Positron-Annihilation Study of Icosahedral AlPdMn Alloys

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We measured the positron-annihilation lifetime in $Al_{71.4}Pd_{20.2}Mn_{8.4}$, $Al_{71.9}Pd_{19.7}Mn_{8.4}$, $Al_{70.2}Pd_{20.3}Mn_{9.5}$, and $Al_{69.1}Pd_{21.5}Mn_{9.4}$ polyquasicrystalline icosahedral quasicrystals. As-grown and plastically deformed single quasicrystals of $Al_{70.6}Pd_{21.1}Mn_{8.3}$ were also studied. In every sample the lifetime spectrum consists of a single component with the lifetime of 206 ± 4 ps. The results indicate that icosahedral quasicrystalline AlPdMn contains a dense distribution of vacancy-type sites. These trapping sites seem to remain unaltered during plastic deformation at high temperature. [S0031-9007(97)04002-7]

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Up to now the general structure of quasicrystalline materials appears to be well understood. Structure determinations by scattering methods, electron microscopy, and scanning tunneling microscopy reveal large clusters as the basic structural elements within ternary (mostly thermodynamically stable) icosahedral systems like AlMnSi [1–3], AlLiCu [4], AlCuFe [5], and AlPdMn [6–9].

However, it is still difficult to confirm certain details of the structure. One example is the question of whether the centers of the clusters are occupied or remain empty. These cluster centers may be important for some physical properties such as the electronic states and thermal stability of quasicrystals [10]. Thus the investigation of vacant centers of clusters in quasicrystals is of great importance.

Positron annihilation measurements (PAMs) already proved to be well suited for such kind of investigations due to their high sensitivity to structural vacancies [11]. Recent PAMs [12–14] suggested that the volume of the vacant center of the Mackay icosahedron in AlMnSi and AlMnSiRu quasicrystals is much reduced or those centers are occupied with atoms such as manganese.

In the case of icosahedral AlLiCu quasicrystals it has been clarified that there exists a high density of the triacontahedral clusters with a vacant center as in the cubic R phase (a related crystalline phase) [15]. For AlCuFe quasicrystals Lawther and Dunlap [16] have recently shown by means of PAM that most positrons are trapped at intrinsic structural vacancies such as vacant cluster centers surrounded by Al atoms in icosahedral coordination.

The stable icosahedral phase of very good structural quality in AlPdMn alloys discovered by Tsai *et al.* [17] is recognized to be one of the typical F-type quasicrystals of which the structure can be described in terms of a face-centered six-dimensional hypercubic lattice. Up to now it is the only known system where by conventional solidification it is possible to obtain centimeter-sized single quasicrystals. Such material in turn can be used for a number of experiments in order to explore intrinsic physical properties of quasicrystals like their plasticity. Concerning the plasticity it has been shown that a dislocation mechanism underlies the deformation process at high temperatures [18].

Dislocations introduced in crystals by plastic deformation are also known to act as trapping sites for positrons [19]. So far plastically deformed quasicrystals have not been subjected to PAMs.

Alloy ingots of the average chemical compositions of $Al_{80-x}Pd_{20}Mn_x$ ($x = 8$, 9, and 10) and $Al_{71.5}Pd_{20.3}Mn_{8.2}$ were prepared by arc melting in an argon atmosphere and then annealed for 12 hours at 1023 K in vacuum (2×10^{-6} Torr) in order to obtain equilibrium states. These four chemical compositions were selected from the phase diagram of the AlPdMn system in the region of the quasicrystalline phase [20]. For quality evaluation we performed x-ray diffraction measurements.

A single quasicrystal with the composition of $Al_{70.6}Pd_{21.1}Mn_{8.3}$ was grown by the Czochralski technique from an $Al_{73.2}Pd_{20.2}Mn_{6.6}$ melt (details will be published elsewhere [21]). The single quasicrystal was cut into rectangular specimens of about $3 \times 5 \times 7$ mm^3 in size. All surfaces were carefully ground and polished. Deformation was done under compression along the long sample axis oriented parallel to a twofold direction of the quasicrystal. Experiments were carried out in vacuum at

a crosshead speed of 0.005 mm/min resulting in an initial strain rate of $\dot{\epsilon} = 1.2 \times 10^{-5}$ s^{-1}. Three compression specimens, B, C, and D, were prepared: B was deformed by 0.2% at 1023 K, C by 21% at 1073 K, and D by 22% at 1023 K.

For the PAMs all samples were sliced into plates with a thickness of 0.5 mm. The positron source [^{22}NaCl, activity about 5 μSv (microsievert)], sealed in a thin foil of kapton, was mounted in a specimen-source-specimen sandwich. The positron-annihilation lifetime spectra were recorded with a fast-fast coincidence system employing H2431Q photomultiplier by Hamamatsu and 1×1 in^2 BaF_2 scintillators. The time resolution of this system was 230 ps full width at half maximum. For each spectrum at least 1.0×10^6 annihilations were counted. All measurements were carried out at room temperature. The time-resolution function was assumed to be composed of two Gaussian functions. Using this time-resolution function, the lifetime in the bulk of well-annealed pure Al (purity 99.9999 wt %) was measured as 165 $\pm$ 2 ps. Each χ^2/q was below 1.2.

After subtracting the background positron-annihilation lifetime spectra were analyzed using POSITRONFIT [22].

Close inspection of the x-ray powder diffractograms revealed that all polyquasicrystalline specimens possess quasiperiodic structure with icosahedral symmetry.

The chemical compositions of the AlPdMn alloys were determined by electron probe x-ray microanalyzer (EPMA). The analysis was carried out with an automatic EPMA (model JXA-733) connected to a computer performing a standard correction by the ZAF (Z: atomic number correction, A: absorption correction, F: fluorescence correction) method [23]. For each specimen ten measurements were used to calculate an average value of the chemical composition. The obtained average compositions for the four polyquasicrystalline specimens are $Al_{71.4}Pd_{20.2}Mn_{8.4}$, $Al_{71.9}Pd_{19.7}Mn_{8.4}$, $Al_{70.2}Pd_{20.3}Mn_{9.5}$, and $Al_{69.1}Pd_{21.5}Mn_{9.4}$. The mean deviation from the average value was typically less than 1.0 at. %.

The single quasicrystal has the composition $Al_{70.6}Pd_{21.1}Mn_{8.3}$. It is icosahedral single-phase material of high structural quality [21].

Table I shows the lifetimes of the polyquasicrystalline quasicrystals as well as those of as-grown and deformed single-quasicrystalline specimens. The positron-annihilation lifetime spectra of all samples are composed of a single component; a fit with a two-component spectrum has shown that the intensity of the second component which was found to be below about 1% with respect to the first component. For all specimens an equal lifetime of 206 $\pm$ 4 ps is observed. *A priori* this might seem surprising since specimens different in composition, structural quality, grain size, and deformation state were investigated. However, this can be understood in the way that the positrons are trapped at structural defects which are intrinsically common to all specimens.

First of all, the average lifetime calculated with respect to the composition from the positron lifetimes of the constituent elements ($\tau_{Al} = 165$ ps, $\tau_{Pd} = 103$ ps, $\tau_{Mn} = 103$ ps [24]) is 146 ps for $Al_{70}Pd_{20}Mn_{10}$ (all other samples yield similar values), which is significantly lower than the observed lifetime. Therefore, it is unlikely that the positrons are annihilated during their diffusive motion in the alloy matrix. They are rather annihilated after being trapped at defect sites. As stated in the introduction, the structural analysis reveals clusters of icosahedral symmetry formed by Al atoms which may possess vacant centers. Therefore, those Al clusters, intrinsic entities of the structure, most likely serve as the positron trapping sites.

Besides its sensitivity to vacancies, PAMs can also be used to detect dislocations [19]. Therefore, we performed for the first time PAMs on deformed AlPdMn quasicrystals. For this material, it has been shown that for the described experimental conditions, deformation to 20% strain leads to a dislocation density of 10^8–10^9 cm^{-2} [25]. An example of the electron micrograph showing a typical dislocation structure in specimen C is presented in Fig. 1. We note that in as-grown single quasicrystal dislocation was rarely observed in the area of Fig. 1. In crystalline metals, a dislocation density of the order of 10^8 cm^{-2} is generally the minimum detectable limit [26]. Though reaching this limit with the present samples, no additional lifetime component could be detected. There are two possible reasons for this observation.

TABLE I. Positron lifetime for polyquasicrystalline samples, single-quasicrystalline samples, and deformed single-quasicrystalline samples. Experimental uncertainty is $\Delta\tau = \pm 4$ psec.

Sample	Lifetime (psec)
Poly-$Al_{71.4}Pd_{20.2}Mn_{8.4}$	210
Poly-$Al_{71.9}Pd_{19.7}Mn_{8.4}$	210
Poly-$Al_{70.2}Pd_{20.3}Mn_{9.5}$	206
Poly-$Al_{69.1}Pd_{21.5}Mn_{9.4}$	211
Single-$Al_{70.6}Pd_{21.1}Mn_{8.3}$ (as-grown)	202
Single-$Al_{70.6}Pd_{21.1}Mn_{8.3}$ (deformed by 0.2% at 1023 K)	205
Single-$Al_{70.6}Pd_{21.1}Mn_{8.3}$ (deformed by 21% at 1073 K)	202
Single-$Al_{70.6}Pd_{21.1}Mn_{8.3}$ (deformed by 22% at 1023 K)	200

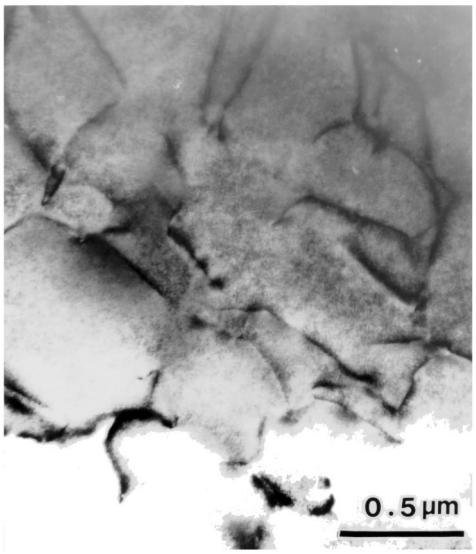

FIG. 1. Electron micrograph taken for deformed single quasicrystal of specimen C.

At first, the density of the trapping sites present in undeformed samples has to be orders of magnitude higher than the density of trapping sites produced by dislocations which are expected to cause a second lifetime component. If the intrinsic structural defects are the vacant centers of the icosahedral clusters, this is explained as follows. Since the icosahedral clusters are present in the icosahedral phase at spatial intervals of $\tau^3 a_q$ [$a_q = 4.8$ Å is the quasilattice constant, $\tau = (1 + \sqrt{5})/2$, in this case being the golden mean] the density of the icosahedral clusters is about $1/(\tau^3 a_q)^3 \approx 1 \times 10^{20}$ cm^{-3}. On the other hand, assuming that for every atomic distance along the dislocation line one trapping site is typically provided the density of trapping sites due to dislocations ρ_d/a (ρ_d: dislocation density, a: atomic distance ≈ 3 Å), which yields 3×10^{16} cm^{-3} for $\rho_d = 10^9$ cm^{-2}. This is 4 orders of magnitude lower than the former density. Thus, if the second component exists, it is far below the detectable limit.

Second, the result indicates that the plastic deformation did not destroy the trapping centers of the structural defects to an extent that a change in the positron lifetime could be induced. Usually the density of trapping sites of the order of 10^{17} cm^{-3} is large enough for all the injected positrons to be trapped. Taking into account the estimated density of vacant clusters the experimental conditions already have been far above the saturation limit. In other words, to affect the positron lifetime by plastic deformation 99.9% of the structural defects have to be destroyed. Even if structural defects are destroyed by plastic deformation, 20% deformation appears to be insufficient to destroy the structural defects to such a high percentage. Further, this is in agreement with recent high temperature deformation studies which indicated that the icosahedral clusters act as strong obstacles to dislocation glide [9]. Hence the glide of dislocations is expected to happen preferentially in between the arrays of the clusters without significant destruction of them.

In conclusion, the present results indicate that there exists a high density of vacancy type structural defects in AlPdMn icosahedral quasicrystal. The presence of a high density of structural defects hinders detection of an effect of dislocations on the positron lifetime which is usually observed in crystalline metals.

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