

STRUCTURAL TRANSFORMATIONS DURING DECOMPOSITION IN Cu–Be ALLOYS

A. G. KHACHATURYAN¹ and D. E. LAUGHLIN²

¹Department of Mechanics and Materials Science, Rutgers University, Piscataway, NJ 08855-0909
and ²Department of Metallurgical Engineering and Materials Science, Carnegie Mellon University,
Pittsburgh, PA 15213–3890, U.S.A.

(Received 21 June 1989; in revised form 28 March 1990)

Abstract—In this paper we consider the decomposition that occurs in Cu-rich Cu–Be alloys. The decomposition process is regarded as an isostructural decomposition of the f.c.c. phase into Be-rich and Be-depleted regions followed by the transformation of the Be enriched f.c.c. regions into Be enriched b.c.c. regions via the Bain strain. Concomitant with and after this process, the b.c.c. regions atomically order to form the CsCl (B2) structure. Consideration of the coherency strain results in the conclusion that the habit plane of the emerging B2 phase changes during decomposition to minimize the elastic strain energy. The habit change is accompanied by a change in crystal structure induced by the coherency. The changes are rationalized in terms of material constants. The predicted habit planes and lattice parameters agree with the X-ray and electron microscopy observations. The morphology and structure of the intermediate γ'' and γ' phases are interpreted as constrained states of the same precipitate B2 phase (γ) with different habit planes.

Résumé—Dans cet article on étudie la décomposition qui se produit dans les alliages Cu–Be riches en Cu. Le processus de décomposition est considéré comme une décomposition isostructurale de la phase c.f.c. en régions riches ou appauvries en béryllium suivie de la transformation des régions c.f.c. enrichies en béryllium en régions c.c. via la déformation de Bain. Pendant et après ce processus, les régions c.c. s'ordonnent pour former la structure CsCl (B2). En considérant les déformations de cohérence, on conclut que le plan d'accrolement de la phase B2 résultante change pendant la décomposition pour minimiser son énergie élastique. Le changement de plan d'accrolement est accompagné par une variation de la structure du cristal induite par la cohérence. Les variations sont rationalisées en fonction des constantes du matériau. Les plans d'accrolement prévus et les paramètres du réseau sont en accord avec les observations par rayons X et par microscopie électronique. La morphologie et la structure des phases intermédiaires γ'' et γ' sont interprétées comme des états contraints de la même phase précipitée B2 (γ) avec différents plans d'accrolement.

Zusammenfassung—In dieser Arbeit betrachten wir die Entmischung, die in Cu-reichen Be-Legierungen auftritt. Der Entmischungsprozeß wird als eine isostrukturelle Entmischung der kfz. Phase in Be-reiche und Be-verarmte Bereiche angesehen; dieser folgt eine Umwandlung der Be-reichen k.f.z. Bereiche in Be-reiche k.r.z. Bereiche über die Bain-Spannung. Während dieses Prozesses und danach ordnen sich die k.r.z. Bereiche atomar und bilden die CsCl (B2)-Struktur. Aus einer Betrachtung der Kohärenzspannungen folgt, daß die Habitebene der entstehenden B2-Phase sich während der Entmischung verändert, um die elastische Verzerrungsenergie zu minimieren. Diese Änderung der Habitebene ist begleitet von einem Wechsel in der Kristallstruktur, der durch die Kohärenz induziert wird. Diese Änderungen werden anhand der Materialkonstanten erklärt. Die vorausgesagten Habitebenen und Gitterparameter stimmen mit Röntgenmessungen und elektronenmikroskopischen Beobachtungen überein. Morphologie und Struktur der Zwischenphasen γ'' und γ' werden als erzwungene Zustände derselben Ausscheidungs-B2-Phase (γ) mit verschiedenen Habitebenen interpretiert.

1. INTRODUCTION

The decomposition of an alloy is a subject that continues to be of interest in the field of materials science. A supersaturated solid solution may decompose into its equilibrium multiphase mixture via a plethora of decomposition paths. Such paths may include changes in atomic composition, atomic ordering, magnetization, precipitate shape, etc. For many of these processes, the path can be followed by measuring the appropriate structure parameter as a function of time. This structure parameter may change either abruptly, in a discontinuous fashion, or

slowly, in a continuous fashion. Also, in many situations the decomposition of alloys may include either a sequence or a set of concomitant processes. When more than one process occurs at a time, the structural parameters may be coupled or linked together. Clearly the specific path that occurs during decomposition determines the microstructure of the phases in the decomposed alloy. This in turn plays a significant role on the resulting physical properties such as strength, coercivity, etc.

It is widely recognized that the elastic strain caused by a crystal lattice mismatch between a precipitate

and its matrix phase is a major factor in determining the morphology of a decomposing alloy. The crystal lattice mismatch characterizing the geometrical difference between the crystal lattices of the coexisting phases may be particularly regarded as a structural parameter. The important point, which is often missed when coexisting phases with different symmetry are considered, is that the crystal lattice mismatch is coupled to the composition of the phases. Since the compositions may change during decomposition, the crystal lattice mismatch may change as well. This would result in a morphology change, such as habit plane orientation, during decomposition. We believe the foregoing situation is not something very exotic and should be observed in many alloy systems. Particularly, we think that the low temperature decomposition of the supersaturated solid solution of Be in Cu (α phase) is an example of such morphology changes.

The decomposition process in Cu-Be alloys has been extensively studied. On the Cu rich end of the equilibrium diagram, a supersaturated solid solution of Be in Cu may be quenched in, and the resulting decomposition process studied. Decomposition depends on the degree of supersaturation, as measured by either composition or temperature. At large supersaturations, the following processes have been documented

- (i) $\alpha' \rightarrow \alpha_1 + \text{equiaxed GP}$
- (ii) $\alpha' \rightarrow \alpha_2 + \text{GP}$
- (iii) $\alpha' \rightarrow \alpha_3 + \gamma''$
- (iv) $\alpha' \rightarrow \alpha_4 + \gamma'$
- (v) $\alpha' \rightarrow \alpha_{\text{eq}} + \gamma$

where α' is a supersaturated solid solution of Be in f.c.c. Cu, α_i are the various compositions of α in metastable equilibrium with the various precipitate phases listed in (i)–(iv), α_{eq} is the composition of the f.c.c. Cu based phase in equilibrium with the equilibrium phase γ , which has the B2 (CsCl) structure, equiaxed GP are the Be rich equiaxed regions in the α' f.c.c. solution, GP zones are plate-like zones of Be, lying on the $\{001\}$ planes of the Cu solid solution, and γ'' and γ' are transient or metastable phases related to the γ , CuBe (CsCl structure) phase. Rioja and Laughlin [1] have reviewed the crystal structures of these phases, and Chakrabarti *et al.* [2] have reviewed the various phase equilibria described in equation (i)–(v) (see also Butler and Cohen [3]).

There exist a wide variety of interpretations in the literature as to morphology, crystallography and habit planes of metastable phases formed prior to the equilibrium phase γ . In this paper we suggest an interpretation that considerably simplifies the above transformation scheme and seems to be consistent with the X-ray and electron microscopy observations of the early stages of decomposition. The interpret-

ation is based on the idea that transient structures formed along the transformation path are determined by the elastic strain generated by the crystal lattice accommodation. For their characterization we use the theory of the strain-induced morphology proposed by one of the authors [4, 5].

In particular, we propose that the process is divided into the following three simple processes:

1. Isostructural $\alpha \rightarrow \alpha' + \alpha''$ decomposition within the f.c.c. α Cu-Be parent lattice resulting in the formation of Be enriched regions, or precipitates of the Be-rich α'' phase.
2. $\alpha'' \rightarrow \gamma$ crystal lattice rearrangement of these regions into the b.c.c. disordered precipitates occurring by means of the Bain distortion of the regions.
3. The atomic b.c.c. \rightarrow B2 ordering within the Be enriched precipitates.

Of course, the transformation need not proceed in the above sequence: (3) and (2) could proceed concomitantly.

The first stage of decomposition is assumed to be governed by the coherent metastable diagram with the miscibility gap where both coexisting phases, the Be-rich and the Be-lean, have the same f.c.c. structure (see curve on Fig. 1 which shows the free energy versus composition dependence). As has been shown by one of the authors before [4, 5], this stage may result in either equiaxed particles or $\{001\}$ platelet precipitates of the solute-rich f.c.c. phase within the solute-lean f.c.c. matrix, depending on the value of the crystal lattice mismatch, interfacial energy and the precipitate volume. The equiaxed shape is expected for very small precipitates with small crystal lattice mismatch and high interfacial energy, whereas the platelike shape with the $\{001\}$ habit is expected in the opposite case. A $\{001\}$ GP zone is the extreme case of a thin platelike precipitate when its thickness consists of several Be-rich monolayers or one monolayer, the minimum possible value permitted by the crystallography. This value is the interplanar distance $d_{(001)} \approx \frac{1}{2} a_z$. In the latter case the

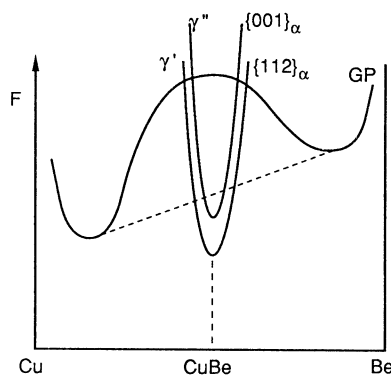


Fig. 1. Schematic energy curves of the phases present in the Cu-Be system. The GP zones are assumed to be isostructural with the α phase. γ' and γ'' have distorted B2 structures, namely tetragonal and monoclinic respectively.

corresponding segregation is a $\{001\}_x$ monolayer GP zone.

The second stage of decomposition involves the f.c.c. \rightarrow b.c.c. crystal Bain lattice rearrangement of the Be-rich $\{001\}$ precipitates, followed by or accompanied by the b.c.c. \rightarrow B2 ordering required by the stable diagram. This results in the formation of the $\{001\}_x$ precipitates of the B2 phase inherited from the $\{001\}_x$ precipitates of the α'' phase. The key factor here is that the Bain crystal lattice rearrangement dramatically changes the crystal lattice mismatch. The crystal lattice accommodation after the Bain distortion results in the rotation of the habit plane from $\{001\}_x$ to a new optimum habit plane, $\{hhl\}_x$ (to be more precise, the habit changes from $\{001\}_x$ to about $\{112\}_x$ after the f.c.c. \rightarrow b.c.c. crystal lattice rearrangement). Even if multilayer $\{001\}$ platelets of the f.c.c. Be-enriched precipitates don't develop and the regions of Be segregations are monolayer $\{001\}$ GP zones, the B2 phase precipitates may still grow on the GP zones. The GP zones then play the role of nucleation sites and may themselves develop into the $\{001\}_x$ B2 phase precipitates. Because the crystal lattice mismatch does not depend on how the initial $\{001\}_x$ B2 precipitate is formed, either by the Bain transformation of the f.c.c. α'' phase or by the growth of the B2 phase on GP zones, the crystal lattice accommodation in both cases will be exactly the same. In both cases the initial habit plane of the product B2(γ) precipitates will be $\{001\}_x$ and in both cases the habit will rotate from the initial $\{001\}_x$ to the $\{hhl\}_x$ plane.

Since the elastic energy of a platelet precipitate as well as its chemical free energy is proportional to its volume and depends on the habit plane orientation, the volume dependent part of the elastic energy turns out to be dependent on the specific habit plane. In other words the habit plane orientation becomes an internal thermodynamic parameter. This means that from the thermodynamic viewpoint, precipitates with different habit planes behave as particles of different phases.

2. THE BASIC EQUATIONS

According to [4, 5], the elastic energy generated by the crystal lattice mismatch is minimized when a coherent precipitate is "rolled out" in a thin and extended platelet whose habit plane is normal to a certain "soft" direction determined by the elastic moduli anisotropy and crystal lattice mismatch. The equation for the elastic energy of a thin plate normal to a unit vector, \mathbf{n} , is

$$E(\mathbf{n}) = \frac{1}{2} [C_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 - \sigma_{ik}^0 n_k \Omega(\mathbf{n})_{ij} \sigma_{jl}^0 n_j] V \quad (1)$$

where V is the precipitate volume, C_{ijkl} is the elastic modulus tensor of the precipitate phase, $\sigma_{ij}^0 = C_{ijkl} \epsilon_{kl}^0$ is the stress-free transformation strain, $\Omega(\mathbf{n})_{ij}^{-1} = C_{ikjl} n_k n_j$ and $\Omega(\mathbf{n})_{ij}$ is a matrix reciprocal to $\Omega(\mathbf{n})_{ij}^{-1}$; in (1)

the summation over twice repeated indexes is implied. The habit plane is determined by minimizing the elastic energy (1) with respect to the habit orientation specified by the vector \mathbf{n} normal to the habit. The minimization allows one to express the habit plane orientation in terms of the materials constants, the stress-free crystal lattice parameters of the matrix and precipitate phases and elastic moduli.

A constrained coherent platelike precipitate is homogeneously distorted so that it provides an exact epitaxial matching between the precipitate lattice and the undistorted matrix lattice along the habit plane. According to [5], the total strain within a platelet precipitate with its habit normal to the unit vector, \mathbf{n} , is

$$\epsilon_{ij}^* = \frac{1}{2} [S(\mathbf{n})_i n_j + n_i S(\mathbf{n})_j] \quad (2)$$

where

$$S(\mathbf{n})_i = \Omega(\mathbf{n})_{ik} \sigma_{kl}^0 n_l. \quad (3)$$

If the total homogeneous strain, ϵ_{ij}^* , within the precipitate is known, the actual precipitate crystal lattice parameters, which are different from the crystal lattice parameters of the stress-free precipitate phase, can be calculated. The crystal lattice continuity across the habit plane, which is the precipitate/matrix boundary, results in not only the homogeneous strain ϵ_{ij}^* but also the rigid body rotation of the precipitate lattice specified by the vector product

$$\phi = \frac{1}{2} S(\mathbf{n}) \times \mathbf{n} \quad (4)$$

whose absolute value is the rotation angle in radians and direction is parallel to the rotation axis [4]. The sum of the homogeneous strain (2) and the rigid body rotation (4) yields the total distortion

$$u_{ij}^* = S(\mathbf{n})_i n_j. \quad (5)$$

An example of a habit plane determination for the cubic \rightarrow tetragonal transformation is given by Wen *et al.* [6]. The \mathbf{n}_0 minimizing the energy (1) of a precipitate formed due to this transformation is

$$\mathbf{n}_0 = (\sin \theta, 0, \cos \theta), \quad (6)$$

if $c_{11} - c_{12} - 2c_{44} < 0$ ($c_{11} = C_{1122}$, $c_{12} = C_{1122}$, $c_{44} = C_{1212}$). The components of the vector (6) are given in the Cartesian system whose axes are parallel to the [100], [010], and [001] precipitate phase directions, respectively; θ is the angle between \mathbf{n}_0 and the [001] direction. The angle, θ , is specified by the equation

$$\cos^2 \theta = 1 + \frac{c_{11} + 2c_{12}}{c_{11} + c_{12}} \frac{t}{1-t} = 1 + \frac{1+2\beta}{1+\beta} \quad (7)$$

which is valid when $t < 0$. In (7) $\beta = (c_{12}/c_{11})$, $t = (\epsilon_{11}^0/\epsilon_{33}^0)$, ϵ_{11}^0 and ϵ_{33}^0 are the components of the stress-free tetragonal transformation strain perpendicular to and along the tetragonal axis [001], respectively.

3. DECOMPOSITION WITHIN THE F.C.C. α PHASE MATRIX

The first stage of the decomposition of the α Cu-Be solid solution is formation of regions enriched in Be within the f.c.c. matrix. This process is governed by the metastable miscibility gap describing the $\alpha \rightarrow \alpha' + \alpha''$ isostructural decomposition into two f.c.c. phases with different Be compositions. It should be accompanied by elastic strain since the atomic radius of a Be atom is considerably less than that of a Cu atom. The stress-free transformation strain in this case is pure dilatational and is determined by the equation

$$\epsilon_0 = \frac{da_x}{a_x dc} (c_{x''} - c_{x'}) \quad (8)$$

where $da_x/a_x dc \approx -0.088$ [7] is the concentration expansion coefficient of the α phase solution, a_x is the f.c.c. lattice parameter, $c_{x''}$ and $c_{x'}$ are compositions of the precipitate (α'') and matrix (α') phases, respectively. It is noteworthy that this coefficient has almost the same value as that for the Al-Cu alloys and is one of the largest in metallic substitutional alloys.

The optimum shape of a coherent cubic phase precipitate in a cubic phase matrix is determined by the competition between the elastic and interfacial energies [5, 8]. The elastic energy tends to flatten the precipitate in an infinitely thin and infinitely extended platelet while the interfacial energy tends to reshape it into a spheroid (if, of course, the interfacial energy is isotropic). The parameter which describes the relative contribution of the interfacial and elastic energies is an aspect ratio K of the material constant r_0 [8], which has dimension of length, and the effective precipitate size, $\sqrt[3]{V}$, where V is the precipitate volume, i.e.

$$K = \frac{r_0}{\sqrt[3]{V}} \quad (9)$$

where

$$r_0 = \gamma_s \frac{c_{11}(c_{11} + c_{12} + 2c_{44})}{(2c_{44} + c_{12} - c_{11})(c_{11} + 2c_{12})^2 \epsilon_0^2}$$

and γ_s is the surface tension. If $K > 1$, the contribution of the interfacial energy dominates and the precipitate is thus equiaxed. It follows from (9) that this may be the case for a small precipitate. When the precipitate grows, the value K decreases and the elastic energy contribution increases. When $K \ll 1$, the equiaxed precipitate transforms into a platelet. If the elastic moduli, c_{11} , c_{12} , c_{44} , meet the requirement, $c_{11} - c_{12} - 2c_{44} < 0$, the habit plane of the platelet is $\{001\}$ [4]. This type of argument can be used for the critical nucleus of the precipitate phase. If the length constant, r_0 , is small (small interfacial energy, γ_s , along with a large crystal lattice mismatch, ϵ_0) and the critical nucleus size, $\sqrt[3]{V_c}$, is such that $K \ll 1$, then the critical nuclei are formed as $\{001\}_x$ platelets from the very beginning. The computer simulation of the decomposition reaction under such conditions

demonstrates that in this case precipitates can be monolayer segregations whose composition is close to the equilibrium composition of the solute rich phase [4]. These Be enriched regions are just GP zones. In the relevant case of the Cu-Be alloy when the crystal lattice mismatch is exceptionally high, the formation of the $\{001\}_x$ GP zones could be expected as in the case of Al-Cu alloys where the crystal lattice mismatch is almost the same. This conclusion is in agreement with the observation of the $\{001\}_x$ GP zones in both systems during the early stage of decomposition. If, however, $K > 1$, the critical nuclei are formed as equiaxed Be enriched regions.

The atomic displacement of solvent atoms adjacent to a $\{001\}_x$ Be-rich monolayer was calculated before [5]. It is given by equation

$$u = \left(1 + \frac{2c_{12}}{c_{11}}\right) \epsilon_0 \frac{a_x}{4} \quad (10)$$

The displacement, u , is directed normal to the $\{001\}_x$ GP zone plane. For example, using elastic constants and the parameter, a_x , of Cu and equation (8) for ϵ_0 and assuming that the $\{001\}_x$ plane in the GP zone is completely filled by Be atoms and that the Be lean matrix is pure Cu, i.e. $c_{x''} \approx 1$ and $c_{x'} \approx 0$, we have $u = -0.19 \text{ \AA}$. The minus sign shows that the solvent Cu atoms in the two adjacent (001) planes are displaced towards the (001) plane filled by Be atoms. The Be filled (001) monolayer and two adjacent Cu-filled planes displaced by $u \approx -0.19 \text{ \AA}$ can be regarded as a unit cell thick (001) platelet composed of tetragonally distorted unit cells of the B2 structure (Fig. 2). The "tetragonal axial ratio" within the layer is then

$$\frac{c}{a} = \frac{a_x + 2u}{a_x} = \frac{3.612 + 2 \times (-0.19)}{3.612} \approx 0.89.$$

This value is between the axial ratio 1, related to the f.c.c. phase and the Bain tetragonal axial ratio $c/a \approx 0.707$ which is required to transform the f.c.c. lattice into the b.c.c. lattice. Therefore the elastic strain induced by a $(001)_x$ GP zone strongly facilitates the f.c.c. \rightarrow b.c.c. (or B2) transformation, which demonstrates that GP zones are possible precursors of the $\alpha \rightarrow \gamma$ transformation.

The X-ray [9] and electron diffraction studies [10, 11] confirm this viewpoint if γ'' precipitates are attributed to the elastically distorted precipitates of the γ (B2) phase (the elastic distortion is imposed on the precipitates by their coherent conjugation with the f.c.c. matrix along the $(001)_x$ habit plane). These studies describe the formation of γ'' as the "piling up" of the $(001)_x$ GP zones.

4. STRUCTURAL TRANSFORMATION OF THE γ PHASE PRECIPITATES

We propose that only two precipitate phases, the α'' Be-rich phase with the f.c.c. structure (or GP zones) and the γ -phase with the B2 structure occur in

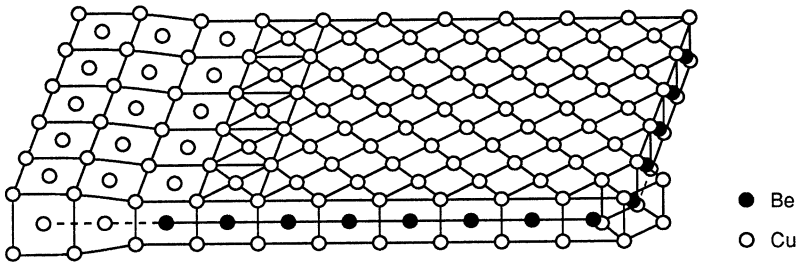


Fig. 2. Schematic representation of the Be monolayer in the f.c.c. Cu matrix.

these alloys. The coherent adjustment of the B2 phase platelets to the f.c.c. matrix results in their homogeneous distortion and the formation of transient structural states which have been called the γ'' and γ' phases. The homogeneous elastic strain imposed on the B2 lattice produces a precipitate phase whose crystal lattice is different from the cubic B2 lattice of the stress-free γ phase. According to equation (5), the homogeneous elastic distortion and thus the crystal lattice symmetry of the distorted precipitate phase is dependent on the precipitate habit. Therefore if the habit changes during aging, the constrained coherent precipitates will respond by the strain-induced changing of their crystal lattice symmetry and crystal lattice parameters. This effect has to be taken into account in any interpretation of the diffraction data. Ignoring it may be misleading since the strained precipitates of the stable phase may be erroneously regarded as transient metastable phases occurring along the decomposition path. We propose that the γ'' and γ' phases are not transient metastable phases whose crystal lattice in the stress-free state is different from that of the equilibrium γ phase. Rather we assume that they are just precipitates of the product B2 (γ) phase with the $\{001\}_x$ and $\{hhl\}_x$ habits, respectively, which are shown to be homogeneously distorted to provide the epitaxy along the habit plane. The difference between their crystal structures (symmetry and lattice parameters) is caused by their different habit planes.

4.1. F.C.C. \rightarrow B2 transformation of the $\{001\}_x$ precipitates

We have shown that the first stage of the decomposition process in the f.c.c. α Cu-Be alloy results in the occurrence of the GP zones or $\{001\}$ platelets of the f.c.c. Be-rich phase. The platelets of the f.c.c. Be-rich metastable phase transform into the platelets of the b.c.c. derivative (B2) phase by means of the diffusionless Bain crystal lattice rearrangement followed by atomic ordering. The rearrangement changes the crystal lattice but not the habit of the precipitates since the habit change is controlled by the slower diffusion process. Thus, the initial habit plane of γ (B2) is inherited from the $\{001\}_x$ habit of the α'' f.c.c. precipitates. However, this habit plane does not minimize the elastic energy of the γ phase precipitate since the $\alpha \rightarrow \gamma$ transformation dramatically affects

the initial crystal lattice mismatch between the f.c.c. α phase matrix and the α'' phase precipitates. Prior to the Bain f.c.c. \rightarrow b.c.c. transformation the mismatch was described by the pure dilatational strain [8]. However, after the transformation, the mismatch is described by a large tetragonal stress-free strain, ϵ_{ij}^0 , where the tetragonal stress-free strain components are determined from the Bain correspondence between the f.c.c. and B2 lattices

$$\epsilon_{11}^0 = \frac{a_\gamma \sqrt{2} - a_x}{a_x} = \frac{a_\gamma}{a_x} \sqrt{2} - 1$$

and

$$\epsilon_{33}^0 = \frac{a_\gamma}{a_x} - 1 \quad (11)$$

where a_x and a_γ are the stress-free parameters of the matrix f.c.c. α phase and the precipitate B2 phase. The normal to the habit plane, \mathbf{n}_0 , minimizing the elastic energy (1) is given by equation (6) where the components of the vector \mathbf{n}_0 are presented in the Cartesian coordinate system related to the cubic axes of the B2 (γ) phase precipitates. In the new coordinate system, related to the cubic axes of the matrix f.c.c. phase lattice and related to the old system by the Bain correspondence, the components of the vector, \mathbf{n}_0 , are

$$\mathbf{n}_0 = \left(\frac{1}{\sqrt{2}} \sin \theta, \frac{1}{\sqrt{2}} \sin \theta, \cos \theta \right)_x \quad (12)$$

where $\cos \theta$ is specified by equation (7). The Miller indices of the optimal habit plane perpendicular to \mathbf{n}_0 given by (12) and related to the γ phase with B2 structure are then $\{hhl\}_x$.

Therefore the second stage of decomposition starts by the formation of the $\{001\}_x$ platelets of the γ phase imbedded into the α phase matrix. It is followed by the diffusion-controlled rotation of the habit to its new $\{hhl\}_x$ optimum orientation minimizing the elastic energy after the $\alpha \rightarrow \gamma$ rearrangement.

4.2. Initial stage: γ phase precipitates with the $\{001\}_x$ habit

It follows from equations (2) and (3) that the accommodation strain imposed on a γ phase precipitate with the $\{001\}_x$ habit transforms the cubic B2 lattice of the precipitate into a tetragonal

lattice. Indeed, substituting the habit plane normal $\mathbf{n}_0 = (0, 0, 1)_\gamma$ to equation (A1) of the Appendix transforms equation (3) to

$$S(\mathbf{n}_0) = \frac{1}{c_{11}} \sigma_{33}^0 \mathbf{n}_0 \quad (13)$$

where $\sigma_{33}^0 = C_{33nl} \epsilon_{nl}^0 = 2c_{12} \epsilon_{11}^0 + c_{11} \epsilon_{33}^0$. Using (13) in (2) gives

$$\begin{aligned} \epsilon_{ij}^* = u_{ij}^* &= \left(\epsilon_{33}^0 + \frac{2c_{12}}{c_{11}} \epsilon_{11}^0 \right) n_i^0 n_j^0 \\ &= \left(\epsilon_{33}^0 + \frac{2c_{12}}{c_{11}} \epsilon_{11}^0 \right) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \end{aligned} \quad (14)$$

The strain (14) is a uniaxial distortion along the $[001]_x$ axis which describes the $\alpha \rightarrow \gamma$ rearrangement producing a constrained γ phase precipitate with the (001) habit and provides its strain-induced tetragonality. This strain does not affect any crystal lattice vector of the α phase parallel to the $(001)_x$ plane during the γ phase formation.

For example, the f.c.c. lattice vectors $\mathbf{a}(1)_x = a_x(\frac{1}{2}, \frac{1}{2}, 0)_x$ and $\mathbf{a}(2)_x = a_x(\frac{1}{2}, \frac{1}{2}, 0)_x$ which are parallel to the $(001)_x$ plane are not affected by the $\alpha \rightarrow \gamma$ rearrangement in the constrained state. According to the Bain transformation scheme these two vectors, $\mathbf{a}(1)_\gamma$ and $\mathbf{a}(2)_\gamma$, after the $\alpha \rightarrow \gamma$ rearrangement should lead to parameters $a_\gamma = b_\gamma$ of the B2 lattice in the directions $[100]_\gamma$ and $[010]_\gamma$. This means that a tetragonally distorted $(001)_x$ platelet of the γ phase with the distortion, ϵ_{ij}^* , has lattice parameters, $a_\gamma^{\text{prec}} = b_\gamma^{\text{prec}}$ which are exactly equal to the corresponding $|\mathbf{a}(1)_x|$ and $|\mathbf{a}(2)_x|$ parameters

$$a_\gamma^{\text{prec}} = b_\gamma^{\text{prec}} = |\mathbf{a}(1)_x| = |\mathbf{a}(2)_x| = a_x \left| \left(\frac{1}{2}, \frac{1}{2}, 0 \right)_x \right| = \frac{a_x}{\sqrt{2}}.$$

As for the f.c.c. lattice vector $\mathbf{a}(3)_x = a_x(0, 0, 1)$, it is transformed according to the Bain scheme to the a_γ , crystal lattice parameter of the B2 lattice along the $[001]_\gamma$ direction. It follows from equations (11) and (14) that in the tetragonal constrained state this parameter becomes tetragonal parameter, c^{prec} , which is

$$c_\gamma^{\text{prec}} = a_x + \left(\epsilon_{33}^0 + \frac{2c_{12}}{c_{11}} \epsilon_{11}^0 \right) a_x = a_\gamma + a_x \frac{2c_{12}}{c_{11}} \epsilon_{11}^0 \quad (15)$$

since by definition of the Bain strain, $a_x(1 + \epsilon_{33}^0) = a_\gamma$.

Therefore the B2(γ) precipitate with the $(001)_x$ habit in the constrained state has a tetragonal rather than a cubic lattice. It is coherent along its $(001)_\gamma$ plane. The elastic accommodation results in the Poisson expansion of the B2 phase crystal lattice along the $[001]_x \parallel [001]_\gamma$ direction.

To calculate the crystal lattice parameter c_γ^{prec} of constrained precipitate, we have to know a_x and a_γ , as well as the elastic moduli ratio, c_{12}/c_{11} , for the B2 phase. We know the crystal lattice parameter of the stress-free α matrix [11] and the stress-free lattice parameter of the B2 CuBe stoichiometric γ phase.

They are $a_x = 3.612 \text{ \AA}$ and $a_\gamma = 2.70 \text{ \AA}$, respectively. Unfortunately, we don't know the elastic properties of CuBe γ phase and thus do not have the c_{12}/c_{11} ratio. The ratio can, however, be found indirectly by comparing equation (15) with the observed results. Shimizu *et al.* [10] report the $(001)_\gamma$ plane spacing, $c_\gamma^{\text{prec}} = 2.9 \text{ \AA}$, for a constrained γ'' precipitate with the $(001)_x$ habit. Using the above numerical values, $a_\gamma = 2.70 \text{ \AA}$, $a_x = 3.612 \text{ \AA}$ and $c_\gamma^{\text{prec}} = 2.9 \text{ \AA}$, in equation (15), we have

$$2.9 = 2.70 + 2 \frac{c_{12}}{c_{11}} \left(\frac{2.70}{3.612} \sqrt{2} - 1 \right) 3.612.$$

The solution of this equation gives $c_{12}/c_{11} \approx 0.5$ which is a quite reasonable value.

4.3. Next stage: γ phase precipitate with the optimal $(hhl)_x$ habit

The $(001)_x$ habit of the γ phase precipitates is formed immediately after the f.c.c. \rightarrow B2 diffusionless crystal lattice rearrangement of the $\{001\}_x$ precipitates of the α'' phase. This is inherited from the isostructural decomposition process occurring within the f.c.c. phase. The best crystal lattice accommodation after the f.c.c. \rightarrow B2 crystal lattice rearrangement is, however, provided by the $(h^0h^0l^0)_x$ habit whose orientation is given by equations (12) and (7). Using in equation (7) the set of the numerical values

$$\begin{aligned} \epsilon_{11}^0 &= \frac{a_\gamma}{a_x} \sqrt{2} - 1 = 0.0571, \\ \epsilon_{33}^0 &= \frac{a_x}{a_\gamma} - 1 = -0.252, \\ t &= \frac{\epsilon_{11}^0}{\epsilon_{33}^0} = -0.225 \end{aligned} \quad (16)$$

obtained from the crystal lattice parameters, $a_\gamma = 2.70 \text{ \AA}$, $a_x = 3.612 \text{ \AA}$, and the ratio $c_{12}/c_{11} \approx 0.5$ obtained above yields

$$\begin{aligned} \cos^2 \theta &= 1 + \frac{1 + 2 \times 0.5}{1 + 0.5} \times \frac{-0.225}{1 + 0.225} = 0.758, \\ \theta &= 29.6^\circ. \end{aligned} \quad (17)$$

Therefore, according to equation (12) and (6), the normal to the optimum habit plane of a coherent γ phase precipitate is

$$\mathbf{n}_0 = (0.349, 0.349, 0.869)_x \quad (18a)$$

or

$$\mathbf{n}_0 = (0.495, 0, 0.869)_\gamma. \quad (18b)$$

The corresponding calculated optimal habit plane, $(hhl)_x$, which is actually irrational, is located between the nearest rational $(113)_x$ and $(112)_x$ planes. For comparison with (18a), the normals to the $(113)_x$ and $(112)_x$ planes are

$$\mathbf{n}_{(113)} = (0.301, 0.301, 0.904)_x,$$

$$\mathbf{n}_{(112)} = (0.408, 0.408, 0.816)_x.$$

The optimum plane deviates from the nearest rational $(113)_x$ and $(112)_x$ planes by $\sim 4^\circ$ and $\sim 5^\circ$, respectively. According to X-ray measurements by Geisler *et al.* [9] the habit plane of γ' precipitates, which we attribute to the constrained γ phase with the habit normal to the vector (18a), is $(112)_x$. Electron microscopy observations by Rioja and Laughlin [1] give the habit which changes between $(112)_x$ and $(113)_x$ during isothermal aging. The above theoretical prediction for the habit plane orientation is therefore in good agreement with the experimental results. It is especially true considering that (i) no fitting parameters were used; the habit plane orientation was calculated utilizing the crystal lattice parameters obtained in the independent X-ray measurements as the only input parameters, (ii) the calculated habit proves to be very sensitive to the crystal lattice parameters which, thus, rules out the accidental coincidence.

4.4. Strain-induced symmetry transformation of the precipitate γ phase

The total distortion of the f.c.c. lattice caused by the f.c.c. \rightarrow B2 transformation in the constrained state includes the Bain distortion, the homogeneous elastic strain and the crystal lattice rotation required to maintain the crystal lattice continuity across the habit boundary plane. As has been shown above, the sum of all these displacement modes is given by the distortion (5). With distortion (5) any f.c.c. lattice translation, \mathbf{r} , involved in the $\alpha'' \rightarrow \gamma$ crystal lattice rearrangement transforms to \mathbf{r}' . The transformation is described by the relation

$$\mathbf{r}'_i = \mathbf{r}_i + \mathbf{u}^*_{ij} r_j = \mathbf{r}_i + S(\mathbf{n})_i(\mathbf{n}\mathbf{r}). \quad (19)$$

The total distortion (5) which has a form of a dyadic product is an invariant plane strain. It follows from (19) that the invariant plane is a plane normal to the vector \mathbf{n} , i.e. the habit plane of the constrained precipitate is always an invariant plane. Indeed, since any f.c.c. translation vector lying in the habit plane, \mathbf{r}_{hab} , is, by definition, orthogonal to the habit plane normal, \mathbf{n} , we have $(\mathbf{r}_{\text{hab}} \mathbf{n}) = 0$. With the latter condition equation (19) gives that $\mathbf{r}'_{\text{hab}} = \mathbf{r}_{\text{hab}}$, i.e. that any f.c.c. translation lying in the habit plane is not affected by the $\alpha'' \rightarrow \gamma$ transformation in the constrained state. In other words, if, for example, the habit plane is $(hhl)_x$, the f.c.c. lattice translation, $\mathbf{a}(2)_x = a_x(\frac{1}{2} \frac{1}{2} 0)_x$, along the $[\bar{1}10]_x$ direction which is located in the $(hhl)_x$ plane irrespective of values h and l , is exactly the same after the transformation as it was before. In particular, when the habit plane of constrained γ phase platelet changes from the $(001)_x$ to the $(112)_x$ assuming the intermediate $(hhl)_x$ indices, this translation does not change its value and orientation. It will be still directed along the same $[\bar{1}10]_x$ axis and will assume exactly the same absolute value $b^{\text{prec}}_x = |\mathbf{a}(2)_x| = a_x/\sqrt{2} = 3.612/\sqrt{2} = 2.554 \text{ \AA}$, where b^{prec}_x is related to b_γ of the B2 structure of the γ phase. This translation is a unit translation of the constrained B2 phase along the $[010]_y$ direction and can

be regarded as its crystal lattice parameters. Therefore one of the crystal lattice parameters of the B2 constrained phase, $b_\gamma = a(2)_x = a_x/\sqrt{2} = 2.554 \text{ \AA}$, is the same for all intermediate states arising along the transformation path.

The crystal lattice rearrangement (19) transforms the crystal lattice of the parent f.c.c. phase to the crystal lattice of the constrained precipitate γ phase. This crystal lattice rearrangement results in the rearrangement of the reciprocal lattice which is described by the relation

$$\mathbf{H}' = \mathbf{H} - \mathbf{n} \frac{S(\mathbf{n})\mathbf{H}}{1 + S(\mathbf{n})\mathbf{n}} \quad (20)$$

where \mathbf{H} and \mathbf{H}' are the corresponding reciprocal lattice vectors related to the parent and precipitate constrained γ phase [5].

The other conclusion concerns the orientational relations. Since the habit plane is an invariant plane, it is not affected by the transformations. That means that the $(hhl)_x$ habit plane of the parent f.c.c. phase and the $(h0l)_y$ plane of the distorted precipitate phase formed from the $(hhl)_x$ plane are parallel to each other and maintain exactly the same atomic arrangement. This conclusion immediately results in the orientation relationships

$$(hhl)_x \parallel (h0l)_y, [\bar{1}10]_x \parallel [010]_y \quad (21)$$

as well as the equality $b^{\text{prec}}_y = a_x/\sqrt{2} = 2.554 \text{ \AA}$ which is not affected by the habit transformation. The habit plane evolution from the $(001)_x$ to the $(hhl)_x$ is described by rotation of the habit plane normal, \mathbf{n} so that the normal has a form

$$\mathbf{n} = \left(\frac{\sin \theta}{\sqrt{2}}, \frac{\sin \theta}{\sqrt{2}}, \cos \theta \right)_x \quad (22a)$$

if it is related to the coordinate system whose axes are parallel to the $[100]_x$, $[010]_x$, $[001]_x$ directions of the f.c.c. α phase, and a form

$$\mathbf{n} = (\sin \theta, 0, \cos \theta)_y \quad (22b)$$

if it is related to the coordinate system whose axes are parallel to the $[100]_y$, $[010]_y$, $[001]_y$ directions of the γ phase B2 lattice (parallel to $[110]_x$, $[\bar{1}10]_x$, $[001]_x$). The $S(\mathbf{n})$ vector has a form similar to \mathbf{n}

$$S(\mathbf{n}) = \left(\frac{S(\mathbf{n})_x}{\sqrt{2}}, \frac{S(\mathbf{n})_x}{\sqrt{2}}, S(\mathbf{n})_z \right)_x \quad (23a)$$

or

$$S(\mathbf{n}) = (S(\mathbf{n})_x, 0, S(\mathbf{n})_z)_y. \quad (23b)$$

Since the direction of the rotation angle is given by the vector product of vectors (22) and (23) [see equation (4)], the rotation axis is $[010]_y \parallel [\bar{1}10]_x$. These two directions, $[\bar{1}10]_x$ and $[010]_y$ are invariant. They are not affected by the change of the habit plane.

Unfortunately, the components of the vector $S(\mathbf{n})$ cannot be calculated exactly since the γ phase elastic moduli ratios, c_{12}/c_{11} and c_{44}/c_{11} , are not known. The

only thing which is exactly predicted by the theory, irrespective of the numerical values of the elastic constants, is that the shear direction given by the vector $S(\mathbf{n})$ lies in the $(\bar{1}10)_x \parallel (010)_\gamma$ plane. We nevertheless may give reasonably good estimate of the vector $S(\mathbf{n})$ and therefore estimate the crystal lattice parameters of the constrained γ phase precipitates with the $\sim(112)_x$ habit which we attribute to the γ' phase. The calculation of the crystal lattice parameters of the constrained γ phase is carried out in Appendix. It is based on the following estimates for the c_{12}/c_{11} and c_{44}/c_{11} ratios.

We already estimated the ratio $c_{12}/c_{11} \approx 0.5$ using the diffraction data [10]. To estimate the c_{44}/c_{11} ratio, we may use the negative elastic anisotropy (the inequality $c_{11} - c_{12} - 2c_{44} < 0$) and the fact that it is physically unrealistic to expect the shear modulus c_{44} to exceed one half of the Young modulus c_{11} . These two conditions give the physically plausible range for the c_{44}/c_{11} ratio

$$0.25 < \frac{c_{44}}{c_{11}} < 0.5. \quad (24)$$

The calculations in Appendix were made for the $c_{12}/c_{11} \approx 0.5$ together with two different ratios, $c_{44}/c_{11} = 0.3$ and $c_{44}/c_{11} = 0.5$, both of them being within the range (24). It is very fortunate that calculations for both values give essentially the same result: the constrained precipitate of the γ phase, perceived as the γ' phase, has the monoclinic lattice with

$$\begin{aligned} a_\gamma^{\text{prec}} &= 2.7 \text{ \AA}, & b_\gamma^{\text{prec}} &= 2.55 \text{ \AA}, \\ c_\gamma^{\text{prec}} &= 2.81 \text{ \AA} & \text{and } \beta &= 87.2^\circ. \end{aligned}$$

This lattice rotates as a rigid body by the angle $\alpha \approx 8.4^\circ$ about the $[\bar{1}10]_x$ axis. This lattice may be regarded approximately as a tetragonal lattice with

$$\bar{a}_\gamma^{\text{prec}} = \frac{2.77 + 2.81}{2} = 2.79 \text{ \AA}$$

and

$$\bar{c}_\gamma^{\text{prec}} = b_\gamma^{\text{prec}} = 2.55 \text{ \AA}$$

and the same $\alpha \approx 8.4^\circ$ rotation if the slight monoclinic distortion is neglected.

5. DISCUSSION

As has been shown above, the formation of coherent γ phase precipitates with the B2 structure from the f.c.c. parent phase of the Cu-Be alloys is accompanied by a large stress-free transformation strain. The $\alpha \rightarrow \gamma$ transformation strain is actually the Bain strain. The best elastic accommodation of the Bain strain is attained when the γ phase precipitates are platelets with the optimum habit minimizing the elastic energy. For a thin platelet with an aspect ratio, K , much smaller than unity, the elastic strain is homogeneous within the platelet and vanishes asymptotically outside it. The strain within the matrix

caused by platelike precipitates can then be ignored in the most thermodynamic applications. If the undistorted α phase f.c.c. matrix is chosen as a reference state, the total transformation strain in the precipitate, the Bain strain + elastic strain + rigid body rotation of the precipitate lattice, is described by the invariant plane strain [5], the invariant plane being parallel to the habit plane. Physically this effect is associated with the fact that the coherent platelet precipitate is epitaxial with the parent phase along its habit plane. These conclusions are valid irrespective of differences between the elastic moduli of the parent and precipitate phases. The elastic strain induced by coherent precipitation affects the observable crystal lattice symmetry and crystal lattice parameters of the precipitate. It cannot be ignored in any interpretation of the structural transformations of precipitates at early (coherent) stage of decompositions. It especially cannot be ignored in the case of precipitation in Cu-Be alloys where the f.c.c. \rightarrow B2 crystal lattice rearrangement is very large.

The effect of coherency strain on the crystal lattice parameters, and sometimes on the symmetry of the precipitates phase, has been observed in different systems: α'' phase in Fe-N [13], θ'' phase and θ' phase in Al-Cu [14], η' phase in Al-Zn-Mg [15], the strain-induced tetragonality of Cu-Ni-Fe alloys [16, 17] (a review of these systems may be found in [5]). This effect is especially interesting in Cu-Be alloy where the habit of the precipitate phases changes during aging time which results in changes of the symmetry and magnitude of the coherent elastic strain within the precipitates.

The main morphological and crystallographic details of the decomposition path of Cu-Be alloys can be naturally explained, if the widely recognized concept that the low temperature decomposition in a Cu-Be alloy starts as a isostructural decomposition within the f.c.c. matrix, $\alpha \rightarrow \alpha' + \alpha''$, is accepted. The $\alpha \rightarrow \alpha' + \alpha''$ reaction results in formation of monolayer or multilayer $\{001\}_x$ GP zones which may be interpreted as precipitates of the Be-rich f.c.c. α'' phase. This decomposition reaction is controlled by the metastable diagram with the miscibility gap. The second stage of the decomposition is usually associated with formation of the transient γ'' and γ' phases with the $\{001\}_x$ and $\{112\}_x$ habit, respectively, whose structure is closely related to the B2 structure of the equilibrium B2 (γ) phase (see e.g. [1]).

It has been established before that the cubic \rightarrow cubic phase transformation may result in the shape transformation of precipitates upon their growing. Small precipitates whose interfacial energy exceeds the volume dependent elastic energy are equiaxed (if the interfacial energy is isotropic). When the elastic energy contribution exceeds the interfacial energy during the precipitate growth, a transformation of the equiaxed precipitates into the platelike ones occurs. If $c_{11} - c_{12} - 2c_{44} < 0$ for the precipitate phase, the habit corresponding to the elastic energy minimum

is $\{001\}_x$ [4]. This theoretical result agrees with observations of the early stages of decomposition in Cu-Be alloys. Indeed, multilayer $\{001\}_x$ GP zones observed in Cu-Be alloys, in fact, are extremely thin coherent precipitates of the Be-rich f.c.c. α'' phase which are tetragonally distorted due to their epitaxy along the $\{001\}_x$ habit plane. Monolayer $\{001\}_x$ GP zones may always be regarded as the limiting case of an extremely thin $\{001\}_x$ Be rich-precipitate. It is interesting that Rioja and Laughlin [1] reported the observation of equiaxed precipitates of the α'' phase when the alloy is aged at room temperature prior to the formation of the platelet $\{001\}_x$ GP zones. These equiaxed precipitates with 15–30 Å in diameter are precursors of $\{001\}_x$ platelet GP zones. This observation is in agreement with the predictions of the theory (see Section 3).

The $\{001\}_x$ habit of the γ phase precipitates is formed immediately after the $\alpha'' \rightarrow \gamma$ transformation. The $\{001\}_a$ precipitates of the constrained γ phase are usually called γ'' . This habit does not provide the best elastic strain accommodation. The calculations presented in Section 4.3 result in the conclusion that the elastic energy minimum is attained when the γ phase precipitates are thin coherent platelets whose habit is located between the $(112)_x$ and $(113)_x$ planes. These theoretical predictions also agree with the observations of platelets of the precipitate phase with these habits attributed to the metastable transient phase called γ' .

The theory correctly predicts the crystal structure of the constrained precipitates relating their structure to the precipitate habit. So the tetragonal structure of the $\{001\}_x$ precipitates of the γ phase with $a_{\gamma}^{\text{prec}} = b_{\gamma}^{\text{prec}} = a_x/\sqrt{2}$ predicted by the theory coincides with the model of the crystal structure of the $\{001\}_x$ γ'' precipitates proposed by Guinier and Jacquet [18] and Guy *et al.* [19]. It also coincides with the model of the γ'' phase lattice proposed by Shimizu *et al.* on the basis of their diffraction data [10]. Geisler *et al.* [9], however, suggested a slightly different monoclinic model for the γ'' phase precipitates which differs from the model by Shimizu *et al.* by a monoclinic shear in the $(\bar{1}\bar{1}0)_x \parallel (010)_y$ plane. According to the model by Geisler *et al.*, the monoclinic structure is characterized by the parameters

$$a_{\gamma}^{\text{prec}} = b_{\gamma}^{\text{prec}} = \frac{a_x}{\sqrt{2}}, \quad \text{and} \quad \beta = 85.2^\circ.$$

Because the precipitates of the constrained γ phase are $\{001\}_x$ platelets, the Laue diffraction conditions are relaxed and the diffraction maxima are $\langle 001 \rangle_x$ reldrods rather than distinct spots. As has been emphasized in [1], this is a reason why it is very difficult to distinguish between the model by Shimizu *et al.* and Geisler *et al.* Besides, the difference between the structure of the γ'' phase proposed by Shimizu *et al.*

[10] and Geisler *et al.* [9] may be attributed to the fact that the later investigators, in fact, observed the later stage of the aging process when the habit already started to deviate from the $\{001\}_x$ plane. Then both observation results are rationalized by the above proposed mechanism. Indeed, the monoclinic shear with the strain direction lying in the $(\bar{1}10)_x \parallel (010)_y$ plane suggested by Geisler *et al.* for the γ'' phase formation is exactly what follows from the theory when the habit plane starts to rotate from the $(001)_x$ towards $(112)_x$ since the shear direction is determined by the vector $S(\mathbf{n})$, which according to (23) should lie in the $(\bar{1}10)_x$ plane.

The theory also correctly predicts the transformation of the shape of the $(001)_y$ superlattice reflections. Since the habit plane reorientation from $(001)_x$ to $\sim(112)_x$ predicted by the theory occurs by diffusion, the coarsening process should result in a spectrum of the habit planes, $(hhl)_x$, within this range. The normals, \mathbf{n} , to these planes form a "fan" in the $(\bar{1}10)_x^*$ reciprocal lattice plane. Positions of the $\{001\}_y$ superlattice diffraction maxima of constrained γ phase platelets (which, of course, are elongated along the direction \mathbf{n} normal to the habit plane) are affected by two factors, by the value of spacing $d_{(001)_y}$, distorted by the homogeneous strain and by the crystal lattice rotation maintaining crystal lattice continuity across the $(hhl)_x$ habit plane boundary. The combination of both these effects is described by the invariant plane strain (5) which provides the $\alpha \rightarrow \gamma$ transformation in the constrained state.

The displacement, $\Delta\mathbf{H} = \mathbf{H}' - \mathbf{H}$, of a diffraction spot, \mathbf{H}' , of the precipitate from the corresponding diffraction spot, \mathbf{H} , of the matrix phase is given by equation (20). It follows from equation (20) that the $(001)_y$ diffraction spot of a constrained γ phase platelet should be shifted from the $(001)_x$ point of the reciprocal lattice of the undistorted α matrix in the direction \mathbf{n} normal to the habit plane. Figure 3(a) shows the position of the $(001)_y$ diffraction spot from a $\{hhl\}_x$ platelet of the constrained γ phase which is predicted by equation (20). It is completely determined by the direction of the habit plane normal, \mathbf{n} , and by the spacing $d_{(001)_y}$ of the $(001)_y$ plane. This spacing, $d_{(001)_y}$, is related to the (001) reciprocal lattice vector of the γ phase by the conventional relation, $|\mathbf{H}'| = 1/d_{(001)_y}$. For the initial $\{001\}$ habit plane $d_{(001)_y} = 2.9 \text{ \AA}$ and the γ phase diffraction spot is then at $\sim(0\ 0\ \frac{4}{3})_x$.

During the elastic strain relaxation upon the habit plane change from $\{001\}_x$ to $\{112\}_x$, the spacing $d_{(001)_x}$ of the constrained γ phase should reduce its value from 2.9 Å for the $(001)_y$ habit towards the value of the stress-free parameter of the γ phase, $a_\gamma = 2.7 \text{ \AA}$, which is the least possible value occurring for the stress-free γ phase. The $\{001\}_y$ diffraction maximum is actually generated by the system of platelets with the spectrum of different $\{hhl\}_x$ habits which is formed during the coarsening reaction. Because of that the diffraction from

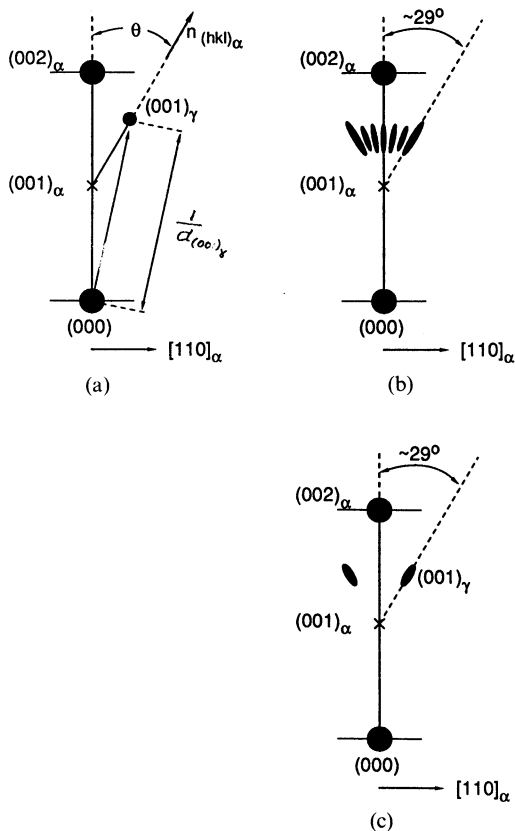


Fig. 3. Schematic sections from a $[110]_x$ diffraction pattern showing: (a) $(001)_x$ reflection of a coherent γ phase precipitate with the $(hhl)_x$ habit; (b) superposition of the $(001)_x$ reflections from the γ phase precipitates with different habits ranging from $(001)_x$ to $(112)_x$. (c) the $(112)_x$ variant of the coherent γ phase attributed to the γ' phase. Note that as a consequence of the accommodation strain, all reflections streak towards the $(001)_x$ point of the reciprocal lattice of the undistorted f.c.c. matrix.

such a system is actually a superposition of the pictures shown on Fig. 3(a) with different directions of the vectors \mathbf{n}_{hhl} and different values $\mathbf{H}' = \mathbf{H}_{(001)_x} = 1/d_{(001)_x}$, increasing with the deviation of the vector \mathbf{n} from the $[001]_x$ direction. The result of this superposition is shown in Fig. 3(b). In Fig. 3(b) two additional factors are also taken into account: that the $(001)_x$ diffraction maximum from each γ phase platelet is actually a relrod normal to its habit plane rather than a diffraction spot (i.e. the relrod along the direction \mathbf{n}), and that the deviation of the habit plane from $(001)_x$ to $(112)_x$ should result in reduction of the $d_{(001)_x}$ from the value 2.9 \AA typical for the (001) habit towards the stress-free value $a_x = 2.7 \text{ \AA}$ mentioned above and thus should result in the increase of the reciprocal lattice vector, $\mathbf{H}_{(001)_x}$.

It is very interesting that the $(001)_x$ diffraction maximum shown on Fig. 3(b) which is obtained this way has an "arrowhead" shape. The tip of the arrowhead is located exactly at the midpoint, $(001)_x$,

of the $(002)_x$ reciprocal lattice vector of the undistorted parent phase. This shape follows from the proposed theoretical model as a consequence of the coherency and the diffusional strain-induced habit plane reorientation resulting in the spectrum of different $(hhl)_x$ habits within the range between the $(001)_x$ and $(112)_x$. The center of gravity of this spectrum should shift towards the $(112)_x$ while its width should reduce during the stress-induced coarsening. The effect of fanning out of the $\sim \frac{2}{3}(002)_x$ maximum into an "arrowhead"-like shape was discussed by Rioja and Laughlin [1].

The further coarsening process leads to disappearance of all habits other than the optimal one situated between the $(112)_x$ and $(113)_x$ (narrowing the width of the habit plane spectrum), and to thickening the optimal $\{112\}_x$ platelets of the γ phase (transformation of the relrods from each platelet on the diffraction pattern into the diffraction spots). This effect should be manifested on the diffraction pattern by formation of the separate diffraction spots which are schematically shown on Fig. 3(c). These spots are usually attributed to the γ' phase.

The TEM observation by Rioja and Laughlin [1] confirms the diffraction pattern predicted by the theory and schematically shown in Fig. 3. Figure 4 taken from [20] shows the diffuse scattering associated with the $[110]_x$ zone axes during the later stages of the decomposition process in f.c.c. Cu-Be alloys. In Fig. 4(a), the long $[001]_x$ streak, characteristic of monolayer G.P. zones, "bunches" up at a position about 0.7 of the way from $(000)_x$ to $\pm(002)_x$, i.e. at, $\sim(0 \ 0 \ \frac{4}{3})_x$ (see Section 4). With further aging, the diffuse scattering appears in the form of an "arrowhead" [Fig. 4(b)]. As it is predicted by the theory, the tip of the "arrowhead" is at the position $(001)_x$, and the streaks which make it up are approximately within $\pm 29^\circ$ of the $[001]_x$. Finally distinct reflections occur after further aging. These reflections are $(001)_x$ phase reflections, and they demonstrate that the habit plane is now fixed at $(112)_x$. See Rioja and Laughlin [1] and Section 4 for further discussion of this phenomenon.

Since a platelike precipitate with a $(hhl)_x$ habit always has the $[\bar{1}10]_x$ direction in the habit plane, irrespective of its orientation with respect to the $[001]_x$ direction, the theory predicts that the $b_y^{\text{prec}} = a_x(\frac{1}{2}, \frac{1}{2}, 0)_x$ is invariant and does not change upon the habit plane transformation. It is always equal to $a_x/\sqrt{2} = 2.55 \text{ \AA}$. The transformation mode in the constrained state is then predicted to be

$$\left\langle \frac{S(\mathbf{n}_{hhl})_x}{\sqrt{2}}, \frac{S(\mathbf{n}_{hhl})_x}{\sqrt{2}}, S(\mathbf{n}_{hhl})_x \right\rangle_{(hhl)_x}$$

i.e. it is described by a shear with the shear direction in the $(\bar{1}10)_x$ plane. In the case of the $(112)_x$ habit, which is usually attributed to the γ' phase, this is exactly the transformation mode proposed by Geisler *et al.* [9] for the γ' phase formation. These authors

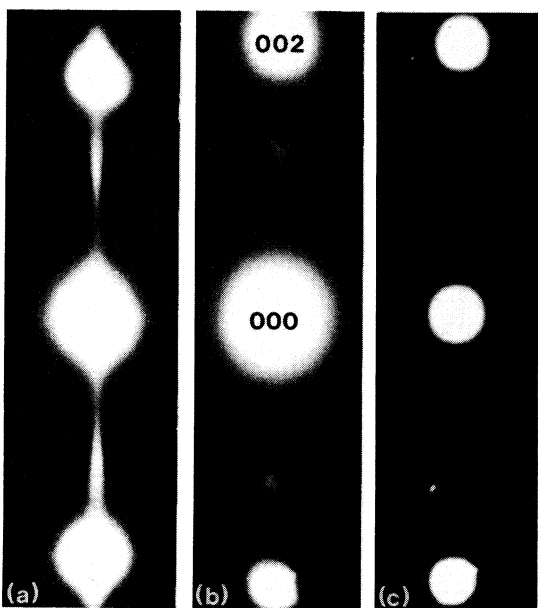


Fig. 4. The $[110]_z$ diffraction patterns from Cu-Be at different stages of aging [20]. (a) Diffraction from the stage attributed to the γ'' phase. (b) The "arrowhead" intensity corresponding to the stage prior to the γ' phase formation. (c) Diffraction from the stage attributed to the γ' phase. Note that the tip of the "arrowhead" is located exactly at the position $(001)_z^*$ of the reciprocal space of the α phase.

reported the parameter $b_z^{\text{prec}} = a_x/\sqrt{2} = 2.55 \text{ \AA}$ and orientation relations

$$(112)_x \parallel (201)_\gamma \quad \text{and} \quad [1\bar{1}0]_x \parallel [010]_\gamma$$

which are in agreement with the theory (see Section 4.4).

As has been mentioned above, we do not know the elastic moduli of the $\gamma(\text{CuBe})$ phase but we may estimate the physically reasonable range assumed by these moduli. It is made in Section 4.2 and in Appendix. The calculation in Appendix of the parameters of the $\sim(112)_x$ platelets of the γ phase attributed to the γ' phase predicts the monoclinic lattice with $a_z^{\text{prec}} = 2.7 \text{ \AA}$, $b_z^{\text{prec}} = 2.55 \text{ \AA}$, $c_z^{\text{prec}} = 2.81 \text{ \AA}$ and $\beta = 87.2^\circ$. This lattice rotates as a rigid body by the angle $\alpha = 8.4^\circ$ about the $[\bar{1}10]_x$ axis. As it was discussed in Section 4.4, this crystal lattice may be regarded as a tetragonal lattice with

$$\bar{a}_z^{\text{prec}} = 2.79 \text{ \AA} \quad \text{and} \quad \bar{c}_z^{\text{prec}} = b_z^{\text{prec}} = 2.55 \text{ \AA}$$

rotated about the $[\bar{1}10]_x$ axis by the same angle $\alpha = 8.4^\circ$ and slightly monoclinically distorted.

With an accuracy of small monoclinic distortion which may be not detected by the X-ray measurements, these results are in a good agreement with the observations by Geisler *et al.* [9] who reported for the γ' phase the tetragonal symmetry with

$$a_z = 2.79 \text{ \AA}, \quad c = 2.55 \text{ \AA}.$$

The γ' phase lattice rotation about the $[\bar{1}10]_x$ axis by the angle 8.7° reported in [9] is also in a good agreement with the theoretically calculated value 8.4° . The orientation relations suggested in [9] exactly coincide with the orientational relations predicted by the theory.

The γ phase precipitates with the optimal $\{112\}_x$ habit (γ' phase) have the lowest elastic strain energy, but their energy still does not completely vanish. Therefore the further elastic strain accommodation reducing the elastic energy to zero should be expected. This relaxation process which can be called stress-induced coarsening is an elastic strain accommodation by the aggregation of various orientation variants of γ phase precipitates into a plate whose macroscopic stress-free shape change in the stress-free state is described by the invariant plane strain. The structure and the elastic strain accommodation of such a plate is expected to be exactly the same as those of a martensitic crystal where different orientation variants of the martensitic phase are formed by the Bain transformation. The formation of the martensite-like structure during the stress-induced coarsening of tetragonal precipitates in the cubic phase matrix was observed in Nb-O suboxides by van Landuyt [21]. It seems to be the case with the Be-Cu system as well. As has been shown by Bowles and Tegart the orientation relations between the α and γ phases in Cu-4 wt% Be alloy can be very well described in terms of the geometrical theory of martensitic transformation [22].

Acknowledgements—One of the authors (AGK) gratefully acknowledges the support from the National Science Foundation under Contract No. DMR-88-17922. Mr D. K. Cheong of CMU is thanked for his comments on the manuscript.

REFERENCES

1. R. J. Rioja and D. E. Laughlin, *Acta metall.* **28**, 1301(1980).
2. D. J. Chakrabarti, D. E. Laughlin and L. E. Tanner, *Bull. Alloy Phase Diagr.* **8**, 269 (1987).
3. B. D. Butler and J. B. Cohen, *J. appl. Phys.* **65**, 2214 (1989).
4. A. G. Khachaturyan, *Sov. Phys. Solid St.* **8**, 2163 (1967).
5. A. G. Khachaturyan, *Theory of Structural Transformations in Solids*. Wiley, New York (1983).
6. S. Wen, E. Kostlan, M. Hong, A. Khachaturyan and J. Morris, *Acta metall.* **9**, 1247 (1981).
7. H. Tanamura and G. Wassermann, *Z. Metall.* **25**, 179 (1933).
8. A. G. Khachaturyan, S. V. Semenovskaya and J. W. Morris Jr, *Acta metall.* **36**, 1563 (1988).
9. A. H. Geisler, J. H. Mallery and F. E. Steigert, *Trans. Am. Inst. Min. Engrs.* **194**, 307 (1952).
10. K. Shimizu, Y. Mikami, H. Mitani and K. Otsuka, *Trans. Japan Inst Metals* **12**, 206 (1971).
11. V. A. Phillips and L. E. Tanner, *Acta metall.* **21**, 441 (1973).
12. M. Nakagawa, *Japan J. appl. Phys.* **4**, 760 (1965).
13. A. V. Suyazov, M. P. Usikov and V. M. Mogutnov, *Phys. Metallogr.* **42**, 755 (1976).

14. J. M. Silkok, T. J. Heals and H. K. Hardy, *J. Inst. Metals* **82**, 239 (1953).
15. L. F. Mondolfo, N. A. Gjostein and D. W. Levinson, *J. Metals* **6**, 1378 (1956).
16. M. E. Hargreaves, *Acta crystallogr* **4**, 301 (1951).
17. E. F. Butler and G. Thomas, *Acta metall.* **18**, 347 (1970).
18. A. Guinier and P. Jacquet, *Cor. Acad. Sci.* **217**, 22 (1943); *Revue Metall.* **41**, 9 (1944).
19. A. G. Guy, C. S. Barrett and R. F. Mehl, *Trans. Am. Inst. Min. Engrs* **175**, 216 (1948).
20. R. J. Rioja, Ph.D. thesis, Carnegie Mellon Univ. Pittsburgh, Pa (1979).
21. J. van Landuyt, *Physica status solidi* **6**, 957 (1964).
22. J. S. Bowles and W. J. McG. Tegart, *Acta metall.* **3**, 590 (1955).

APPENDIX

Calculation of Crystal Lattice Parameters of a Constrained Precipitate of the B2 (γ) Phase

The components of the tensor $\Omega(\mathbf{n})_{ij}$ defined in equation (1) for a cubic lattice of the γ phase precipitate are

$$\Omega(\mathbf{n})_{ii} = \frac{c_{44} + (c_{11} - c_{44})(n_i^2 + n_k^2) + \zeta(c_{11} + c_{12})n_i^2 n_k^2}{c_{44}D(\mathbf{n})}$$

for diagonal elements and

$$\Omega(\mathbf{n})_{ij} = -\frac{(c_{12} + c_{44})(1 + \zeta n_k^2)}{c_{44}D(\mathbf{n})n_i n_j} \quad (\text{A.1})$$

if $i \neq j$, where $\mathbf{n} = (n_1, n_2, n_3)$ is a unit vector, i, j, k form the cyclic sequence (summation over the repeating indexes in (A.1) is not implied)

$$\zeta = \frac{c_{11} - c_{12} - 2c_{44}}{c_{44}}$$

$$D(\mathbf{n}) = c_{11} + \zeta(c_{11} + c_{12})(n_1^2 n_2^2 + n_2^2 n_3^2 + n_1^2 n_3^2) + \zeta^2(c_{11} + 2c_{12} + c_{44})n_1^2 n_2^2 n_3^2.$$

The representation (A.1) of the tensor $\Omega(\mathbf{n})_{ij}$ is related to the cubic axis, $[100]_x$, $[010]_y$, $[001]_z$, of the precipitate B2 phase. For the habit plane normal

$$\mathbf{n}_0 = (0.4939, 0, 0.869), \quad (\text{A.2})$$

given by equation (6), the nonzero components of the tensor (A.1) are

$$\begin{aligned} \Omega(\mathbf{n}_0)_{11} &= \frac{c_{44} + (c_{11} - c_{44})(n_3^0)^2}{c_{44}[c_{11} + \zeta(c_{11} + c_{12})(n_1^0)^2(n_3^0)^2]} \\ \Omega(\mathbf{n}_0)_{33} &= \frac{c_{44} + (c_{11} - c_{44})(n_1^0)^2}{c_{44}[c_{11} + \zeta(c_{11} + c_{12})(n_1^0)^2(n_3^0)^2]} \\ \Omega(\mathbf{n}_0)_{13} &= -\frac{c_{12} + c_{44}}{c_{44}[c_{11} + \zeta(c_{11} + c_{12})(n_1^0)^2(n_3^0)^2]} n_1^0 n_3^0 \end{aligned} \quad (\text{A.3})$$

where according to equation (18b)

$$n_1^0 = 0.4939, n_3^0 = 0.869. \quad (\text{A.4})$$

Measuring all elastic moduli in units c_{11} , we may use the ratios, $1, c_{12}/c_{11}, c_{44}/c_{11}$, instead of the elastic constants c_{11}, c_{12}, c_{44} , respectively. Assuming $c_{44}/c_{11} \approx 0.3$ and using the ratio $c_{12}/c_{44} = 0.5$ determined from the experimental data, we then have from (A.3) and (A.4) the following dimensionless values for $c_{11}\Omega(\mathbf{n})_{ij}$

$$\begin{aligned} c_{11}\Omega(\mathbf{n})_{11} &= 3.0448, \\ c_{11}\Omega(\mathbf{n})_{33} &= 1.7287, \\ c_{11}\Omega(\mathbf{n})_{13} &= -1.2615. \end{aligned} \quad (\text{A.5})$$

For the vector \mathbf{n}_0 specified by (A.2), the vector $f_i = \sigma_{ij}^0 n_j^0$ is

$$\mathbf{f} = (\sigma_{11}^0 n_1^0, 0, \sigma_{33}^0 n_3^0)$$

where according to definition $\sigma_{ij}^0 = C_{ijkl} \epsilon_{kl}^0$

$$\sigma_{11}^0 = (c_{11} + c_{12})\epsilon_{11}^0 + c_{12}\epsilon_{33}^0 \quad \text{and} \quad \sigma_{33}^0 = 2c_{12}\epsilon_{11}^0 + c_{11}\epsilon_{33}^0.$$

Therefore

$$\mathbf{f} = \{(c_{11} + c_{12})\epsilon_{11}^0 + c_{12}\epsilon_{33}^0\} n_1^0, 0, \{2c_{12}\epsilon_{11}^0 + c_{11}\epsilon_{33}^0\} n_3^0\}.$$

Equation for \mathbf{f} may also be presented in the dimensionless form as

$$\frac{\mathbf{f}}{c_{11}\epsilon_{33}^0} = \left\{ \left[\left(1 + \frac{c_{12}}{c_{11}} \right) t + \frac{c_{12}}{c_{11}} \right] n_1^0, 0, \left[2 \frac{c_{12}}{c_{11}} t + 1 \right] n_3^0 \right\}$$

where $t = \epsilon_{11}^0/\epsilon_{33}^0$. The numerical data utilized above, $t = -0.225$ [equation (16)] and $c_{12}/c_{11} = 0.5$, gives

$$\frac{\mathbf{f}}{c_{11}\epsilon_{33}^0} = (0.08026, 0, 0.67348). \quad (\text{A.6})$$

The vector, $S(\mathbf{n}_0)$, determined by equation (3) with numerical values in (A.5) and (A.6) can be rewritten as $S(\mathbf{n}_0) = \epsilon_{33}^0(-0.6056, 0, 1.0636)$. Since $\epsilon_{33}^0 = -0.252$

$$S(\mathbf{n}_0) = (0.1526, 0, -0.268). \quad (\text{A.7})$$

The crystal lattice parameters of the constrained γ phase platelet whose habit is normal to the vector \mathbf{n}_0 are determined by equation (19).

According to the Bain orientational relations, the $\alpha \rightarrow \gamma$ transformation results in

$$\begin{aligned} \mathbf{a}(1)_x &= a_x \left(\frac{1}{2}, \frac{1}{2}, 0 \right)_x = \frac{a_x}{\sqrt{2}} (1, 0, 0)_y \rightarrow \mathbf{a}_y^{\text{prec}} \\ \mathbf{a}(2)_x &= a_x \left(\frac{1}{2}, \frac{1}{2}, 0 \right)_x = \frac{a_x}{\sqrt{2}} (0, 1, 0)_y \rightarrow \mathbf{b}_y^{\text{prec}} \\ \mathbf{a}(3)_x &= a_x (0, 0, 1)_x = a_x (0, 0, 1)_y \rightarrow \mathbf{c}_y^{\text{prec}} \end{aligned} \quad (\text{A.8})$$

where $\mathbf{a}_y^{\text{prec}}, \mathbf{b}_y^{\text{prec}}, \mathbf{c}_y^{\text{prec}}$ are crystal lattice parameter vectors of the constraint γ phase lattice. Because of the crystal lattice constraint, these vectors may deviate from the $[110]_x, [1\bar{1}0]_x$ and $[001]_x$ directions required by the Bain orientational relations and change their absolute value with respect to the stress-free parameter, a_γ of the γ phase. That changes the orientational relations which are not the Bain relations any more. The constrained parameters are described by equation (19)

$$\begin{aligned} \mathbf{a}_y^{\text{prec}} &= \mathbf{a}(1)_x + S(\mathbf{n}_0)[\mathbf{n}_0 \mathbf{a}(1)_x] \\ \mathbf{b}_y^{\text{prec}} &= \mathbf{a}(2)_x \\ \mathbf{c}_y^{\text{prec}} &= \mathbf{a}(3)_x + S(\mathbf{n}_0)[\mathbf{n}_0 \mathbf{a}(3)_x]. \end{aligned} \quad (\text{A.9})$$

Using the components

$$\left(\frac{a_x}{\sqrt{2}} \right) (1, 0, 0)_y, \left(\frac{a_x}{\sqrt{2}} \right) (\bar{1}, 1, 0)_y,$$

and $a_x(0, 0, 1)_y$ of the vectors $\mathbf{a}(1)_x, \mathbf{a}(2)_x, \mathbf{a}(3)_x, a_x = 3.612 \text{ \AA}$ and the components of the vector $S(\mathbf{n}_0)$ given by (A.7) in equation (A.9) yields

$$a_y^{\text{prec}} \approx 2.77 \text{ \AA}, \quad c_y^{\text{prec}} = 2.81 \text{ \AA}, \quad b_y^{\text{prec}} = \frac{a_x}{\sqrt{2}} = 2.554 \text{ \AA}.$$

The axis $\mathbf{a}_y^{\text{prec}}$ rotates by the angle 7° in the $(\bar{1}10)_x$ plane, the axis $\mathbf{c}_y^{\text{prec}}$ rotates by the angle 9.8° in the same plane. The angle between axis $\mathbf{a}_y^{\text{prec}}$ and $\mathbf{c}_y^{\text{prec}}$ becomes 87.2° , i.e. it deviates by the angle $9.8^\circ - 7^\circ = 2.8^\circ$ from 90° angle which was before the $\alpha \rightarrow \gamma$ transformation. Therefore the crystal lattice of the constrained γ phase undergoes the rigid body rotation by the angle $\alpha = (9.8 + 7)/2 = 8.4^\circ$.

The resultant crystal lattice is monoclinic with parameters

$$\begin{aligned} a_y^{\text{prec}} &= 2.77 \text{ \AA}, \quad b_y^{\text{prec}} = 2.554 \text{ \AA}, \\ c_y^{\text{prec}} &= 2.81 \text{ \AA} \quad \text{and} \quad \beta = 87.2 \text{ \AA}. \end{aligned}$$

This monoclinic crystal symmetry is determined by the symmetry of the problem and does not depend on the numerical input data. The rigid body rotation about the $[\bar{1}10]_x$ axis results in substantial deviation from the Bain relations.

The above monoclinic structure may be regarded as a tetragonal structure with

$$\bar{a}_\gamma \approx c_\gamma^{\text{prec}} \approx a_\gamma^{\text{prec}} = \frac{2.81 + 2.77}{2} = 2.79 \text{ \AA}$$

and

$$\bar{c}_\gamma \approx b_\gamma^{\text{prec}} = 2.554 \text{ \AA},$$

which is slightly monoclinically deformed.

If this slight monoclinic distortion is not detected by the experimental technique, the constraint γ phase precipitates may be interpreted as precipitates of the tetragonal γ' phase with the $(112)_x$ habit. It seems to be the case in the Geisler *et al.* observations that reported the tetragonal γ' phase $(112)_x$ platelets with the tetragonal lattice with the parameters

$$a_\gamma^{\text{prec}} = 2.79 \text{ \AA}, \quad c_\gamma^{\text{prec}} = 2.55 \text{ \AA}$$

which rotates about the $[1\bar{1}0]_x$ axis by the angle $\alpha = 8.7^\circ$ (compare with the calculated value, $\bar{a}_\gamma^{\text{prec}} = 2.79 \text{ \AA}$, $c_\gamma = 2.55 \text{ \AA}$, $\alpha = 8.4^\circ$).

The calculation with $c_{44}/c_{11} = 0.5$ gives numerically the same values, i.e. within the physically reasonable range we have approximately the same calculation results.