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A positron annihilation study of Al–Li alloys

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Abstract. The interaction and recovery of deformation induced defects has been studied by positron annihilation techniques in the Al–1.7 at.% Li and Al–9.9 at.% Li alloys. The samples have been deformed at liquid nitrogen and room temperatures for several deformation degrees. In the low temperature region (100–200 K and 200–400 K) the two recovery stages observed in pure Al and phenomena currently interpreted as divacancy and monovacancy migration are present in both alloys. However, it is observed that the presence of Li enhances the vacancy clustering. The effect observed in the high temperature region (400–600 K) in the higher Li content alloy has been interpreted as trapping of positrons by δ' particles.

1. Introduction

Positron annihilation techniques (PAT) have been used extensively in the past to study defects in pure metals. Trapping of positrons has been observed at vacancies, vacancy agglomerates (voids and bubbles) and dislocations. A lot of information on these defect types (formation energy, creation and migration of certain defect types during annealing) has been obtained.

When studying dilute alloys with the PAT several supplementary effects must be taken into account, such as trapping at the precipitate–matrix interface, positron affinity for one of the components of the metallic alloy, and so on. In the past, positron annihilation proved to be an excellent tool for following precipitation processes (Dlubek *et al* 1986, Lühr-Tank *et al* 1987). Moreover, it is known that the addition of alloying elements can strongly affect the point defect behaviour in the matrix (Hautojärvi 1987) and, as a consequence, the response to plastic deformation.

Despite its potential utility in the study of alloys, the PAT has not yet been used as extensively as it has been up to now for the investigation of pure metals. Still, positron annihilation spectroscopy can bring valuable data to the study of submicroscopic effects in alloys.

We have undertaken this work on Al–Li alloys with the aim of going deeper into the potential utility of the PAT for the study of alloys. In addition to the interest of further extending the PAT for the characterization of submicroscopic defects in alloys, the study of Al–Li is itself attractive because of its technological interest.

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In the past few years, it has been recognized that adding lithium to aluminium results in a high strength alloy with applications in the aerospace industry. Adding Li to Al reduces its density and increases the elastic modulus. In the region of interest, the principal phases in the phase diagram are α (Al–Li in solid solution), δ' (Al_3Li coherent ordered phase) and δ (AlLi). It has been proposed by Silcock (1959–60) that precipitation in Al–Li alloys follows the sequence: α-phase (supersaturated solid solution), through the δ' Al_3Li phase to the δ AlLi phase. It is the presence of these phases that affects the mechanical properties of the material and its response to deformation.

In this work two types of Al–Li alloys (dilute and concentrated) will be studied. The interaction of defects after plastic deformation will be investigated using the PAT.

The affinity of the positron for the Li-rich zones is proved and the effect of Li on the behaviour of defects created by the deformation is discussed.

2. Experiment

The samples used in this study were Al–1.7 at.% Li and Al–9.9 at.% Li. Pure 5N Al samples were used as a reference. The alloy samples with 9.9 at.% Li were supplied by Alcan Ltd. The samples containing 1.7 at.% Li were prepared in the HMI für Kernforschung (Berlin) and the preparation method has been described elsewhere (del Río *et al* 1989).

The low-Li-content samples were homogenized at 820 K for one hour and then quenched at room temperature; the higher Li-content samples were homogenized at 820 K for one hour, then annealed at 510 K for four hours and finally quenched at room temperature. In order to remove the Li-depleted zone close to the surface, all samples were chemically polished prior to measurement.

The deformation of the pure Al sample and most of the deformation of the alloys were performed under liquid nitrogen by compression. For comparison, the alloys were also deformed at room temperature. The degree of deformation is indicated by the relative thickness reduction $\Delta D/D_0$, where D_0 is the initial thickness of the samples, whereas $\Delta D = D_0 - D$ is the absolute thickness reduction.

The positron source consisted of 10 μCi ^{22}NaCl between two 7.5 μm thick Kapton foils. This source was mounted between two identically deformed samples. The source–sample assembly was then mounted into a nitrogen flow cryostat. For the deformations under liquid nitrogen all those manipulations were performed under liquid nitrogen in order to prevent the samples from warming up before the measurements. During the measurements the samples were in a nitrogen atmosphere.

The Doppler broadening of the annihilation line was measured with an intrinsic Ge detector having a resolution of about 1.2 keV at the 511 keV annihilation line at a count rate of about 10^4 counts s^{-1}. Two point stabilization was used: the zero of the ADC was stabilized at 661.6 keV of ^{137}Cs. With a biased amplifier, all the pulses below 470 keV were cut off. The calibration was 0.05 keV/channel.

The annihilation line was characterized by the conventional S-parameter, which is defined as the fraction of full energy (i.e. photo peak) counts falling within a central integration window. The measurements were performed fully automatically: the measuring time was one hour, after which the temperature was changed and the data were transferred to the floppy disk of a PC-XT. Measurements were performed at the

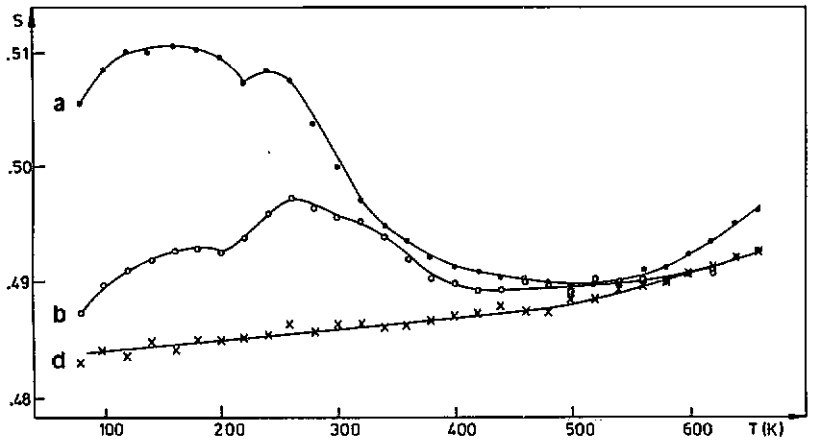

Figure 1. The *S*-parameter as a function of the annealing temperature in samples deformed at liquid nitrogen temperature: (*a*) ●: pure Al, 56% thickness reduction; (*b*) ○: alloy Al–1.7 at.% Li, 30% thickness reduction; (*d*) ×: annealed alloy in the interval 660–80 K.

annealing temperature in the interval 80–660–80 K in steps of 20 K. Transmission electron microscopy (TEM) observations have been performed on several samples in order to investigate their microstructure.

3. Results

As a reference, pure Al was deformed to obtain a 56% thickness reduction. The results are shown in figure 1(*a*). An annealing stage is seen from 80 K to 220 K. A very broad recovery stage extending from 220 K to 580 K is measured. During this stage deformation induced dislocations anneal out. Above 580 K an increase of the *S*-parameter is measured, this being due to the creation of thermal vacancies.

The results are in agreement with previous experiments performed in deformed pure Al (Segers *et al* 1985). It is noted that in pure Al trapping saturation is observed above 30%.

A pair of samples containing 1.7 at.% Li were deformed to obtain a 30% thickness reduction. The results are shown in figure 1(*b*). Both the annealing steps observed in pure Al at 170 and 250 K are present in the alloy, but here the second annealing stage is more prominent (as compared with the first).

In order to study the effect of the Li content during the annealing behaviour, an Al–9.9 at.% Li alloy has been deformed to a comparable thickness reduction (26%). The results are shown in figure 2(*b*). It is noted that the effect observed between 200 and 400 K is much more pronounced in comparison with the lower Li-content sample. A new effect, not present in pure Al, appears between 400 and 600 K.

To study the effect of saturation trapping, several degrees of deformation were performed on the Al–9.9 at.% Li alloys. The results for an 8% thickness reduction are shown in figure 2(*c*); the same annealing stages are present but the effect on the *S*-parameter in the temperature interval 200–400 K is reduced in comparison with that on the 26% deformed sample; a lower reduction is seen in the temperature range 400–600 K.

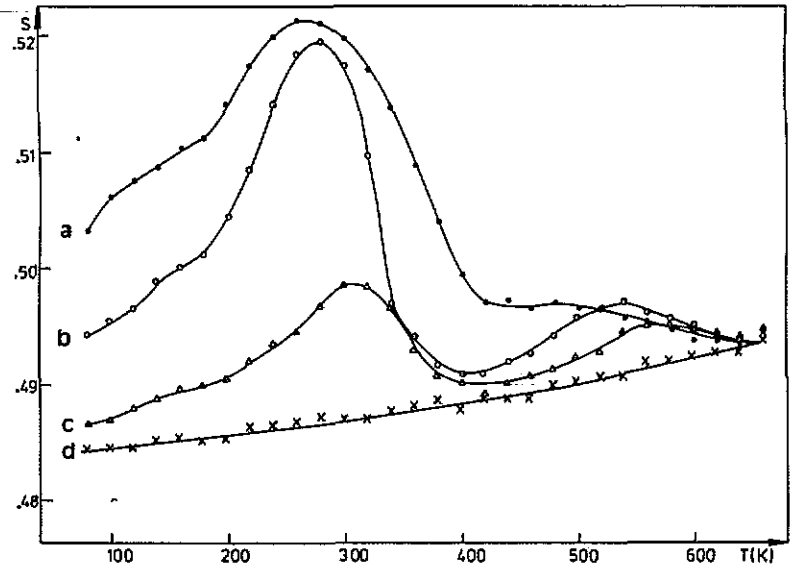

Figure 2. The *S*-parameter as a function of the annealing temperature for the alloy Al–9.9 at.% Li deformed at liquid nitrogen to three different thickness reduction degrees: (*a*) ●: 50%, (*b*) ○: 26%, (*c*) △: 8%, (*d*) ×: annealed alloy in the interval 660–80 K.

Another sample has been deformed to obtain a 50% thickness reduction, comparable with the deformation degree for pure Al (see figure 1(*a*)). The results are represented in figure 2(*a*).

The *S*-parameter value in the as-deformed samples at 80 K is proportional to the deformation degree (see figures 2(*a*), (*b*) and (*c*)). The effect between 200 and 400 K seems to saturate after a 26% thickness reduction (see figures 2(*a*) and 2(*b*)); after annealing at 400 K the *S*-parameter value increases with the deformation degree.

To avoid the effect of the point defects that are mobile below room temperature, an Al–9.9 at.% Li alloy has been deformed at room temperature to obtain a 50% thickness reduction (see figure 3). It is found that below 300 K only a slight temperature effect is present (probably due to thermal expansion); from 300 K up to 400 K a slight decrease of the *S*-parameter value is seen; a peak still exists between 400 and 600 K.

TEM observations were performed for deformed samples having 1.7 at.% Li and 9.9 at.% Li content after annealing at 660 K. Supplementary observations were also made in an as-deformed (20%) Al–9.9 at.% Li alloy.

In the as-deformed Al–9.9 at.% Li alloy (20% deformation degree, room temperature) the presence of the δ' phase is visible in both the diffraction patterns and the dark field micrographs. The spherical particles (diameter $D = 50$ nm) are inhomogeneously distributed in the sample and the distance between them is $d = 400$ nm. A high density of dislocations is also observed. After annealing these samples at 660 K the δ' phase dissolves leading to the formation of δ particles (diameter $D = 1\ \mu$m) that lie mainly at the grain boundaries (grain size = 6 μm) the mean interparticle distance being $d = 5\ \mu$m. Our observations are in agreement with previous work (Silcock 1959–60, Williams and Edington 1975, Samuel and Champier 1987).

The TEM observations performed in the low-content alloy (1.7 at.% Li) show no visible effects of precipitation, in agreement with the literature (Ceresara *et al* 1977).

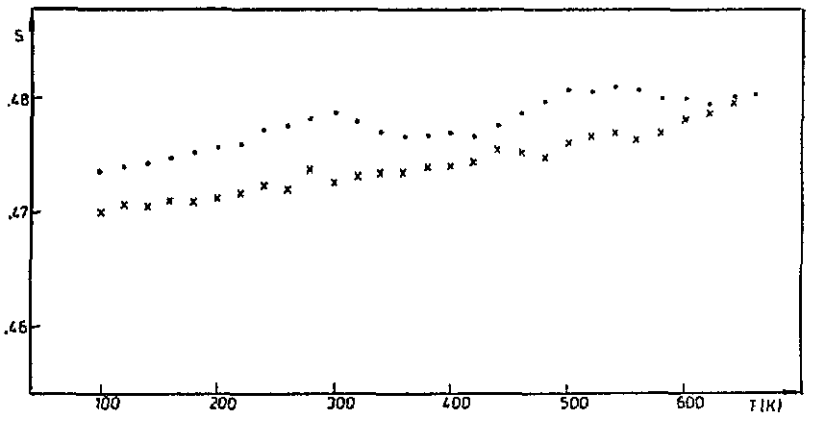

Figure 3. The *S*-parameter as a function of the annealing temperature in the alloy Al–9.9 at.% Li deformed at room temperature. The crosses show the evolution of the *S*-parameter in the annealed alloy from 660 to 80 K.

The two alloy systems were also measured in thermal equilibrium between 80 K and 660 K. Only a slight temperature effect due to thermal expansion was measured. At the highest temperatures no effect of thermally induced vacancies was found.

4. Discussion

4.1. Al–1.7 at.% Li

By comparing the results obtained in this alloy with results obtained for pure Al (see figures 1(*b*) and 1(*a*), respectively) it can be seen that there are some differences in the behaviour of the samples.

In a deformed metal or alloy two kinds of defect capable of trapping positrons are expected: dislocations and vacancies or vacancy clusters. The latter will only be present if the deformation and measuring temperature lies below the vacancy migration temperature. According to the data available in the literature, vacancies in Al migrate below room temperature (Wampler and Gauster 1978, Alam 1981); thus, the trapping effects observed in both the pure Al and the alloy must arise from vacancies, vacancy clusters and dislocations.

The two peaks centred at around 170 K and 250 K in deformed Al (see figure 1(*a*)) have been interpreted in previous work as migration of divacancies and monovacancies, respectively (Segers *et al* 1985). This interpretation is based on the perturbed angular correlation (PAC) measurements by Müller (1982) and the migration enthalpy values for di- and mono-vacancies (Balluffi 1978). The PAC results suggest that the divacancy migrates for a lower temperature than the monovacancy, in agreement with the calculations performed by Takai *et al* (1982). In the annealing curve for the alloy (see figure 1(*b*)) the two peaks centred at 170 and 250 K are also present, and we can tentatively associate them to divacancy and monovacancy migration on the basis of the former interpretation given for Al. However, there are some differences between the annealing curves that deserve further explanation; the lower *S*-values for the alloy and the enhancement of the second annealing stage relative to the first when comparing these results with the pure Al sample curve.

Saturation is observed to take place for room-temperature deformed Al samples compressed to a thickness reduction of approximately 25% or more (Segers *et al* 1985); for Al samples deformed at 77 K, saturation has been found to occur at deformation degrees above 15% (Petersen 1983). According to these data, the lower trapping signal observed in the alloy cannot be explained as being due to the lower degree of deformation (30% for the alloy, 56% for pure Al), and this effect must be related in turn to the presence of Li in the alloy sample.

The positron annihilation technique has recently shown that small Li clusters consisting of few atoms are present in an Al–1.7 at.% Li alloy (del Río *et al* 1989). The lower trapping signal in the alloy compared with the pure Al could be explained by assuming that there is a competitive trapping process between the Li clusters present in the samples and the vacancies generated by the plastic deformation.

Since the lifetime associated with the Li clusters is lower than that associated with vacancies in Al (del Río *et al* 1989), the *S*-parameter value for the Li clusters is also expected to be lower than that associated with vacancies in pure Al. These two hypotheses would explain the relatively small effect measured in the deformed alloy samples, where the signal level is lowered in comparison with the pure Al, due to the presence of the small Li clusters (see figures 1(*a*) and (*b*)).

The increase of the *S*-parameter, starting at around 200 K (see figure 1(*b*)), can be associated with clustering of vacancies. The formation of vacancy clusters has been observed in quenched pure Al, where a peak in the *S*-parameter is found at around 240 K (Wampler and Gauster 1978), and in quenched dilute Al–Li alloys, in which clusters start forming at around 200 K and dissolve at 350 K (Leighly *et al* 1989), in agreement with our results.

From the present discussion it can be concluded that the evolution of the *S*-parameter between 200 and 350 K can be attributed to the formation and dissolution of vacancy clusters, presumably formed by the clustering of monovacancies that become mobile at around 200 K.

The presence of impurity atoms can play an important role in the vacancy kinetics in metals and alloys. The impurities can favour the formation of vacancy clusters or can act as pinning centres shifting the vacancy migration temperature to higher values. Manganese and copper enhance the vacancy clustering in quenched Al but do not change the cluster dissolution temperature (Hood and Schultz 1982). However, a very small addition of In to Al delays the recovery of the quenched alloy in comparison with pure Al, and no vacancy clustering is observed (Hood and Schultz 1983).

In the Al–1.7 at.% Li alloy no shift is observed in the monovacancy recovery temperature in comparison with pure Al; however, the peak due to monovacancies is enhanced when adding Li to pure Al. The resistivity measurements performed in dilute and concentrated Al–Li alloys yield a value of 0.25 eV for the Li atom–Al vacancy binding energy (Ceresara *et al* 1977), which is high enough to allow us to interpret the enhancement observed at 250 K as due to vacancy clustering induced by Li.

Above 350 K the annealing of dislocations is seen in the temperature interval up to 550 K. The slight increase in the *S*-parameter observed for both samples from this temperature could be assigned to the formation of thermal vacancies. Again the lower values found for the alloy in comparison with pure Al suggest the competition trapping between Li clusters and vacancies.

4.2. Al–9.9 at.% Li

The behaviour shown in the high temperature region by the Al–Li alloy having a Li content of 9.9 at.% has a peculiarity when comparing it with the lower content alloy. As

can be observed in figures 2 and 3, the peak centred at around 540 K is present in all of the curves, regardless of the deformation degree and deformation temperature.

It is clear that the dislocations present in the deformed samples must give rise to a trapping effect; however, the distance between δ' particles ($d = 400$ nm) is suitable for positrons to reach the precipitates. In any case, the observed S-parameter behaviour must arise from trapping at dislocations and/or δ' particles, and also presumably from the interaction of the two.

The peak observed at about 540 K in both the low and room temperature deformed samples (see figures 2 and 3) lies well out of the temperature range in which dislocations anneal out in pure Al (between 300 and 500 K, depending on the deformation degree and deformation temperature, (Petersen 1983, Segers *et al* 1985)). Moreover, the increase in the S-parameter reveals the formation of a new defect capable of trapping positrons or the increase in the density of preexisting traps.

According to the theoretical predictions (Stott and Kubica 1975) and experimental results (del Río *et al* 1989) positrons are attracted to Li-rich regions, such as δ' precipitates.

In the light of the preceding reasoning, the effects observed in the temperature range 400–600 K can be due to the presence of the δ' phase that does not precipitate in the low-Li-content alloy (compare figures 2 and 3 with 1(b)). By assuming that positrons are trapped at the δ' phase precipitates, an increase in the S-parameter would indicate an increase in the concentration of δ' phase, the decrease in the S-parameter from 540 K would thus indicate a decrease in δ' phase volume fraction, i.e. a dissolution of δ' precipitates.

Samuel and Champier (1987) have observed an increase with temperature of the δ' volume fraction for ageing periods greater than one hour up to 550 K, at which the δ' phase starts dissolving to give rise to the δ phase. Following the same authors, both phases are completely dissolved at 800 K. Their results could be correlated with the increase in the S-parameter shown in figures 2 and 3 between 400 and 540 K. It is worth noting that the measuring time (30 min) is shorter than the ageing time necessary for detecting an increase of the δ' volume fraction by electron microscopy (Samuel and Champier 1987), indicating that positrons are very sensitive to the growth of the δ' phase.

The samples are completely recovered by annealing at 660 K indicating that the δ' phase has completely dissolved in agreement with the literature and our TEM observations.

As mentioned in section 3, the δ particles are present in the deformed and subsequently annealed at 660 K samples, but they do not contribute to the trapping signal because the distance between them is much larger than the positron diffusion length.

It is to be noted that the trapping signal originating from dislocations is also present up to the temperatures at which they anneal out (about 400 K).

The effects observed in the low temperature region (100–200 K and 200–350 K) have the same origin as the ones found for the low-Li-content samples since, in addition to dislocations and δ' particles, divacancies and monovacancies are present in a low temperature deformed sample. The defect concentration increases with the degree of deformation leading to an increase in the S-parameter value in the as-deformed state.

The same arguments as given in section 4.1 can now be used to explain why no saturation is observed for the 26% deformed sample: in the temperature range 100–200 K there is competition between trapping at Li-rich zones, such as δ' particles and

very probably also small clusters present in the α phase, and vacancy type defects generated during deformation.

It is to be noted that the *S*-parameter in the as-deformed state for the higher deformation degree (50%) is very close to the one in the pure Al deformed samples (see figures 1(*a*) and 2(*a*)), indicating that saturation is achieved at this deformation level.

The small Li clusters (presumably also the δ' precipitates) favour vacancy clustering in the temperature range 200–250 K, leading to a peak value higher than that found for the low-Li-content alloy (see figures 1(*b*) and 2(*b*)), even overcoming the saturation value for pure Al (compare figures 1(*a*) and 2(*a*)).

As expected, the contribution of the point defects is not present in the room temperature deformed samples.

Above 280 K the clusters collapse into loops (Wampler and Gauster 1978) and the annealing of dislocations and loops is seen in the interval up to 400 K. However, the effect is different from that seen in deformed pure Al. For the alloy, the decrease in the *S*-parameter is much steeper. It can be assumed that δ' particles are present in the matrix and on the dislocations lines. Positrons can be trapped by the isolated δ' particles and by the dislocations, at which they can reach the δ' particles or defects associated with the dislocations (vacancies and jogs) by pipe diffusion. The effect at the end of the annealing stage around 400 K, observed for all the deformation degrees (see figure 2), is a competition between annihilation at δ' particles (which grow as a function of temperature with, as a consequence, an increase of the *S*-parameter value) and the annihilation from defects on the dislocation line, whose density is proportional to the degree of deformation.

5. Conclusions

A positron annihilation study of deformation and recovery of the Al–1.7 at.% Li and Al–9.9 at.% Li has shown that Li has a strong effect on the monovacancy behaviour, leading to an enhanced clustering in comparison with pure Al. The presence of δ'-phase particles in the higher Li-content samples is clearly detected by the positrons and it is shown that the sensitivity of this technique to the evolution of the δ'-phase volume fraction is higher than conventional ones such as TEM.

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