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Submicrostructural and microstructural evolution of pure and oxygen contaminated vacuum melt-spun 99.9999% Al and Al:90 at p.p.m. C

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Positron lifetime (PLS) and TEM studies have been completed on a series of pure, carbon-doped (~90 at p.p.m.) and oxygen contaminated (340–670 at p.p.m.) vacuum melt-spun (VacMS) aluminium samples. Both TEM and PLS data have shown pure and carbon-doped samples to be fully annealed at ~473 K. Oxygen-contaminated samples were found to contain defects including dislocations (TEM) and small vacancy clusters (PLS) up to the highest annealing temperatures (853 K) studied. The results show that the presence of oxygen completely dominates the evolution of both microstructure and submicrostructure in VacMS aluminium.

1. Introduction

The advent and refinement over recent years of rapid solidification (RS) techniques has resulted in breakthroughs in powder-metallurgy allowing new refinements of microstructure, extended alloying and production of previously unattainable crystalline and amorphous structures (materials). Improved aluminium alloys have been produced using RS techniques; however, a basic understanding of the underlying mechanisms which control microstructural and thus mechanical characteristics of such materials is often lacking. Property improvements are usually attributed to factors such as superior homogeneity and refined microstructures which result from the initial powder structures. Of particular technological concern is the effect of elevated fabrication temperatures on structures produced by rapid solidification and the ability of such structures to withstand said temperatures.

Some materials produced via consolidation of RS alloy powder have been shown [1, 2] to exhibit highly retarded grain growth compared to similar conventionally produced materials. More recently, in an attempt to clarify the mechanisms which cause retardation of grain growth, Rabin *et al.* [3] have studied gas-atomized 99.999% pure aluminium. These authors concluded that the observed anomalous stability and coarsening of quenched-in defects resulted from the presence of impurities, most likely carbon. Here we report the results of a combined positron (lifetime) annihilation spectroscopy (PLS) and transmission electron microscopy study of rapidly solidified (vacuum melt-spun) pure and oxygen-contaminated 99.9999% pure Al and Al:90 at p.p.m. C. The results show that the presence of oxygen completely dominates both submicrostructural and microstructural behaviour of these materials.

2. Experimental procedure

Vacuum melt-spun (VacMS) samples of 99.9999% pure Al and Al:90 at p.p.m. C were produced using the apparatus described by Wright *et al.* [4]. Oxygen contamination resulted when, in initial production runs, the system was not baked prior to melting the samples. The oxygen concentration was estimated, by Leco analysis, to be between 340 and 670 at p.p.m. (500 at p.p.m.). Raw melt-spun samples were ~ 0.1 mm thick elliptical sheets with major and minor axes of 30 and 20 mm, respectively.

PLS samples were constructed using multi-layer arrangements of material held in pure tantallum templates. The templates were approximately 8 mm square and samples 5 mm square with sufficient thickness to stop all positrons emitted from the 30 μCi ^{22}Na source used. The source was constructed in the way described by Usmar [5] using 8 μm Kapton foils as the source windows.

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Positron lifetime spectra were accumulated using standard "Fast Fast" coincidence spectrometers [6] with a timing resolution of 138–150 ps FWHM depending on the spectrometer used. The resolution of a particular spectrometer varied less than 5 ps for the duration of the experiments described here. Isochronal annealing was completed using the method described by Usmar and Lynn [7]. Two pairs of samples were annealed in the temperature range 293–853 K. Positron lifetime spectra were accumulated after each annealing stage at room temperature, with spectra containing at least 1.75×10^6 counts.

TEM samples were prepared from VacMS materials using conventional electropolishing methods, after annealing. The thin foil TEM samples were examined in a Philips EM 420 electron microscope operated at 120 kV. Samples of pure, carbon-doped and oxygen-contaminated materials were examined in the as-prepared state and after various heat treatments.

3. Positron lifetime measurement

A positron lifetime spectrum (for background and reviews, see [8–10]) generally consists of the sum of at least two decaying exponentials

$$S(t) = \sum_i I_i e^{-\lambda_i t} \qquad (1)$$

Because not all positrons have sufficient energy to pass through the source window (8 μm Kapton) one of these components is associated with annihilations in the window. Further complication occurs because the measured spectra are a convolution of the finite timing resolution, $p(t)$, of the spectrometer and the real spectrum

$$N(t) = \int p(t - t')s(t')\mathrm{d}t' \qquad (2)$$

Thus numerical analysis of the spectra can only be accomplished with the aid of a non-linear curve-fitting computer program. Here the program PFPOSFIT [11], a standard program developed for positron lifetime analysis, was used. The program returns the reduced chi-squared (χ^2_R) as a measure of the quality of a particular fit. Values of $\chi^2_R \leqslant 1.15$ are generally accepted as indicating a good fit.

Figs 1 and 2 show the fitted positron lifetime parameters, τ_2 and I_2, for VacMS 99.9999% pure Al and Al:90 at p.p.m. C, respectively. These parameters were the longest lived components of those returned (excluding source) by PFPOSFIT when spectra were fitted with two components (three including source) I_2 having been corrected for source contributions. In both samples, I_2 is seen to fall to zero at ~ 473 K, i.e. in both pure and carbon-doped aluminium, no positron traps are present above 473 K. The magnitudes of τ_2 remain constant at 208 ± 5 ps for pure aluminium and 247 ± 5 ps for Al:90 at p.p.m. C throughout the temperature range (293–493 K) studied. It is apparent that the active positron trap in pure VacMS Al is smaller than that in VacMS Al:90 at p.p.m. C. In fact, the magnitude of τ_2 for pure aluminium suggests the trap to be a dislocation or dislocation loop whilst that for Al:90 at p.p.m. C suggest a vacancy [12].

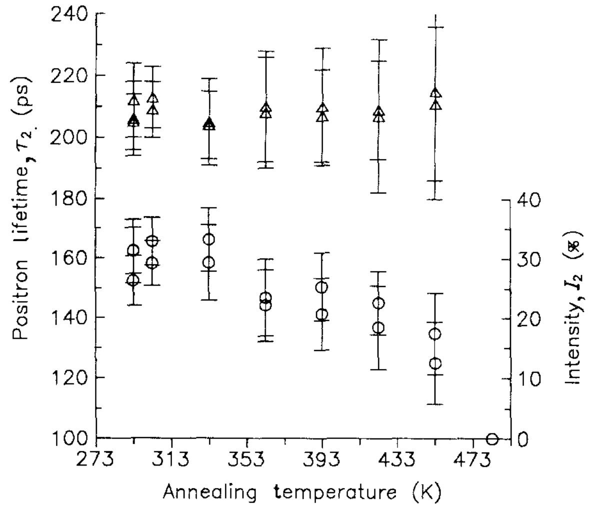

Figure 1 (△) Positron lifetime, τ_2, and (○) intensity, I_2, versus annealing temperature for VacMS pure aluminium.

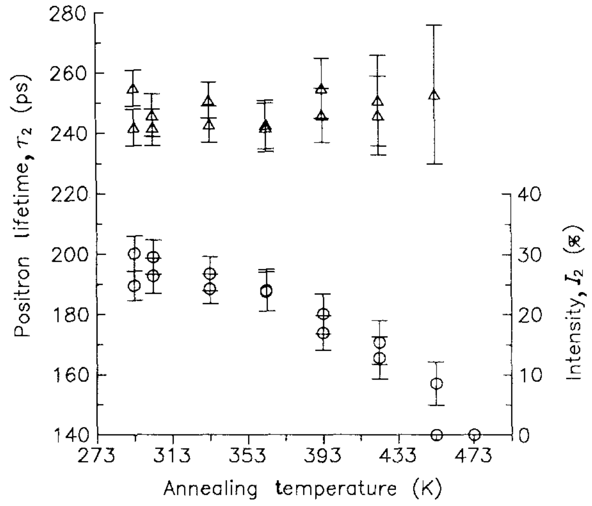

Figure 2 (△) Positron lifetime, τ_2, and (○) intensity, I_2, versus annealing temperature for VacMS Al:90 at p.p.m. C.

The data for pure aluminium are in good agreement with previously published work of Alam [13], who reported positron line shape measurements [9] for quenched and deformed pure aluminium with deformations being completed at 77 K and room temperature. In both cases, an annealing stage between ~ 300 and ~ 450 K was identified as the annealing of dislocations. The onset of this stage in the quenched samples occurred at ~ 330 K, in excellent agreement with the present data.

With respect to the data for Al:90 at p.p.m. C it is evident that because the positron trapping site is a vacancy and native vacancies in pure aluminium are unstable above 190 K [13, 14] these vacancies must be stabilized by carbon and only anneal once either the carbon–vacancy complex or the carbon atom becomes mobile above ~ 293 K. In any case, both pure and carbon-doped VacMS are completely annealed above ~ 473 and 463 K, respectively.

Data for oxygen-contaminated samples of VacMS Al and Al:90 at p.p.m. C were analysed with PFPOSFIT using, after source correction, two component fits. The magnitude, τ_2, and relative intensity, I_2, of the longest lived components returned by PFPOSFIT from these fits for oxygen-contaminated aluminium and Al:90 at p.p.m. C are shown in Figs 3 and 4, respectively. Evidently these samples exhibit markedly different and more complex behaviour than the equivalent components for oxygen-free samples with defects present up to the highest annealing temperature (853 K) reached. The data show some subtle differences but the major features are, within experimental error, identical. The relative intensities, I_2, remain essentially constant between 293 and 593 K and then decreases to zero at ~ 853 K. The lifetime, τ_2, remains constant between 293 and ~ 393 K, falls by ~ 20 ps at 423 K, is constant between 423 and 623 K, and then increases to 300 ps at the highest annealing temperatures reached.

Here the relatively complex behaviour of τ_2 deserves further discussion. In particular, this behaviour must bring into question the validity of the two component fits. The values of χ_R^2 by PFPOSFIT indicate the two component fits to be valid; however, a further test using the two state trapping model [15, 16] was made. If the model was valid, observed spectra have the form

$$N(t) = N_0\left[\frac{(\lambda_b - \lambda_t)}{(\lambda_b - \lambda_t + K_{bt})}\right]\exp[-(\lambda_b + K_{bt})t] + N_0\left[\frac{K_{bt}}{(\lambda_b - \lambda_t + K_{bt})}\right] \times \exp[-\lambda_t t] \quad (3)$$

where λ_b is the bulk annihilation rate; λ_t the annihilation rate from the trapped state; K_{bt} the trapping rate from bulk to trapped state and N_0 is a normalization constant. The parameters τ_1, τ_2, I_1 and I_2 returned by PFPOSFIT can be related to the terms in Equation 3. Subsequent algebraic manipulation reveals the bulk annihilation rate, which can be measured, to be given as

$$\lambda_b = I_1\lambda_1 + I_2\lambda_2 \quad (4)$$

or inversely, the bulk lifetime as

$$\tau_b = \lambda_b^{-1} = (I_1\lambda_1 + I_2\lambda_2)^{-1} \quad (5)$$

Fig. 5 shows the values of τ_b (versus temperature) calculated using Equation 5. Throughout the temperature range, the values of τ_b are in good agreement with the measured value (157 ± 5 ps) of the bulk lifetime of aluminium suggesting the two component fits are valid. Thus it may be concluded that a single positron trap is active throughout the temperature range studied and that the variations in τ_2 indicate a change in the nature of the trap.

Below 623 K, the features exhibited by τ_2 are similar but the magnitude of τ_2 differs between samples. In the Al:500 at p.p.m. O sample, $\tau_2 = 248 \pm 5$ ps, whilst in Al:90 at p.p.m. C:500 at p.p.m. O, $\tau_2 = 261 \pm 5$ ps. The defects present could be vacancies decorated by oxygen or oxygen and carbon. The decrease of τ_2 in both samples between 373 and 423 K might then be associated with reorientation of the vacancy–impurity complex. Alternately, the defects present at room temperature could be small vacancy clusters which subsequently collapse into loops between ~ 373 and ~ 423 K. Differentiating these two possibilities is difficult. In Al:500 at p.p.m. O, $\tau_2 = 248 \pm 5$ ps at room temperature and 225 ± 5 ps between 423 and 623 K. Here the value of τ_2 is very close to that (240 ± 10 ps) for vacancies in pure aluminium which would give credence to the former explanation. The room-temperature value of τ_2 for Al:90 at p.p.m. C:500 at p.p.m. O was 262 ± 5 ps whilst that between 323 and 623 K was 245 ± 5 ps. Thus at room temperature the defect might be a small vacancy cluster; however, between 323 and 623 K the value of τ_2 suggests a vacancy.

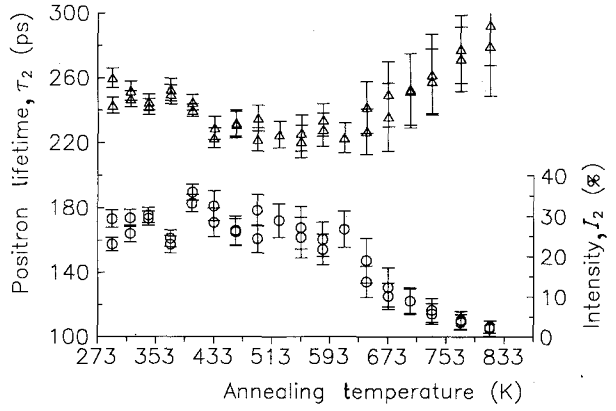

Figure 3 (△) Positron lifetime, τ_2, and (○) intensity, I_2, versus annealing temperature for VacMS Al:500 at p.p.m. O.

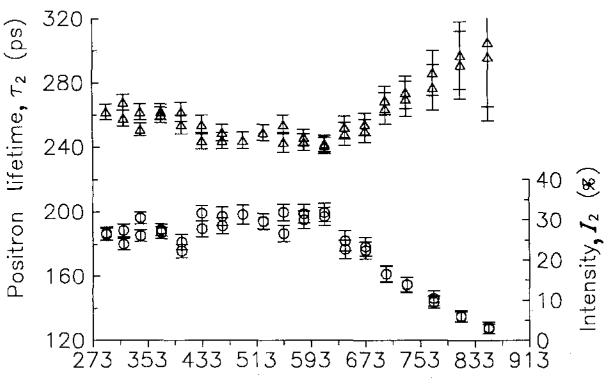

Figure 4 (△) Positron lifetime, τ_2, and (○) intensity, I_2, versus annealing temperature for VacMS Al:90 at p.p.m. C: 500 at p.p.m. O.

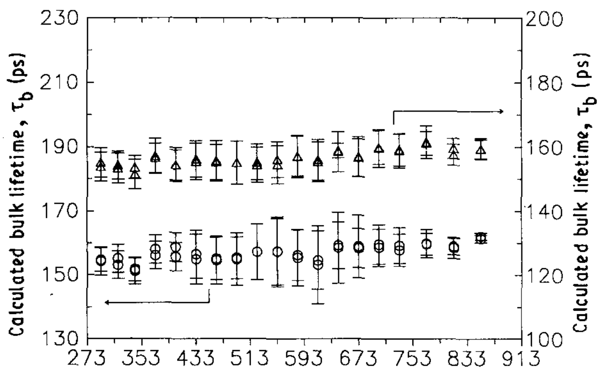

Figure 5 Calculated bulk lifetime, τ_b, versus annealing temperature for (○) VacMS Al:90 at p.p.m. C and (△) Al:90 at p.p.m. C: 500 at p.p.m. O.

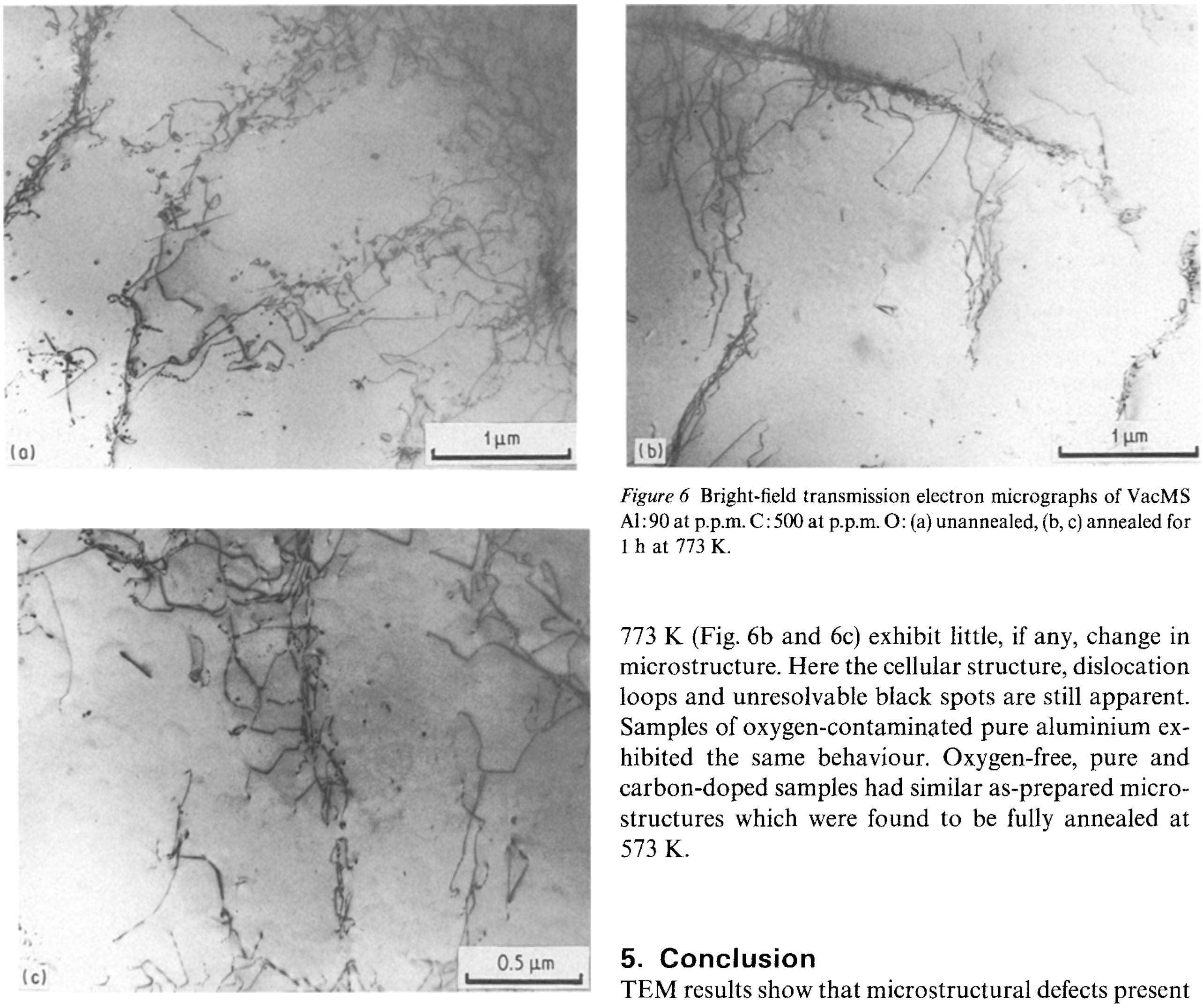

Figure 6 Bright-field transmission electron micrographs of VacMS Al:90 at p.p.m. C:500 at p.p.m. O: (a) unannealed, (b, c) annealed for 1 h at 773 K.

Regardless of the uncertainties associated with the nature of the defects present below 623 K, at the highest annealing temperature the magnitude of τ_2 ($\sim$ 300 ps) indicates the active positron traps to be small vacancy clusters. The calculations of Puska and Nieminen [17] of positron lifetimes for empty vacancy clusters in pure aluminium suggest that the clusters observed here contain no more than five vacancies and more likely three or four. Such clusters cannot be seen using standard TEM. Thus above 623 K the increase in τ_2 and simultaneous decrease in I_2 suggests that stabilized open-volume defects, probably vacancies, which were present at 623 K, agglomerate and coalesce into larger open-volume defects, i.e. vacancy clusters, during annealing. The same effect has been observed in metals containing helium [18, 19] and the noble gases [20].

4. TEM

Examples of bright-field micrographs of oxygen-contaminated carbon-doped VacMS Al are shown in Fig. 6a–c. The microstructure of unannealed samples (Fig. 6a) contains significant densities of interlaced dislocations which form a loose cellular structure similar to that observed by Rabin *et al.* [3]. Within the cells were observed small dislocation loops and unresolvable black spots. Samples annealed for 1 h at 773 K (Fig. 6b and 6c) exhibit little, if any, change in microstructure. Here the cellular structure, dislocation loops and unresolvable black spots are still apparent. Samples of oxygen-contaminated pure aluminium exhibited the same behaviour. Oxygen-free, pure and carbon-doped samples had similar as-prepared microstructures which were found to be fully annealed at 573 K.

5. Conclusion

TEM results show that microstructural defects present in VacMS Al; Al:90 at p.p.m. C; Al:500 at p.p.m. O and Al:90 at p.p.m. C:500 at p.p.m. O are similar to those observed by Rabin *et al.* [3] in gas-atomized aluminium. Positron lifetime spectroscopy has shown that defects in VacMS pure aluminium and Al:90 at p.p.m. C are completely annealed at 473 K, whilst in oxygen-contaminated samples of the same materials, defects are present up to the highest annealing temperature (853 K) studied. Thus it is evident that oxygen plays a dominant role in the stabilization and growth of quenched-in defects in rapidly solidified (VacMS) Al. The tentative suggestion by Rabin *et al.* [3] that the impurity active in stabilizing quenched-in defects in RS Al was most likely in carbon, was incorrect.

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