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LETTER TO THE EDITOR

Annealing of vacancy-type defects and crystallisation of icosahedral Al–Mn–Si

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Abstract. We report a positron annihilation investigation of quasicrystalline-to-crystalline phase transition in the Al–Mn–Si alloy system using both Doppler broadening and lifetime measurement techniques. Our results show the presence of small vacancy clusters in the as-grown icosahedral phase. Iosochronal annealing studies carried out from 100 °C onwards show that the vacancy clusters are annealed out along with the crystallisation process. The positron lifetime results rule out the possibility of a central hole which had been postulated in the icosahedral building block called the Mackay icosahedron.

Although the quasicrystalline phase in the Al–Mn alloy system was discovered [1] almost five years ago, the exact atomic arrangement to describe this new phase remains an open question. The important structural models of the materials can be grouped into two classes. One of them is based on the three-dimensional Penrose tiling [2] (or its generation [3] from six dimensions) and the other is the random packing of icosahedral clusters [4, 5]. It has been shown [6] that both the approaches can describe the observed diffraction patterns qualitatively, including the unusually broad peaks (characteristic of disorder) observed in quasicrystalline phases. In spite of detailed analysis [3] one cannot decide on the appropriate model for this phase on the basis of neutron and x-ray diffraction data alone, and more experimental observations are called for using other complementary techniques. In this letter we present a positron annihilation study of the as-grown icosahedral Al–Mn–Si alloy and its crystallisation by thermal annealing. The positron annihilation technique, by virtue of its defect specificity, has provided valuable additional information and indicates the presence of vacancy-type defects in the quasicrystalline phase, which are annealed out during the crystallisation process. This result has an important bearing on the modelling of the quasicrystalline phase.

Quasicrystalline ribbon samples (of width 3 mm and thickness 30 μm) of the $Al_{74}Mn_{20}Si_6$ alloy, made of high purity constituents, were obtained by the usual melt-spinning technique. Positron studies were made using powder samples that were obtained by gentle grinding of the ribbons. The quasicrystalline character of the ribbons and powder samples were confirmed by electron and x-ray diffraction, respectively. The experimental set-up was identical to that used [7] for the Al–Mn alloy, except that the source was replaced by a stronger (5 μCi) Na^{22} source. The positron source was evaporated onto a thin Ni foil and covered with an identical foil. It was placed inside a cylindrical glass sample holder and the quasicrystalline powder specimen, to a thickness

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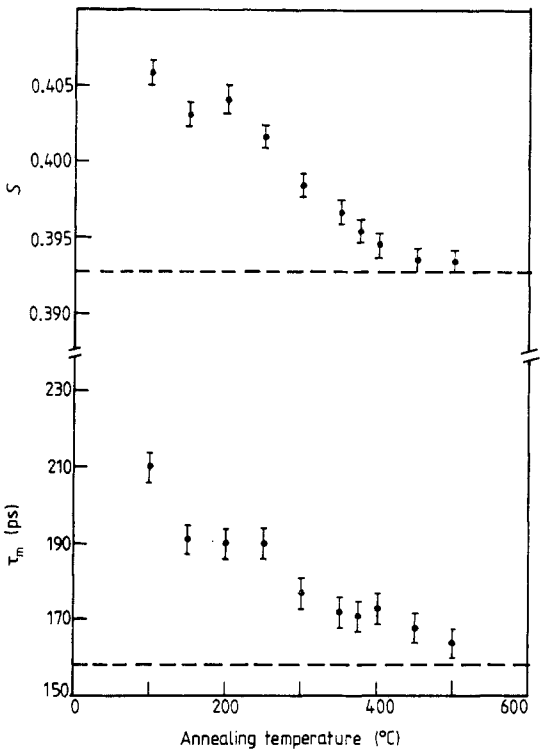

Figure 1. The Doppler broadened annihilation line-shape parameter S and the mean lifetime τ_m of $Al_{74}Mn_{20}Si_6$ as functions of annealing temperature.

of at least 5 mm, was poured all around the source to make sure that annihilations were taking place inside the sample only. For Doppler broadening measurements, a 40 cm^3 HP Ge detector with an energy resolution (FWHM) of 1.10 keV for the 475 keV gamma line of a Rh^{102} source was used. Lifetime measurements were made using a conventional slow–fast coincidence spectrometer [8]. The prompt time resolution (FWHM) of this lifetime spectrometer at the experimental window settings (with the upper 50% of the Comptons of 1.28 MeV and the 0.511 MeV gamma rays accepted in the two channels, respectively) was 260 ps. The observed Doppler-broadened and lifetime spectra were analysed using standard computer codes [9].

The crystallisation process of this alloy was studied using isochronal annealing done at different set temperatures (stability better than ±1 °C) for seven minutes in high vacuum and then slowly cooled, thereby avoiding quenching effects and surface contamination. The annealing time of seven minutes was the same as in our earlier work on the Al–Mn alloy [7]. The reference crystalline phase was obtained by annealing the alloy at 500 °C for one hour and it was found to be α-Al–Mn–Si, similar to that observed by earlier workers [10].

The variation of the S-parameter and the mean lifetime τ_m (the latter being defined as $\Sigma\tau_i I_i/\Sigma I_i$, where τ_i and I_i represent different lifetimes and their intensities) as functions of isochronal annealing temperature are shown in figure 1. The S-parameter has the usual definition, namely, the ratio of the area under the central channels to the total area under the annihilation curve. In our earlier work [7] on the Al–Mn alloy, we could observe a slow fall of the S-parameter before 300 °C and a rapid reduction of S above

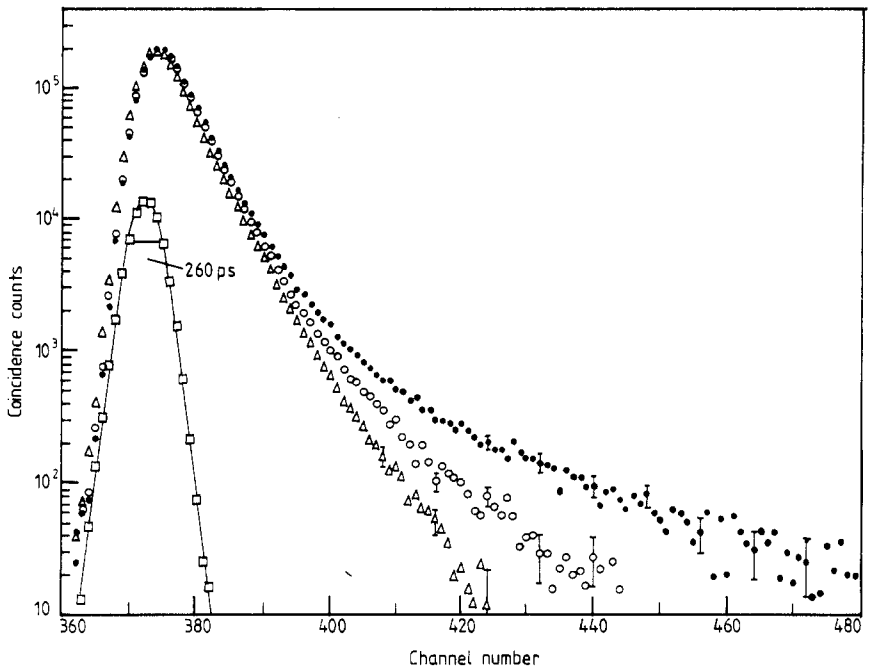

Figure 2. Positron lifetime spectra of $Al_{74}Mn_{20}Si_6$ for the quasicrystalline phase annealed at 100 °C (●) and 250 °C (○) and for the crystalline phase obtained after annealing at 500 °C (△) for one hour. The spectra have been peak-normalised for easy comparison. The prompt curve taken with Co^{60} is also shown (□). (1 channel = 50 ps).

this temperature, indicating structural relaxation and crystallisation processes, respectively. In the Al–Mn–Si alloy we obtain a smoother and more continuous fall of S, showing that the processes of structural relaxation and crystallisation overlap considerably in this system. This is more strikingly shown in the lifetime spectra of figure 2. The higher S-parameter in the quasicrystalline phase of Al–Mn–Si as compared to the crystalline phase was also observed earlier by Dunlap and co-workers [11]. However, no positron lifetime measurements were performed by them.

Although the lifetime spectra of the quasicrystalline Al–Mn alloy could be analysed [12] on the basis of two components, we noticed the presence of a third component in the Al–Mn–Si alloy up to the annealing temperature of 150 °C. The relative intensity (~1.5%) of this third component τ_3 (=1500 ps) is in agreement with the value obtained by the peak-to-peak ratio method [13], which indicated 1% of ortho-positronium in the sample. It should be mentioned here that positronium formation has been observed in silicon compounds [13]. The values of the lifetimes and their relative intensities as a function of annealing temperatures are shown in table 1.

The value of τ_2 (=262 ps) in the as-grown quasicrystalline phase remains more or less unchanged up to 250 °C. This indicates the presence of vacancy clusters in the quasicrystalline phase of the Al–Mn–Si alloy, which persist more or less unchanged up to this temperature. To calculate the size and concentration of these vacancy clusters, the lifetime components were analysed using the two-state trapping model [14]. In this model, it is assumed that annihilations can only occur from either the positron bulk state

Table 1. Results of positron lifetime measurements on the quasicrystalline sample i-$Al_{74}Mn_{20}Si_6$ (VOF is the variance of fit, which should be unity in the absence of systematic errors; the error in I_1 and I_2 is about 3%).

Temperature (°C)	VOF	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	I_1 (%)	U_2 (%)	I_3 (%)
As-grown	1.45	140(2)	262(3)	1500	57.6	40.9	1.5
100	1.17	145	260	1500	58.5	40.1	1.4
150	1.36	157	280	1500	73.8	26.1	0.2
200	1.17	159	276		73.0	27.0	
250	1.36	157	263		69.3	30.7	
300	1.01	177			100.0		
350	0.90	172			100.0		
375	1.14	171			100.0		
400	1.07	173			100.0		
450	1.16	168			100.0		
500	1.41	164			100.0		
Crystal	1.12	158			100.0		
		Using constrained fit analysis					
300	1.4	158(fixed)	228			11.3	
350	1.5	158(fitted)	209			9.3	

or the positron trap state, giving rise to a two-component lifetime spectrum. When de-trapping is neglected, the trapping rate K in the defects can be written as

$$K = (I_2/I_1)(\tau_b^{-1} - \tau_2^{-1}) \tag{1}$$

where τ_b and τ_2 are the positron lifetimes in the defect-free bulk material and in the defect, respectively. For the present analysis we have taken τ_b as 158 ps, which corresponds to the single-component lifetime observed in the reference crystalline phase. The lifetime of the short-lived component is then given by

$$\tau_1 = (\tau_b^{-1} + K)^{-1}. \tag{2}$$

One can approximate the trapping rate K as being a product of the specific trapping rate μ (into unit concentration of defects) and the defect concentration C as

$$K = \mu C. \tag{3}$$

By comparing the increase in τ_2 as against τ_b with the calculated [15] positron lifetimes for different sizes of vacancy clusters in Al, we conclude that the τ_2 value of 260 ps approximately represents a divacancy. It should be mentioned [16] that vacancy clusters could relax to smaller volumes, so the number of vacancies (2 in this case) obtained using calculated lifetimes represents a lower limit of the number of vacancies in the cluster. For this vacancy cluster size a μ of the order of $5.9 \times 10^{14}\ s^{-1}$ is obtained from the work of Nieminen and Laakkonen [14]. Now by putting these numbers in the above equations we get the defect concentration C as 3×10^{-6} and the predicted short-lived component as 123 ps, which is close to the experimentally observed value of 140 ± 3 pS.

It is seen from table 1 that from an annealing temperature of 300 °C onwards the lifetime spectra can be fitted on the basis of a single component. However, the value of this lifetime has increased to 177 ps, indicating that it absorbs the effect of higher lifetime

components. This was verified by doing a constrained fit by fixing the first lifetime component at the bulk value of 158 ps. Then the second lifetime component and its intensity fell rapidly as a function of annealing temperature, indicating that both the vacancy defect volume and defect concentration are coming down rapidly. We get 228 ps and 11% as the values of τ_2 and I_2, respectively, for the sample annealed at 300 °C and 209 ps and 9% at 350 °C. It must be mentioned, however, that the variance of fit in terms of this forced two-component analysis for 300 °C and 350 °C data increased substantially to 1.4 and 1.5, respectively, compared to the near unity value obtained in the unconstrained fittings given in table 1.

It is surprising that the vacancy clusters in the quasicrystalline phase get annealed out from 300 °C onwards well before the crystallisation process is expected to be completed. Calorimetry and other techniques first detect [17] the quasicrystalline–crystalline phase transformation at a much higher temperature; the positron annihilation technique seems to start seeing this process much earlier. Moreover, from the present study it seems that this phase transition could be a continuous-ordering process which starts occurring at 300 °C. The XAFS studies of Ma and Stern [10] show that the icosahedral units in the quasicrystalline phase closely resemble those in α-AlMnSi and are also similarly connected, albeit with a smaller coordination number. Electron diffraction studies [18] also indicated partial crystallisation of these materials by aging at around 325 °C. In order to verify whether the vacancy clusters are an integral part of the quasicrystalline phase or not we are carrying out positron studies in other metastable and stable quasicrystalline alloys.

There has been speculation that the basic icosahedral unit in the quasicrystalline phase of AlMnSi is the so-called 'Mackay icosahedron' with a hole in the centre [19], although the necessity of the Mackay icosahedron as a basic structural unit has been questioned on the basis of recent neutron diffraction data [3] and also on the basis of packing considerations [20]. If such a hole existed in the icosahedral building block for the quasicrystalline phase with a radius of about 90% of that of a monovacancy, it would act as a saturation trap for positrons and give a single-component lifetime spectrum with a mean lifetime a little above 200 ps. There is no evidence of this in our data. In fact our positron lifetime data, comprising a single component of 158 ps in the crystalline phase, do not seem to indicate the existence of such central holes in the icosahedral clusters even in this phase, though they have been predicted in the x-ray structure of Cooper and Robinson [21]. Since the latter was based on visually estimated data, with several strong reflections affected by extinction and the structure refined to an R-factor no better than 0.10, it would seem that this important structure (of α-AlMnSi) requires to be redone with better data. Moreover, it would seem stereochemically difficult to construct an icosahedral cluster in a rapidly quenched alloy with a central hole! It must be mentioned that in the original paper of Mackay the successive layers of atoms were built up around a central atom [22].

Nevertheless, it appears from our results on the Al–Mn–Si alloy that space filling models based either on twinning [20] of large crystalline unit cells or on Penrose tiling [2] cannot easily explain the existence of these large vacancy clusters. One can perhaps generate these clusters in the quasicrystalline model by unrealistically relaxing the matching rules of Penrose tilings. On the other hand, suitably constructed models of random packing of icosahedral clusters, while retaining bond orientational order to be consistent with diffraction data, could easily accommodate this type of vacancy defect as indicated by our present observations.

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