Nanocrystallization of Al-based glassy alloys

N. Boucharat and G. Wilde

Forschungszentrum Karlsruhe, Institut für Nanotechnologie, P.O. Box 3640, 76021 Karlsruhe, Germany.

Abstract

In a number of marginal glass-forming alloys, number densities of nanocrystals as high as \(10^{21}\) m\(^{-3}\) to \(10^{23}\) m\(^{-3}\) can develop during a primary crystallization reaction. These nanostructured materials present an exceptional strength-density performance. The origin of the nanocrystallization process is discussed on the basis of kinetic analyses and calorimetric and structural investigations of Al\(_{92}\)Sm\(_8\). The early stages of the nanocrystal development were monitored by isothermal calorimetry on long time scales. The results strongly indicate that the nanocrystals develop by diffusional growth of quenched-in nuclei. However, the formation of a pronounced concentration gradient at the growing nanocrystal interface increases the kinetic stability and allows the retention of nanostructured materials. Additionally, the effect of thermal treatments, plastic deformation and inoculation of immiscible elements (e.g. Pb, In) on the crystallization behavior of glassy Al\(_{88}\)Y\(_7\)Fe\(_5\) is examined. The results demonstrate the effectiveness of the severe plastic deformation and of the inoculants to promote nanocrystallization. Moreover, it is shown that the modifications of the concentration gradient can affect the nucleation conditions for new phases that allow for an effective control of the phase formation sequence.

1 Introduction

One of the ways to improve the mechanical properties of metallic alloys is to produce materials with a very small grain size [1,2]. Among the techniques that enable the synthesis of such nanostructured materials, thermal treatments and conventional plastic deformation processes of metallic glasses can be applied. Using rapid quenching processing, amorphous Al alloys such as Al-TM (transition metal)-RE (rare earth element) alloys can be produced that partially devitrify upon heating, yielding in a fine dispersion of almost pure Al nanocrystals [3] with an unusually high number density (up to \(10^{23}\) m\(^{-3}\) [4]) in a residual amorphous matrix. Very impressive property enhancements have been achieved e.g. a tensile strength reaching 1560 MPa [5] which is much higher than the strength of coarse-grained Al alloys [1]. Beyond the evidence of improved mechanical properties, an important characteristic is the slow growth of nanocrystals, which allows a more accurate experimental monitoring, offering a new advantage in the investigations of the kinetics involved in the nanocrystallization process. One opportunity for both the enhancement of the nanocrystal number density and an increased understanding of the origin of the nanocrystals is given by promoting the nucleation site density by incorporating immiscible elements into the melt prior to quenching [6]. A different approach is based on plastic deformation-induced nanocrystallization that can be applied as an alternative synthesis route for producing bulk ultrafine nanostructured alloys. In particular, nanocrystallization reactions in metallic glasses have been observed using bending [7-9], tension [8], ball-milling [10] or nanoindentation [11] processes. Moreover, it has been recently demonstrated that severe plastic deformation processes such as high pressure torsion induces nanocrystallization in various glassy alloys.
[12-15]. This process appears to be a promising method to produce bulk nanostructured materials with exceptional high strength [16,17].

In this contribution, Al$_{92}$Sm$_8$ and Al$_{88}$Y$_7$Fe$_5$ glasses serve as model systems to investigate the origin of the nanocrystallization process. Both systems are known [18,19] to yield similar product microstructures during the initial crystallization reaction. However, the different absolute values for the transformation temperatures enable the use of different analysis tools and synthesis procedures. The kinetics of the crystallization process is studied using quantitative structural and calorimetric analyses. Moreover, the impact of thermal treatments, plastic deformation processes and inoculation of immiscible Pb and In nanoparticles on the nanocrystallization and the crystallization sequence of Al$_{88}$Y$_7$Fe$_5$ is examined. The results show that the use of deformation processes and incorporated nucleation catalysts gives new insight on the crystallization kinetics and on strategies for the control of the microstructure and the phase formation sequence.

2 Nanostructure development

Many metallic glasses including Al-based systems require rapid solidification to avoid crystallization and to allow the formation of an amorphous phase. Fig. 1a shows the bright-field TEM image of an amorphous Al$_{92}$Sm$_8$ alloy produced by melt-spinning. Following amorphization by rapid quenching, many metallic glasses do not exhibit a clear glass transition signal upon heating. Instead, exothermic maxima develop that indicate a multiple stage crystallization as show in Fig. 1b [18] for an as-spun Al$_{92}$Sm$_8$ ribbon. Microstructural analyses have established that the primary crystallization peak with an onset at 172°C corresponds to the development of a high number density of almost pure Al-nanocrystals within an amorphous matrix [3,4]. The sharp exothermic peak at higher temperature is attributed to the crystallization of the remaining amorphous matrix with the formation of Al-rich intermetallic phases.

![Figure 1](image)

**Figure 1:** a) Bright-field TEM image and corresponding SAED pattern of as-spun Al$_{92}$Sm$_8$ ribbon. The analyses do not show any signs of crystallinity. b) Continuous DSC trace of as-spun Al$_{92}$Sm$_8$ at 20°C.min$^{-1}$ [18]. The crystallization occurs in two steps. The primary crystallization peak with an onset at 172°C corresponds to the development of a high number density of Al-nanocrystals in the amorphous matrix. The second peak is attributed to the crystallization of the remaining amorphous matrix.

The origin of the Al-nanocrystal development in such systems is still a matter of discussion since it is somewhat unexpected that crystallization would favor the Al solution phase as the primary reaction product over an Al-rich intermetallic phase. In this respect, the formation of
Al-nanocrystals has to be examined in terms of a kinetic competition during nucleation. For the most part the competition is largely determined by the relative magnitudes for the activation barrier for nucleation, $\Delta G^*$ which is proportional to $(\sigma_{ls})^3/(\Delta G_v)^2$ where $\sigma_{ls}$ is the liquid-solid interfacial energy and $\Delta G_v$ is the driving free energy for nucleation. In the present case of nucleation reactions that involve solute partitioning, the maximum value for $\Delta G_v$ is determined by the parallel tangent construction [20]. The result of the parallel tangent analysis at the crystallization temperature of 172°C (Fig. 2 [21,22]) clearly demonstrates that over the composition range of glass formation the Al$_{11}$Sm$_3$ intermetallic phase is favored by almost a factor of two in terms of $\Delta G_v$.

Since the Al solution phase crystallized first, two alternative explanations could be given: the value for $\sigma_{ls}$ for Al$_{11}$Sm$_3$ is almost 50% higher than that for the Al solution (which is not likely) or there is a strong heterogeneous nucleation catalysis to favor the Al phase by reducing the $\Delta G^*$ magnitude. This examination of the kinetic competition during primary crystallization suggests that the presence of quenched-in nuclei plays a controlling role in the devitrification of Al-base amorphous alloys, as proposed earlier [4,18].

In order to study the early stages of nanocrystal development, isothermal microcalorimetry measurements of as-quenched Al$_{92}$Sm$_8$ have been performed at temperature near $T_g$. An advantage of low temperature isothermal measurements is a slowing of the nanocrystallisation reaction to allow for the monitoring of the transformation process on long time scales and a minimization of instrument transient effects. Moreover, low temperature treatment yields a small heat evolution that is below the detection level of DSC instrument but can be readily measured in a microcalorimeter. The measured isothermal heat flows at 120°C and 130°C are given in Fig. 3.

For these measurements, the microcalorimeter has been equilibrated at the respective temperatures prior to the insertion of the specimen. Thus, it was ensured that the microstructure did not change before the onset of the microcalorimetry measurement. The baseline measured for about 7 days indicates the absence of any instrumental
transient effect that exceeds the scatter of the data (0.025 μW/h). Under identical conditions, the temperature of the samples was maintained with an accuracy better than 2x10⁻⁴°C. The sample measurements show a monotonically decreasing signal as well as the absence of any maximum in the heat flow signal indicating that the development of Al-nanocrystals within an amorphous matrix is controlled by diffusional growth and not by a nucleation and growth process [23]. Similar conclusions based on experimental measurements [18] and kinetics analyses [4] have been reported earlier. The investigations clearly provide strong indications for the role of quenched-in nuclei in nanocrystal formation. It appears that the initial quenching process is not sufficiently rapid to completely prevent the formation of nuclei. Then, a cluster distribution with an average size larger than the critical size for growth at large undercooling could be retained in the material after the rapid quench. However, crystallites can not develop due to the rapidly rising viscosity with continued cooling. By subsequent heating a sample containing quenched-in nuclei, rapid crystallization ensues at the glass transition which then roughly coincides with the crystallization temperature [24].

3 Impact of processing pathways on the nanocrystallization in as-spun Al₈₈Y₇Fe₅

3.1 Thermally-induced nanocrystallization

Rapidly quenched Al₈₈Y₇Fe₅ glassy ribbons of about 40 μm in thickness were produced by melt-spinning using a single-roll melt spinner with a copper roll [25]. The DSC signal of the as-spun sample in Fig. 4a shows a primary crystallization peak at about 276°C that corresponds to the formation of Al-nanocrystals. As illustrated in Fig. 5a, samples held at 245°C for 10 min show small spherical nanocrystals with a size of approximately 15 nm in the amorphous matrix. As further growth of nanocrystals proceeds, the initially spherical nanocrystals develop a dendritic shape and the nanocrystal number density increases significantly (Fig. 5b). As reported earlier [19], values as high as 10⁻²¹ m⁻³ are reached in as-spun Al₈₈Y₇Fe₅ after annealing at 245°C.

![Figure 4: Continuous heating DSC traces at 20°C min⁻¹ of a) as-spun Al₈₈Y₇Fe₅ and samples that have been annealed at 245°C for 30 min, 60 min and 300 min, respectively. b) as-spun Al₈₈Y₇Fe₅ and samples that have been cold-rolled to true strains, ε = -1, -2 and -4, respectively. An exothermic signal in addition to the nanocrystallization of Al is detected for both annealed and cold-rolled samples. This signal is related to the formation of a so-called “transient” phase and disappears after annealing for 300 min or after extended rolling (ε = -4).](image-url)
The development of the Al-nanocrystals is accompanied by the slow disappearance of the primary crystallization signal with increasing annealing time, indicating the sluggish growth of the nanocrystals (Fig. 4a). The combination of two effects, the rejection of the solute during nanocrystal growth and the large difference of the component diffusivities, cause the formation of pronounced concentration gradients at the interface of the growing nanocrystal that account for the dendritic morphologies and the stabilization of the nanoscale structure. This result has also been shown by direct experimental analyses using atom-probe measurements [26] and by the modelling of the crystallization kinetics [4]. Moreover, the high density of the Al-nanocrystallites causes a soft impingement of overlapping diffusion fields between neighboring nanocrystals at rather early stages of the nanocrystallization that contributes to the sluggish nanocrystal growth. The significant changes in the thermal responses in Figs. 4a,b that show an additional exothermic signal with an onset at about 320°C are related to the formation of a so-called “transient” phase. This point will be discussed in section 4.

3.2 Deformation-induced nanocrystallization

Cold-rolling

The experimental procedure used to produce cold-rolled Al$_{88}$Y$_{7}$Fe$_{5}$ from as-spun ribbons has been described in detail previously [27]. The thermal responses of as-spun and cold-rolled Al$_{88}$Y$_{7}$Fe$_{5}$ to true strains of -1, -2 and -4 are reported in Fig. 4b. As observed for annealed Al$_{88}$Y$_{7}$Fe$_{5}$, the DSC signal corresponding to the primary crystallization peak vanishes with increasing true strain.

![Figure 5: TEM images of Al$_{88}$Y$_{7}$Fe$_{5}$ a) and b) Bright-field and corresponding SAED images of as-spun samples that have been annealed at 245°C for 10 and 60 min, respectively, c) Dark-field and corresponding SAED images of an as-spun sample that has been cold-rolled to a true strain of $\varepsilon = -10$. Both, thermal treatments and plastic deformation induce the development of Al-nanocrystals. The Dark-field TEM images in the inset show the shape evolution of nanocrystals from a spherical to a dendritic morphology with increasing annealing time.](image)

The dark-field TEM image (Fig. 5c) of a sample that has been cold-rolled to a true strain of -10 shows that the plastic deformation of as-spun ribbons induced nanocrystallization even at a low strain-rate of about 0.01 s$^{-1}$ since Al-nanocrystals can develop with a high number density ($10^{21}$ m$^{-3}$ [28]) with the same magnitude as thermally-treated samples [19]. Subsequent annealing at 220°C for 10 min increases the number density by a factor of 10 indicating the effectiveness of the cold-rolling in promoting Al-nanocrystal formation since as-spun samples thermally treated under the same conditions do not show any crystallites [28]. Experimental observations in amorphous Al$_{90}$Gd$_{5}$Fe$_{5}$ alloys [7] have demonstrated that bending the sample induces the formation of shear-bands that are likely sites for the crystallization to occur. It
was also suggested that the formation of crystallites is caused by a local heating, possibly in shear-bands, but a theoretical analysis of nanocrystallization during nanoindentation of a Zr-based bulk glass revealed a negligible temperature increase above room temperature in shear-bands [11]. Since nanocrystals appear to be distributed homogeneously throughout the sample, the nanocrystal development appears to be not limited to shear-bands in the rolled Al_{88}Y_{7}Fe_{5} ribbons to a true strain of -10. Moreover, samples that have been rolled with liquid nitrogen in the roll gap show the same thermal response as samples that were rolled at room temperature [27]. These results indicate that although shear-bands are not observed for the cold-rolled Al_{88}Y_{7}Fe_{5} ribbons, the nanocrystal development during rolling is not induced by thermally activated processes. Yet, the development of a high density of nanocrystals could be attributed to a dynamic steady-state with the creation and the disintegration of nanocrystals during the deformation process [29]. Alternatively, the shear-bands could not be resolved by the TEM analyses since the low difference of the densities between the shear-bands and the surrounding region renders the detection difficult.

Severe plastic deformation

Al_{88}Y_{7}Fe_{5} disks of 8 mm in diameter and 0.2 mm in thickness were prepared by high pressure torsion straining (HPT), subjecting the as-spun ribbons to five whole turns under an applied pressure of 6 GPa. XRD measurements have confirmed the development of a high number density of Al nanocrystallites since intense peaks were observed in addition to the broad maximum corresponding to the remaining amorphous Al_{88}Y_{7}Fe phase. From the XRD spectrum, the average crystallite size was determined as \( D_{av} = 10 \pm 2 \) nm.

Figure 6: Continuous DSC traces at 20°C.min^{-1} of Al_{88}Y_{7}Fe_{5} disks prepared by the HPT process. a) HPT sample. The signal shows a small decreasing heat flow until about 220°C partly attributed to relaxation processes. b) HPT sample annealed at 200°C for 60 min. The signal does not show significant changes compared to the non pre-annealed HPT sample (a). c) HPT disk that has been cycled twice up to 220°C and subsequently heated up to 320°C. The thermal response reveals the presence of a small exothermic peak with an onset at about 222°C corresponding to the primary crystallization peak.

Fig. 6a presents the thermal response of a HPT sample. The sharp exothermic peaks at temperature above 350°C are linked to the formation of intermetallic phases also obtained after heating as-spun Al_{88}Y_{7}Fe under similar conditions. The signal of HPT Al_{88}Y_{7}Fe_{5} does not show a markedly primary crystallisation peak, as observed for the as-spun sample (Fig. 4a), but a small decreasing heat flow at temperatures below 220°C. This is mainly attributed to strain relaxation since the HPT process induces a large amount of additional strain that can
later relax upon heating. In order to minimize the relaxation contribution to the DSC signal, the HPT sample was cycled twice up to 220°C and subsequently heated up to 320°C. The thermal response depicted in Fig. 5c reveals the presence of a small exothermic peak with an onset at about 222°C that is close to the observed shift for the primary crystallization peak of cold-rolled Al₈₈Y₇Fe₅ at the true strain of -4 (Fig. 4b). In agreement with the onset temperature of the primary crystallization peak, a sample was annealed at 200°C for 60 min and subsequently heated up to 450°C (Fig. 6b). No significant changes in the DSC response are observed, compared to the signal of the non pre-annealed HPT sample (Fig. 6a). Moreover, both signals do not show any exothermic peak at about 320°C as observed in Figs. 4a,b for rather shortly annealed samples and for cold-rolled samples, that indicates a high thermal stability of the sample subjected to plastic deformation at very large strains.

While the amorphous nature of the as-spun Al₈₈Y₇Fe₅ was clearly evidenced by TEM analyses, typical microstructures associated with the severely deformed samples reveal that an extremely high number density of nanocrystals develops as shown in the dark-field image in Fig. 7a. The evaluated nanocrystal size of about 12 nm is consistent with that obtained from XRD data. The inserted SAED pattern depicts spots and a halo corresponding to α-Al reflections and the remaining amorphous Al₇YFe phase, respectively. The HRTEM micrograph and the corresponding Fast Fourier Transformation (FFT) in Fig. 7b show the {111} Al lattice fringes that are surrounded by the amorphous phase and the <111> Al reflections, respectively. The number density of Al-nanocrystals has been determined. Particles have been counted from a dark-field TEM image. The sample thickness was determined by Electron Energy Loss Spectroscopy (EELS) [30]. The number density thus obtained amounted to about 10^22 m⁻³. This has to be regarded as a lower limit since some particles have certainly been omitted from counting due to a low contrast. Taking the different experimental uncertainties into account results in a cumulative error of a factor of 2 in the number density value.

The results shows clearly that, despite the errors involved in the counting, the increase of the nanocrystal number density after severe plastic deformation process is remarkable since the value is about 10 times higher than the extreme number density already presents after cold-rolling at a true strain of -10 or after annealing at 245°C (Fig. 5a-c).
3.3 Inoculation by immiscible Pb or In

Based upon the experimental results discussed above and previous investigations [18], it is apparent that the formation of the extreme nanocrystal number densities in Al-based glasses is inherently coupled to the presence of a high initial nucleation site density. A new approach in enhancing the nanocrystal number density, and thus to improve both property performance and microstructure stability, is to promote quenched-in nuclei in the undercooled melts. One opportunity is given by small variations of the processing pathway such as the precipitation of an immiscible liquid component, as reported for Al and Fe-based alloys [31,32]. For this reason, 1 at% Pb and 1 at% In were substituted for Al in Al$_{88}$Y$_7$Fe$_5$ during melt spinning. Both elements are not reported to form stoichiometric compounds with the other constituent elements and are immiscible in the majority component, i.e. in Al. Moreover, the difference of the melting temperature of both elements could affect the crystallization sequence differently since Pb melts at a temperature above the onset temperature of the primary crystallization in Pb-free samples and In melts at a lower temperature. The thermal responses of as-spun Al$_{87}$Y$_7$Fe$_5$Pb$_1$ and Al$_{87}$Y$_7$Fe$_5$In$_1$ alloys are depicted in Figs. 8a and 8b, respectively. The primary crystallization peak that appears in the first heating run displays strong shifts to lower temperatures and does not display a relatively sharp onset but a gradual decrease of the heat flow at the beginning of the reaction as well as a wider temperature range compared to the thermal response of as-spun Al$_{88}$Y$_7$Fe$_5$ (Fig. 4a). In the second heating run, small endothermic peaks are detected (dotted squares) that correspond to the melting of Pb (Fig. 8a) and In (Fig. 8b and enlargement in the inset), respectively.

![Figure 8](image_url)

**Figure 8:** Two successive continuous heating DSC traces at 20°C min$^{-1}$ of a) as-spun Al$_{87}$Y$_7$Fe$_5$Pb$_1$ and b) as-spun Al$_{87}$Y$_7$Fe$_5$In$_1$. The thermal responses show in both cases a marked shift of the primary crystallization peak to lower temperatures. The endothermic peaks in the frame (dotted square) indicate the melting of Pb and In that are detectable in the second heating run. An enlargement of the In melting peak is given in the inset of the figure b. Both peaks shift to lower temperatures.

It is worth noting the reduction of both melting points compared to those of the bulk elements that is related to the nanosizes of Pb and In particles and the presence of the crystallized AlYFe matrix. The melting point modifications of Pb and In at small sizes have also been reported in as-spun Al-Pb and Al-In alloys as a consequence of the inoculant particles sizes and morphologies [33, 34].
The significant shifts of the primary crystallization reaction indicate that the incorporation of Pb and In particles into the ternary alloy alters the nucleation and growth conditions of the Al-nanocrystals. These results are consistent with previous TEM investigations [6] that have shown the effectiveness of Pb particles to promote the development of nanosized Al since an annealing at 245°C for 10 min enhances the number density by a factor of 10, compared to Al<sub>88</sub>Y<sub>7</sub>Fe<sub>5</sub> thermally treated under similar conditions. Al-nanocrystals forming on Pb particles have been observed, demonstrating that the Pb nanoparticles act as heterogeneous nucleation sites increasing the nucleation rate by lowering the energetic barrier. However, careful analysis has shown that a large amount of Al-nanocrystals are not attached to Pb nanoparticles, suggesting that in addition to conventional heterogeneous catalysis, other mechanisms have to be taken into account for a full description of the nanocrystallization process. Especially, the fact that the inoculants introduce a large amount of interface area which acts to decrease the heat transfer during quenching needs to be considered. This effect leads to a slowing-down of the local cooling rate, which promotes the retention of additional quenched-in nuclei. By subsequent thermal treatments, additional Al-nanocrystals can develop that contribute to the increase of the number density. The shift of the primary crystallization reaction in In-containing samples agrees with this latter interpretation. Indeed, a heterogeneous nucleation reaction on the In particles is unlikely since Al-nanocrystals develop upon heating in an amorphous matrix containing liquid In particles. However, the more pronounced decrease compared to the Pb-containing samples remains surprising, suggesting that additional mechanisms could impact the nanocrystallization process. Thus, the significant changes in the DSC signals (Figs. 8a,b) coupled to the different melting behavior of Pb and In indicate that the inoculant particles have a large impact on the kinetic balance between crystallization and vitrification during rapid quenching that controls the generation of the nanocrystal dispersion.

4 Phase sequence control during devitrification of as-spun Al<sub>88</sub>Y<sub>7</sub>Fe<sub>5</sub>

The impact of thermal treatments and mechanical deformations on the phase formation sequence during devitrification of glassy Al<sub>88</sub>Y<sub>7</sub>Fe<sub>5</sub> has been investigated. The calorimetric signals given in Fig. 4a show an additional maximum in the range of 320-360°C for all Al<sub>88</sub>Y<sub>7</sub>Fe<sub>5</sub> samples that have been annealed at 245°C and that was not observed in the as-spun samples. Moreover, samples that were annealed for 300 min did show a marked decrease of the crystallization signal of this additional phase during subsequent heating experiments. DSC measurements of cold-rolled samples yield similar results (Fig. 4b). The additional signal is detected for true strains of -1 and -2, respectively and disappears at a higher true strain (ε = -4). In both, annealed and cold-rolled samples, the appearance of the additional signal is coupled with the decrease of the primary crystallization peak indicating that the slow Al-nanocrystal growth occurs with the precipitation of a so-called transient phase. XRD measurements of as-spun samples that had been continuously heated up to 348°C did not show any crystalline phase except the Al-nanocrystals [25]. In contrast, XRD measurement on samples that had been annealed at 245°C for 60 min and that were subsequently reheated up to 355°C exhibited strong peaks in addition to the Al-reflections that correspond to the formation of a so-called transient phase (Fig. 9). The same pattern was obtained from cold-rolled samples at ε = -2 followed by isothermal annealing at 325°C for 4 min. In order to analyze the reason for the nucleation of the transient phase, TEM analyses have been performed on samples annealed at 245°C for 60 min and subsequently reheated up to 355°C. The observations have shown that such treatments produce a large nanocrystal volume fraction within the residual amorphous phase [25]. As shown in Figure 10, the sample regions
surrounding a nanocrystal exhibit the presence of fringes that cannot be attributed to the fcc-Al and that correspond to the transient phase. Detailed analyses indicate that the interface between the Al-nanocrystal and the transient phase seems to be semi-coherent indicating that the transient phase nucleated at the Al-nanocrystal/glass interface. This situation can be analyzed within the framework of nucleation in a concentration gradient as proposed by Desré [35]. After short time annealing (e.g. during heating the as-spun material at a constant rate), the resulting concentration gradient is rather steep [4] and prevents the formation of any additional phase near the interface. Moreover, the width of spatial regions that have a composition suitable for the nucleation of an intermetallic phase can be smaller than the critical radius for nucleation. However, the diffusion fields are broadened if limited interdiffusion has occurred during a pre-annealing treatment. The resulting decrease of the concentration gradient involves two effects: the activation barrier for nucleation is decreased and the spatial regions of compositions that allow the nucleation of an additional phase with limited stability range are broadened. Thus, nucleation and growth of metastable phases are expected to be favored during the development from initial sharp gradients towards full diffusional equilibrium. At the late stages of the interdiffusion process, the solute concentration along the diffusion path is not sufficient for the nucleation of metastable phases. Thus, the nucleation of the stable phase is again favored and – as observed experimentally - the calorimetric signal due to the formation of the transient phase disappears after long annealing periods (Fig. 4a,b).

Figure 9: Al_{88}Y_{7}Fe_{5} that has been annealed at 245°C for 60 min and subsequently heated at 20°C min^{-1} up to 355°C. The XRD pattern shows additional peaks (●) to the Al-reflection peaks (│) corresponding to the transient phase.

Figure 10: High resolution TEM of Al_{88}Y_{7}Fe_{5} annealed at 245°C for 60 min and re-heated up to 355°C. The image of the boundary region of an Al-nanocrystal shows lattice fringes in the matrix surrounding the Al-nanocrystal that correspond to the transient phase.

Thus, the present results are in complete qualitative agreement with the conclusions drawn from the concept of nucleation in a concentration gradient [35], indicating the existence of a critical value of the concentration gradient that favors the nucleation of the transient phase. Moreover, these results indicate a new opportunity for the selection of a nucleating phase, since the phase formation sequence can be modified by controlling the concentration gradient at the interface.
5 Summary

The achievement of new types of marginal glass-forming systems such as Al$_{92}$Sm$_8$ and Al$_{88}$Y$_7$Fe$_5$ has extended the understanding and the description of the kinetics of the nanocrystallization process underlying the nanostructure development. The combination of different synthesis routes and analysis methods indicate that the nanocrystal development during the primary crystallization reaction is related to the formation of quenched-in nuclei. During the diffusional growth of the nanocrystals, the large disparities of the component diffusivities cause a soft diffusion field impingement between neighboring nanocrystals that provides for a kinetic stabilization of the nanoscale structure. Moreover, the experimental investigations clearly show that both thermally and deformation-induced nanocrystallization can be applied for nanostructure development in Al$_{88}$Y$_7$Fe$_5$. However, the microstructure control on the nanoscale, e.g. the increase of the nanocrystal number density, requires the control of the nucleation site density in the molten material. Here, severe plastic deformation and the incorporation of immiscible Pb and In particles into the Al$_{88}$Y$_7$Fe$_5$ melt have shown to be successful. The investigations highlight the possibility to synthesize ultrafine nanostructures by plastic deformation or inoculation of marginally glass-forming alloys. Moreover, it is demonstrated that the formation of a pronounced concentration gradient at the growing nanocrystal interface provides for the modification of the phase evolution sequence of the crystallization reactions. These investigations indicate the attractive opportunities, e.g. to produce specific microstructures and to the select nucleating phase by controlling the concentration gradient.

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7 References