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Natural ageing of Al–Cu–Mg revisited from a local perspective

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ABSTRACT

Although Al alloys based on the Al–Cu–(Mg) system have been investigated for decades, information about the evolution of microstructure on the atomistic level during natural ageing is scarce. Therefore, the early stages of natural ageing in laboratory Al–Cu–(Mg) alloys and in AA2024 were investigated using positron annihilation and X-ray absorption spectroscopy. This complementary approach allows for accessing both essential components of Al alloys, namely vacancies and alloying elements. It is found, that during natural ageing the chemical environment of vacancies is formed both of Cu and Mg atoms and that the rearrangement of vacancy surroundings persists the hardness increase of Al–Cu–Mg alloys. During natural ageing two different regimes of vacancy environment are detected and interpreted in terms of cluster growth and vacancy capture. Features of the near edge structure of the X-ray absorption are interpreted using theoretical calculations obtained by the FEFF8.4 code. Thus the agglomeration of Cu and Mg, which is accompanied by lattice distortions around Cu atoms, can be probed. A minimal size of Cu–Mg co-clusters is proposed for later stages of natural ageing.

1. Introduction

The decomposition or precipitation process taking place in Al based light alloys implicates their extensive usage in application areas, in which a combination of relatively high strength and light weight is indispensable. The effect of precipitation on mechanical properties of Al alloys was first observed for an Al–Cu–Mg alloy by Wilm in 1911 [1]. Nevertheless, the explanation of the hardness increase during natural ageing in terms of precipitation of Cu platelets had to wait more than 20 years until the discovery of Cu enriched zones by Guinier and Preston [2,3]. Nowadays, Al–Cu–Mg based alloys (2xxx series) are extensively used as structural materials in the aerospace sector and are potential alloys for car body applications.

The technological relevance of these age hardenable alloys has stimulated enormous research activities during the last century [4], for which the early works by Wilm, Guinier, Preston and Bagaryatsky [5] are the starting points. Employing the whole spectrum of materials science techniques the precipitation sequence of Al–Cu–Mg alloys as well as the hardening structures produced during artificial ageing could be clarified to a great extent [6]. Nevertheless, the decomposition process during natural ageing, which leads to the industrially important T4 state of Al–Cu–Mg based materials, still requires elucidation. This is mainly due to the size of the structures formed during the very early stages of decomposition at temperatures below 323 K, which do not entail sufficient contrast to be visible with, e.g. transmission electron microscopy or related techniques. It is thus the aim of this work to tackle the different stages of natural ageing in Al–Cu–Mg alloys by means of the spectroscopic techniques of positron annihilation and X-ray absorption fine structure. The usage of these methods is thereby motivated by the essential ingredients not only of Al–Cu–Mg based alloys but also of nearly all age hardenable Al alloys, namely vacancies and alloying atoms, respectively. Both the methods are highly sensitive to one of these ingredients, which in turn allows for taking up a local perspective on ageing.

Positron annihilation spectroscopy (PAS) and its related techniques are unique tools for the investigation of vacancies in Al alloys. Accordingly, PAS has been applied successfully to determine the role of vacancies in the precipitation process for decades [7,8]. However, most PAS studies concerning Al alloys investigated vacancies during artificial ageing, so that the behaviour of vacancies during natural ageing is a largely unexplored area, which especially applies for Al–Cu–Mg alloys. By contrast, X-ray absorption fine structure spectroscopy (XAFS) has rarely been used for the investigation of structural Al based light alloys until recently [9–12]. This is remarkable in as far as XAFS allows for the selective observation of distinct chemical species and their surroundings. Representative of PAS and XAFS the Doppler broadening of annihilation radiation and the X-ray absorption near edge structure, respectively were employed in this work for the investigation of vacancies and alloy-

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ing atoms as well as their environment during natural ageing in Al–Cu–Mg alloys. Additionally, ab initio calculations of the X-ray near edge structure were carried out, in order to support the experimental X-ray absorption data.

2. Materials and methods

2.1. Samples and heat treatment

Three different Al–Cu based alloys were investigated, a commercial alloy AA2024, a binary Al–Cu laboratory alloy and a ternary laboratory Al–Cu–Mg alloy. The alloying additions in the laboratory alloys are close to those in the commercial one, so that the influence of Mg as well as of minor alloying additions can be assessed. The composition of all three alloys is given in Table 1. The laboratory alloys were melted in an induction furnace using high purity base materials. In order to access the different stages of natural ageing of these alloys, first a solid solution was obtained by a heat treatment at 768 K for 45 min. The samples were then quenched to water at room temperature (RT) and subsequently aged at RT.

2.2. Hardness measurements

The evolution of hardness in the course of natural ageing was measured using a Shimadzu HMV-M3 hardness tester employing a Vickers hardness indenter with a force of 2 N for 20 s loading time. Each hardness value reported in this work represents the mean of at least five measurements.

2.3. Doppler broadening spectroscopy

Among the different experimental techniques based on positron annihilation the spectroscopy of the Doppler broadening of annihilation radiation (DBAR) is well suited both to detect vacancy-like defects and to determine the chemical nature of their next neighbours simultaneously [13,14]. The momentum distribution of electrons taking part in the annihilation process induces a broadening of the 511 keV annihilation peak $\Delta E = (1/2)cp_L$, where p_L is the longitudinal momentum component of the annihilating electron in the direction of the γ-ray emission and c is the speed of light. A change of the positron annihilation site or a change of its surroundings usually coincides with a characteristic change of Doppler broadening. Thereby changes of annihilation site are reflected in the low momentum region, i.e. the low energetic or central part of the annihilation peak roughly corresponding to $p_L \leq 10 \times 10^{-3} m_0 c$, where m_0 is the electron rest mass. The chemical environment mostly affects the high momentum region, i.e. $p_L > 10 \times 10^{-3} m_0 c$, in which annihilation with element specific core electrons dominates. Line shape parameters, which quantify annihilation events in the central part (the S-parameter) or the wing region (the W-parameter) of the annihilation line, then allow for the determination of the positron annihilation site and its surroundings. Besides, ratio-plots obtained by taking the ratio of a complete Doppler broadening curve with a DBAR curve of a reference material can be used to visualize differences in electron momentum distribution. This procedure is sometimes referred to as fingerprint analysis, since especially in the high momentum region each element causes a specific ratio-plot shape. Fig. 1 shows the ratio-plots of some pure metals with respect to annealed Al. The differences in electron momentum distribution are clearly visible and can be used to determine, e.g. the next neighbours of a vacancy even in dilute alloys.

Table 1
Compositions of the investigated alloys given in wt.%. Since this AA2024 contains only very small amounts of Fe and Si, their influence on the decomposition process can be neglected.

Alloy	Cu	Mg	Mn	Fe	Si
Al–Cu	4.0	–	–	–	–
Al–Cu–Mg	4.4	1.6	–	–	–
AA2024	4.4	1.6	0.6	0.1	<0.05

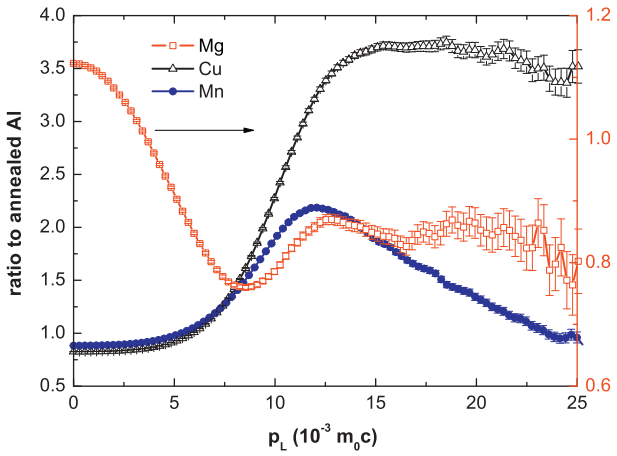

Fig. 1. Ratio-plots of metallic Cu, Mg and Mn. Each alloying element causes a characteristic shape of the DBAR with respect to pure annealed Al. These shapes are used to identify the vacancy surroundings in Al alloys.

All DBAR data presented in this work were measured using a single high purity Ge detector. The acquired spectra were analysed employing the High Momentum Analysis (HMA), which is a specialised method of background reduction [15]. Employing the HMA method the high momentum region could be resolved in spite of using only a single Ge detector. Consequently, the radioactive isotope ^{68}Ge emitting only an insignificant fraction of disturbing high energetic γ-radiation was used as the positron source with an activity of about 0.3 MBq. The 478 keV γ-line of ^{7}Be was used for stabilisation purposes. The energy resolution of the setup at 478 keV in terms of full width half maximum (FWHM) was about 1.35 keV.

2.4. X-ray absorption near edge structure

Structural changes around Cu atoms were investigated measuring the X-ray absorption near edge structure (XANES). Essentially, the explanatory power of this method bases on the modulation of the X-ray absorption coefficient, which strongly depends on the local (electronic) structure around a certain chemical species [16]. In the near edge region, which typically spans the first 100 eV after the actual absorption edge, the excited photoelectron mainly probes the density of empty states in the vicinity of absorbing atoms. This is correlated with the local structure around the absorbing atoms, e.g. coordination number and the type of neighbouring atoms, and thus the XANES is often used for the determination of unknown structures.

The XANES experiments were carried out at the Cu K-edge in fluorescence mode using the 7T-MPW-MAGS beamline [17] at the storage ring BESSY II. The Cu Kα fluorescence radiation was detected employing a NaI scintillation detector, whereas the primary beam intensity was measured using an ambient air ion chamber. The cross-section of the incident X-rays on the sample was about 3 mm × 0.5 mm. Though the X-ray absorption of a metallic Cu reference could not be recorded simultaneously with the actual measurement, subsequent measurements proved the stability of the energy calibration. The alloy samples used for XANES investigations were at least 1 mm thick. Acquired data was further analysed using the software package ATHENA [18] including appropriate self-absorption corrections.