Formation of Quasicrystalline AlCuFe by Physical Vapor Deposition: Phase Selection via Nanocluster Nucleation

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We study the crystalline state of a very thin AlCuFe film, sputter deposited at the relatively low substrate temperature of 460 °C. High-resolution transmission electron microscopy shows that the layer consists of isolated quasicrystalline nanoparticles, although, at the given composition and deposition temperature, the quasicrystalline state is metastable. The nucleation process of the quasicrystalline phase is discussed in terms of a liquidlike to solid transition of nanoclusters. [S0031-9007(96)02058-3]

Since the discovery of materials showing crystallographically forbidden icosahedral symmetry [1], the formation and the physical properties of these and other quasicrystalline phases have been studied extensively. Most quasicrystalline materials obtained so far have been produced by melt spinning or, in the case of thermodynamically stable quasicrystals, by conventional casting [2]. Thin films of metastable quasicrystals such as AlMn were produced by heating amorphous films or from a stack of elemental layers, or were formed directly by physical vapor deposition on heated substrates [3]. Also thin films of quasicrystals stable at high temperatures such as AlCuFe were studied. These films were deposited at low substrate temperatures in either the amorphous or the crystalline state [4,5] or as a stack of elemental layers [6]. The icosahedral i phase was obtained by subsequent annealing between 400 and 700 °C.

However, the phase diagram of AlCuFe is very complex and extremely temperature dependent [7,8]. The crystalline rhombohedral R phase, the orthorhombic O phase [8], pentagonal phases [9], as well as modulated [10] and perfect i phases show only small differences in x-ray diffraction (XRD) patterns [7]. These small differences are hardly detectable in very thin films due to disturbing effects, such as the finite size of crystallites, stresses, and defects. In most studies of AlCuFe films so far, only XRD was used to characterize their crystalline state [4,5,6]. Furthermore, the i phase of AlCuFe is—if at all—stable only in a very small range of composition at low temperatures: Below about 700 °C rhombohedral, pentagonal, modulated, and other phases are dominant [8]. The i phase obtained by rapid quenching transforms into the modulated phase by atomic diffusion at temperatures [11] above $\approx$520 °C [10].

Thus, high-resolution transmission electron microscopy (HRTEM) seems to be indispensable to discern the crystalline state of thin films or nanoparticles of quasicrystalline and related alloys. To our knowledge there exists so far only one HRTEM study of AlCuFe films [12]. In this study rather thick films (50−200 μm) were deposited at 600–650 °C and, according to HRTEM, the pentagonal phase was formed, which at this temperature is possibly stable.

The question arises whether much thinner quasicrystalline AlCuFe films or nanoparticles can be formed in a direct way, i.e., without postdeposition annealing, and at lower deposition temperatures T_D, for which the i phase is not stable and the atomic diffusion is small. We used HRTEM to demonstrate that sputter-deposited thin layers of AlCuFe can be directly nucleated in its metastable quasicrystalline phase. We interpret this result with regard to the liquidlike state of nanoparticles at high temperatures.

Recently, thin AlCuFe films (thickness $\approx$160 nm) were sputter deposited at T_D up to 490 °C [13]. Two films produced at 460 and 490 °C showed XRD patterns as expected for the i phase, while films deposited at 410 °C and lower mainly contained peaks of the crystalline cubic β phase. The room temperature dc resistivity of the film deposited at 490 °C reached comparatively high values of $\approx$1900 × 10^{-8} Ω m [14]. The composition of the films was measured with elastic recoil detection analysis (ERDA) and found to be Al$_{64.5}$Cu$_{22.5}$Fe$_{13}$, with an error of 1 at. %. A small oxygen contamination of about 2 at. % was detected [13].

In the present work, a very thin AlCuFe film sandwiched between Al$_2$O$_3$ films was prepared under conditions identical to the thicker films mentioned above ($T_D = 460$ °C). The deposition apparatus used and the experimental conditions have been described earlier [13]. Briefly, a rotating target consisting of pieces of Al, Cu, and Fe in the appropriate sizes is sputtered with an argon ion beam. The background pressure was $\approx$10^{-4} Pa, and during sputtering the argon pressure was 2 × 10^{-2} Pa. A Si wafer, which was pressed to a heated copper holder, was used as a substrate. The film thickness was measured during deposition with an oscillating quartz

monitor and after deposition with cross-sectional TEM. A sequence of various layers was deposited at room temperature: 35 nm amorphous Al_2O_3, 140 nm copper, and 32 nm Al_2O_3 [15]. After the deposition of these films the temperature was increased to 460 °C for growing the Al-CuFe film and another 37 nm amorphous Al_2O_3 layer.

The AlCuFe film was produced with a measured growth rate of 0.16 nm/s and a nominal thickness of 7.5 nm according to the quartz monitor. It was calibrated by grazing incidence x-ray reflectometry, using a thick film deposited at 200 °C. Plan-view TEM analysis revealed that the AlCuFe layer was not continuous but consisted of isolated nanoparticles with a mean diameter of about

15 nm. The projected layer thickness amounted to only 13–14 nm according to the cross-sectional TEM. With the fraction of AlCuFe particles of $25 \pm 5\%$ in this layer, the thickness of an equivalent homogeneous film would be only ≈ 3.5 nm or less than half of the expected thickness. This discrepancy can be explained by re-evaporation or re-sputtering occurring especially in the first stages of growth and at high T_D [16].

The TEM preparation of the as-grown multilayered structure was done by conventional mechanical prethinning and final argon ion milling using the specimen cooling unit to prevent post growth annealing. The amorphous Al_2O_3 layers protected the AlCuFe film during the thinning
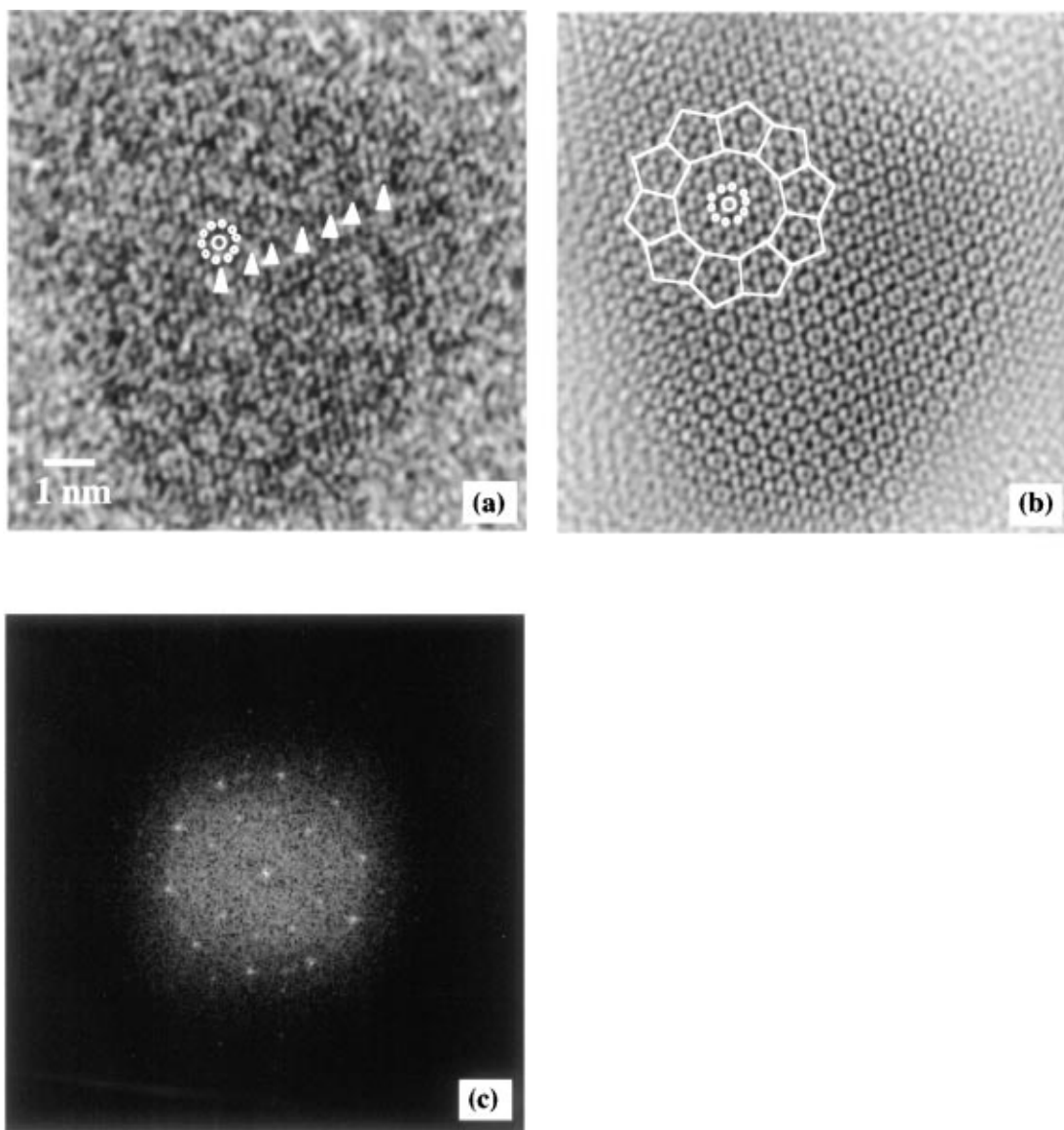

FIG. 1. HRTEM of an isolated AlCuFe particle embedded in amorphous Al_2O_3 in the direction of a fivefold zone axis. (a) Original micrograph: Tenfold rings with an aperiodic sequence of distances are marked by arrows. (b) Fourier-filtered micrograph: Fivefold symmetric elements (pentagons) are outlined. (c) Fourier spectrum of (a): Bright spots are well aligned.

process used to obtain the plan-view samples. In order to determine the structure of the AlCuFe phase by HRTEM, it is indispensable to tilt the sample in a low-index orientation with respect to the electron beam. This procedure is practically impossible in the case under consideration because of the small size of the randomly oriented particles; a texture was not observed. In the plan-view dark field TEM images, however, some grains appeared especially bright. These grains are likely to show an orientation which allows the observation of the quasicrystalline or crystalline structure in high-resolution mode. We studied a large number of these grains which turned out to be nearly exactly oriented along a threefold, fivefold, or twofold zone axis.

Figure 1(a) shows a very small particle (diameter $\approx$ 8 nm) imaged along a fivefold zone axis. The noise level of all micrographs is high due to the amorphous Al_2O_3 films in which the particles are embedded. Nevertheless, the characteristic rings with tenfold rotational symmetry can be discerned, and the sequence of distances between these rings is aperiodic (arrows). The fivefold symmetric structure of the particle can be recognized more clearly in the Fourier-filtered micrograph in Fig. 1(b). The Fourier spectrum belonging to Fig. 1(a) is shown in Fig. 1(c): Two rings of ten diffraction spots are detected; the spots lie on straight lines within an experimental uncertainty of 0.5°. For the R phase a misalignment of 1.4° is expected [17], demonstrating that the nanoparticle is in the quasicrystalline state. Also, particles viewed along a twofold zone axis show the properties expected for the i phase. In Fig. 2 irregular octagons as described in Ref. [18] are drawn. These octagons correspond to the projection of an icosadodecahedron, which is a polyhedron with icosahedral symmetry; their presence indicated that the particle is quasicrystalline. The dots are well aligned in the twofold symmetry direction indicated by an arrow, while the R phase shows kinks in the connection lines between the spots [19].

The crystallographic differences between the i phase and modulated and pentagonal phases are small and are usually observed along a twofold axis in HRTEM studies. In the case of the modulated i phase, long sequences of distances between lattice planes are repeated in a way which is not allowed for perfect quasicrystals [10]. Pentagonal phases include "platelets" of considerable size (5.2 and 8.5 nm) [9]. Both features were not observed or appear to be unobservable in particles of, e.g., 8 nm diameter. Because of the presence of large and clearly recognizable irregular octagons, as shown in Fig. 2, we believe that the particles are indeed of the i phase.

These particles were formed directly by sputtering onto a heated substrate at a comparatively low $T_D = 460\,°C$. The phase diagram of AlCuFe at 600 °C [8] shows that the R phase, a tetragonal ω phase, and a monoclinic λ phase are stable at the composition of the present sample. The composition region with stable i phase is very small at lower temperatures and 2–3 at. % richer in
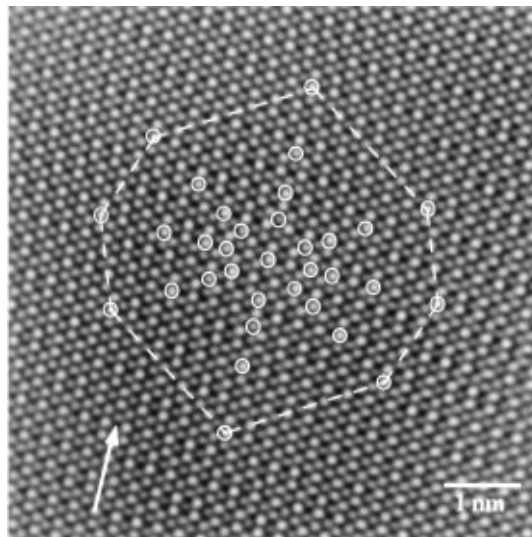

FIG. 2. Fourier-filtered HRTEM micrograph of an AlCuFe particle in the direction of a twofold zone axis. The isolated particle has a diameter of $\approx$18 nm, only a part is shown. The drawn irregular octagons are the projection of an icosadodecahedron, which is a polyhedron with icosahedral symmetry. These octagons and the absence of kinks in the twofold symmetry direction (marked by an arrow) are indicative for the i phase.

copper. Thus, we believe that the observed i phase is not the thermodynamically stable one, even though the oxygen contamination might somewhat influence the region of stability.

Films deposited at $T_D \leq 410\,°C$ are amorphous or consist mostly of the β phase [4,5,13]. According to Ref. [5] the i phase can be obtained by annealing such films at 400 °C, while Ref. [4] states a transformation from the β phase to the i phase at 515 °C. We annealed a β-phase film (160 nm thickness) prepared at 300 °C (sample 1 of Ref. [13]) in vacuum at 510 °C for 18 h. No change of the crystalline state was found with XRD except for the position of the dominant peak of the β phase, which shifted to slightly larger angles. This is in accordance with the result that transformations between R phase and modulated and perfect i phase were found only at temperature above about 520 °C [10,11]. Thus, T_D was not sufficient to allow i-phase formation due to solid state diffusion.

We conclude that the formation of quasicyrstalline nanoparticles takes place by a direct nucleation process within a narrow temperature interval above about 410 °C and below about 520 °C. With a small change in T_D the formation of two different metastable phases, cubic and icosahedral, with completely different local order and crystal symmetry is favored. We speculate that this behavior can be explained with the particular properties of nanoparticles. While the number of atoms necessary for the formation of a cube is rather small, the building block of the i phase contains about 50 atoms [20], and a critical nucleus will probably be much larger. Thus, we suggest that the formation proceeds along the following three steps: (1) In the

first stage of growth, extremely small clusters are formed which show structural [21] and shape fluctuations [22]. According to the literature, these fluctuations occur since the clusters may be in a "liquidlike" or quasimolten state. (2) During further deposition the nuclei grow and, with increased size, a transition from the liquidlike state to the truly solid state takes place. The deposition temperature T_D controls the size at which this transition occurs: At lower temperature the critical nuclei are small and the β phase is frozen in. At higher temperature larger nuclei include a sufficient number of atoms to form the more complicated i-phase structure. (3) The frozen-in nuclei act as seeds for continued growth resulting in larger particles which maintain the crystalline structure of the initial nucleus. Although the proposed mechanism for the phase-selection of nanoparticles was not observed directly, we believe that the reported indirect evidence is convincing. Furthermore, this new mechanism should not be restricted to AlCuFe or other quasicrystalline materials. It might also be observed during nucleation of other materials showing crystalline phases of very different structural symmetry or complexity.

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