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Hyperbolic grain boundaries

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In the amorphous-to-crystalline phase transformation of thin film $CoSi_2$, all grain boundaries in the crystalline microstructure viewed in projection have the shape of a hyperbola. This is due to the continuous nucleation and constant growth rate which gives circular $CoSi_2$ grains before impingement. Such a mode of transformation results in a macroscopic nonequilibrium state at the triple points where a grain boundary meets two amorphous-to-crystalline interfaces.

Most solid materials are polycrystalline and consist of an assembly of variously oriented grains which meet at grain boundaries. Grain boundaries are transition regions, one or two atoms wide, where the crystal structure adjusts from the orientation of one grain to that of another. A consequence of this disturbance to the crystal structure is that grain boundaries almost invariably increase the internal energy of materials. Except for systems such as rare gases adsorbed on graphite, grain boundaries are never thermodynamically stable defects. The formation and evolution of grain-boundary networks are generic questions concerning the microstructure of polycrystalline materials and have been subjects of many experimental and theoretical investigations. In this Rapid Communication we present results concerning crystallization in a thin-film system, which is uniquely suitable for characterization by experiment and simple enough for the data to offer a test for the validity of theories of nucleation and growth.

Based on the concept of nucleation and growth, the formation of a polycrystalline microstructure comes from the impingement of individually growing grains with different orientations. Johnson and Mehl[1] and others[2,3] have described the case where nucleation is continuous and growth is isotropic and constant. Avrami[4] emphasized the case of simultaneous nucleation, which results in a microstructure that consists of Voronoi polygons. Recently, computer simulation has been employed to study the formation and evolution of microstructures. Mahin, Hanson, and Morris[5] performed the simulation of three-dimensional microstructures resulting from continuous and simultaneous nucleation. Frost and Thompson[6] studied two-dimensional thin-film microstructures with various nucleation modes. The work of Anderson and coworkers[7,8] stressed microstructure evolution starting from a random polycrystalline microstructure. The simulation of a soap film model has also been presented by Weaire and Kermode.[9] Results from these simulations showed that microstructures originating from different nucleation and growth modes are distinguishable, e.g., the continuous nucleation and constant growth mode produces hyperbolic-type grain boundaries, and the simultaneous nucleation and constant growth mode produces only straight grain boundaries. While much progress has been achieved in microstructure simulation, very few direct comparisons between experiments and theoretical models were available. In this Communication, we report the formation of a polycrystalline microstructure in the amorphous-to-crystalline transformation of thin film $CoSi_2$. We show that the transformation obeys the Johnson-Mehl model and indeed forms hyperbolic grain boundaries. We further show that the configuration of growth in this mode is nonequilibrium.

Experimentally, we prepared amorphous thin films of $CoSi_2$ of 500 Å in thickness by *e*-gun deposition in a vacuum of 10^{-7} Torr into a Si wafer containing arrays of etched windows each about $\frac{1}{4}$ mm^2 in area. The windows were coated with a 200-Å-thick Si_3N_4 film for viewing the $CoSi_2$ crystallization. Direct observations of the crystallization, which occurs around 150 °C, were performed *in situ* in a Phillips 420 transmission-electron microscope. The crystallization temperature was determined by a thermocouple in the specimen holder and was verified by *in situ* resistivity measurements. The composition of the amorphous film was determined by using Rutherford backscattering spectroscopy. The crystallized phase was

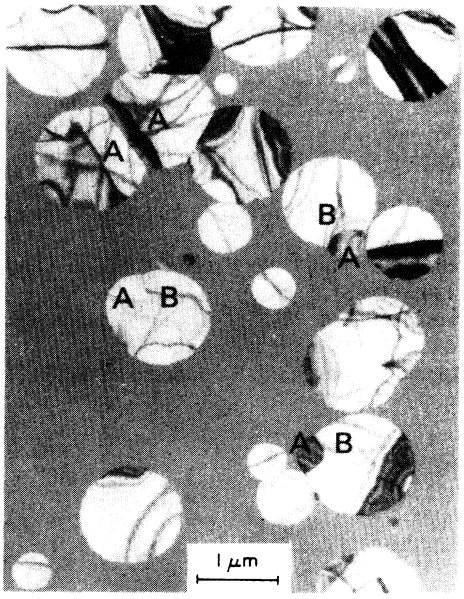

FIG. 1. A bright-field transmission electron microscopic image of amorphous-to-crystalline transformation of $CoSi_2$ thin film at 150 °C.

determined to be $CoSi_2$ with the CaF_2 crystal structure by electron diffraction and x-ray diffraction.

Figure 1 shows a bright-field image of a partially crystallized sample. The crystallization occurs by nucleation and growth of individual grains. The $CoSi_2$ grains are approximately circular, prior to impingement with their neighbors, indicating an isotropic growth. Some evidence for faceting is revealed when the crystallites are viewed at higher magnifications. Each grain is a single crystal as indicated by the continuity of its bend contours. The individual grains are randomly oriented as shown by selected area diffraction. The nucleation appears to be random.

When two growing grains meet each other, a grain boundary is formed. In Fig. 2, a sequence of four images taken with time intervals of one minute is presented to show the formation of grain boundaries between grains at a constant growth rate. If the two grains are equal in size, i.e., if they nucleate at the same time and grow at the same rate, the boundary formed is straight, as exemplified by the A-A pair in Fig. 1. On the other hand, the boundary becomes curved if the two grains are unequal in size, i.e., they do not nucleate at the same time even though they grow at the same rate. Examples are the A-B pairs shown in Fig. 1 and Fig. 2.

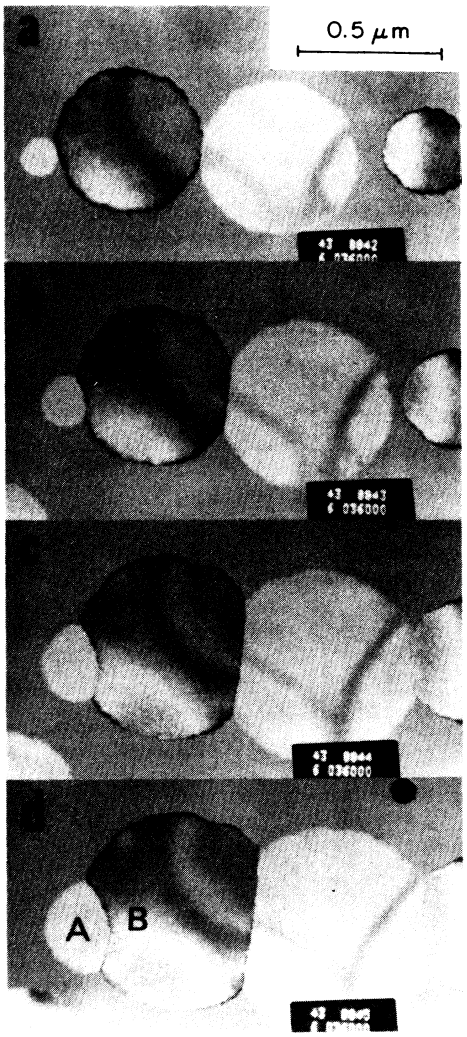

FIG. 2. A sequence of four bright-field transmission electron microscopic images of the growth of $CoSi_2$ grains at 150 °C. The interval between the images was 1 min.

If we assume that (a) the nucleation is random and continuous, (b) the growth is constant and isotropic, and (c) the grain boundaries do not migrate, which is a good assumption when the crystallization temperature is much lower than the melting temperature T_m, of the crystalline phase ($T_m = 1325$ °C for $CoSi_2$), all the grain boundaries formed are hyperbolic.[5,6] (Strictly, the boundaries are hyperboloids, but since the grain diameter is much greater than the film thickness, the two-dimensional approximation is good.) Following Frost and Thompson,[6] we represent the successive positions of the growth fronts by sets of concentric circles centered at A and B, as shown in Fig. 3. The family of broken lines, including the straight one, which connect the points of intersection of these circles are hyperbolas and represent the grain boundaries which can be formed when grains nucleated at the points A and B impinge. We have enlarged a few of the A-B pairs in Fig. 1 and have checked that the grain boundaries can indeed be fitted to a hyperbola.

The bold lines in Fig. 3 depict a large grain and a small grain joined by a hyperbolic grain boundary. If we let the distance between A and B be $2c$, the time interval between the nucleation events at A and B be Δt, and the growth rate be u, the hyperbola is described by

$$\frac{x^2}{a^2} - \frac{y^2}{b^2} = 1 \ , \tag{1}$$

where $a = u\Delta t/2$ and $b = (c^2 - a^2)^{\frac{1}{2}}$. The x axis passes through A and B, and the y axis passes through their midpoint. We note that all the parameters, i.e., c, u, and Δt can be measured experimentally. In fact, for a pair of grains, the Δt can be calculated by knowing c and u. It means that we can reconstruct the nucleation events in a given microstructure. In the case of three-dimensional growth, the growth fronts are spherical, so the grain boundary can be obtained by a revolution of the hyperbola around the A-B axis.

While the above geometrical analysis is adequate in

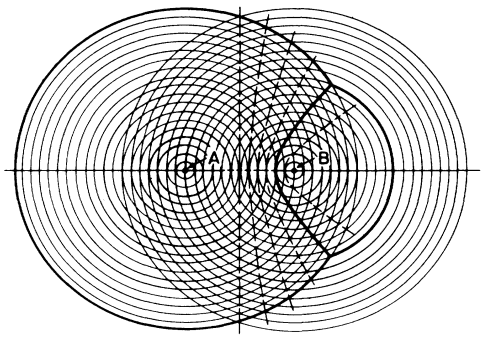

FIG. 3. The family of broken curves, which connect the successive interesting points of the two sets of concentric circles, are hyperbolas. The bold curve depicts the formation of a hyperbolic grain boundary between a large and a small grain.

describing the experimental observation, no consideration is given to energy, e.g., at triple points where a grain boundary meets two amorphous-to-crystalline interfaces. We note that the triple-point geometry changes with growth (see Fig. 3) suggesting a nonequilibrium state in general. In the simple case, where the two growing grains are equal in size, the grain boundary is straight, and the configuration is, therefore, invariant in energy with respect to growth since the amorphous-to-crystalline interfaces are assumed to be isotropic; the triple point must maintain a fixed geometry in order to satisfy the equilibrium condition. In Fig. 4, if θ is assumed to be the equilibrium angle at the triple point, we have $\sigma = 2\sigma_i \cos\theta$ where σ and σ_i are grain-boundary and interfacial energy, respectively, yet the formation of the grain boundary starts with an angle smaller than θ and then becomes greater than θ. The same applies to hyperbolic grain boundaries. Clearly, the macroscopic nonequilibrium situation is due to a dominant isotropic growth. However, whether or not local equilibrium may prevail in a microscopic or atomic scale remains to be studied. We note that in the Johnson-Mehl-Avrami analysis of phase transformation,[10] their growth model is geometrical, i.e., without imposing an equilibrium condition at triple points. Hence, the $CoSi_2$ system as compared to other silicides[11,12] is ideal for studying this kind of transformation.

The hyperbolic grain boundaries themselves are also in nonequilibrium states because of their curvature. Upon heating, they will migrate under a driving force which is inversely proportional to the curvature which varies from point to point on the boundary.

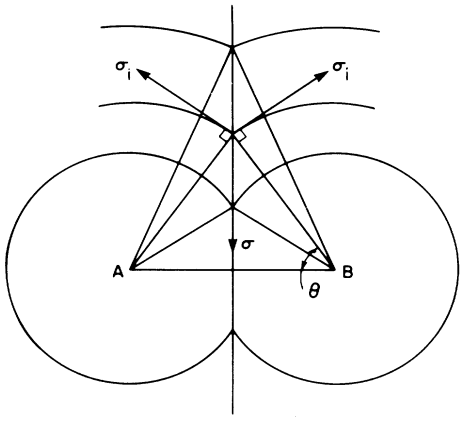

FIG. 4. The geometry of nonequilibrium states at the triple point of a straight grain boundary joining two circular amorphous-to-crystalline interfaces.

In conclusion, we have presented here a simple case of formation of a polycrystalline thin-film microstructure which has a well-defined grain-boundary network. The formation process itself can be used to study theories of phase transformation and percolation. The microstructure obtained can serve as the initial state for observations of the evolution of a grain-boundary network. The coalescence and grain growth phenomena are both in a system which can readily be compared with theoretical models.

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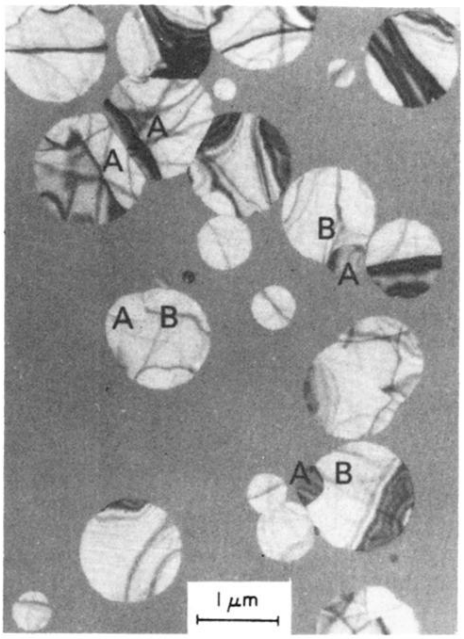

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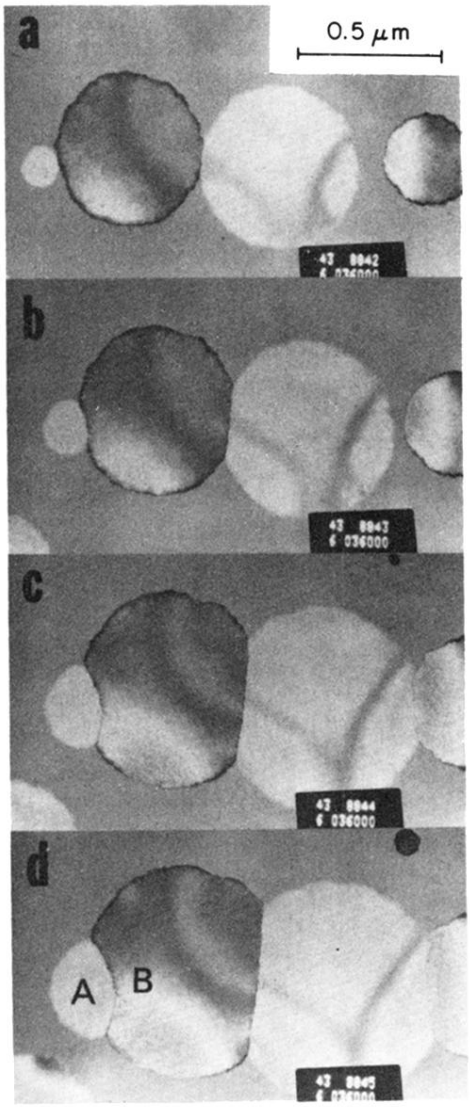

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