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# Some observations on deformation-related discontinuous precipitation in an Al-14.6at.%Zn alloy

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ABSTRACT

The discontinuous precipitation (DP) in a supersaturated Al-14.6at.%Zn alloy in relation to different forms of deformation structures has been investigated with optical and electron microscopy. It has been found that intense surface scribing, followed by short-term ageing at 65 °C, resulted in a recrystallized duplex structure with nanoscale equiaxed $\beta$-Zn particles and $\alpha$-Al grains. In the absence of recrystallization and shear banding, moderate surface grinding increased the transformation kinetics of DP on the alloy surface by an order of magnitude compared with that of the undeformed counterpart. The enhanced transformation kinetics is attributed to intragranular nucleation and growth of DP colonies associated plausibly with dislocation cell wall structures induced by the surface strain. In contrast, bulk deformation by means of cold-rolling (13–66% reduction) and *in situ* stress-ageing (~1% strain) both suppressed the development of DP in the alloy. The role of deformation bands as nucleation sites of DP and the driving force determining the development of DP colonies in deformed matrices are discussed.

## 1. Introduction

Discontinuous precipitation (DP) refers to a solid-state phase transformation in which a supersaturated phase ($\alpha_o$) dissociates into a two-phase ($\alpha + \beta$) aggregate typically behind a mobile (high-angle) grain boundary. It has attracted considerable interest [1–3] over the last three decades with regard to both initiation and growth mechanisms and transformation kinetics. There has, in particular, been a considerable amount of research effort devoted to investigation of the discontinuous precipitation in alloys subjected to prior plastic deformation [4–12]. There is a common view that the strain energy associated with either local or general plastic deformation may impart a driving force for the migration of grain boundaries [13] that is complementary to the contribution from chemical free energy. However, experimental observations of whether or not prior plastic deformation promotes the kinetics of DP appear to vary depending upon the alloy system and the nature and degree of deformation, even when similar deformation structures are produced.

Deformation twins have, for example, been reported to be favoured nucleation sites for DP in Cu–Mg [14] and Cu–In [15] alloys, whereas they are proposed [9] to be the obstacles that impede the growth of DP in Mg–Al. Deformation substructures, such as dislocations and deformation bands, which occur more regularly in deformed alloys, may also lead to diverse precipitation behaviours. While it is generally believed that continuous precipitation occurs preferentially in association with dislocations and deformation bands, and compete thermodynamically to suppress DP development [1,6,12], it has been suggested that deformation bands may serve as nucleation sites for DP [16]. In contrast, the enhanced DP development within cold-deformed surface layers of Ni–In [7] and Cu–Ag [8] alloys has been attributed to recrystallization in advance of DP. However, direct microstructural evidence that verifies the initiation of DP from recrystallized grain boundaries rather than other substructures is not readily available.

To determine the influence(s) of prior strain on the formation of DP, it is pertinent to identify the actual deformation structures which initiate the discontinuous reactions. The current work focuses on the microstructural examination of DP development in connection with deformation structures in a binary Al-14.6at.%Zn alloy. Localized and bulk deformation techniques have been employed to induce different degrees of plastic strain and, in turn, various forms of deformation structure(s). Special attention has been paid to the initiation behaviour of DP at the early stages of decomposition.

## 2. Experimental procedure

An Al-14.6at.%Zn alloy was prepared from commercially-pure grade (above 99.9%) elemental Al and Zn metals by conventional casting under normal atmosphere. Traces of impurities including Si and Fe, each below 0.1 at.%, were detected as per quantitative composition analysis. The ingot was homogenized at 450 °C for 50 h in an air furnace, followed by cold-rolling to facilitate grain size reduction. Samples of the rolled sheet were solution-treated in a salt-bath at 350 °C for 1 h and

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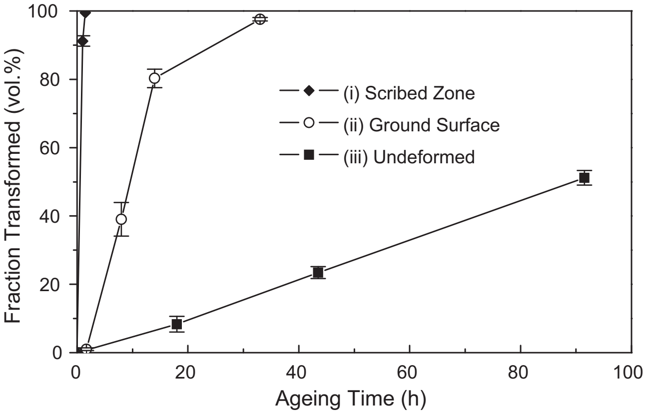

**Fig. 1.** The rates of DP transformation measured for the alloy (i) within an intense scribe mark, (ii) on an alloy surface uniformly ground with 1200-grit paper and (iii) on a strain-free specimen isothermally aged at 65 °C.

then water-quenched. The resulting grain size of the samples was approximately 120 μm on average. Plastic deformation of the specimens prior to ageing was performed by (i) uniform mechanical grinding of the specimen surface on water-cooled 1200 grit (40 μm) SiC papers, (ii) localized scribing with a carbide tip (90° vertex angle) under steady load to a depth of around 200 μm, and (iii) varying degrees of cold-rolling from 13% up to 66% reduction in multiple passes, with typically less than 9% reduction per pass. In order to study the dynamic interactions between deformation structures and the growth of DP cells, isothermal ageing treatments of the alloy, under a unidirectional stress of 40 MPa, were performed using a standard constant-load creep test rig equipped with an oil-bath. All isothermal ageing was carried out in the temperature range of 65–150 °C, over which the DP occurred most favourably in the present alloy.

Microstructural characterization was performed with a reflected-light microscope, a JEOL 840A scanning electron microscope (SEM) equipped with a backscattered electron detector, and a Philips CM20 transmission electron microscope (TEM) operating at 200 kV. The surfaces of alloy specimens for quantitative analyses were fine-polished to 0.05 μm finish using colloidal silica, chemically etched with a solution containing 100 ml $H_2O$, 4 ml $HNO_3$ and 22 ml HF, and examined under polarized light. The fraction of transformation was measured on digitized micrographs using the image analysis software ImageJ. Thin-foil specimens for TEM observations were prepared by mechanical dimpling to a thickness of around 100 μm, followed by ion beam milling using a Gatan PIPS$^{TM}$ system operating at ion energy of 4 keV.

## 3. Results and discussion

### 3.1. Localized severe plastic deformation and uniform surface grinding

Quantitative reflected-light metallography revealed marked variations in the rate of transformation detectable at the surface regions of the alloy specimens subjected to uniform mechanical grinding and localized severe plastic deformation (scribing) of the surface. Fig. 1 depicts the change in fraction of DP detectable as a function of time during isothermal ageing at 65 °C for each of the deformed specimens, when compared with a specimen fine-polished and chemically-etched (i.e. a comparatively undeformed surface). It is noted that the locally-deformed (scribed) surface exhibits a rapid transformation rate immediately within the deformation zone defined by the boundaries of the scribe mark, which covers an area of ∼400 μm × 4 mm, resulting in almost complete (>90 vol.%) transformation within 1 h ageing at 65 °C. The backscattered SEM (BS-SEM) micrograph of Fig. 2a reveals the near-complete transformation to apparently discontinuous product within the deformation zone defined by the scribe mark, while the polarized light micrograph in Fig. 2b confirms transformation in the zone of severe plastic deformation and highlights the preferred formation of DP product in association with localized deformation bands within the matrix immediately adjacent to the scribed zone. Fig. 2c illustrates that the major deformation bands in the vicinity of the scribe favour the initiation of DP colonies from one side of the band in a similar fashion to a mobile high-angle grain boundary. The propensity for the bands to initiate DP is noted to decline progressively with the distance away from the scribe. In those regions subjected to a reduced magnitude of plastic strain, where the deformation bands become finer and less densely distributed, a dispersion of fine continuous precipitates (sized 30–80 nm along the longer dimension) emerged as the dominant decomposition product in place of DP, as shown in Fig. 2d. It is also seen in the figure that the size scale of the continuous precipitation is more pronounced at the locations of deformation bands. The above observations indicate that the extent of the localized DP products decreases with the apparent severity of the localized deformation bands and the dominant mode of decomposition may vary across the plastic strain gradient.

Further microstructural examination was carried out within the scribed zone. Thin foil specimens for TEM were prepared from the scribed sample by ion-beam milling preferentially and selectively from the reverse side of the sample to the deformed surface, towards the location of the scratch. Fig. 3 shows bright field TEM micrographs typical of the deformed zone after ageing 1.5 h at 65 °C, for a period in which transformation to discontinuous product was essentially complete. There is direct evidence that the f.c.c. (Al-rich) α-phase has a nanoscale, equiaxed grain structure (average grain diameter $d \sim 300$–400 nm), while contrast variations indicate a preponderance of high-angle grain boundaries. This implies that recrystallization has occurred within the deformed region, and the ultra-fine scale of the recrystallized α structure is consistent with levels of strain in the scribed zone that constitute severe plastic deformation (SPD) [17].

Selected area electron diffraction (SAED) analysis, such as that in Fig. 3b, revealed that the nanostructure was in fact dual-phase, comprising predominantly the f.c.c. (Al-rich) α-phase and a lower volume fraction of the h.c.p. (Zn-rich) β phase. The β phase typically took the form of irregularly shaped, globular particles, located exclusively at the grain boundaries and grain boundary junctions within the α, with a scale typically in the range of 50–200 nm in diameter. This suggests that the β phase is most likely a product of heterogeneous grain boundary nucleation and, in this respect, the resulting structure might be interpreted as indicative of a discontinuous product, for the early-stages of discontinuous reactions typically involve the formation of precursor grain-boundary nuclei of the solute-rich phase. However, the duplex equiaxed nanostructure developed is not the lamellar configuration typical of DP in such an alloy system at conventional grain sizes [12,18,19] and, while it has developed under conditions in which DP would be expected, it may not be readily classified as a conventional discontinuous product in morphological terms.

It is possible that the scale of the nanostructure developed in the severely deformed zone, and large fraction of grain boundary area per unit volume ratio associated with it, are sufficient to modify the form of the conventional decomposition product(s). Such nanostructure will likely enhance the nucleation rate for the solute-rich constituent, while the depletion of solute content within the α grains will be accelerated by enhanced grain-boundary diffusion. The chemical driving force for decomposition may well be diminished before a conventional discontinuous reaction front can be mobilized. The observation that the conventional form(s) of a discontinuous transformation product may be constrained at ultra-fine grain size is potentially worthy of further study in material subjected to more uniform severe plastic deformation at larger scale. From a practical perspective, this behaviour suggests a potentially novel route to the synthesis of ultra-fine scale duplex metallic composites from a supersaturated alloy by means of severe deformation.

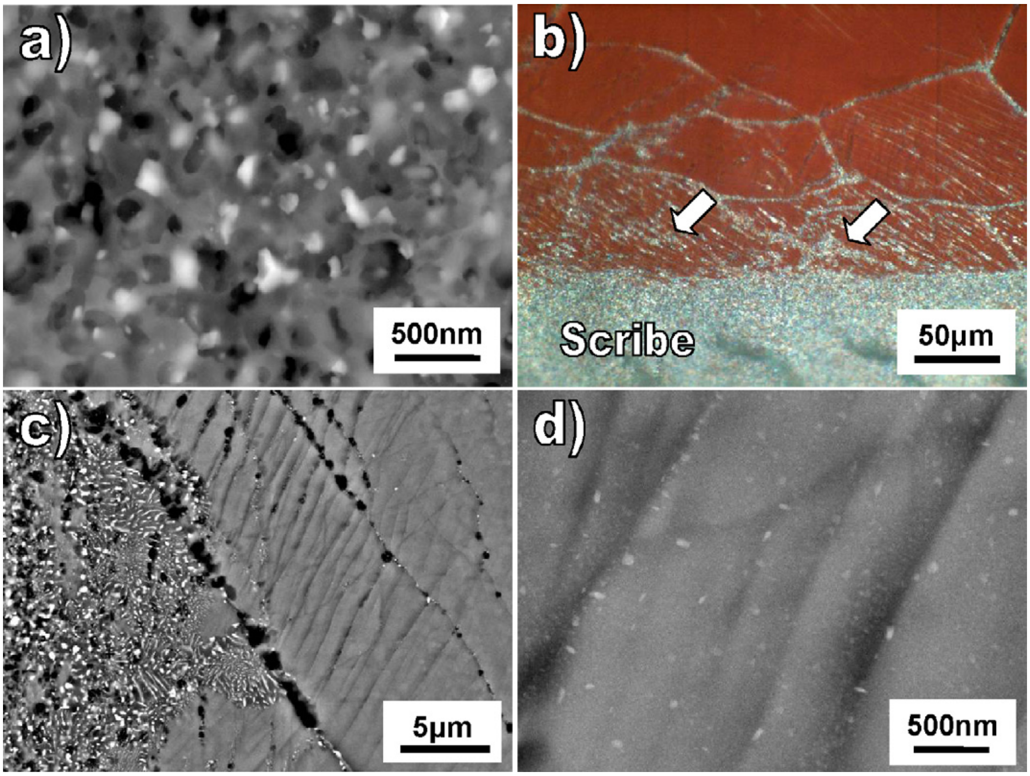

**Fig. 2.** Microstructures of the scribed specimen after 1 h ageing at 65 °C. (a) BS-SEM micrograph of the transformed structure within the scribe mark. The dimples and cavities were caused by preferential etching of the Zn-rich phase. (b) Polarized light micrograph showing the occurrence of DP (arrowed) associated with deformation bands adjacent to the scribe mark. (c) BS-SEM micrograph of the DP colonies indicated in (b). (d) BS-SEM micrograph showing continuous precipitation in the less severely deformed region away from the scribe.

In comparison, for the sample deformed more uniformly and qualitatively less severely by surface mechanical grinding, the fraction of DP product detected during isothermal ageing at 65 °C increased more slowly and at a rate of ~6 vol.% per hour over the first 14 h of ageing (Fig. 1). While diminished with respect to the rate of transformation within the localized scratch zone, this still represents a rate of increase in total transformation product fraction that is an order of magnitude greater than that observed on the surface of an undeformed control specimen. As shown in Fig. 1, the increase in DP volume fraction in the fine-polished and etched specimen was of the order of 0.55 vol.% per hour throughout the first 100 h of isothermal ageing. These experimental observations would appear to support the notion that prior plastic deformation, in the present case localized to the sample free surface, will tend to accelerate the formation of discontinuous transformation products within the deformation zone during subsequent isothermal decomposition. The rate of transformation scales qualitatively with the degree of plastic strain and may be very rapid in volumes of material subjected to severe plastic deformation.

Fig. 4 illustrates the evolution of DP immediately adjacent to the free surface of specimens polished, etched and surface ground with 1200 grit SiC paper, then aged isothermally at 65 °C, and finally lightly diamond polished and etched to reveal the transformation product(s). When compared in terms of local stress intensity, depth of penetration and degree of local strain, uniform mechanical grinding at this scale (40 μm abrasive) is expected to yield less intense surface cold work than a single scribe mark, in a deformation layer that may extend in excess of 100 μm sub-surface. The reduced severity of deformation would appear to be confirmed by the preservation of the original grain structure (average grain diameter ~ 120 μm) (Fig. 4). After 100 min ageing, the DP product within the deformation zone took the form of finely dispersed intragranular cells (~1 to 5 μm in diameter) within the supersaturated $\alpha_o$ matrix, Fig. 4a, together with conventional cellular colonies originating from pre-existing grain boundaries. Backscattered SEM images of the early-stage intragranular DP cells, Fig. 4b, revealed a conventional duplex lamellar substructure, with no evidence of deformation bands or locally recrystallized structure such as observed in the scribed sample. Prolonged ageing for 1100 min led to more extensive cellular structures, which comprised aggregates of individual DP colonies with diverse growth directions (Fig. 4c and d).

In thermodynamic considerations, the intragranular nucleation of DP in the absence of interphase interfaces and structural inhomogeneity is anticipated to be energetically unfavourable, and it is conjectured that such nucleation would be associated with some other form of structural heterogeneity. However, the origin(s) of the apparently intragranular colonies of DP could not be determined unambiguously. Second-phase particles have been suggested to assist the heterogeneous nucleation of discontinuous colonies in a Cu–In alloy [20]. In the present alloy, a limited quantity of iron-rich phase particles were found at grain boundaries after the homogenization treatment at 450 °C, due possibly to impurity segregation to the grain boundaries. While these particles may become embedded in the recrystallized grains following the rolling and solution treatment, it is unlikely that there could be the density of constituent/inclusion particles to account for the apparent nucleation rate. On the other hand, the degree of plastic deformation, in the present example, is unlikely to be sufficient for the development of localized shear bands. No such heterogeneities could be detected by TEM in thin foil specimens prepared selectively from the near-surface zone.

The initiation of the discrete DP colonies observed in Fig. 4a and b might plausibly be associated with dislocations or dislocation arrays, which might themselves become progressively annihilated in the course of isothermal ageing (recovery). Low to moderate

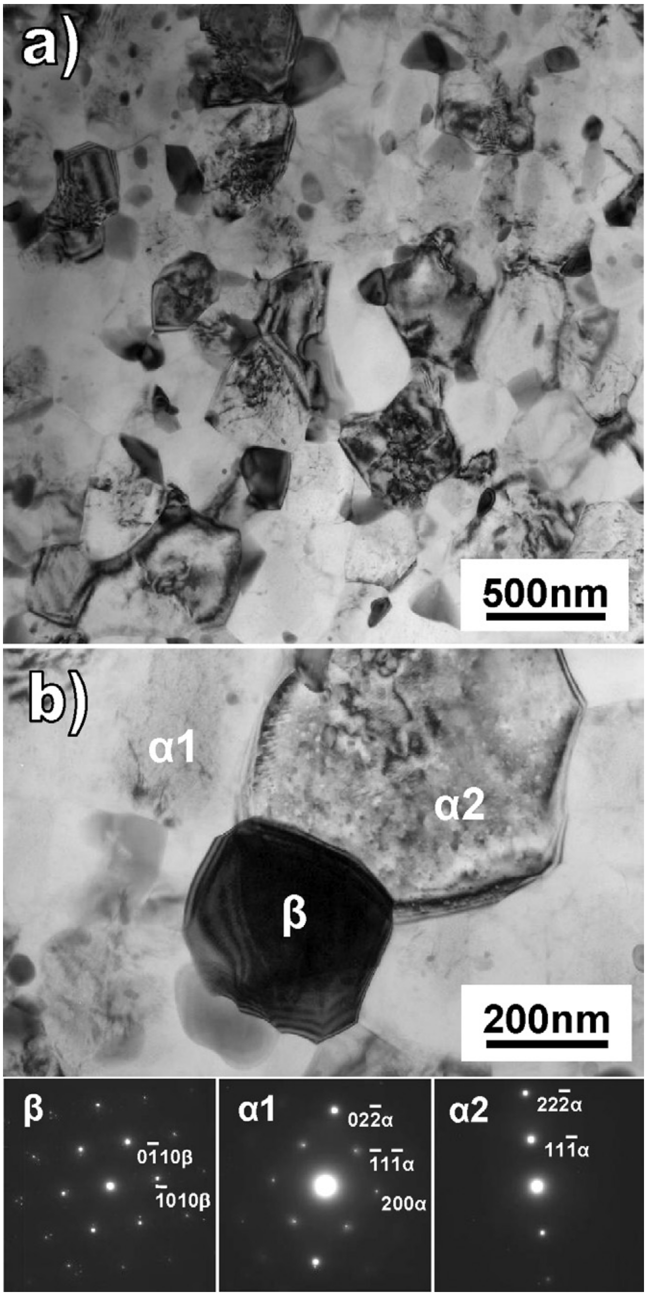

**Fig. 3.** (a) TEM micrograph showing an equiaxed nanostructure within the scribe after ageing at 65 °C for 1.5 h. (b) SAED patterns associated with an intergranular (h.c.p.) β-phase and the neighbouring (f.c.c.) α grains. $B = \langle 0\,0\,0\,1\rangle_{\beta}$.

plastic deformations are known to lead to cell and sub-grain structures that are partitioned by dislocation walls that may be diffuse or discrete, depending on the degree of deformation. Such walls are typically low-angle boundaries and their effectiveness in initiating DP remains to be established. However, it has been suggested that individual dislocations may be sufficient for nucleation of discontinuous products in a Cu–In alloy [15], in which the product phases and the supersaturated matrix are significantly different in specific volume. In the present case, the array of discontinuous colonies, in Fig. 4a for example, was such that they could readily be imagined to decorate the boundaries of a cellular network, with an average cell dimension of typically ~10 μm. However, it proved difficult to obtain more direct evidence of any such model.

**Table 1**
Total volume fraction of DP measured for undeformed and cold-rolled specimens after 90 h ageing at 65 °C.

| Cold roll reduction (%) | 0 | 13 | 24 | 50 | 66 |
|---|---|---|---|---|---|
| Total fraction of DP (vol.%) | 51.2 | 5.0 | 3.1 | 3.7 | 2.9 |

### 3.2. Cold rolling and stress ageing under uniaxial load

In contrast to the pronounced effects of localized surface prestrains, more uniform bulk deformations by cold rolling had effectively negligible influence in promoting DP in the present alloy and, indeed, inhibited the discontinuous reaction observed in undeformed samples. With isothermal ageing at 65 °C, the total volume fractions of discontinuous transformation product were commonly observed to saturate at levels of around 3–5% after 90 h of ageing for samples subjected to cold-rolling in the range of 13–66% thickness reduction. A comparison of the fraction transformed among the samples cold-rolled to various degrees together with an undeformed sample is given in Table 1. In agreement with a previous work [12], metallographic examination revealed plastic strain to be heterogeneous with localized deformation bands prominent in the cold-rolled specimens. The polarized light micrograph in Fig. 5a is representative of the near-surface region parallel to the rolling plane, for a sample rolled to 13% total reduction and aged 1.5 h at 65 °C. The original grain structure is preserved and there is apparent intensification of decomposition product(s) at the grain boundaries and at irregularly spaced deformation bands within the grains. Transmission electron microscopy revealed, Fig. 5b, a dense distribution of predominately Zn-rich particles having the form of lenticular platelets with rational crystallographic habit, and thus apparently the product of a continuous precipitation reaction. Similar precipitates were observed throughout the adjacent (dislocated) matrix, but on a finer scale and at much lower number density. It appeared that there had been an accelerated rate of nucleation and increased rate of growth for continuous precipitation occurring within the deformation bands.As shown in Fig. 5c, there was also evidence of a competing reaction mode or an anomalous coarsening of the continuous precipitates within some segments of the bands, leading to coarse globular and/or elongated (fibrous) particles in arrays that resemble a DP product. Competitive coarsening of existing coherent precipitates by discontinuous reaction has been reported for Al–Li [21] and Cu–Ni–Fe [22] alloys, with the driving force being attributed to the difference in the effective interfacial energies associated with the continuous and discontinuous products. As with generic DP reactions, mobile, high-angle boundaries are normally a prerequisite for discontinuous coarsening [1], but in the present case there was no indications of such boundaries associated with the clusters of coarsened precipitates. It is thus not possible to be definitive about the mechanism by which such clusters were formed.However, additional evidence was obtained that the discontinuous reaction is able to initiate from deformation bands within the present Al–Zn alloy. The electron micrographs of Fig. 6 show a deformation band which is defined in Fig. 6a by the strain contrast associated with the dislocation substructure within the band. Multiple colonies of DP were observed to have originated predominately at the boundaries of the deformation band in the presence of continuous products, as evidenced in Fig. 6b. These colonies were found to extend across the band and, in some cases, protrude for a limited distance into the adjacent matrix. The initiation of classical discontinuous products is dependent upon, firstly, the occurrence of heterogeneous grain boundary precipitates and, secondly, the availability of thermodynamic driving force sources such as differences in chemical (volume) free energy and/or elastic strain energy to drive the boundary movement [1]. In this regard, the pre-existing continuous precipitates

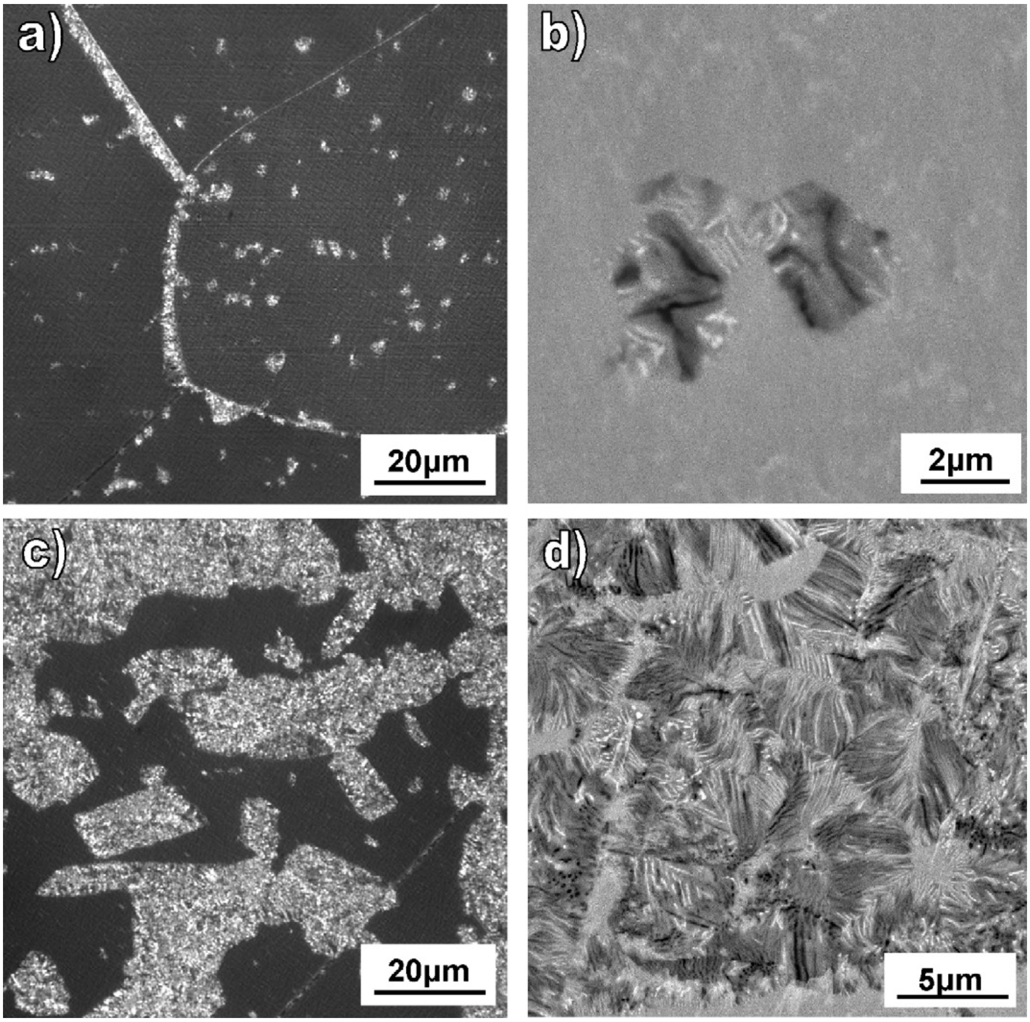

**Fig. 4.** Polarized-light and BS-SEM micrographs showing the evolution of intragranular DP colonies on the surface of the mechanically ground specimen aged at 65 °C for 100 min (a and b) and 1100 min (c and d).

situated at the band/matrix interface, given sufficient interfacial lattice misfit, may be considered analogous to conventional grain boundary precipitates in terms of their roles on the initiation of DP cells. The propagation of the cell fronts from the band/matrix interface towards a region of high defect density clearly suggests that the elastic strain energy associated with the defect substructures and continuous products within the band, rather than the chemical free energy, constitutes the dominant driving force for the DP reaction. However, the discontinuous reaction is confined to the deformation bands and the immediate vicinity of the bands and conventional metallography revealed virtually discontinued development of DP beyond the immediate vicinity of the deformation bands and the grain boundaries, even with prolonged ageing.To complement the observations on samples pre-strained and aged isothermally, selected samples of the alloy were subjected to isothermal ageing under a uniaxial tensile stress in an effort to better understand any dynamic interactions between deformation structures and the DP colonies under development. A pair of backscattered SEM micrographs in Fig. 7 shows the form of the DP product in a specimen subjected to an axial stress of 40 MPa and *in situ* ageing at 150 °C for 24 h. The applied stress at this temperature has produced a permanent tensile strain of ~1% in the tensile specimen during this exposure. As in the case of prior cold-rolling, the formation of DP in stress-aged samples was found to be significantly retarded compared with the unstressed counterparts under identical isothermal ageing conditions. The overall DP transformation of the stress-aged sample shown in the figure is measured to be 27 vol.%, compared to 70 vol.% for a control specimen aged side-by-side without applied loading. Within the resulting microstructure, the DP colonies were observed to originate preferentially from those grain boundaries approximately normal to the stress axis, as in Fig. 7a; and they were commonly found to exhibit a triangular morphology, with apexes pointing in the loading direction and slanted edges aligned on average at ~45° to the stress axis. The observed cell morphologies are consistent with those from earlier studies of the effect of stress on the formation and growth of discontinuous products in Cu–Cd [23] and Al–Zn [24] alloys. In both earlier studies, discontinuous cell fronts having 'saw-tooth' geometries were reported and explained in terms of the differential driving force (coherency strain energy) experienced by local DP boundary segments oriented differently with respect to the applied stress. In the present case, it is particularly noteworthy that the 'saw-tooth' boundary segments defining cell edges were very commonly aligned with local deformation bands having traces at ~45° (on average) to the applied stress axis (Fig. 7b).

While limited in scope, the present microstructural observations demonstrate that the role of prior plastic deformation on the discontinuous precipitation reaction in this Al-14.6at.%Zn alloy is complex, and strongly dependent upon the nature of the deformation and the form of deformation structure that is induced.

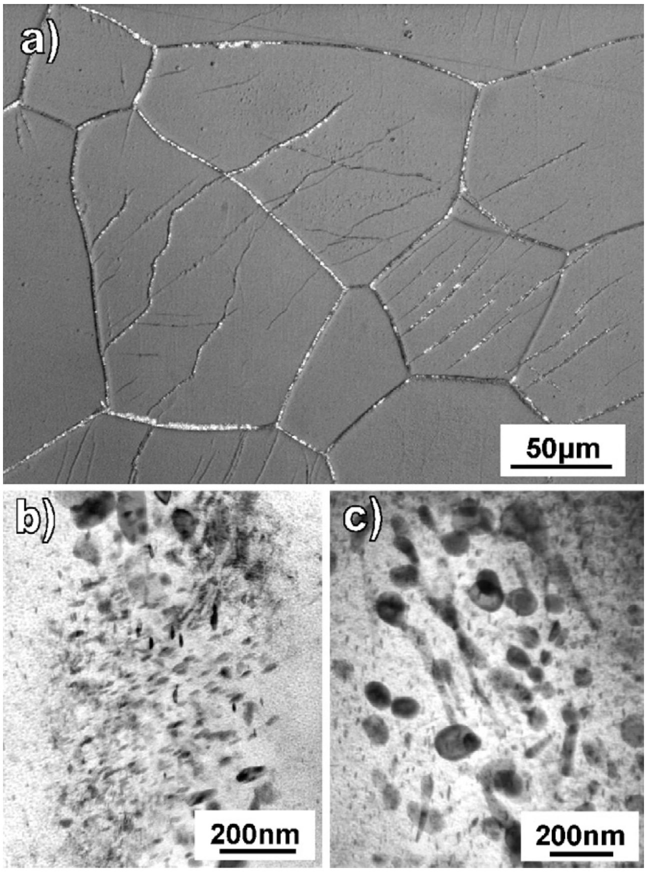

**Fig. 5.** Deformation bands in the specimen cold-rolled by 13% and aged at 65 °C for 1.5 h. (a) Polarized light micrograph. (b and c) TEM micrographs showing ordinary continuous precipitates and abnormally coarsened precipitates inside a deformation band, respectively.

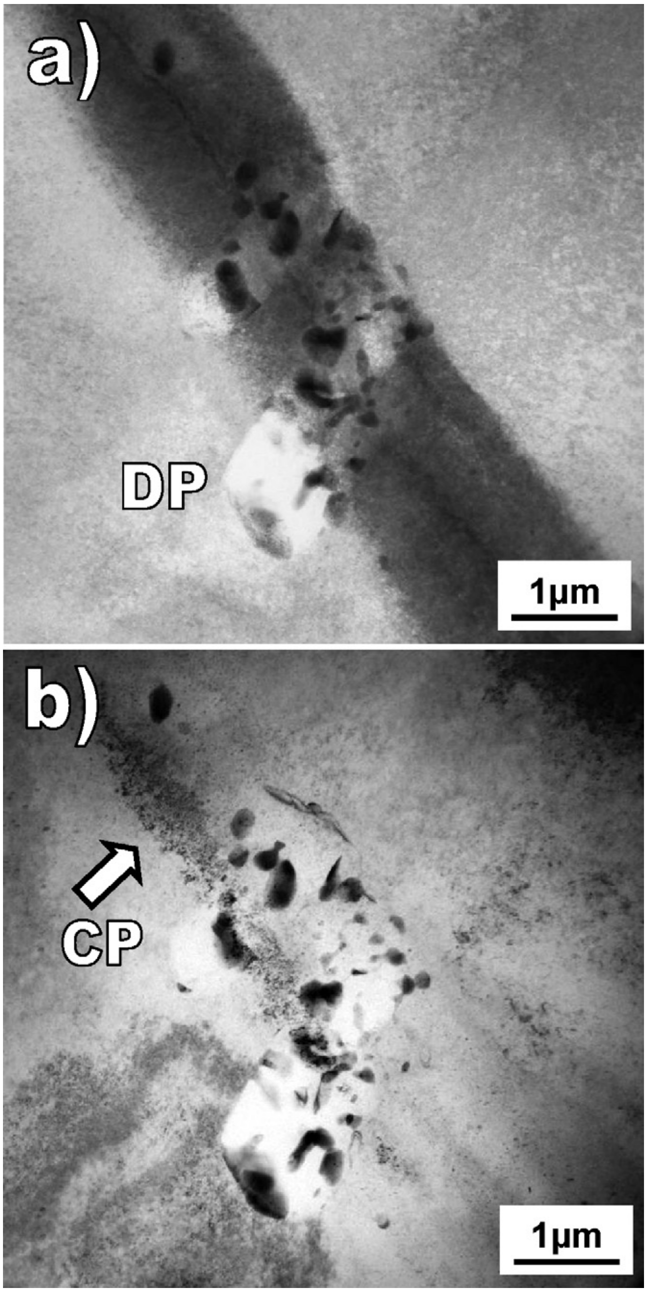

**Fig. 6.** TEM micrographs showing (a) DP cells originated from the interface of a deformation band and (b) a high density of continuous precipitates (CP) inside the band under different tilt conditions. Specimen cold-rolled 13% and aged at 65 °C for 1.5 h.

The kinetics of DP will be most noticeably enhanced if both the nucleation and growth rates are accelerated. In the above examples, it seems that the nucleation rate, and most particularly the intragranular nucleation rate, may be significantly enhanced if prior deformation leads to the formation of planar assemblies of dislocations, across which there emerges the combination of chemical and/or strain energy gradients appropriate to the formation DP colonies. Such assemblies might be found in cell walls or sub-grain boundaries that are the product of deformation or post-deformation recovery, or in the walls of deformation bands. But whether an increase in nucleation rate translates into an increase in the volume fraction of DP product under given ageing conditions will still depend upon the ease of subsequent growth of DP colonies. For instances, in the case of the alloy material within a ground surface zone, growth appears unimpeded and transformation kinetics are enhanced with respect to an undeformed free surface. However, in samples bulk-deformed by cold rolling, regardless of the fact that the localized deformation bands are able to facilitate the intragranular nucleation of DP cells, these cells are found to protrude into the deformed matrix only by a minimal extent. This would therefore imply that, apart from the actual forms of local deformation heterogeneities (dislocation cell walls, deformation bands, etc.) created by prior deformations, the availability of adequate driving forces that will sustain DP development in the matrix regions surrounding these deformation heterogeneities is yet another crucial factor that governs the overall kinetics of DP.

Kim and Park [19] investigated the effect of prior continuous precipitation on the subsequent growth of DP in an Al-14.6at.%Zn alloy and concluded that the kinetics of DP scales directly with the stored elastic strain energy associated with the early-stage metastable continuous products (coherent G.P. zones). Under the premise that continuous and discontinuous precipitations are mutually competitive decomposition processes and the diffusional growth of continuous products occurs concurrently with the DP counterparts in the alloy during ageing, it is reasonable to predict that the elastic strain energy term may diminish beyond a critical stage of the decomposition as the metastable continuous products evolve into other transitional phases or stable equilibrium phase, through which the precipitates progressively lose their coherency with the matrix lattice. The current TEM investigation has evidenced the occurrence of continuous products in the deformed matrix of the specimens subjected to cold rolling. The inhibition of discontinuous transformation within the less-severely deformed

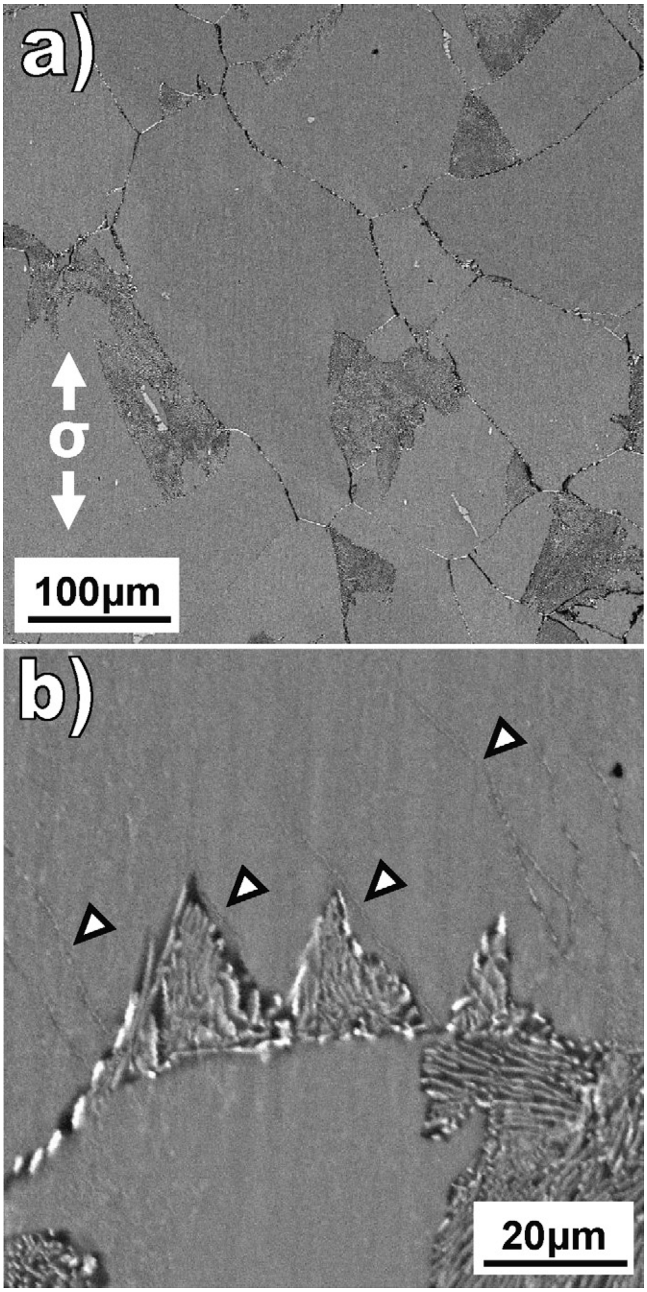

**Fig. 7.** BS-SEM micrographs of a specimen aged at 150 °C for 24 h under a unidirectional stress of 40 MPa showing (a) the general morphology of the DP cells and (b) the interactions of deformation bands (arrowed) with individual cells.

matrix in the cold rolled samples, which occurred over the entire range of reduction (13–66%), could plausibly be explained by an enhanced kinetics of the continuous precipitation process within the highly dislocated matrix, which in turn accelerates the evolution of the early stage coherent products into partially coherent or incoherent forms, such as the rhombohedral R-phase and cubic $\alpha'$ phase [25], leading to a subcritical level of coherency strain energy that is no longer adequate to constitute the driving force for the development of existing DP colonies.

As far as the undeformed alloy specimens are concerned, the higher kinetics of DP transformation recorded for the specimen aged at 150 °C (3 vol.%/h) with respect to those aged at 65 °C (0.55 vol.%/h) is in qualitative agreement with the results reported in Ref. [19]. The DP cells in the specimen stress-aged at 150 °C have been shown to develop into characteristic triangular geometries with apexes roughly aligned with the stress direction. Based upon the assumption that a lattice diffusion zone of some interatomic distances exists ahead of migrating cell fronts, Sulonen [23] predicted that the diffusional coherency strain energy associated with the lattice misfit across a DP interface will serve as the driving force for the interface migration. Accordingly, depending on the relative orientations of the boundary segments with respect to the stress axis, the driving force acting on these segments and, in turn, their local migration velocities will be subjected to systematic variations. While the above treatment lends rationale to the formation faceted cell morphologies, the assumption of volume diffusion that underlies the above proposition is not readily validated. The present work shows that the production of permanent strain and, hence, deformation structures in the matrix by the applied stress is likely to introduce additional microstructural factors that may influence the overall transformation kinetics and the morphological development of DP. From a microstructural perspective, the impeded DP development observed in the specimen stress-aged at 150 °C, as compared to the unstressed counterpart, appears to be closely connected to formation of deformation bands which facilitated competitive continuous reactions. The geometrical correspondence among the traces of deformation bands and the DP boundary segments provides an insight into the possibility that such local heterogeneities in a mildly deformed structure may impose certain influence on confining growth of the discontinuous product as a result of locally diminished thermodynamic driving force and contribute, at least in part, to the characteristic geometry of the DP cells developed in the stress-aged specimen.

## 4. Conclusions

Prior deformations have been shown to influence the rate of transformation and morphological development of DP colonies in an Al-14.6at.%Zn alloy. It is demonstrated that when the deformation is sufficiently intense, as in the case of a linear scribing ($\sim$200 μm depth) on the alloy surface, recrystallization precedes or accompanies the discontinuous reaction upon ageing at 65 °C and results in a characteristic nanostructure which comprises dispersed particulate $\beta$-phase (50–200 nm) in a $\alpha$-grain structure of average diameter 300–400 nm. Such a combined structural transformation sheds light on a potentially novel route to the synthesis of ultra-fine scale duplex metallic composites by means of severe deformation.

Depending on the local severity of the deformation heterogeneities such as deformation bands and, perhaps, dislocation cell wall structures, these heterogeneities may either behave as preferred nucleation sites for discontinuous products (as discussed in the cases of localized surface scribing/grinding and uniform bulk deformation by 13–66% rolling reduction) or as potential barriers which limit the growth and cell morphologies of DP (as in the case of stress-ageing). The mobility of DP reaction fronts in the deformed alloy matrix is considered to be strongly dependent upon the level of stored strain energy associated with the competitive continuous products and defects in the matrix.

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