Chemistry of grain boundary environments in nanocrystalline Al 7075

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ABSTRACT

Positron annihilation spectroscopy in two variants (coincidence Doppler-broadening CDB and lifetime spectroscopy LT) was used for the characterisation of severely deformed nanocrystalline 7075 Al alloy, with specific attention to the distribution of solute in the proximity of grain boundaries. The 7075 samples were deformed via the high pressure torsion (HPT) technique after solution treatment and quenching. The grain size at the end of the deformation was sub 100 nm. The deformed samples have undergone 3 months of natural ageing post-processing. CDB and LT measurements consistently indicate that the fraction of trapped positrons in these samples is near to 90%. The analysis of CDB data shows that the environment of the positron traps is enriched with solute up to 50 at.%, nearly evenly divided between Mg and transition metals (Zn and Cu). The CDB results indicate an enhancement of solute concentration at grain boundaries associated with HPT deformation.

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1. Introduction

Bulk nanostructured (NS) materials have high strength but low ductility [1]. Therefore, many efforts have been paid to develop strategies to improve the poor ductility of NS materials [2]. Among various strategies, introducing nano-precipitates in NS Al alloy matrix by low-temperature aging can enhance the ductility while further gaining rather than sacrificing the strength [3,4]. The phase transformation (i.e. precipitation) and diffusion processes of NS alloys are therefore of significant importance from viewpoints of both basic science and engineering application.

The solute segregation and precipitation kinetics in NS alloy might be altered by the presence of high-density lattice imperfections, such as dislocations and grain boundaries [5,6]. Three-dimensional atom probe tomography (APT) is ideally suited for observing these phenomena [7]. An alternative method for characterising the chemical environment of grain boundaries in nanocrystalline materials is coincidence Doppler-broadening (CDB) positron annihilation spectroscopy. When the grain size is significantly smaller than the positron diffusion length (of the order of 100 nm in Al), the largest majority of positrons are able to reach the grain boundaries, where they become trapped by misfit defects similar to vacancies. In these conditions, CDB spectra give information on the chemistry in contact with these defects [8].

2. Experimental details

Table 1 shows the chemical composition of the commercial 7075 Al alloy analyzed in a commercial laboratory (Luvak Inc., Boylston, MA).

The 7075 Al samples were solution treated at 480 °C for 5 h then quenched into water at room temperature to form coarse-grained (CG) solid solution. High pressure torsion (HPT) was performed immediately following quenching by applying 10 rotations under a pressure of 6 GPa at room temperature (RT) to obtain nanocrystalline (NC) 7075 Al alloy sample. The original HPT die used in this experiment allows processing samples with 20 mm in diameter (see Ref. [9]). Both solution-treated + quenched CG and HPT processed NC 7075 Al samples were naturally aged (NA) for 3 months before analysis.

Conventional transmission electron microscopy (TEM) was performed on a Philips CM12 operated at an accelerating voltage of 120 kV. The TEM specimens were prepared through electro-chemical and ion milling. The CDB and LT measurements and the analysis were carried out following procedures described elsewhere [8,10]. Total counts were more than 2×10^7 for each CDB measurement. The analysis of the CDB data, based on the fitting of the Doppler-broadening annihilation line with a linear combination of reference spectra taken for pure elements, with and without vacancies, gives an approximate evaluation of the positron trapping fraction F (fraction of positrons that are annihilated in the sample after having been trapped by vacancies or vacancy-like defects at misfit interfaces) and of the fractional concentrations of the elements in contact with vacant atomic sites. In the present case, the analysis did not include the minority elements as Fe, Si, Mn, Cr and Ti since these metals form relatively well dispersed particles [11] that are not expected to contribute significantly to positron trapping. They also do not play a

Table 1
Chemical composition of the 7075 Al alloy. Others elements <0.15 wt.%.

	Al	Zn	Mg	Cu	Fe	Si	Mn	Cr	Ti
at.%	93.6	2.55	2.89	0.61	0.08	0.11	0.006	0.10	0.01
wt.%	89.6	5.96	2.51	1.39	0.16	0.11	0.005	0.19	0.02

part in the ageing process. The fitting function therefore takes the form:

$$\rho_{fit} = (1 - F)\rho_{Al} + F(C_{Al}\rho_{Al}^{vac} + C_{Zn}\rho_{Zn}^{vac} + C_{Mg}\rho_{Mg}^{vac} + C_{Cu}\rho_{Cu}^{vac}) \qquad (1)$$

where ρ_{Al} is the experimental momentum distribution measured for annealed Al, ρ_{Al}^{vac}, ρ_{Zn}^{vac}, ρ_{Mg}^{vac}, ρ_{Cu}^{vac} the momentum distributions expected for vacancies in pure elements, as obtained from measurements on deformed samples after subtracting the contribution of annihilations from free positrons [10]. The fitting parameters are the trapping fraction F and the fractional concentrations C_{Al}, C_{Zn}, C_{Mg}, C_{Cu}. Here it should be noted that the above fractional concentrations are to be interpreted as representing the atomic composition in immediate contact with the vacancy where the positron is trapped. These values can differ from the average composition of the vacancy-solute aggregates.

3. Results and discussion

A bright-field TEM image of the NC 7075 Al sample, shown in Fig. 1, indicates that the grain size was refined to sub 100 nm by severe plastic deformation. Given the grain size of the NC 7075 Al sample is an order of magnitude smaller than the diffusion length of positrons in bulk aluminium (about 100 nm), grain boundary characterisation is expected to be the dominant source of data, although a minor contribution to F may also come from vacancies associated to solute aggregates (solute clusters, GP zones and precipitates) within the grains [8,12]. The results of a two-component analysis of the positron lifetime spectra in the NC 7075 Al samples are presented in Table 2. I_D is the fractional intensity of the long living component; the intensity of the other component (not reported in Table 2) is $I_{free} = 1 - I_D$. The lifetime τ_D, which is to be attributed to positrons trapped at open volume defects, is lower than the value obtained for vacancies and dislocations (typically between 225 and 245 ps) in pure Al [13,14]. This is a symptom of vacancy decoration with the transition metals Zn and Cu. The shorter lifetime τ_{free} must be interpreted as the mean survival time of a positron as a free particle in the matrix. According to the positron trapping model (PTM) [15]:

$$\tau_{free} = (\lambda_{bulk} + \kappa)^{-1}, \qquad (2)$$

where λ_{bulk} represents the annihilation rate of free positron in the bulk of the matrix and κ the trapping rate in defects. As a check of consistency of the two-component analysis with the PTM, Table 2
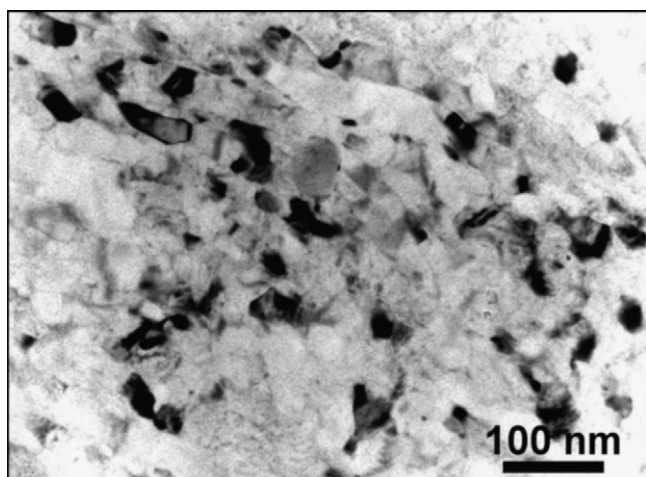

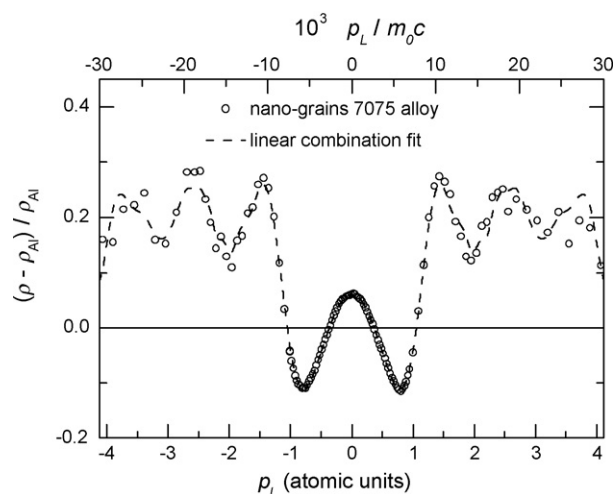**Fig. 1.** Bright-field TEM micrograph depicting the sub 100 nm grain size.

Fig. 2. CDB momentum distribution of the positron-electron annihilation radiation (relative difference to pure Al). The dashed line represents a fit with a linear combination of reference spectra for pure elements (see Ref. [8]).

includes the lifetime $\tau_{bulk} = \lambda_{bulk}^{-1}$, obtained from:

$$\tau_{bulk} = \left(\frac{I_{free}}{\tau_{free}} + \frac{I_D}{\tau_D}\right)^{-1}, \qquad (3)$$

which represents the reciprocal of the annihilation rate in the matrix and is expected to be near to the positron lifetime in bulk aluminium. The trapping fraction F, which was calculated in accordance with the PTM equation:

$$F = I_D\left(1 - \frac{\tau_{free}}{\tau_D}\right), \qquad (4)$$

is near to 90%. The high value of F is consistent with expectation for a nanocrystalline system, in agreement with previous LT analysis and estimations for other fine grain Al alloys [13], which indicate strong positron trapping at vacancy-like defects associated to grain boundaries. For the CG sample, no reliable two-component analysis of the lifetime spectrum was obtained. The average positron lifetime is, in this case, 214 ± 2 ps, which is slightly longer than in the UFG sample (about 210 ps). The difference may reflect the different morphology (free volume size) and chemical composition of the vacancy-like defects where the positrons are trapped. More information on the composition comes from CDB measurements discussed below.

Fig. 2 shows the CDB momentum distribution of the annihilation radiation in the NC 7075 Al sample. The data are presented by means of the relative difference function $(\rho - \rho_{Al})/\rho_{Al}$, where ρ is the momentum spectrum of the annihilation radiation measured in NC 7075 Al samples and ρ_{Al} is the reference momentum spectrum measured for annealed aluminium. The statistical noise has been reduced by averaging groups of three subsequent points from 1 to 2.6 atomic momentum units and of six points above 2.6 atomic units. This presentation is frequently adopted in CDB studies; it has the advantage of enhancing the details of the spectrum ρ in the low intensity tails at high momentum, where the information on the chemical species is more explicit. The dashed line is a fit with a linear combination of reference spectra obtained for samples of pure metals (Eq. (1)). The results of the best-fit procedure are presented in Table 3.

The fraction of trapped positrons from the CDB analysis confirms the independent LT result ($F \cong 90\%$). It also confirms that positrons trapped at grain boundaries probe an important amount of solute (above 50 at.%). Of the 12 nearest neighbours of a vacancy, about 6 are Al atoms; the remaining part is nearly evenly divided between

Table 2
Positron lifetime LT results. τ_D is the lifetime associated to defects obtained in the nanocrystalline 7075 Al alloy; I_D is the intensity of the spectral component associated to τ_D; *F* is the corresponding fraction of positrons trapped by defects according to the positron trapping model; τ_{free} is the lifetime of free positrons and τ_{bulk} is the bulk lifetime in the 7075 Al alloy matrix (the bulk positron lifetime for pure Al is 162 ps). The absolute statistical errors are included into the parenthesis.

Sample	τ_D (ps)	I_D	F	τ_{free} (ps)	τ_{bulk} (ps)
NC 7075 Al	219 (2)	0.95 (0.03)	0.89 (0.04)	10–20	155–170

Table 3
CDB results. *F* is the fraction of positron annihilated in vacancy-like defects and C_i is the average atomic fraction associated to defects. The absolute statistical errors are included into the parenthesis.

Sample	F	C_{Al}	C_{Mg}	C_{Zn}	C_{Cu}	$C_{Zn} + C_{Cu}$
NC 7075 Al	0.90 (0.02)	0.47 (0.02)	0.26 (0.02)	0.18 (0.03)	0.09 (0.03)	0.27 (0.02)
CG 7075 Al	0.64 (0.02)	0.08 (0.03)	0.32 (0.03)	0.55 (0.03)	0.05 (0.03)	0.60 (0.02)

Mg and transition metals (Zn and Cu). With the CDB method the separation of Zn and Cu is difficult, due to the similar electronic structure of these elements; however, the fit suggests that a balance of 2 atoms of Zn for each atom of Cu is highly probable.

Table 3 includes the results of the CDB analysis for the reference CG samples. In this situation, Guiner–Preston (GP) zones are formed (see Refs. [16–19] for a similar commercial alloy and Ref. [20] for a laboratory alloy). The fraction of positrons trapped by defects in the CG sample is lower than in the NC sample (64% against 90%). The environment of the positron traps is very rich in solute with a small presence of Al (only about 8 at.%). The most abundant solute is Zn (about 55 at.%). The dominant positron traps are expected to be vacancies, which are normally associated to GP zones in Al–Zn–Mg to minimize the internal energy.

The fractional solute concentration around vacancies in the GP zones of the CG 7075 Al sample formed at room temperature (RT) is different from the concentration associated to the positron traps in NC 7075 Al samples. The ratio $(C_{Zn} + C_{Cu})/C_{Mg}$ in the CG 7075 Al samples is 1.87 ± 0.15, in agreement with recent CDB determinations [8]. On the other hand, in deformed NC 7075 Al samples the ratio $(C_{Zn} + C_{Cu})/C_{Mg}$ ratio is 1.04 ± 0.05. The different composition of the environment of the positron annihilation site in NC and CG samples also indicates a different structure of the solute aggregates formed by segregation at grain boundaries or by dynamical precipitation near to grain boundaries. In this regard, it can be noted that several studies show that heterogeneous segregation and nucleation on dislocations and grain boundaries is promoted by the atomic movement generated during deformation [5,6].

4. Conclusions

1. The present study demonstrates that in NC 7075 Al samples positrons are strongly trapped at open volume defects where the environment is enriched with solute up to about 50 at.%.
2. The dominant positron traps are most probably localised at empty sites on large angle grain boundaries, but it is not possible to exclude a substantial contribution of vacancy-like defects associated with precipitates near to grain boundaries or inside the grains.

3. In deformed samples the Mg concentration in contact with the empty site is dominant above Zn and Cu.
4. In non-deformed materials, where the positron traps are vacancies deeply embedded in GP zones, the solute enrichment is even stronger (about 92 at.%).

Acknowledgements

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