytypic forms of the reagents play an insignificant role in the formation of the first phase during solid-phase SHS. The energy of activation E_a of the solid-phase reaction must include the binding energy and the energy of reagent transfer. In the reactions considered, the transfer energies are the same. Hence, the difference in the energies of activation of the solid-phase SHS reactions

Fig. 2. Diffraction patterns from the Al/α-Co/MgO(001) film structure before the SHS reaction. Crystallographic epitaxial relations of the MgO(001) substrate and the initial α-Co phase are shown on the right of the figure.

taking place in the Al/β-Co/MgO(001) and Al/α-Co/MgO(001) systems equals that in the binding energies of cobalt in the hexagonal and cubic modifications. This difference is insignificant because the enthalpy $\Delta H^{\beta \to \alpha} = -220$ cal/mol is small [11]. The SHS front velocity V_f depends on the temperature T_s by the near-Arrhenius law: $V_f \sim \exp(-E_a/kT_s)$; therefore, a change in the energy of activation will insignificantly influence only the temperature dependence of the front velocity. This means that the low-energy difference in the reagent structures affect the SHS basic parameters in thin films (initiation temperature and the formation of the first phase) only slightly. Specifically, the SHS parameters in amorphous films may not differ from those in polycrystalline and single-crystal layers, since the enthalpy of amorphous–crystalline transition is low (≈ 1000 cal/mol for most alloys). These conclusions agree with those drawn in [12], where the solid-phase reaction at the titanium–aluminum interface was shown to form a single $TiAl_3$ phase irrespective of whether fine- or coarse-grained aluminum was used as a substrate. The formation of the $TiAl_3$ phase was also insensitive to the sequence of layer deposition in the Ti/Al bilayer system.

The prediction of the onset of the first phase (or of the SHS initiation temperature T_0) is of great importance for applications. At the initiation temperature, solid-phase transformations are accompanied by bond breaking and atomic rearrangements with the formation of new bonds. Therefore, as the annealing temperature rises, a phase having the lowest temperature of solid-phase transformation must appear first at the interface between reagents in a bilayer system. For example, in a S/Fe bilayer system, the temperature T_0 of initiating the solid-phase reaction producing FeS iron monosulfide and the temperature of metal–insulator phase transition

were shown to coincide [13]. In Cu/Au thin bilayer films (the Cu–Au system is a model system for studying ordering in alloys), the SHS initiation temperature T_0 was shown [14] to coincide with the Kurnakov temperature T_K of the CuAu ordered alloy, which is a reaction product: $T_0(Cu/Au) = T_K(CuAu)$. Later [15], this equality was confirmed for Al/β-Co/MgO(001) and other bilayer systems having superlattices in their reaction products.

Thus, the study of SHS in Al/hexagonal Co and Al/cubic Co bilayer structures revealed the following.

(1) In the thin films, the polytypic modifications of the reagents and the low-energy difference in their structures do not influence the SHS initiation temperature and the first phase of the reaction products.

(2) In the film reagents, the SHS initiation temperature correlates with the Kurnakov temperature of the phase forming in the reaction products provided that there are no solid-phase transformations preceding the order–disorder transition.

(3) Synthesis mechanisms, which are responsible for the reaction product microstructure, depend on the crystal orientations of reacting pairs.

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