Homogeneous nucleated annihilation of the $2q$ phase in $\text{Cu}_{0.78}\text{Pd}_{0.22}$

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The kinetics of the phase transition in $\text{Cu}_{0.78}\text{Pd}_{0.22}$ from the two-dimensional to the one-dimensional long-period structure ($2q$ to $1q$) has been investigated by time-resolved x-ray scattering. Over a period of two-and-a-half decades an exponential-decay law is accurately obeyed. Model considerations of bulk and interfacial annihilation at the $1q$ - $2q$ interface show that the annihilation is bulk and not interfacial driven.

Current approaches in the analysis of the kinetics of phase transitions are generally based on principles of universality and scaling.^{1,2} In the case of phase transitions which are accompanied by a decrease in translational or orientational symmetry, the growth of the new phase can be considered as a two-stage process. On the very short-time scale, the growth behavior is governed by the difference in the free energies of the two phases and is consequently exponential. However, on the longer time scale the growth behavior becomes a question of competition between domains on different sublattices. For non-conserved systems this competition leads to algebraic growth of the domain size with exponents such as $\frac{1}{2}$ and $\frac{1}{4}$.³ Experimental attempts to verify algebraic-growth laws include studies of Ni_3Mn (Ref. 4) and Cu_3Au (Refs. 5–7). If the order parameter is conserved, the exponent is generally expected to be $\frac{1}{3}$ in accordance with the Lifshitz-Slyozov law.⁸

In the case of phase transitions which are accompanied by an increase of symmetry, no additional domain fragmentation is involved while domain boundaries corresponding to restored symmetry operations will disappear. Experimental approaches to this second type of (inverse) transition are hampered by the short-time scale involved. The transition from a high-temperature orthorhombic ($2q$) to a low-temperature tetragonal ($1q$) phase in $\text{Cu}_{0.78}\text{Pd}_{0.22}$ (two-dimensional to one-dimensional structure) is exceptional in the sense that the decay of the diffracted intensity from the disappearing $2q$ phase can be followed over several days.

An explanation for the slow decay rate must be found in an analysis of the topology of the $1q$ and $2q$ phases. Since the $1q$ modulation is common to both phases, mechanisms for the $2q$ - $1q$ transition should deal with the annihilation of this second family of domain walls. High-resolution electron microscopy studies of “frozen-in” configurations during the transformation from the $1q$ phase to the $2q$ phase provide unambiguous evidence for the role of hairpin-like topological defects in the transformation.^{9–11} In this paper, the kinetics of the $2q$ - $1q$ transition has been

studied in $\text{Cu}_{0.78}\text{Pd}_{0.22}$ by means of x-ray diffraction. It is shown that the time-resolved x-ray diffraction data strictly follow an exponential decay. Therefore, in accordance with simple model considerations, we find that the annihilation is a bulk process.

A (100) oriented disk of diameter 7 mm and thickness 1.5 mm of a Cu-Pd single crystal was diamond-paste and electropolished. The sample composition was verified by electron microprobe analysis and found to be 78% Cu and 22% Pd, the uncertainty being 0.5%. Prior to the x-ray experiment, the sample was annealed at 480°C for two weeks and the $2q$ state was fully achieved. The x-ray source was a rotating anode (Cu $K\alpha$) operated at 50 kV, 150 mA, and the diffractometer was configured in the two-circle geometry. The scattering plane was ($h, 0, l$). To study the sample *in situ* at high temperature, it was mounted in a small furnace, and kept under vacuum using a diffusion pump. The relative stability of the temperature was 0.3°C and the absolute accuracy was better than 3°C.

At high temperatures, Cu-Pd alloys form a disordered solid solution on a fcc lattice. For the composition of our sample we found the order-disorder transition temperature to be 484°C. Just below this temperature, $\text{Cu}_{0.78}\text{Pd}_{0.22}$ has a two-dimensional long-period structure (the $2q$ structure). At about 465°C, the alloy undergoes a first-order phase transition to the one-dimensional long-period structure ($1q$). These long-period structures can be conceived of as being derived from the Cu_3Au (L_2) structure by antiphase boundary modulations.¹⁰ Figures 1(a) and 1(b) show the $1q$ and $2q$ structure schematically in the [010] projection. Along the [001] direction, the $1q$ structure can be conceived as an alternation of pure Cu layers and mixed Cu-Pd layers. It is the interchanging of the Pd and Cu sites within the mixed layers that leads to the antiphase domain structure; the displacement vector is $\mathbf{R} = \frac{1}{2} [110]$, with the antiphase boundaries lying in the (001) plane. The $2q$ structure can be considered as due to an additional modulation with a second set of antiphase boundaries lying in the (100) planes ($\mathbf{R} = \frac{1}{2} [101]$) super-

FIG. 1. Schematic drawing of the $1q$ and $2q$ structures, (a) and (b), respectively. Palladium atom positions with the correct displacement vectors are shown to illustrate the antiphase character. The domain walls are not necessarily as compact as the figure may indicate. The $1q$ modulation is depicted along the c axis of the crystal, the $2q$ modulation along the a axis, (c) and (d) show the corresponding reciprocal lattices. Only the first harmonics of the modulations are shown.

posed on and perpendicular to the $1q$ antiphase boundaries. A schematic representation is given in Fig. 1(b). Figures 1(c) and 1(d) show the corresponding reciprocal spaces. For simplicity, only the first harmonics are shown. The x-ray diffraction patterns are complicated by the superposition of the different orientation variants.

We studied the disappearance of the $2q$ phase at 462°C , which is a few degrees below the transition temperature. Consequently, decomposition due to the narrow two-phase coexisting region of the phase diagram is avoided. Figure 2 shows a $(10l)$ scan around the (103) super-

FIG. 2. The diffraction pattern along $(10l)$ as obtained at times 0, 60, and 216 ksec. The pattern consists of the central superlattice peak (103) and of two sets of satellites $(103^-)_{1D}$, $(103^+)_{1D}$, and $(103^-)_{2D}$, $(103^+)_{2D}$ from the $1q$ and $2q$ modulations, respectively. The outermost peaks are located at the $1q$ positions ($a^* = 1.690 \text{ \AA}^{-1}$).

lattice point for three different times selected. On the scan marked 0 ksec, five peaks are present. The two outermost peaks are the $(103^-)_{1D}$ and $(103^+)_{1D}$ satellites from the $1q$ modulation along the l direction. This modulation is common to the one and two q phases and therefore survives the phase transition. The central peak is the (103) Bragg peak due to the $1q$ structure and comes from variants with the q vector along the k direction. Because of the tetragonal distortion, the $(103^-)_{1D}$ and $(103^+)_{1D}$ peaks are not symmetrical around the (103) Bragg peak. The appearance of this peak in the scan marked 0 ksec is due to the time it takes to lower the temperature to 462°C . The symmetrical satellites $(103^-)_{2D}$ and $(103^+)_{2D}$ around the (103) peak represent scattering from the $2q$ phase and disappear with time.

In order to obtain a background-subtracted value of the intensity of the $(103^-)_{2D}$ peak, we performed a least-squares fitting of the neighboring peaks. Figure 3 shows the scan at 86 ksec. The $(103^-)_{1D}$ peak was fitted by a Lorentzian line shape, convoluted with a Gaussian representing the experimental resolution. The (103) peak was fitted by a sum of two Lorentzians, convoluted by the Gaussian. Figure 4 shows the background subtracted intensity on a logarithmic scale of the $(103^-)_{2D}$ peak as a function of time. Over the full two-and-a-half decades the data points accurately follow a straight line. During this decay we do not observe any change in the width of the $(103^-)_{2D}$ peak.

Because of the finite difference in the free energy of the $1q$ and $2q$ phases, mean-field theory predicts that the annihilation shall be exponential, as is the case for the initial growth of an ordered phase.^{1,3} However, due to the antiphase nature of the domain walls, the annihilation of the $2q$ phase cannot be homogeneous on an atomic scale but must require the simultaneous dissociation of two domain walls. To understand the time behavior, it is therefore necessary to take into account the topology of the structure.

FIG. 3. Expanded view of the diffraction pattern, the multiplication factor used is 50 and the time was 86 ksec. The solid curve is the result of the fitting of the $(103^-)_{1D}$ and of the superlattice peak to allow for the subtraction of the background from the $(103^-)_{2D}$ peak ($a^* = 1.690 \text{ \AA}^{-1}$).

FIG. 4. A single logarithmic plot of the background subtracted peak intensity of $(103^-)_{2D}$ vs time. The straight line is the best fit to the data by an exponential.

A topological defect is needed in the mesh of domain walls if the annihilation takes place by local rearrangements of atoms. We propose to consider a two-stage process involving nucleation of topological defects and the subsequent motion of these. Figure 5 shows a dark-field image of Cu-Pd taken with a transmission electron microscope. Hairpin-like structures made up of two joined domain walls are present at the $1q$ - $2q$ interface. This has been studied in detail with high-resolution electron microscopy.⁹⁻¹¹ A nucleation process which involves the creation of a pair of hairpin defects will be slow since "phason-like" excitations have to overcome the repulsion between the domain walls. The second process is the backward migration of the tips of the hairpins. This process corresponds to localized short-range diffusion in which the minority atoms close to the domain wall change their sublattice.

To interpret the x-ray diffraction result, it is necessary to consider some simple kinetic models. For a two-step process we may write the differential equation $dV/dt \sim M$, V being the fraction of the total sample volume having the $2q$ structure at time t and M the number of topological defects at time t . For topological defects nucleated with equal probability anywhere in the bulk $M \sim \int V dt$, for topological defects nucleated on the $1q$ - $2q$ interface

FIG. 5. The center of the photo shows hairpin defects in a Cu_3Pd alloy as observed in the electron microscope. This dark-field micrograph (which was made using the cluster of satellites at 100 fcc for the imaging) is a static observation during the kinetic transformation process, which was blocked by a rapid cooling to room temperature where the diffusion rate is vanishing.

$M \sim \int V^{2/3} dt$. The former case gives an exponential time decay whereas the latter case gives a power law. However, the time development of a two-stage process is governed by the slowest process. Therefore, if we assume that nucleation rate of the topological defects (e.g., hairpins) is significantly slower than their migration, then an "equilibrium" defect density results, and M becomes simply proportional to V and to $V^{2/3}$ for bulk and interface nucleation, respectively. Such bulk nucleation gives rise to an exponential decay, while interface nucleation to a power law; in this case with the exponent three. Interfacial nucleation at a fractal interface with dimension η leads to a modified power law with an exponent $3/(3-\eta)$.

The x-ray-diffraction data clearly show exponential time dependence. Hence, the simple models considered above show that the nucleation is homogeneous in the bulk and not driven by the $1q$ - $2q$ interface. During the time development of the $(103^-)_{2D}$ peak no broadening was observed. Following the nucleation of a topological defect, either an avalanche wipes out an entire $2q$ domain, or the remaining smaller $2q$ domains are pinned such that they still scatter coherently over the observed coherence length of about $300 \text{ \AA}$.¹² This is consistent with the proposed two-stage process where the kinetics is driven by a slow homogeneous nucleation of topological defects.

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FIG. 5. The center of the photo shows hairpin defects in a Cu_3Pd alloy as observed in the electron microscope. This dark-field micrograph (which was made using the cluster of satellites at 100 fcc for the imaging) is a static observation during the kinetic transformation process, which was blocked by a rapid cooling to room temperature where the diffusion rate is vanishing.