PHYSICAL REVIEW B VOLUME 60, NUMBER 21 1 DECEMBER 1999-I

Kinetics of phase transitions in equiatomic CuAu

O. Malis and K. F. Ludwig, Jr.
Boston University, Boston, Massachusetts 02215

(Received 22 April 1999)

The detailed ordering kinetics in equiatomic CuAu was studied using *in situ* time-resolved x-ray scattering. A subtle competition between the modulated CuAu II phase and the simple ordered CuAu I phase was found to occur across the CuAu I/CuAu II phase boundary. The correlation between ordering and the tetragonal distortion was also investigated, in particular the crossover from a heterogeneous incoherent nucleation to a continuous, coherent growth of the tetragonal lattice. The late stage coarsening process was found to obey the expected $t^{1/2}$ growth law but at high temperatures the kinetics is slowed down, possibly by the competition between the two ordered phases or the interaction between grain and domain boundaries.
[S0163-1829(99)02542-4]

I. INTRODUCTION

Bulk metallic alloys exhibit a wide variety of ordered structures in the solid phase, some of which have interesting technological properties. In contrast to the disordered solid solutions where the different chemical species are distributed on the positions of the crystalline lattice with a probability equal to their composition, in the ordered phases each species occupies specific atomic positions which form single-component rich sublattices. Traditionally, ordering in binary metallic alloys has often been modeled by an Ising antiferromagnet on a fixed lattice. Starting from this Ising model a coarse-grained, Ginzburg-Landau free-energy functional can be defined and used to describe the phase transition between the disordered and the ordered phases. The kinetics of the ordering transformation is concerned with the time evolution of the order when a phase transition occurs and is often investigated theoretically using a Langevin equation.[1] Even within the mean-field context the Langevin equation cannot be solved exactly in the general case and must be simplified by adding strong constraints to the model, constraints which make the solutions valid only in limited time regimes. For the earliest stages of the process, Cahn, Hilliard, Cook, de Fontaine, and Khachaturian[2–7] developed a linear theory by assuming that the order parameter is sufficiently small that the higher-order terms of the Ginzburg-Landau expansion of the free-energy can be neglected. Despite its simplicity and the uncertainty concerning its breakdown time,[8,9] the linear theory is often used as a first model to interpret early stage experimental data.[10] For the late stages of the coarsening process, Allen and Cahn[11] derived an equation for the time dependence of the average domain size. The predicted $t^{1/2}$ growth law of the ordered domains has been confirmed by numerical simulations[12] and x-ray scattering experiments[13] on several ordering systems.

The theories mentioned above are expected to be valid for simple ordering systems in very specific time regimes of the transformation. There is, however, a broad range of intermediate stages for which no simple analytical solution for the Langevin equation can be constructed. Nonlinear theories have been proposed for this regime but they involve a number of uncontrolled approximations.[14–16] Moreover, real alloy systems often display complicated ordered structures that involve long-period superlattices or lattice distortions. Relatively little experimental and theoretical work has been done so far to approach the rich phenomena associated with phase transition kinetics in these systems. The goal of the present paper is to investigate experimentally the ordering kinetics of such a complex binary alloy, equiatomic CuAu. Currently, there is no single theoretical model that can fully explain the behavior we observe in CuAu. Though there has been some success in comparing the experimental results to Langevin simulations based on the effective medium theory of cohesion in metals (EMT),[17] clearly more sophisticated theories and Monte Carlo simulations have to be developed in order to provide insight into the subtle interplay between order and strain in CuAu.

In the 50-50 at. % concentration range the equilibrium phase diagram of CuAu exhibits a sequence of two first-order phase transitions. Above 410 °C the stable phase is disordered; Cu and Au atoms occupy with equal probability the four sublattices of a fcc lattice. Below 385 °C the equilibrium phase is a simple $L1_0$ ordered phase, CuAu I, in which Cu and Au occupy alternating atomic layers. Between these two transition temperatures CuAu orders into a one-dimensional long-period superlattice (LPS) structure, called the CuAu II or modulated phase, which consists of a periodic array of antiphase boundaries with an average modulation wavelength approximately ten times the size of the underlying CuAu I cell. The origin of the modulated phase is still under debate[18] and most theoretical models encounter difficulties in predicting the correct CuAu II stability in a narrow temperature range.

In addition to ordering, the phase transitions in CuAu are accompanied by a change of the lattice from cubic in the disordered phase to orthorhombic in CuAu II and tetragonal in CuAu I. If, by convention, the c axis of the lattice is taken to be the stacking direction of the Cu and Au layers, also called the ordering direction, the orthorhombic distortion of the unit cell b/a is small and will be neglected but the tetragonal distortion c/a is significant and reflects the large size difference between Cu and Au atoms (12%). The tetragonal lattice is compressed by approximately 7% in the ordering direction and dilated by about 1% in the plane perpen-

0163-1829/99/60(21)/14675(8)/$15.00

dicular to the ordering direction (in-plane directions) with respect to the cubic disordered lattice.

Using *in situ* time-resolved x-ray scattering we studied in detail the kinetics of CuAu I formation from the disordered and modulated phases. We found that the CuAu II phase plays a major role in the ordering process. Our investigation focuses on the competition between the two ordered phases and on the correlation between order and strain as the lattice changes from cubic to tetragonal. We also examine the late stages of the transformation within the context of the Cahn-Allen theory of coarsening.

II. EXPERIMENT

The x-ray scattering experiment was performed at the National Synchrotron Light Source, Brookhaven National Laboratory, on the IBM-MIT beamline X20C. The x-ray data we report here were taken with a flat double-crystal Si(111) monochromator at a photon energy of 6.9 keV while the beam intensity was monitored with two ion chambers. The beam was focused at the sample and the typical beam size was 0.5-mm vertical by 1-mm horizontal.

The samples studied were polycrystalline free standing films and ribbons 3–10-μm thick deposited by thermal evaporation on metallic foil. The composition of the samples was determined by x-ray microanalysis and fluorescence and found to be within 1.5 at. % of stoichiometry. This uncertainty in the composition of the samples is consistent with a 10° uncertainty in our determination of the modulated to disordered transition temperature. The relative ratios of the measured Bragg peak intensities indicates that the CuAu grains do not exhibit significant preferred orientation.

During the experiment the samples were rapidly quenched from the disordered or modulated phase into the ordered or modulated phase region and the time evolution of the x-ray scattering pattern was recorded by a linear position-sensitive detector or a CCD array in reflection geometry. In order to avoid oxidation at high temperatures and to improve temperature homogeneity, the samples were kept in a high-purity He atmosphere. Two different experimental setups have been used to achieve the desired quench rates. For the examination of slower processes such as the competition between the two ordered phases the samples were heated on a boron-nitride heater which is in thermal contact with a water-cooled Cu block. The temperature is measured by a thermocouple and controlled by a Eurotherm controller. This setup allowed quench rates of up to 6 °C/sec.

In order to achieve faster quenches and therefore study earlier stages of the transformation some of the polycrystalline films were deposited on 25-μ Mo foil and cut into 2-mm wide ribbons. These ribbons were resistively self-heated and the temperature was monitored with an infrared pyrometer which was calibrated so that the modulated to disordered transition temperature corresponds to the known value. This setup allowed quench rates of up to 250 °C/sec. Qualitatively similar behavior was observed in the ribbons and the thin films.

III. COMPETITION BETWEEN CuAu I AND CuAu II

The ordering kinetics in CuAu has been investigated by studying the time evolution of the scattering pattern in the (110) and (001) Bragg peak ranges. In both these regions of reciprocal space, CuAu I exhibits single superlattice points while CuAu II exhibits pairs of superlattice points. For a polycrystalline sample, due to the radially averaging nature of the scattering, the CuAu II pair produces only one diffraction maximum in the (001) q range and two maxima in the (110) q range. Moreover, the significance of the peak widths is also different: the (001) width is given by the domain size in the ordering direction (i.e., along the local c axis) while the widths of the (110) peaks reflect domain sizes in the plane perpendicular to the ordering direction.

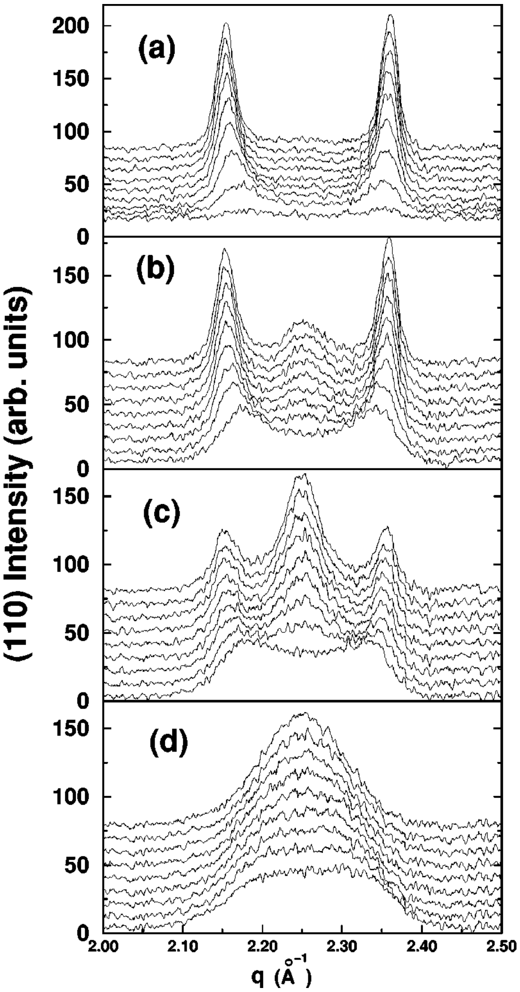

FIG. 1. Time evolution of the (110) scattering pattern for quenches from 430–390 °C (a), 380 °C (b), 370 °C (c), and 320 °C (d). In each case the lowest diffraction pattern is obtained 90 sec after the quench. Subsequent patterns at 90 sec intervals are offset by 10 units upwards. The exposure time for each pattern is 3 sec.

We found evidence for a competition between the two ordered phases which occurs across the CuAu II/CuAu I phase boundary and takes the form of an interesting metastability of the modulated phase into the CuAu I stability range.

Figure 1 shows the evolution of the scattering pattern in the (110) reciprocal vector range for a sequence of quenches from the disordered state (430 °C) to different points below the modulated/disordered phase boundary. The two side peaks are characteristic of the modulated phase while the central peak is the single (110) peak of CuAu I. It is noteworthy that for quenches in the vicinity of the CuAu I/

CuAu II phase boundary both ordered phases appear and grow regardless of the position of the final temperature with respect to the equilibrium phase boundary.

If the sample is quenched into the CuAu II stability region, to 390 °C [Fig. 1(a)], the scattering pattern is dominated by the strong growth of the modulated satellites. At all times, however, there is a small amount of extra intensity between the two modulated peaks which develops into a weak central peak and indicates the presence of simple ordered regions. Moreover, for a shallow quench into the CuAu I stability range, 5° below the transition at 385 °C [Fig. 1(b)], the CuAu II satellites still appear and grow significantly but the CuAu I peak grows faster than at 390 °C. For increasing quench depth the relative growth rate of the ordered phase with respect to the modulated phase increases so that at approximately 355 °C it is not possible any more to identify three separate peaks in the late stages of the process and the scattering exhibits a single very broad peak.

To quantify the competition between CuAu I and CuAu II, we fit the x-ray scattering pattern with three Lorentzian-square functions of independent heights, positions, and widths. The fit results were used to calculate the integrated intensities of the CuAu I single peak and CuAu II side peaks which are proportional to the volumes of the two phases, respectively. The separation into simple ordered and modulated phase is somewhat arbitrary because, especially in the early stages of the transformation, there are likely no distinct boundaries between the two phases. The sample probably exhibits an interconnected structure of modulated and simple ordered regions. From the analysis point of view, however, it is natural to make this separation which helps characterize the overall features of the structure.

In order to discuss concretely the different stages of the transition for a shallow quench below the CuAu I/CuAu II transition line we will focus on the quench from 430–360 °C. Figure 2 displays the time evolution of the integrated intensities, peak positions, and domain sizes for this particular case. The domain sizes were estimated from the peak widths after correcting for experimental resolution.

In the early stages of the transformation the (110) total integrated intensity grows rapidly and then levels after approximately 75 sec indicating that most of the material has ordered by this time. Consistent with the (110) behavior, the integrated intensity of the (001) peak saturates on the same time scale. In this time regime the scattering pattern around (110) has an interesting double-peak shape which is shown in detail in Fig. 3. This peak shape suggests that, when they first appear, the ordered domains exhibit in-plane periodic antiphase boundaries similar to the ones present in CuAu II. The wavelength of the modulated regions, however, is approximately 44% larger than the equilibrium CuAu II value and is reflected in the smaller separation of the two peaks. This double peak is also reminiscent of the diffuse scattering peak shape reported in disordered CuAu.[19,20] The equilibrium fluctuations above 410 °C exhibit antiphaselike medium-range correlations with a modulation wavelength approximately equal to 13 unit cells.[20] It seems that in the early stages of ordering these fluctuations grow in amplitude to become ordered regions with a similar in-plane structure. On this time scale the structure consists of a mixture of modulated regions with an average width of 23 unit cells and simple ordered regions with an average width of 13 unit cells.

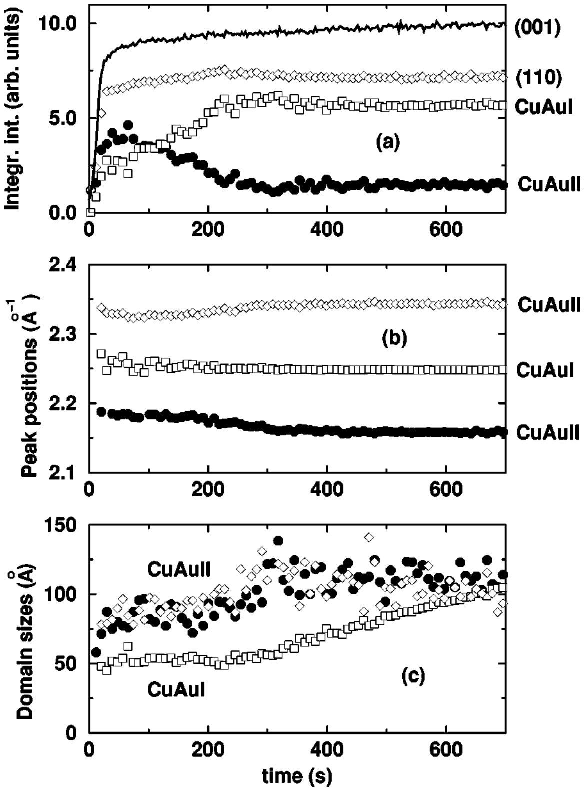

FIG. 2. Time dependence of the integrated intensities (a), peak positions (b), and domain sizes (c) of the (110) modulated and simple ordered peaks for a quench from 430–360 °C. Time zero is the quench time and the exposure time of each point is 3 sec.

Simultaneously with the ordering process, during the first 100 sec following the quench, the tetragonal distortion of the lattice also occurs and can be seen in the shift of the three peaks towards lower *q* values. This topic will, however, be discussed in detail in Sec. IV below.

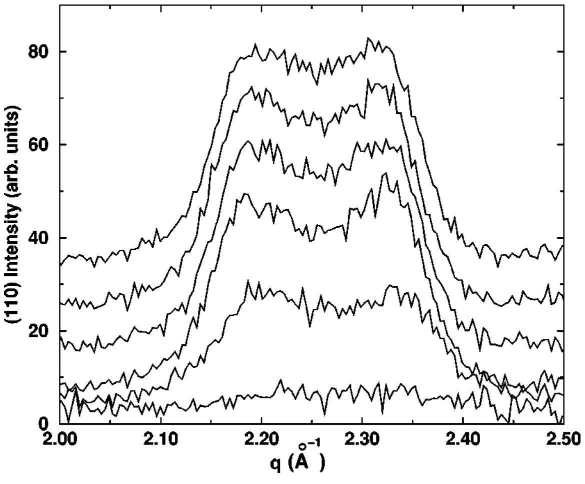

FIG. 3. Early stage evolution of the scattering pattern around the (110) superlattice peak. The lowest diffraction pattern is obtained 15 sec after the quench. Subsequent patterns at 15 sec intervals are offset by 10 units upwards. The exposure time of each pattern is 3 sec.

After the initial onset of the ordering, some of the modulatedlike regions begin to transform into simple ordered regions as can be seen from the decrease of the CuAu II integrated intensity and the continuous increase of the CuAu I integrated intensity. For approximately 125 sec this process occurs without significant changes of the modulation wavelength and in-plane domain size which would suggest that it is mainly due to coarsening in the ordering direction. Soon, however, the CuAu II peaks begin to shift outwardly indicating the rapid decrease of the modulation wavelength towards the equilibrium value. This process, which lasts for approximately 100 sec, is also accompanied by an increase of the average in-plane domain sizes of the two ordered phases. After about 300 sec the material enters the coarsening stage of the transformation which is characterized by a more rapid increase of the CuAu I average domain size. This process is more complicated than the classic coarsening mechanism and will be discussed in more detail in Sec. V below. It is interesting, however, that the modulated phase persists to relatively long times and does not disappear completely even after 1500 sec. This behavior is in qualitative agreement with Langevin simulations reported elsewhere.[17]

The split-peak feature of the scattering in the early stage of the transformation can be observed for quenches to temperatures above 350 °C. For quenches below 350 °C, the x-ray scattering around (110) displays a single maximum but this peak is very broad and has an unusual flat-topped shape [Fig. 1(d)]. This peak gradually narrows into the Lorentzian-square shape expected for the late stage coarsening process but its width remains large, corresponding to a relatively small in-plane domain size of approximately 13 unit cells at 320 °C after 800 sec.

In order to further investigate the CuAu II metastability into the CuAu I region of the phase diagram we have also studied the effect of the initial state on the ordering kinetics. As mentioned above, a quench from the disordered phase to 320 °C produces a CuAu I phase with small in-plane domain size. However, if the sample is first ordered thoroughly into the modulated phase at 390 °C, i.e., the diffraction pattern displays only the modulated satellites and no ordered central peak, and is subsequently quenched to 320 °C, the CuAu I growth rate is very small and depends on the quality of the starting CuAu II phase. In certain cases no growth was observed on the time scale of the experiment, which is the same as in Fig. 1(d). This behavior suggests that the modulated phase is metastable deep into the ordered phase region and the CuAu I growth from CuAu II occurs mainly through nucleation on defects. A similar behavior was also observed in the Langevin simulations based on EMT.[17]

IV. CORRELATION BETWEEN ORDER AND THE TETRAGONAL DISTORTION

As was mentioned in the previous section, in the early stages of the transformation, the sample orders almost completely as can be seen by the rapid saturation of the (001) integrated intensity. This process is expected to occur through a nucleation and growth mechanism for quenches above the instability point and through continuous ordering for quenches below this temperature. In the nucleation regime, the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory[21] predicts that the volume fraction of the transformed phase should grow as $1-\exp(-kt^n)$, where n is the Avrami exponent and k is a constant depending on nucleation and growth rates. This functional form provides a good fit to the time dependence of the (001) integrated intensity for shallow quenches. Moreover, the Avrami exponent has values less than 2 which indicates a heterogeneous nucleation mechanism in the ''site saturation'' regime. For quenches below 375 °C the rapid initial increase of the (001) integrated intensity in the early stages is followed by a slower growth process which extends to late times. For these quenches the time of nucleation and growth becomes comparable to the time of the relaxation of the fluctuations and in this sense the process becomes more continuous on time scales above 10 sec. In this temperature range the JMAK form cannot fit the integrated intensities across the experimental time scale.

Simultaneously with the ordering, in the early stages the lattice changes from cubic in the disordered phase to tetragonal in the ordered phases. In a recent electron microscopy and x-ray-diffraction study,[22] Tanaka and his collaborators provided evidence for the existence of a crossover from an incoherent to a coherent growth of the ordered phases, a crossover which was first suggested by Borelius.[23] Making use of Cook's concept of a coherent phase boundary,[24] Tanaka *et al.* identified three mechanisms of formation of the ordered tetragonal phases from the disordered state: incoherent nucleation at grain boundaries between the incoherent and coherent phase boundaries, coherent nucleation within the disordered grains between the coherent phase boundary and the coherent spinodal, and continuous ordering below the coherent spinodal. The values they proposed for the coherent phase boundary and the spinodal are 375 and 357 °C, respectively.

We have investigated the kinetics of the tetragonal distortion by performing a systematic study of the temperature and time evolution of the {200} fundamental peaks. These peaks are not directly sensitive to the ordering process and therefore cannot distinguish between the two ordered phases, but they provide direct information about the changes in lattice parameter. Figures 4(a) and 4(b) show the maps of the scattered x-ray intensities around the (200) reciprocal lattice position for a quench from 442–390 °C and a quench from 440–352 °C, respectively. The peak at largest q is the (002) fundamental of the ordered phases which reflects the lattice parameter in the c direction while the peak at lowest q is due to the (200) and (020) reflections and gives the in-plane lattice constant a. The central peak is the fundamental reflection of the cubic disordered phase.

For quenches above 360 °C [Fig. 4(a)] the tetragonal peaks appear and grow close to the positions expected from the equilibrium values of the lattice parameter while the disordered peak subsides. This behavior suggests that the ordered phases form through an incoherent nucleation process with an incubation period. The time dependence of the integrated intensity at the higher temperatures can be well fit with the JMAK form and the Avrami exponent is consistent with a heterogeneous nucleation process in the ''site saturation'' regime. Figure 5 shows in detail the time evolution of the three peak positions obtained from a fit of the x-ray intensities with three Lorentzian-square peaks for the quench to 390 °C. At the earliest times we were able to fit the data, the tetragonal peaks are closer to the disordered peak than

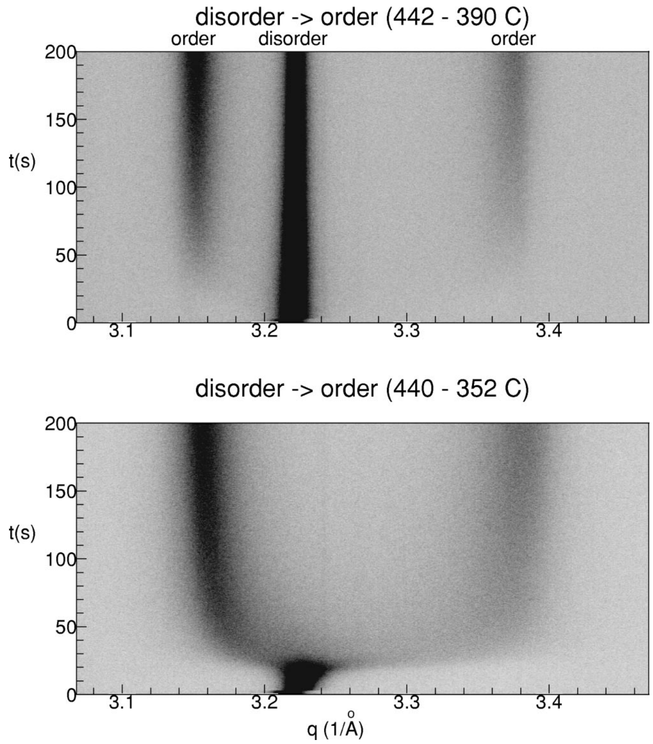

FIG. 4. Time evolution of the {200} fundamental peaks for a quench from 442–390 °C and a quench from 440–352 °C. The quench occurred at $t=5$ sec and the exposure time of each pattern is 0.5 sec.

expected from the equilibrium positions. This suggests that, when they first form, the tetragonal grains are subject to significant stresses from the surrounding cubic phase, stresses which relax in time and the peaks shift outwards. A small shift of the disordered peak can also be observed, perhaps due to the stresses acting on the disordered grains which, as the grains decrease in size, become strong enough to increase the average disordered lattice parameter.

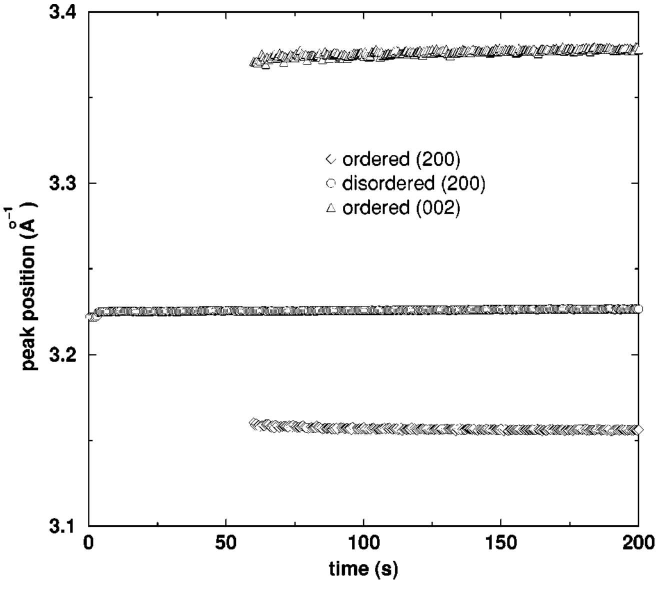

FIG. 5. Time evolution of the disordered (200) and ordered (200) and (002) fundamental peak positions for a quench from 442–390 °C. The quench occurred at $t=5$ sec and the exposure time of each point is 0.5 sec.

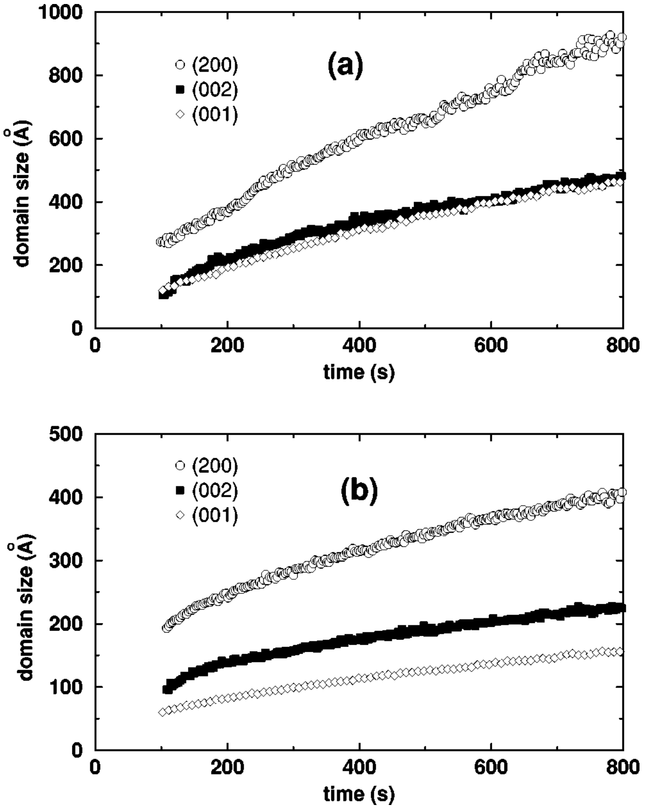

FIG. 6. Time dependence of the domain sizes in the ordering direction [calculated from the (001) peak widths] and grain sizes in the ordering direction [from the (002) peak widths] and in-plane direction [from (200) peak width] for a quench from 430–390 °C (a) and a quench from 430–320 °C (b). The quench occurred at $t=0$ sec but the data could not be fit in a reliable way before $t=100$ sec. The exposure time of each point is 3 sec.

For deeper quenches, however [Fig. 4(b)], a qualitatively different process was observed. Immediately following the quench, the disordered fundamental starts to broaden and decrease in intensity suggesting that the lattice breaks into many small grains. After this brief period of lattice fragmentation the central peak splits into the two tetragonal peaks which gradually shift toward the equilibrium positions as the average lattice parameters continuously change from the disordered to the ordered values.

We have also been able to extract detailed information about the shape and average size of the ordered domains and grains from the widths of the (001) and (200) peaks after the instrumental resolution has been subtracted. The tetragonal grains have a ''pancake'' shape with the size in the ordering direction approximately equal to half the in-plane size (Fig. 6). At all temperatures the in-plane grain size also grows at a higher rate than does the grain size in the ordering direction. For shallow quenches (390 °C) the size of the ordered domains in the ordering direction is comparable to the corresponding size of the tetragonal grains and grows at the same rate [Fig. 6(a)]. For deeper quenches, however, the grains are larger than the average domain size in the ordering direction and contain more than one ordered domain. Both the grain and the domain sizes appear, however, to be growing at approximately the same rate [Fig. 6(b)].

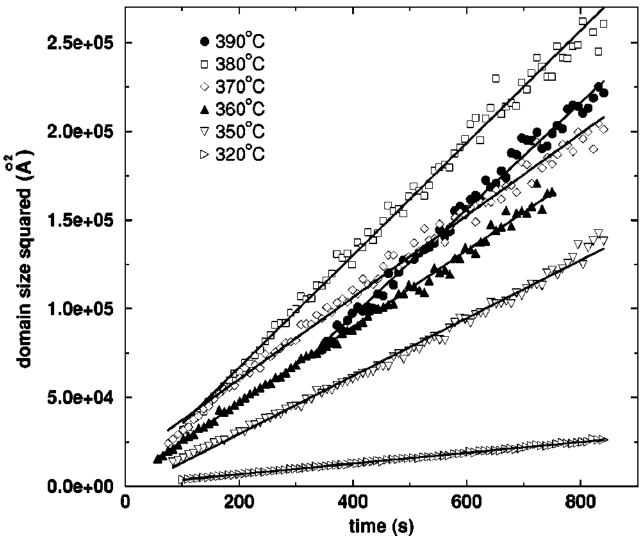

FIG. 7. Late stage coarsening in the ordering direction. The exposure time of each point is 3 sec.

V. LATE STAGE COARSENING

For the late stage curvature-driven coarsening process in an ordering alloy, Cahn and Allen predicted that the average size of the ordered domains grows in time as $t^{1/2}$.[11] In CuAu, where the ordering process is complicated by the tetragonal distortion and the in-plane competition between CuAu I and CuAu II phases, there is no *a priori* reason for this scaling law to be valid. Figure 7 shows the time dependence of the square of the average ordered domain sizes calculated from the (001) peak width for a series of quenches below the transition temperature at 410 °C. At each temperature the late stages are considered to start when the (001) integrated intensity reaches 90% of the maximum value and only the data points after this time are displayed. It is interesting that, for every temperature, the domain size squared can be well fit to straight lines. This suggests that across the entire temperature range investigated, in this time regime, coarsening within each grain is curvature driven. This is true even for the quench to 390 °C where Fig. 6 shows that the domain and grain sizes are approximately equal and therefore we would expect the interaction between domain and grain boundary to influence the domain growth. Moreover, the grain growth in both directions seems to follow the same $t^{1/2}$ law.

In order to examine the coarsening process in the plane perpendicular to the ordering direction we plot the time dependence of the in-plane domain size squared calculated from the (110) peak widths in Fig. 8. In the modulated phase region [Fig. 8(a)] as well as in the ordered phase region [Fig. 8(b)] the in-plane sizes of the CuAu II and CuAu I domains, respectively, seem to obey the same $t^{1/2}$ coarsening law in the late stages of the transformation. It is noteworthy that simulations of coarsening in the two-dimensional (2D) axial next-nearest-neighbor Ising model found that the characteristic length scale of the modulated phase also grows as $t^{1/2}$.[25]

Cahn-Allen theory predicts that the slope of the domain size squared as a function of time depends on temperature only through the diffusion constant and therefore should have a simple exponential dependence on inverse absolute temperature, e^{-E/k_BT}, where E is the diffusion activation energy. Figure 9 shows the temperature dependence of the slopes from the fit of the domain sizes squared in the ordering and in-plane directions calculated from the (001) and (110) peak width, respectively, for two different samples. It is noteworthy that the slopes in the in-plane direction are smaller than the slopes in the ordering direction. A similar asymmetry was reported by Nagler *et al.* in Cu_3Au.[13]

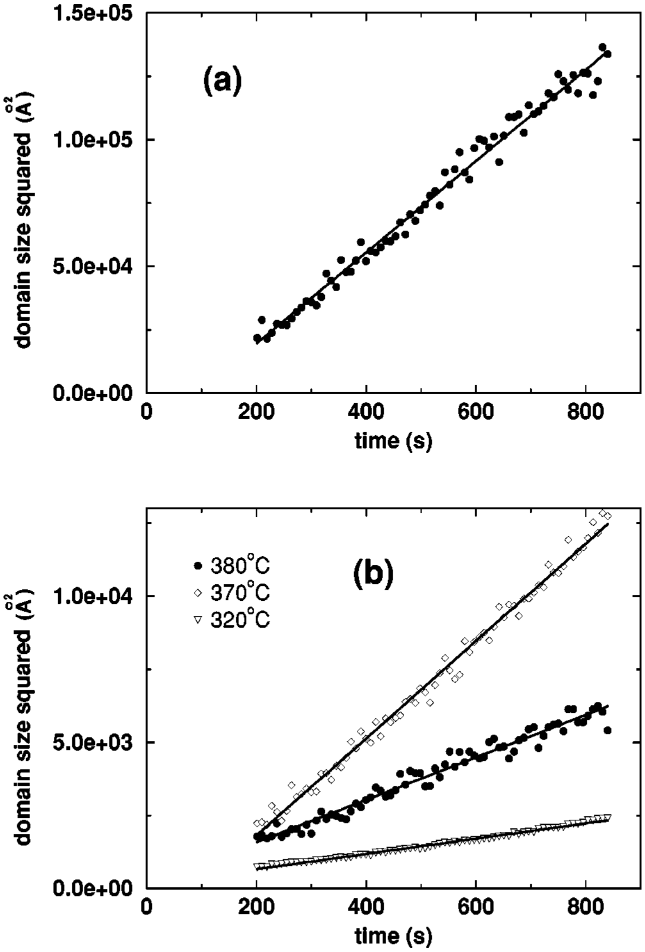

FIG. 8. Late stage coarsening in the in-plane direction for the modulated phase in a quench from 430–390 °C (a), and for the simple ordered phase in quenches from 430–380, 370, and 320 °C (b). The exposure time of each point is 3 sec.

At low temperatures the slopes exhibit thermally activated behavior and the calculated activation energy, approximately 1.74 eV, is in agreement with diffusion activation energies reported in the literature.[26] At high temperatures, however, the slopes fall below the values expected from the extrapolation of the straight lines fit through the low-temperature points. In the ordering direction, this slowing down might be caused by the interaction between the domains and the grains boundaries and/or by the competition between the two ordered phases. In the in-plane direction, though, where the grain sizes are considerably larger than the domain sizes, this slowing down is likely an effect of the competition between the two ordered phases.

VI. DISCUSSION AND CONCLUSIONS

In the earliest stages of the transformation we were able to study, the sample orders almost completely as can be seen

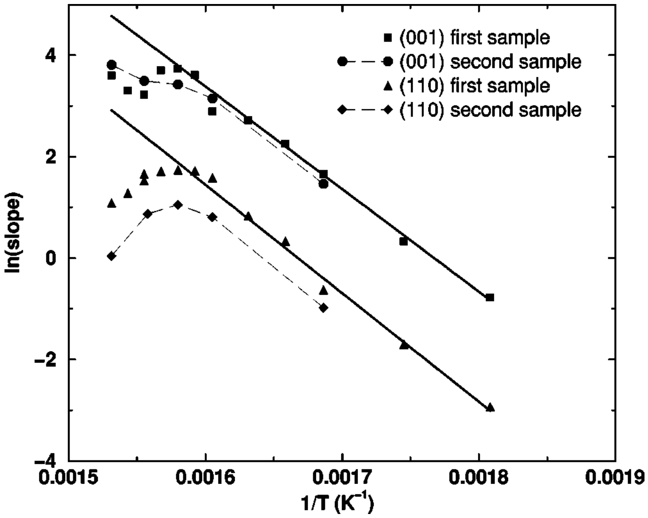

FIG. 9. Temperature dependence of the slopes from the linear fit of the domain size squared as a function of temperature in the ordering direction [from the (001) peak width] and in the in-plane direction [from the (110) peak width] for two different samples. The straight lines are fits through the low-temperature data points.

from the rapid saturation of the (001) superlattice peak. Thus we were not able to directly observe the initial relaxation of fluctuations as had been done in, for example, Cu_3Au.[10] For temperatures above 350 °C, the ordered structures which initially form have features strikingly similar to the antiphase correlations existing in the disordered phase. In this time regime the material likely consists of a complex, intermingled, mixture of simple ordered regions and modulated regions. Apparently, there is no need for simple-ordered regions to develop before the appearance of modulated structures. Moreover, as in the disordered phase, the modulated-like regions have a modulation wavelength larger than the equilibrium value in CuAu II. This would suggest that the equilibrium fluctuations in the disordered phase play a major role in the kinetics of the ordering process. Preliminary results from studies of Cu_3Pd and Pd_3V suggest that in these systems the initial ordering process is also dominated by the growth of pre-existing fluctuations from the disordered phase.[27]

It is particularly interesting that the ordered domains have a modulated in-plane structure even for shallow quenches, where the initial onset of the ordering occurs through heterogeneous nucleation and growth. It appears that the ordered nuclei consist of an intricate network of antiphase domains which grow simultaneously and maintain the relatively long-range correlations necessary to form modulated regions. It is possible that the evolution in the early stages is triggered by the strain field around dislocations which makes the fluctuations present in the disordered phase transform into ordered regions by ''filling in'' (i.e., growing in amplitude). As the tetragonal distortion advances into the volume it will also continue to favor the growth of those fluctuations which have an appropriate orientation.

With decreasing quench temperature, the integrated intensities suggest that there is an effective change from heterogeneous nucleation and growth to a more continuous ordering process. This occurs at temperatures well above the spinodal temperature of 320 °C determined from measurements of the correlation length above the transition,[20] and may be related to the anomalous rapid growth in antiphase correlation susceptibility with decreasing temperature observed in the disordered phase.[20]

We have found evidence for two regimes of growth of the tetragonal distortion. Above 360 °C, the tetragonal distortion appears through an incoherent nucleation mechanism. Below this temperature regime, there is a continuous, coherent change of the lattice parameters from the disordered to the equilibrium ordered values. These results are in general agreement with the observations of Tanaka *et al.*[22] We see, however, no clear regime in which ordering domains nucleate without an accompanying tetragonal distortion. We believe that the tetragonal relaxation of the ordered nuclei occurs simultaneously with the ordering.

Elder and his collaborators performed 2D Langevin simulations of an EMT-based Landau model of CuAu and found good qualitative agreement with some of our experimental results.[17] The Langevin simulations correctly reproduced the competition between the two ordered phases across the CuAu I to CuAu II phase boundary as well as the metastability of CuAu II deep into the CuAu I range. The Landau model, however, predicts that the disordered phase exhibits spinodals with respect to the modulated and CuAu I phases, and, since both these spinodals are located in the CuAu II region, the growth below the CuAu I/CuAu II phase boundary occurs through a continuous ordering mechanism. In contrast to the Landau model, the real alloy does not have an instability point in this temperature range, and therefore the degree of qualitative agreement between the simulations and the experimental results is quite surprising. Moreover, the Langevin simulations were not able to reproduce the details of the ordering process such as the evolution of the modulation wavelength. It is also noteworthy that the Langevin simulations were performed on a 2D lattice and no attempt was made to study the kinetics of the tetragonal distortion. In order to explain the evolving relationship between order and strain from a theoretical point of view, more sophisticated Monte Carlo simulations may be necessary.

We have also investigated in detail the time and temperature dependence of the domain and grain sizes and the evolving relationship between them. In the late stage of the ordering process we found that the average size of the ordered domains and grains in the ordering and in-plane directions obeys the $t^{1/2}$ growth law expected for a curvature-driven growth mechanism. However, the complicated temperature dependence of the slopes indicates that the growth process is slowed down, possibly by the competition between the two ordered phases or the interaction with the tetragonal distortion. It is noteworthy that the Langevin simulations of CuAu performed by Chakraborty, Elder, and Goldenfeld[28] suggest that the coarsening kinetics in the modulation plane is slowed down by the formation of small antiphase droplets which have a size equal to half the modulation wavelength and pin the domain boundaries.

In conclusion, using *in situ* time-resolved x-ray scattering we have investigated the kinetics of phase transition in equiatomic CuAu, a classic alloy system displaying a modulated phase and a tetragonal distortion. The results of our experimental study were correlated with the information available from diffuse scattering measurements in disordered CuAu and Langevin simulations based on EMT in order to provide insight into the ordering process of such a complex system.

ACKNOWLEDGMENTS

This work was supported by NSF Grant No. DMR-9633596. The NSLS is supported by DOE Division of Materials Sciences and Division of Chemical Sciences.

---

[1] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8.

[2] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **31**, 688 (1959).

[3] J. W. Cahn, Acta Metall. **9**, 795 (1967).

[4] J. W. Cahn, Trans. Metall. Soc. AIME **242**, 165 (1968).

[5] H. E. Cook, D. de Fontaine, and J. E. Hilliard, Acta Metall. **17**, 765 (1969).

[6] H. E. Cook, Acta Metall. **18**, 297 (1970).

[7] A. G. Khachaturian, Fiz. Tverd. Tela (Leningrad) **9**, 2594 (1967) [Sov. Phys. Solid State **9**, 2040 (1968)].

[8] N. A. Gross, W. Klein, and K. Ludwig, Phys. Rev. Lett. **73**, 2639 (1994).

[9] N. A. Gross, W. Klein, and K. Ludwig, Phys. Rev. E **56**, 5160 (1997).

[10] K. F. Ludwig, G. B. Stephenson, J. L. Jordan-Sweet, J. Mainville, Y. S. Yang, and M. Sutton, Phys. Rev. Lett. **61**, 1859 (1988).

[11] S. M. Allen and J. W. Cahn, Acta Metall. **27**, 1085 (1979).

[12] M. K. Phani, J. L. Lebowitz, M. H. Kalos, and O. Penrose, Phys. Rev. Lett. **45**, 366 (1980).

[13] S. E. Nagler, R. F. Shannon, Jr., C. R. Harkless, M. A. Singh, and R. M. Nicklow, Phys. Rev. Lett. **61**, 718 (1988).

[14] J. S. Langer, M. Bar-on, and H. D. Miller, Phys. Rev. A **11**, 1417 (1975).

[15] C. Billotet and K. Binder, Z. Phys. B **32**, 195 (1979).

[16] K. Kawasaki, M. C. Yalabik, and J. D. Gunton, Phys. Rev. A **17**, 455 (1978).

[17] K. R. Elder, O. Malis, K. Ludwig, B. Chakraborty, and N. Goldenfeld, Europhys. Lett. **43**, 629 (1998).

[18] A. T. Paxton and H. M. Polatoglou, Phys. Rev. Lett. **78**, 270 (1997), and references therein.

[19] S. Hashimoto, Acta Crystallogr., Sect. A: Found. Crystallogr. **A39**, 524 (1983).

[20] O. Malis, K. F. Ludwig, W. Schweika, G. E. Ice, and C. J. Sparks, Phys. Rev. B (to be published).

[21] J. W. Christian, *The Theory of Transformations in Metals and Alloys* (Pergamon Press, New York, 1975), Part I.

[22] Y. Tanaka, K-I. Udoh, K. Hisatsune, and K. Yasuda, Philos. Mag. A **69**, 925 (1994).

[23] G. Borelius, J. Inst. Met. **74**, 17 (1948).

[24] H. E. Cook, Mater. Sci. Eng. **25**, 127 (1976).

[25] T. Ala-Nissila, J. D. Gunton, and K. Kaski, Phys. Rev. B **33**, 7583 (1986).

[26] F. Lantelme and S. Belaidouni, Electrochim. Acta **26**, 1225 (1981).

[27] K. F. Ludwig (private communication).

[28] B. Chakraborty, K. Elder, and N. Goldenfeld, Physica A **224**, 113 (1996).