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Early and late stages of demixing of a commercial Al-Li alloy

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A detailed *in situ* SAXS investigation is presented on the phase separation process in a commercial aluminum-lithium alloy. Taking advantage of conventional and synchrotron X-ray sources, it has been possible to probe both slow and fast kinetics. Both early and late stages of demixing are probed in a range of different temperatures between 75 and 200°C. The corresponding SAXS data are interpreted in terms of the currently accepted theories. The large temperature range covered in these measurements allows obtaining information on activated processes occurring in these materials. © *2002 Kluwer Academic Publishers*

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1. Introduction

Aluminum-lithium alloys are of outstanding relevance in the aeronautical industry, on account of their low density and high strength [1–9]. The increase in mechanical performance due to Li addition is related to the presence of a segregated coherent $L1_2$-δ' phase, which precipitates from the homogeneous solid solution at temperatures lower than the critical temperature. The segregated phase has an approximate composition corresponding to Al_3Li [8–12]. The nature of the whole phase separation process in isothermal conditions is of both practical and industrial relevance, as a consequence of the strong influence of this phenomenon on the macroscopic properties of the alloy.

A detailed knowledge of the nature of the whole process is then highly desirable as it would allow an understanding of and improvement in the performance of the material.

There has been a great deal of research relating to both the early [see e.g. 13, 14] and late stages [15, 16] of demixing in metallic alloys and understanding of the whole matter is constantly improving. Moreover, the possibility of accessing high brilliance X-ray sources is allowing more and more detailed investigations of the early stages of the fast processes [14].

In the last few years we have reported a series of structural characterizations of commercial Al-Li alloys, describing essentially the late stages of demixing and showing relevant structural details of the nature of the phase separation [7–9, 17–19]. We now report on detailed Small Angle X-ray Scattering (SAXS) measurements with higher temporal resolution performed on Al-Li alloys aged at a series of temperatures in the range 75–200°C. The kinetics at high temperatures are too fast for conventional SAXS devices, while the kinetics at low temperatures are definitively too slow to devote synchrotron beam line to an in situ study of the temporal evolution of the SAXS pattern. Accordingly, the low temperature aging has been studied with a conventional SAXS instrument, thus obtaining a temporal resolution of 15 minutes, while faster kinetics at high temperature were investigated using a synchrotron source collecting SAXS frames every 10–20 seconds. In this way a large kinetic regime has been covered, allowing the characterization of aging in a wide temperature range. In this report a general description of the results obtained during the early and late stages of demixing will be given concentrating mainly on the aging at the lowest temperature. In a following report the results obtained at higher temperatures will be described.

2. Experimental

The alloy studied was a commercial 2090 Al-Li sample (90.71 at.% Al, 8.00 at.% Li, 1.12 at.% Cu). The samples were solution treated at 520°C for 20 min in a molten salt mixture, in order to homogenize the microstructure. Samples were then quenched in a water-ethanol solution at ca. −20°C, and then kept at that temperature until shortly before use. Once ready for measurement, samples were moved to a thermostated sample holder, which allowed the temperature to be determined with a precision of ±1°C.

SAXS measurements for characterizing slow aging kinetics (i.e. for aging temperatures between 75 and

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150°C) were performed using the 10-m camera at the W. C. Kohler Centre for Small Angle Scattering at the Oak Ridge National Laboratory (USA) [20]. Data were collected with Cu K_α radiation, using different sample-to-detector distances depending on the aging temperature: accordingly the explored Q-range ($Q = 4\pi \sin\theta/\lambda$, with 2θ the scattering angle and λ the wavelength of the scattered radiation) was from 0.1 to 4.8 nm^{-1}.

The sample scattering data, collected with a 2-D position-sensitive proportional detector of dimension $20 \times 20\ \mathrm{cm}^2$, were corrected for detector efficiency and background and then converted to one-dimensional radial averages. Further comparison with secondary calibration standards allowed the data to be converted to scattering cross sections per unit volume ($\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega\ (\mathrm{cm}^{-1})$) [21].

To probe the demixing kinetics at high temperatures, when the process is too fast to be followed with a conventional SAXS instrument, use was made of the high brilliance synchrotron sources, specifically the station 8.2 of the Synchrotron Radiation Source at the Daresbury Laboratory, Warrington, UK. Details of the storage ring, radiation camera geometry and data collection system can be found elsewhere [22]. The SAXS data were collected on a multiwire quadrant detector positioned at 3.5 m from the sample with a time resolution of 10 sec. To convert channels into momentum transfer values, scattering from a rat tail tendon standard was used.

3. Results and discussion

3.1. Early stages of demixing

Fig. 1 shows the time dependence of the SAXS pattern at the aging temperature of 75°C. These data have been collected on a conventional SAXS instrument and cover the different early and late stages of demixing, as indicated by the time dependence of the segregated phase volume fraction, ϕ, which saturates to a final value of approximately 0.17 at late aging times.

In Fig. 2, the time dependence of the SAXS invariant [23], Q_o, is reported for the temperature range 75–150°C. Q_o is defined as:

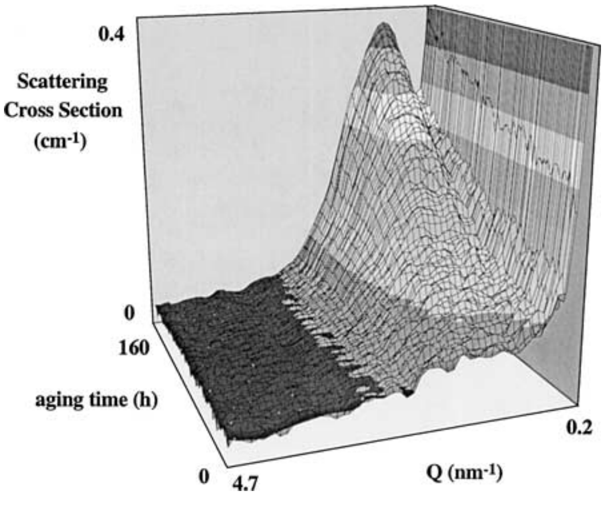

Figure 1 Time dependence of the SAXS pattern for 2090 Al-Li alloy, during thermal treatment at 75°C. The measurements span a period of ca 160 hours, while the Q range is between 0.2 and 4.7 nm^{-1}.

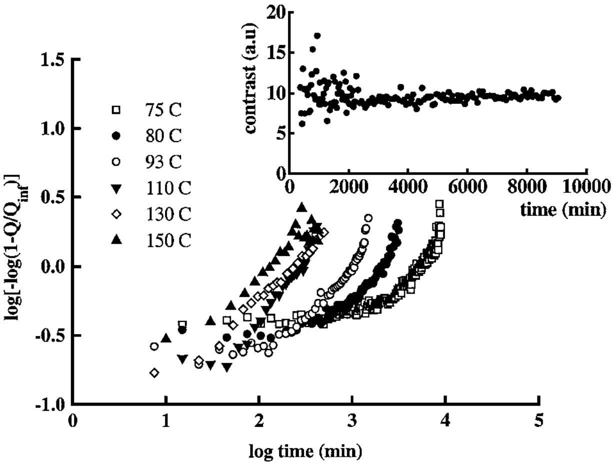

Figure 2 Time dependence of the SAXS invariant (on a $\log[-\log(1 - Q_\mathrm{o}/Q_{\mathrm{o},\infty})]$ vs $\log t$ scale) for the aging of 2090 Al-Li alloy at different temperatures in the range 75–150°C. In the inset the time dependence of the contrast between matrix and the phase segregated clusters is reported.

$$Q_\mathrm{o} = \int_{Q_\mathrm{min}}^{Q_\mathrm{max}} Q^2\, \mathrm{d}\Sigma(Q)/\mathrm{d}\Omega\, \mathrm{d}Q \qquad (1)$$

where Q_min and Q_max are the lowest and highest Q values covered by the measurements. Strictly values of 0 and ∞ should be used as the lower and upper integration limits. However for $Q < Q_\mathrm{min}$ and $Q > Q_\mathrm{max}$ the kernel in the integral was essentially equal to zero. Q_o is related to the microscopic details of the phase-segregated material according to:

$$Q_\mathrm{o} = \Delta\eta\phi(1-\phi) \qquad (2)$$

where $\Delta\eta$ is the electron density contrast between the homogeneous matrix and the phase segregated clusters and ϕ is the volume fraction of the minority δ' phase. Changes in the invariant can be attributed either to a change in the volume fraction of the minority phase or of the contrast, or to both of these effects. In the following, it will be shown that, apart from an initial change, the contrast soon saturates to a constant value, which is shown in the inset of Fig. 2. In Fig. 2 two different time regimes can be identified in that two substantially different slopes can be observed for the SAXS invariant. The same behavior can also be found at the other aging temperatures, although it is less obvious. It has been observed that during the second regime (long aging times) the contrast remains constant, and therefore the observed change in Q_o is entirely due to a change in the amount of the segregated phase. The SAXS invariant in the two regimes was fitted with a linear relationship. In Fig. 3, these fits are reported for the study at 75°C. A similar quality of fit has been obtained for the other aging temperatures. These results allowed a characteristic time, τ^*, i.e. the transition time when the SAXS invariant changes from one linear behavior to the other to be defined. The temperature dependence of such a parameter is reported in Fig. 4. It is noteworthy that τ^* shows Arrhenius-like behavior, thus indicating that the second process, occurring at a later stage, is an activated one. The energy barrier for this process is calculated to be 59.0 kJ/mol.

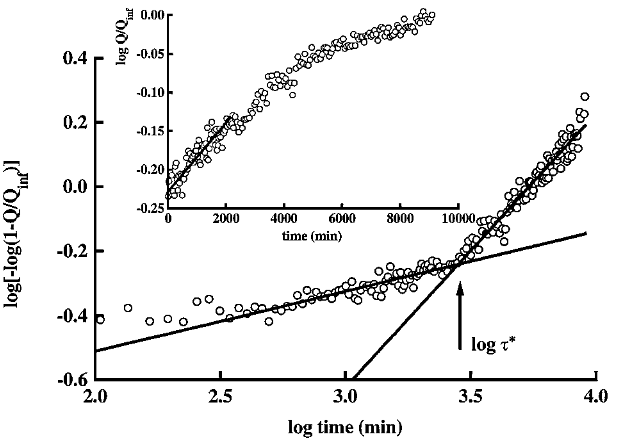

Figure 3 Representative description of the time dependence of the SAXS invariant (on a $\log[-\log(1 - Q_o/Q_{o,\infty})]$ vs $\log t$ scale) for the aging of 2090 Al-Li alloy at 75°C. The occurrence of a discontinuity at the characteristic time t^* is evident. In the inset the linear growth of $\log Q_o/Q_{o,\infty}$ with aging time during the early stages of demixing is shown.

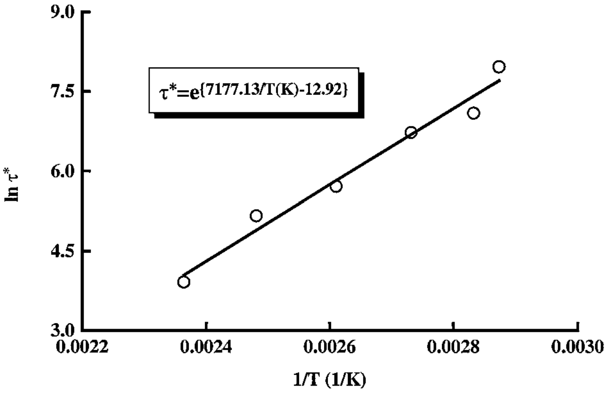

Figure 4 Arrhenius-like plot for the temperature dependence of the characteristic time t^*.

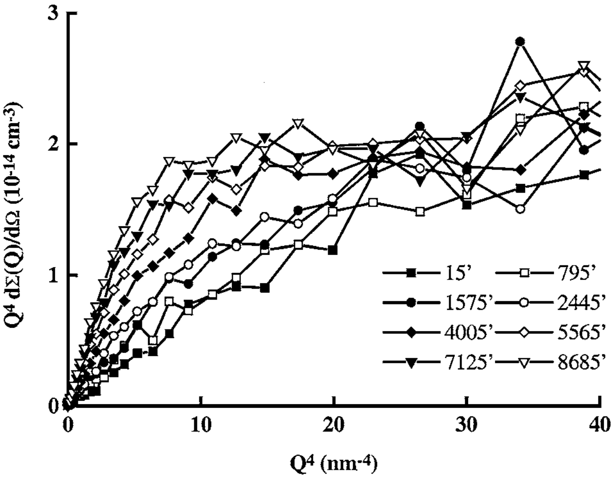

Figure 5 Time dependence of $Q^4 d\Sigma(Q,t)/d\Omega$ vs Q^4 at selected aging times for 2090 Al-Li alloy at 75°C. It can be observed that only at late stages (i.e. approximately $t > 4000'$), do the curve reaches a plateau, corresponding to the Porod regime.

It is interesting to relate the existence of an Arrhenius-like activated process to the final achievement of constant electron density contrast. This latter event is supposed to be related to the completeness of the phase separation process, which develops during aging.

Obviously, the occurrence of a dual mechanism during the phase separation process can be directly related to the well-known distinction between early and late stages of demixing. In the past, it has been shown that pure Al-Li alloys with Li contents equal to 9.5 and 11.4 at.% during the early stage follow a spinodal behavior [24]. In the present study a commercial Al-Li (i.e. containing non-negligible amounts of other components has been used). Moreover the nominal at.% content of Li corresponds to ca 8%, i.e., below the composition range explored in the past [24]. In order to check the early stage behavior of the present sample the Porod behavior was examined: it is well known that phase separating systems which follow the spinodal mechanism generally present continuously variation in the roughness of the interface between the matrix and the segregating clusters. Due to the spinodal mechanism, a transition from a diffuse to a sharp interface is expected. It is well known that using Small Angle Scattering techniques it is possible to characterize the nature of the interface. Accordingly, in the presence of a sharp interface, it can be expected that:

$$\lim_{q\to\infty} Q^4\, d\Sigma(Q,t)/d\Omega = \text{constant}, \tag{3}$$

where the constant value is related to specific surface of the interface. In Fig. 5 the time dependence of $Q^4\, d\Sigma(Q,t)/d\Omega$ vs Q^4 is reported for selected aging times. It can be observed that only in the late stages (i.e. approximately $t > 4000'$), do the curves reach a plateau, corresponding to the Porod regime. A similar observation [24] led to the conclusion that the early stages of demixing for Al-Li alloys are dictated by spinodal decomposition. In order to further check this hypothesis, the Cahn-Hilliard-Cook (CHC) approach [25–27] was used to describe the first stage of demixing. This approach rationalizes the early stage exponential growth of $d\Sigma(Q,t)/d\Omega$, according to the following relationship:

$$d\Sigma(Q,t)/d\Omega = d\Sigma(Q,0)\big/ d\Omega e^{2R(Q)t}, \tag{4}$$

where $R(Q)$ is the amplification factor and $d\Sigma(Q,0)/d\Omega$ is the scattering pattern of the quenched material, i.e. before the occurrence of any phase separation. Assuming an exponential growth as suggested by Equation 4, the time dependence of the invariant becomes

$$Q_o(t) = e^t \int_0^\infty Q^2\, d\Sigma(Q,0)/d\Omega\, dQ \tag{5}$$

Accordingly, the logarithm of the invariant should grow linearly with time if a time evolution of the form of Equation 4 is assumed for the early stages of demixing. In the inset of Fig. 3 a plot of $\log Q_o$ vs time is reported, showing the occurrence of a linear behavior in the early stages of phase separation.

Further tests for the validity of the CHC model were applied to the available data. In Fig. 6, the time dependence of $\log d\Sigma(Q,t)/d\Omega$ for selected values of Q is reported. The CHC model suggests that a linear behavior

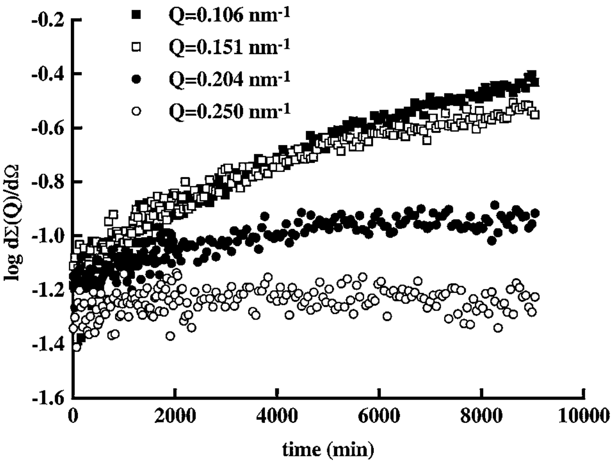

Figure 6 Time dependence of log $d\Sigma(Q,t)/d\Omega$ for selected values of Q during the aging at 75°C for 2090 Al-Li alloy.

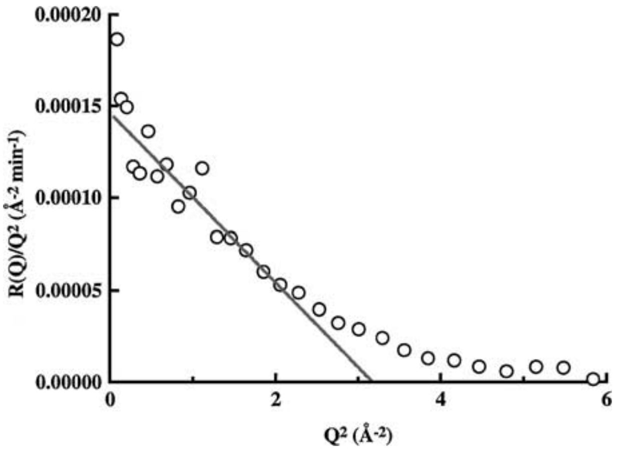

Figure 7 Q^2 dependence of $R(Q)/Q^2$. The linear regime in which CHC model is applied is shown.

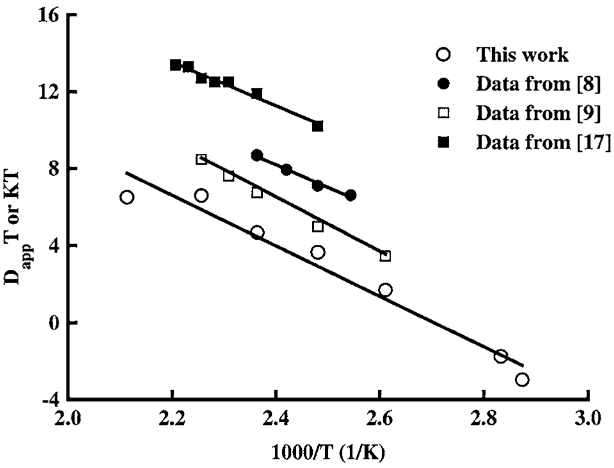

Figure 8 Temperature dependence of the apparent diffusion coefficient, D_{app}. For comparison, data from other SAXS characterizations are reported.

should be obtained for these plots, during the initial stage of spinodal decomposition. In Fig. 6, the slopes of the different curves at early aging times correspond to the values of the amplification factor, $R(Q)$, at the various Q's. In its simple form, which considers only linear terms in the diffusion equation, the CHC model implies that $R(Q)/Q^2 = -D_{\text{app}} - \alpha Q^2$, where D_{app} is the apparent diffusion coefficient and α is a term related to the Helmholtz free energy per unit volume of the system. In Fig. 7 $R(Q)/Q^2$ vs Q^2 is shown. From the CHC model, the intercept of the straight line across the linear portion of Fig. 7 corresponds to the apparent diffusion coefficient D_{app}, related to the diffusion process leading to the phase separation. Similar plots have been obtained for the early stages of phase separation during aging at different temperatures. At the highest temperatures, it was necessary to take advantage of the high brilliance of synchrotron radiation, as the phase demixing process occurred too quickly to be detected by means of conventional SAXS instruments. In Fig. 8 the temperature dependence of the apparent diffusion coefficient is reported for the whole range of temperatures investigated (in particular the two highest temperatures were investigated with synchrotron radiation, due to the high Li diffusivity at those temperatures). The occurrence of an Arrhenius-like behavior, with an activation energy of 110 ± 5 kJ/mol, can be observed. This value compares favorably with the activation energy reported for similar commercial alloys, investigating the late stage (coarsening) regime by means of SAXS [8, 9, 17]. Although the results reported in Fig. 8 refer to measurements collected in two different regimes (i.e. the early stage for data concerning the present report and the late stage in the other studies), we believe that this agreement is not at all fortuitous. The activated process is in fact the diffusion of the lithium atom, which is responsible for both the coarsening process and the spinodal decomposition. The observed agreement in the SAXS data is also an extension of the agreement in the whole body of data on coarsening behavior of the δ'-Al-Li phase in different Li-containing alloys, which is reviewed in ref. [28]. An activation energy for the coarsening behavior of 115 ± 4 kJ/mol, in excellent agreement with this result is reported. In a more recent work from Noble and Bray [29], combined use of Transmission Electron Microscopy and Electrical Resistivity led to the determination of the activation energy for the δ' coarsening in a A1-7.6 at.% Li alloy: these authors measured a value of 118 kJ/mol, again in good agreement with this result.

The measurements presented here suggest that the early stages of demixing for the 2090 alloy occur by means of spinodal decomposition, in the temperature range between 75 and 200°C. This result was not expected on the basis of the available literature [24].

3.2. Late stages of demixing

Having presented results for the early stages of the phase separation, attention is turned to describing the experimental evidence concerning the late stages of the demixing. A more detailed description will be presented in a forthcoming communication. Here results obtained for the aging at 75°C are presented. At this temperature, the coarsening process occurs very slowly, so that no relevant stresses are induced in the matrix due to the cluster formation and growth. Accordingly, almost spherical aggregates rather monodisperse in size are found at this temperature. In these conditions, the whole SAXS curve can be modeled in terms of intra-cluster and inter-cluster contributions [7], such that:

$$d\Sigma(Q)/d\Omega = N_{agg}P(Q)S(Q) + B/Q^4 + BKG, \quad (6)$$

where BKG is the incoherent background, B/Q^4 is a term describing the scattering contribution arising from inter-grain macro clusters [7], N_{agg} is the concentration of minority phase clusters, $P(Q)$ and $S(Q)$ being the monodisperse spherical particles Form Factor (FF) and the Structure Factor (SF), respectively [7]. Therefore, FF depends on the average particle diameter, R_{core}, while SF is calculated using the Percus Yevick approximation and is a function of the average interparticle distance, R_{str}, and of the volume fraction of the minority phase, η. For details of the analytical expression of FF and SF refer to e.g. [7]. The calculated scattering cross sections are in excellent agreement with the experimental data as shown in Fig. 9, where a typical fit for a sample aged at 75°C is reported. Fits of the same quality were obtained for all the data collected for aging periods in the coarsening regime. In Fig. 10 the time dependence of R_{core} and R_{str} is reported. As previously reported [9], the two parameters differ, but their ratio remains almost constant during the late stages and approaches the value of 1.4–1.5. The difference between these two parameters is related to the existence of the so called depletion zone and the fact that R_{core}/R_{str} remains constant indicates that during the coarsening the whole morphology evolves in a self-similar way [15]. Accordingly R_{core} and R_{str} show the same dependence with time, which is of the form $R \approx t^{-\alpha}$, with $\alpha = 0.14$. This power law is substantially different form the value expected from the Lifshitz-Slyozov (LS) model ($\alpha = 0.33$) [30], suggesting that the whole coarsening process may not follow the dissolution-condensation route. Finally, the occurrence of a discontinuity in their time dependence can be noticed around τ^*, this indicating that these parameters are also sensitive to the occurrence of a dual aging stage during phase separation.

In Fig. 11, the time dependence of the SAXS invariant, Q_o, and of the volume fraction, in the Avrami plot $(\log[-\log(1 - X(t)/X(\infty))]$, where $X = Q_o$ or $\eta)$ is reported. The ratio of the two quantities is the contrast between the minority phase and the matrix and its time dependence has been reported in the inset of Fig. 2. In this context it is also relevant to stress that both quantities show a discontinuity around τ^*.

To further describe the late stages of demixing, Fig. 12 shows the temperature dependence of Q_{max} and

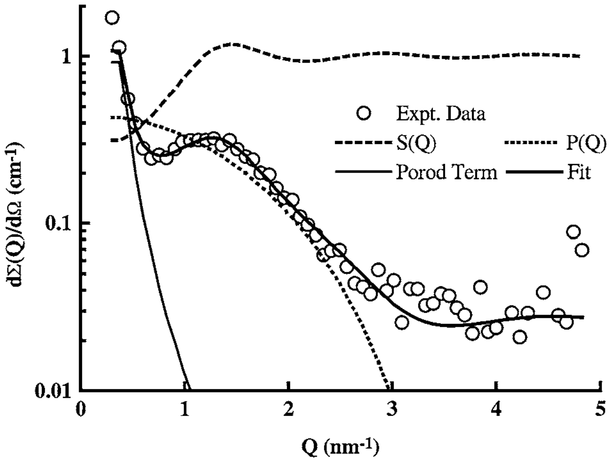

Figure 9 Typical fit of SAXS data for a 2090 Al-Li alloy during late stage of demixing at 75°C.

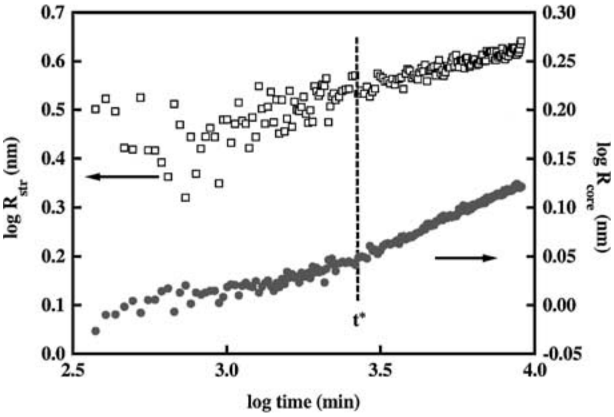

Figure 10 Time dependence of R_{core} and R_{str}, during the aging process of a 2090 Al-Li alloy at 75°C.

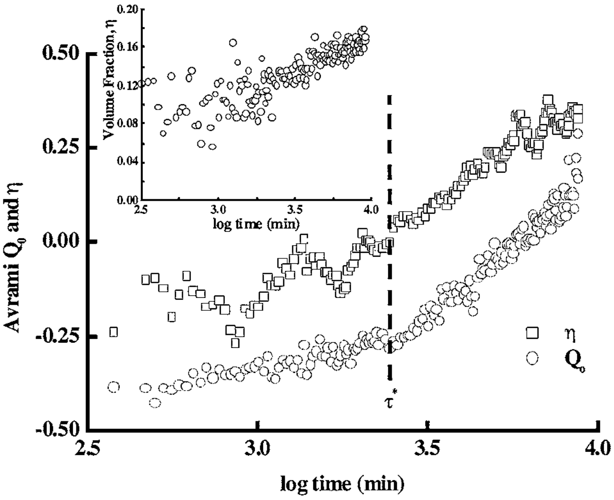

Figure 11 Comparison between the Avrami plots of Q_o and η during the aging of a 2090 Al-Li alloy at 75°C. In the inset, the time dependence of the Volume Fraction, η, is reported at the same temperature. It can be seen that η saturates at ca. 0.2 at long aging times.

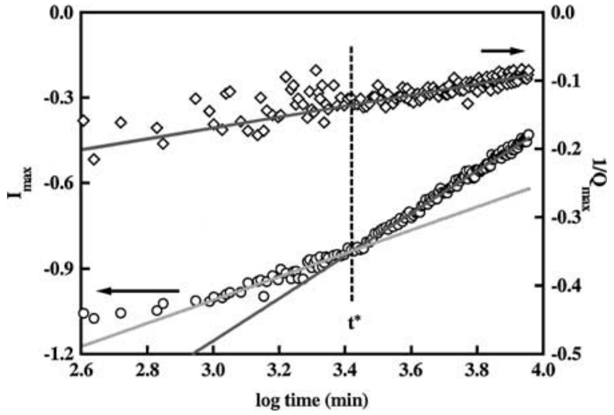

Figure 12 Time dependence of I_{max} and $1/Q_{max}$ during the aging of a 2090 Al-Li alloy at 75°C. The plotted lines are linear fits to describe the power law behavior.

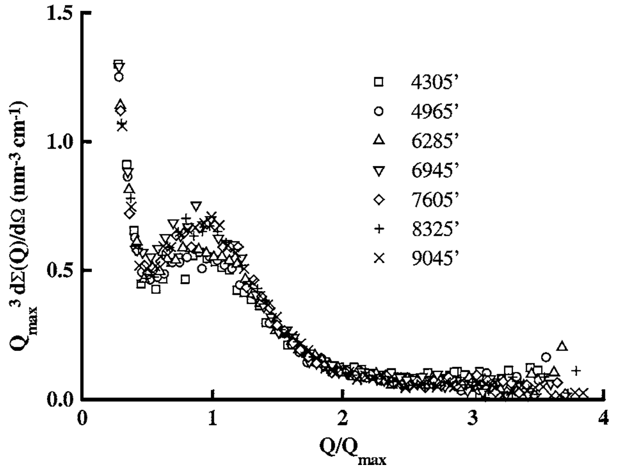

Figure 13 Test of dynamic scaling for the late stages SAXS pattern for the aging of a 2090 Al-Li alloy at 75°C.

$I_{\max}$ (the abscissa and ordinate of the peak in the SAXS pattern, respectively). Once more a discontinuity can be observed around τ^*, and a power law behavior is found for both the quantities. As already observed for R_{core} and R_{str}, in the late stages of demixing the LS law is not followed. $Q_{\max}$ follows an even slower time dependence than R_{core} and R_{depl} ($\alpha = 0.04$), while $I_{\max}$ shows a power law behavior: $I_{\max} \approx t^{\beta}$, with $\beta = 0.75$. Therefore the expected relationship: $\alpha = 3\beta$ is not followed.

Finally in Fig. 13, the validity of the dynamic scaling behavior [31–33] on the late stages of phase separation at 75°C is tested. $Q^3_{\max}\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega$ is plotted versus $Q/Q_{\max}$ and it can be appreciated that a substantial superimposition of the curves occurs when the late stages of demixing are considered. This result indicates that the growth of the minority phase occurs in a self similar way and that the only parameter changing during the aging is a scaling length, affecting the size distribution of the particles.

4. Conclusion

A detailed SAXS investigation has been reported for the early and late stages of phase separation in a commercial Al-Li alloy. The combined use of conventional SAXS instruments and synchrotron radiation allows both early and late stages in a fairly large aging temperature range to be examined. The transition from an early to a further stage has been identified and it has been shown to present an Arrhenius-like behavior.

The early stage of phase separation in the commercial material has been shown to occur via a spinodal decomposition mechanism. Much evidence supports this finding. The available data have been interpreted in terms of the CHC model and the apparent diffusion coefficient has an Arrhenius-like temperature dependence, with an activation energy which is very close to the one obtained from the investigation of the coarsening stage. This result suggests that the process involves lithium diffusion in the matrix.

The late stage of demixing has been described for aging at 75°C. A detailed fitting of the whole scattering curve in terms of a structural model has been presented and the corresponding fitting parameters allow a precise characterization of the time evolution of the morphology. Deviations from the evaporation-condensation mechanism for cluster growth has been found, although it was possible to establish the self-similarity of the growth by means of dynamical scaling.

Acknowledgments

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