Detection of nano-particles by dynamic dislocation-defect analysis

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Abstract. Dynamic dislocation-defect analysis is derived from precise determination of the activation volume \( \nu \) and distance \( d \). Upon precipitation of nano-particles of Al\(_6\)Fe in nominally pure aluminum, the Haasen plots can reveal their existence and a new activation distance plot can determine their magnitudes for specific obstacles from which particle size can be assessed.

1. Introduction

Nano-sized precipitates can be produced in nominally pure aluminum (Al) due to the low solubility of iron (Fe) but a special processing is required to overcome the low Fe diffusivity. This methodology first observed in electrical grade Al has been pursued and culminated in a quantitative kinetics of grain growth in very dilute Al-Fe alloys [1]. To achieve Fe solute levels below 1 ppm atomic, long-term anneals at 230 °C segregated Fe solutes to dislocations followed by Al\(_6\)Fe precipitation [2]. Subsequent anneals at 275 and 300 °C showed that three different levels of purity were attained [1] according to the phase diagram determined by precision strain rate sensitivity (PSRS) [3]. Furthermore the ultra-fine precipitates act as Zener drag on grain boundaries to limit grain growth resulting in continuous recrystallization (CREX) as described elsewhere [4]. Following this microstructural evolution, the thermodynamic response during tensile testing at low temperature was investigated. The Haasen plot determined by PSRS results in precise determination of the activation volume \( \nu \) such that it was shown that the up strain-rate change is sensitive to the strong obstacles, primarily the forest dislocations, whereas the down-rate change incorporates the weaker defects termed deformation debris [5]. On the other hand, the less thermally activatable obstacles such as fine particles give rise to a steeper slope in the Haasen plot during the initial (yield) or micro-strain region and its analysis has been described [3]. Most recently it was shown that a plot of the inverse work-hardening coefficient \( \theta \) versus the ratio of mean slip distance \( \lambda \) to the activation volume results in a slope which depicts the ratio of the activation distance \( d \) to the Burgers vector \( b \) [6]. The latter plot designated the activation distance diagram (ADD) together with the Haasen one and the log \( \lambda \) versus log flow stress \( \tau \) plot comprise the primary relations for dynamic dislocation analysis (DDDA) as shown below:

\[
\lambda = \phi \frac{b^2}{2} \frac{\partial \gamma}{\partial \tau} \tag{1}
\]

\[
\tau = \frac{\sigma_{\mu} b}{\ell} \tag{2}
\]
\[
\frac{d}{b} = \frac{(k/S)(d\theta^3)}{4 \mu} \approx \frac{\theta_{II}/\theta}{b^3 \lambda / \nu}
\]  
(3)

where \(\mu\) is the shear modulus at test temperature \(T\); \(\theta_{II}\), the Stage II work-hardening slope for [001] crystal; \(\phi = f(\alpha)\), a calibrating factor [6]; \(k\), the Boltzmann constant and others are defined in text or retain their usual meaning. The ADD of equation (3) is unique in that the inter-obstacle length \(\ell\) which inversely correlates to \(\tau\) intrinsically cancels since \(v\) is defined as \(db\ell\) and derived from the stress drop. Hence the only modeling parameter which is encompassed in this evaluation is \(\alpha\), the strength of obstacle parameter, which ranges from 0 to 1.0. For the dislocation-forest (D-F) interaction this value for Al is taken to be 0.4 [6]. Thus the ADD plot gives rise to the thermodynamic signature of the obstacles which are statistically being intersected by the mobile dislocations and elucidates the interpretation of the Haasen plot; whereas \(\lambda\) is a linear function of \(\alpha\) and is dependent on the choice of \(\sigma_0\) used to define the flow stress \(\tau\) from \((\sigma - \sigma_0)/M\) where \(\sigma_0\) is the proof stress at 0.02% strain and \(M\), the Taylor factor of 3.

In this report, the purest Al matrix achieved by annealing at 230 °C for 100 h (RC1 in Ref. [1]) were tensile tested at 78 K. To validate that fine precipitates exist, the DDDA of specimens which were annealed for CReX at 255 °C for 1, 3 and 12 h was compared to that of super-pure Al of large (300 µm) grain size. The results clearly show that particles in the nm range are present.

2. Experimental approach.

The 27 mm as-cast slab of chemical composition (Al-8Cu-43Fe-55Mn-5Ni-67Si-112Ti in ppm atomic) was homogenized for 48 h at 600 °C; processing details are found elsewhere [1]. Tensile specimens with gauge section of about 40 x 2.4 x 0.9 mm^3 with an etched-reduced section were prepared prior to annealing at 255 °C in a salt bath. The PSRS tests [3] were performed with strain rate changes of \(1/4\) and \(1/10\) down from \(6 \times 10^{-5} \text{ s}^{-1}\) with sustained strain intervals of about 0.5% prior to up-change determinations. The microstructure was examined by electron channeling contrast in a scanning electron microscope after electro-polishing coupons after various heat treatments. In this examination, the one-µm sized CReX grains could be clearly recorded but no particles could be detected by this means. As reported [1], grain growth in the prepared sheets underwent a two stage process whereby the initial one was very slow. Thus even after 12 h at 255 °C, the grain size was
about 2.3 µm. Super-pure Al was rolled after pre-cooling at 78 K but grain size smaller than 300 µm could not be attained by annealing at 80 °C for 2 h.

3. Results and Discussion
Figure 1 shows the Haasen plots derived from tensile testing of RC1 specimens aged at 255 °C for times t of 1, 3 and 12 h compared to that of super-pure Al which was recrystallized at 80 °C for 2 h. This figure shows that compared to the super-pure Al, the RC1 series manifests an initial steeper slope in the yielding process, the magnitude of which seems to increase with ageing time. The σ₀ for RC-1 series was larger compared to the super-pure Al due to the fine grain size and the expected presence of nano-particles. Previous analysis [3] had shown that the strain rate sensitivity for less thermal particles S_p can be calculated from \( (S_{D,F})^{2/3} \) and is tabulated in table 1. The particle size is inversely related to \( S_p \) and the plot in figure 2 reveals a coarsening kinetics of \( t^\kappa \) where theoretically \( \kappa \) is 0.33 for three dimensional ageing, 0.25 for interfacial and 0.20 for linear reactions. Although the derived value is 0.243 suggesting ageing within the grain boundaries, the particles which affect \( \sigma_0 \) are located within the grains. For particle size calculation, the parameter \( \alpha \) is involved as indicated in table 1 and it is expected to be larger than that for dislocations of the assumed 0.4 and its maximum is 1.0. Thus the change in particle size could affect the magnitude of \( \alpha \). For this reason log \( S_p \) versus log t was plotted, in case this effect of \( \alpha \) become obvious. The slopes corresponding to 0.33 and 0.20 is also shown to depict the possible range. The supposition is that Fe solute segregate to dislocations via Cottrell-Bilby [7] mechanism and precipitate by means of pipe diffusion during the preliminary anneal at 230 °C. During subsequent CReX the grain boundaries are stabilized by the pre-set precipitates which would coarsen by grain boundary diffusion but the intra-granular particles, if connected by the residual dislocation network after recrystallization, will coarsen by pipe diffusion. The current data is insufficient to resolve this subtle difference.

![Figure 2. Log plot of coarsening kinetics with inset of Table 1 depicting derived values.](image)

The role of fine particles should also manifest itself in the log \( \lambda \) versus log \( \tau \) plot as shown in figure 3. For the super-pure case, yielding as expected takes place with the grown-in dislocations widely spaced in the 10 µm range and decreases as the dislocation density increases with strain. However for the RC1 cases, the opposite effect is observed in the micro-strain region whereby the mean slip
distance increases from a minimum $\lambda_m$. For dislocation motion through randomly dispersed obstacles, the mean slip distance increases till slip becomes homogeneous [8]. This process of percolation [9] means that $\lambda_m$ is smaller than the mean inter-obstacle spacing. Examination of this model indicates that a typical value for $\ell$ is about 2 $\lambda_m$ and hence $\ell$ of 0.5 $\mu$m, results in calculated $\sigma_0$ of 40.8 MPa compared to the measured 70.12 MPa. The increase in $\alpha$ also imply an increase in the $\lambda_m/\ell$ ratio. Taking the case of very strong obstacles with $\alpha = 0.81$ [8] and $\lambda_m = \ell$, the calculated $\sigma_0$ of 101.6 MPa is found. Although both $\alpha$ and $\lambda_m/\ell$ are both directly related to the strength of obstacle defined by the internal angle between the bowing dislocation components around the obstacle, the models [8,10] has various geometrical terms which makes the predictions ambiguous.

The third aspect of the DDDA is the ADD plot shown in figure 4. The initial slope in units of $d/b$ is that from the micro-strain region and the second designated slope is the least square fit from the 1/10 up-change data-points, the response of which is attributed to dislocation-forest interaction [5]. The D-F $d/b$ values for all the specimens are near the 0.25 expected for the Peierls dislocation. Previously the value in Stage II for [001] Al crystal tested at 78 K was 0.35 which decreased to 0.22 during Stage III [6]. Hence the observed lower slope for the down-change data-points indicates the incorporation of debris as for Stage III. Thus the determinations in the higher strain regions are fairly self-consistent. In the micro-strain region for RC1, an effect is observed for the 12 h-age case wherein a zig-zag pattern is evident. This type of pattern was observed in age-hardening alloys [11] and may be due to punching out of loops around particles which are too strong to be cut through. Thus the passing dislocations intersect these very small weak loops with lower value of $\alpha$ [8] than the 0.4 used for data analysis. On the other hand the smaller zig-zag effect for the super-pure case must be due to the debris-loops left behind from the low temperature recrystallization temperature and hence manifest slopes similar to RC1 aged for 1 and 3 h. The lower $\alpha$ values for loops [8] means that a correction to the initial slope is required, which increases the $d/b$ determined by using $\alpha = 0.4$ since $\lambda$ is linearly related to $\alpha$.
Figure 4. $\Theta/\theta$ versus $b^{2}\lambda/\nu$ ADD plot derived from equation (3) depicting the $d/b$ values for the yield region and the dislocation-forest (D-F) interactions. The unfilled symbols are for up-change and filled ones for down-change. The square symbols indicate \( \frac{1}{4} \) change whereas the diamond the $\frac{1}{10}$ ones; the latter are used for all least square fits. The RC1 plots are offset for clarity.

4. Conclusion

The dynamic dislocation-defect analysis examines the interrelation of $\tau$ with $\theta$, $\alpha$, $\lambda$, $\nu$ and $d$. The activation distance can only be determined dynamically as illustrated to characterize the dislocation-defect intersection with thermal assistance. Using the dislocation-forest as a calibration factor, the obstacle species can be compared and their thermodynamic response categorized. In this manner, the formation of nano-sized $\text{Al}_6\text{Fe}$ precipitates were confirmed upon suitable heat treatment to getter the Fe solutes by segregation to dislocations.

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