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Vacancy-type defects in amorphous and nanocrystalline Al alloys: Variation with preparation route and processing

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Positron annihilation spectroscopy was performed in order to study the influence of preparation route and processing on atomic free volumes in amorphous and nanocrystalline aluminium alloys. In melt-spun amorphous $Al_{88}Y_7Fe_5$, structural free volumes smaller than a lattice vacancy are predominant, whereas in amorphous $Al_{92}Sm_8$ prepared by repeated cold rolling larger free volumes occur. In the early stages of nanocrystallization of $Al_{88}Y_7Fe_5$, an indication of Y enrichment at interfacial free volumes in the growth front of the Al nanocrystallites is found.

Keywords: Accumulative roll bonding (ARB); Melt-spinning; Positron annihilation (PAL); Aluminium alloys; Defects

Owing to the relevance of aluminium alloys as high-strength lightweight materials, further improvements of their mechanical properties by structural refinement is highly attractive. For this purpose, severe plastic deformation and rapid solidification, which are suitable methods for the preparation of nanoscaled crystalline and amorphous Al alloys, are currently the subject of intensive research [1–4]. The complex processes of structural refinement during synthesis as well as the resulting mechanical properties are sensitively affected by atomic-sized free volumes in these structurally complex materials including lattice vacancies and vacancy–solute complexes in the crystallites or structural free volumes in the interfaces and the amorphous phases.

In the present work, the highly sensitive and specific methods of positron annihilations are used for a comparative study of the pattern of free volumes in Al-based alloys prepared by severe plastic deformation and rapid solidification, i.e. accumulative rolling bonding of $Al_{92}Sm_8$ [2] and melt-spinning of $Al_{88}Y_7Fe_5$ [1,4], respectively. The central issue pertains to the variation of the free volumes with preparation route and processing, and in particular, whether and to what extent the pattern of free volumes in melt-spun amorphous $Al_{88}Y_7Fe_5$ differs from that in amorphous $Al_{92}Sm_8$ prepared by accumulative rolling bonding (referred to as folding & rolling (F&R) in the following). Of further interest is the character of free volumes in the interfaces which are introduced in a different manner in both alloys during processing. In melt-spun amorphous $Al_{88}Y_7Fe_5$, interfaces occur between the nanocrystallites and the amorphous matrix during annealing-induced nanocrystallization, whereas in $Al_{92}Sm_8$ interfaces are formed in the course of deformation-induced amorphization.

Positron annihilation [5] serves as a well-established, highly specific technique for studying vacancy–solute interaction and precipitation phenomena in Al-based alloys (see e.g. [6–8]). While positron lifetime spectroscopy yields information on the size of free volumes, two-dimensional Doppler broadening (2DDB) spectroscopy of the electron–positron annihilation radiation [9] is sensitive to the local chemical environment of open-volume positron annihilation sites [7,8]. The chemical information is derived from the core electron momenta of the atoms surrounding the annihilation site [8]. The 2DDB method can also be used to study processes of interfacial segregation [10–12].

Despite the great technological relevance of Al-based alloys as lightweight structural materials, there have been relatively few studies on the structural refinement of these alloys [13,14]. Positron annihilation measurements were initiated recently in order to study the behaviour of precipitates in Al–Cu–Mg–Mn under severe plastic deformation by high-pressure torsion [13]. The focus of the present study is on amorphization and nanocrystallization of Al-based alloys.

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For the present studies, F&R-processed samples were prepared by folding and rolling of stacks of high-purity elemental foils with nominal composition $Al_{92}Sm_8$. The starting thickness was 38 μm for the Al foil of 99.9995% purity and 35 μm after initial polishing and rolling for the Sm foil of 99.9% purity. Of all binary Al-rich glass-forming alloys, Al–Sm offers the largest composition window and the least stringent requirements on processing for glass formation [2]. One F&R cycle denotes folding of a 200 μm multilayer once, with subsequent multiple cold rolling until the original thickness is reached, i.e. one cycle corresponds to a thickness reduction of 50%. The details of this synthesis are described elsewhere [10]. Amorphous $Al_{88}Y_7Fe_5$ was prepared by melt-spinning yielding ribbons with a thickness of about 40 μm and a width of about 5 mm. An ingot with nominal composition $Al_{88}Y_7Fe_5$ for melt-spinning was prepared by arc-melting from the high-purity constituent metals (Al 99.999%, Y 99.9%, Fe 99.995%). Subsequent annealing was performed in a vacuum furnace. X-ray diffraction (XRD) was used to investigate the microstructural evolution of $Al_{92}Sm_8$ and $Al_{88}Y_7Fe_5$ during F&R-processing or thermal annealing, respectively. The XRD measurements were performed with a Bruker D8 Advanced diffractometer with θ–2θ geometry. The microstructure was further checked by transmission electron microscopy (TEM).

Studies of positron lifetime and 2DDB were performed in the same manner as recently described elsewhere [10]. Summarizing briefly, a conventional spectrometer with a time resolution of 230 ps full width at half maximum (FWHM) was used for the positron lifetime measurements. Lifetime spectra of about 5×10^6 coincident counts were analyzed by the program PFPOSFIT [15] taking into account a source correction. The 2DDB measurements were performed using a coincidence setup of two Ge detectors, giving an energy resolution of 0.88 keV (FWHM) related to the 511 keV γ-line. A peak-to-background ratio greater than 8×10^5 was achieved, which ensured sensitivity to annihilation events with high-momentum (core) electrons. Two-dimensional spectra with an energy width of about 1 keV per channel and 6–8 $\times 10^7$ counts were collected, from which the background-free Doppler spectra were obtained. All measurements were performed at room temperature. The chemical-sensitive high-momentum part of the Doppler broadening spectra F was fitted by a linear combination $F = k_{Al}$, $F_{Al} + k_{Sm/Y}$, $F_{Sm/Y}$ of the momentum distribution of the pure constituent metals (F_{Al}, $F_{Sm/Y}$), where k_{Al} and $k_{Sm/Y}$ denote the relative fraction of F_{Al} and $F_{Sm/Y}$ ($k_{Al} + k_{Sm/Y} = 1$). $k_{Sm/Y}$ is presented below. For $Al_{88}Y_7Fe_5$, the minor contribution of Fe is not considered in the spectral analysis. A second type of spectral analysis ([16], not shown in the following), which is based on the ratio of Doppler broadening curves (see Ref. [10] for method), yields the same trend as the two-component fit. This shows the reliability of the results obtained from 2DDB, similar to earlier findings for a Cu–Zr alloy [10].

The sensitivity of the positron annihilation method for studying the chemical environment of vacancy-type defects in the present Al-based alloys is demonstrated by measurements on the dilute alloy $Al_{99.5}Sm_{0.5}$. Upon solution annealing and quenching, an increase in the relative fraction k_{Sm} is deduced from Doppler broadening spectroscopy (Table 1), indicating unambiguously the formation of vacancy–Sm complexes. This is further supported by the positron lifetime component $\tau_2 = 217$ ps (Table 1), which is smaller than that in a lattice vacancy of pure Al ($\tau_V = 253$ ps [17]) as expected for positron annihilation in vacancy–solute complexes [6,8]. For a further check, a second $Al_{99.5}Sm_{0.5}$ sample was subjected to severe plastic deformation by means of high-pressure torsion. In this state the relative fraction k_{Sm} is strongly reduced (cf. Table 1) since grain boundaries and dislocations caused by deformation-induced structural refinement act as competing positron traps in addition to vacancy–Sm complexes. This is also shown by the enhanced positron lifetime component $\tau_2 = 238$ ps (Table 1), which characterizes free volumes slightly smaller than a lattice vacancy as typical of grain boundaries and dislocations [18].

Based on this sensitivity test, positron annihilation was applied to study the structural refinement and amorphization of $Al_{92}Sm_8$ in the course of repeated cold rolling (Fig. 1). According to XRD and TEM analysis (not shown) amorphization of $Al_{92}Sm_8$ sets in at 30 F&R cycles. After 60 F&R cycles a predominantly (~75%) amorphous structure is obtained with a residual crystalline phase consisting of nanocrystallites [19]. The nanocrystallites are mostly embedded individually in the amorphous phase, though minor amounts of agglomerates of nanocrystallites exist. By means of Doppler broadening spectroscopy a characteristic variation of the local chemical environment of free volumes in the course of F&R cycling is observed (Fig. 1a). In the first regime up to 30 F&R cycles, the intensity of Sm is relatively high ($k_{Sm} \sim 50\%$), indicating that a high fraction of free volumes is decorated with Sm. Since in this regime the fraction of amorphous phase appears to be small or negligible (see above), dominant free volumes

Table 1. Positron annihilation parameters measured on F&R-prepared, predominantly amorphous (~75%) $Al_{92}Sm_8$ (60 F&R cycles) and on melt-spun amorphous $Al_{88}Y_7Fe_5$. For comparison the data for Al before and after F&R (40 cycles) as well as for $Al_{99.5}Sm_{0.5}$ after annealing (600 °C, 2 h) and furnace cooling and after subsequent solution annealing (600 °C, 1 h) and quenching or subsequent deformation by high-pressure torsion (HPT) are given. τ_1, τ_2: positron lifetime components; I_2 ($I_1 = 1-I_2$): relative intensities; τ_m: mean positron lifetime; $k_{Sm/Y}$: relative intensity of Sm or Y obtained from two-component analysis of Doppler broadening spectra.

Sample		τ_1 [ps]	τ_2 [ps]	I_2 [%]	τ_m [ps]	$k_{Sm/Y}$ [%]
$Al_{92}Sm_8$	60 F&R	183 ± 4	275	63 ± 2	241 ± 1	19 ± 10
$Al_{88}Y_7Fe_3$	Melt-spun	226 ± 1	–	100	226 ± 1	11 ± 6
Al	Annealed	165 ± 1	–	–	165 ± 1	–
	40 F&R	198 ± 18	312 ± 10	72 ± 9	280 ± 1	–
$Al_{99.5}Sm_{0.5}$	Annealed	157 ± 4	289 ± 15	23 ± 4	188 ± 1	19 ± 8
	Quenched	96 ± 6	217 ± 1	82 ± 1	195 ± 1	50 ± 11
	HPT	138 ± 9	238 ± 3	75 ± 4	213 ± 1	13 ± 17