Self-propagating high-temperature synthesis and formation of quasicrystals in Al/Mn bilayer thin films

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Self-propagating high-temperature synthesis in Al/Mn bilayer thin films was investigated. It was found that a quasicrystalline phase forms after the passage of self-propagating high-temperature synthesis through the sample. It is shown that after multiple initiation ($n>5$) of self-propagating high-temperature synthesis in a sample the quasicrystalline phase transforms into a stable Al_6Mn phase. It is conjectured that self-propagating high-temperature synthesis can play the main role in the formation of quasicrystals in other film systems as well. © *1998 American Institute of Physics.* [S0021-3640(98)00514-3]

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After the discovery of a quasicrystalline phase in the alloy Al–Mn,[1] works describing the formation of this phase in Al/Mn thin films by ion irradiation[2,3] and by the implantation of manganese in an aluminum film[4] appeared. Quasicrystals in other systems are also being investigated on ribbons or films. At the same time, the kinetics of the formation of a quasicrystalline phase is unclear in many respects, and the conditions under which a quasicrystalline phase forms are determined by experimental search.

The present work is devoted to an investigation of self-propagating high-temperature synthesis (SHS) in Al/Mn bilayer thin films and a determination of the conditions under which a quasicrystalline icosahedral (i) phase forms in them. Powder-based SHS is used to obtain divers compounds and has been well studied.[5,6] Film-based SHS exhibits features which distinguish it from powder-based SHS and is only now becoming an object of study.[7,8] The samples used for investigations of SHS in thin films consist of up to 500-nm thick layers of reactants which are deposited successively on a substrate. Initiation of SHS occurs when the temperature T_s of the sample exceeds the initiation temperature T_0. In this case, the combustion front propagates along the surface of the film sample.[7,8] An important feature of SHS in thin films is that it can be of two types. In type-I SHS, after the passage of the wave of SHS the reaction is completed by the formation of compounds. An example of this type is the system Al–Ni, where a Ni_2Al_3 phase forms as a result of the passage of a SHS front, and no traces of pure Ni and Al remain.[8] In type-II

SHS a second wave passes over the surface of the sample after the passage of the SHS wave. The passage of the second wave results in phase separation into the initial reactants. At the same time, metastable phases can form in the sample. Type-II SHS arises in Al/Ge films, where the products of the reaction contain mainly solid solutions of Al and Ge, and a negligible quantity of the metastable AlGe phase forms.[8] The temperature T_{ps} at which the phase-separation front appears equals the initiation temperature T_0 ($T_{ps}=T_0$). Since phase separation arises at substrate temperatures $T_s<T_0$, it is possible to reinitiate SHS in this sample by heating it above the temperature T_0. It follows that SHS can be initiated several times in the same sample. After the first initiation, SHS gives rise to mixing of the layers of reactants. For Al/Ge films the initiation temperature is $T_0=600-550$ K. The system Al–Ge has a simple phase diagram of the eutectic type with a eutectic temperature $T_E=697$ K. The microstructure of Al/Ge films after the passage of a wave of SHS consists of clusters which have a dense-branching morphology (DBM clusters). DBM clusters are investigated in many natural sciences and the kinetics of the formation of DBM clusters is widely studied. In Al/Ge films DBM clusters are fractals (the fractal dimension is $d_f=2$ and clusters consist of a solid solution of germanium) in an aluminum matrix.[8] Phase separation into fractal clusters, DBM clusters containing mainly germanium, and a single-crystal aluminum matrix in Al–Ge films proceeds from the amorphous phase. Different models explaining phase separation have been proposed. However, the mechanisms leading to phase separation remain unclear (see references cited in Ref. 8). It is surmised that multiple initiation of SHS in thin films is an analog of a repeated transition through the eutectic temperature in bulk samples. A very unexpected result is that SHS and phase separation in thin films occur in the solid phase, in contrast to eutectic separation, which proceeds from the liquid phase.

The Al/Mn films were obtained by successive deposition of thin layers of manganese, followed by aluminum, on glass substrates. The chosen ratio of the aluminum layer thickness d_{Al} to the manganese layer thickness d_{Mn} was $d_{\mathrm{Al}}:d_{\mathrm{Mn}}=7:1$, which corresponds to ~ 14 at. % Mn in the sample. The total film thickness was in the range 200–800 nm. The details of the production of film samples and the method of initiating SHS in them are described in Refs. 7 and 8. SHS in Al/Mn films is of the second type and proceeds similarly to SHS in Al/Ge samples. The initiation temperature T_0 is higher than in Al/Ge films and lies in the interval 750–800 K. The characteristic features of the motion of the SHS and phase-separation fronts can be easily observed visually. However, they are hardly noticeable after $n\sim 10$ cycles. The velocity V_{ps} of the phase separation front increases strongly with increasing degree of supercooling $\Delta T=T_0-T_s$, where T_s is the substrate temperature. In the experiments, two extreme values of V_{ps} permitted by the experimental conditions were used:

$$V_{ps}^{\min}=(1-2)\times 10^{-3}\ \text{m/s} \quad \text{and} \quad V_{ps}^{\max}=(0.1-0.2)\ \text{m/s}.$$

In Ref. 9 all of the reflections from the quasicrystalline phase were indexed, and the x-ray diffraction data obtained correspond well to the observed diffraction pattern. In the present work the quasicrystalline phase arising after the passage of a SHS wave in an Al(90 nm)/Mn(630 nm) sample was determined according to the two strongest reflections: $d_1=0.217$ nm and $d_2=0.2065$ nm. The phases formed in the synthesis process were identified on a DRON-4-07 diffractometer at room temperature ($\mathrm{Cu}K_\alpha$ radiation). Fragments of diffraction patterns obtained from the Al(90 nm)/Mn(630 nm) sample before and after SHS are presented in Fig. 1. The initial sample (Fig. 1a) contains an

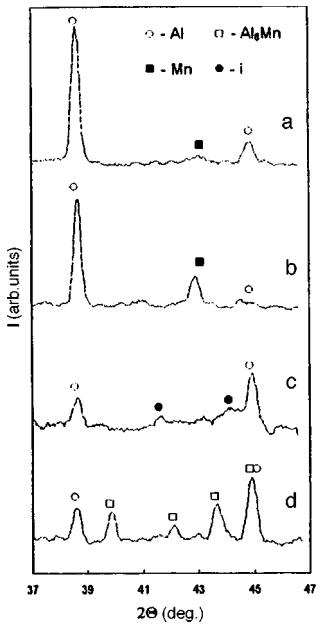

FIG. 1. Diffraction patterns of Al(80 nm)/Ge (630 nm) thin-film samples as a function of the phase separation velocity V_{ps} and the number of SHS cycles n: a) Initial sample, b) $n=1$, $V_{ps}^{\max}=(0.1-0.2)$ m/s, c) $n=1$, $V_{ps}^{\min}=(1-2)\times 10^{-3}$ m/s, d) $n=5$, $V_{ps}^{\max}$ and $n=5$, $V_{ps}^{\min}$.

amorphous layer of α-Mn (broadened peak with $d=0.210$ nm) and a polycrystalline Al film. The post-SHS phase composition depends on both the velocity V_{ps} of the phase separation front and the number n of SHS cycles. For $n=1$ and $V_{ps}^{\max}=(0.1-0.2)$ m/s (Fig. 1b) the sample contains polycrystalline aluminum and manganese. For low velocities $V_{ps}^{\max}=(1-2)\times 10^{-3}$ m/s and $n=1$ (Fig. 1c) the diffraction pattern contains reflections from polycrystalline aluminum and a quasicrystalline icosahedral (i) phase. The intensity of the reflections from aluminum and manganese decreases compared with the initial sample, which suggests formation of a substantial fraction of the quasicrystalline phase. At velocities $V_{ps}^{\max}$ and $n=1$, however, the manganese crystallizes, but there is not enough time for the quasicrystalline phase to form. The diffraction pattern changes radically with multiple initiation of SHS $n>5$ (Fig. 1d). The quasicrystalline phase transforms into an equilibrium Al_6Mn phase, irrespective of the velocity of phase separation.

The microstructure of Al/Mn films consists of clusters in an aluminum matrix and is similar in many respects to the microstructure of Al/Ge films. However, these clusters differ from the DBM clusters in Al/Ge samples, since they are round, 10–20 μm in size, and have a uniform internal structure. Apparently, the same microstructure is described in Ref. 1. In Refs. 2 and 3, layer mixing also was observed in Al/Mn films under ion irradiation. This presupposes that in this case SHS was initiated and participated in the formation of a quasicrystalline phase. The study of SHS in film samples shows that intense diffusion of reactants between layers or grains occurs exclusively at the SHS initiation temperature T_0 and, as we have said, it occurs in the solid phase. The formation of the metastable phases and amorphous state is also surmised[7,8] to occur at temperature

T_0. Since the free energy of the quasicrystalline phase falls between that of the crystal and the amorphous states,[2] the formation of a quasicrystalline phase during SHS is not unexpected. It is surmised that after the passage of the first SHS front with $T_s > T_0$ an amorphous phase forms as a result of the reaction between the aluminum and manganese layers and then decomposes at temperatures $T_s < T_0$, depending on the velocity of the phase separation front and the number of SHS cycles, into the components indicated in Fig. 1. Such a scenario, where a quasicrystalline phase forms from an amorphous phase in Al/Mn films, was studied in Refs. 2 and 3.

As we have said, the initiation temperature of SHS in Al/Ge bilayer film samples is 100–150 K lower than the eutectic temperature for the equilibrium Al–Ge system. The SHS initiation temperature in Al/Mn is also 100–150 K lower than the Al–Mn eutectic temperature of the equilibrium system $T_E = 820$ K.[10] Therefore the SHS initiation temperature T_0 for other systems must also be lower than their eutectic temperatures. Since the motion of the SHS front can be seen visually, it is not difficult to find the temperature T_0. Aluminum enters easily into SHS with many elements of the periodic system,[5] so that SHS should be expected to participate in the formation of aluminum-based quasicrystalline phases.

All this suggests that SHS can play an important role in the formation of quasicrystalline phases, and investigation of the phase composition of the products of reaction in film systems where quasicrystalline and metastable phases form will make it possible to gain a deeper understanding of the physicochemical nature of SHS and the micromechanisms of phase separation in thin films.

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