A FIRST STEP TOWARDS SELF HEALING IN ALUMINIUM ALLOYS

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Positron lifetime and Doppler broadening spectroscopy have been applied to probe the free volume generation (vacancies, dislocations and nano-cracks) during plastic deformation of a commercial aluminium AA2024 (T3) alloy. Aim of the total program is to study how solute atoms can be driven to the areas where initial cracking may occur in order to prevent the failure of the specimen. The phenomenon of closing the nano-crack is called Self Healing, and can provide extra strength and ductility to the alloy under some loading conditions. Plastic deformation of over-aged aluminum alloy at room temperature increases the average positron lifetime from initial value of 190 ps to 203 ps. The low momentum parameter S increases in agreement with the increase of open volume defects. The elastic deformation of the sample does not have a recordable effect on the positron annihilation data. It is also shown that the induced damage does not recover after loading the sample, i.e. the AA2024 in the T3 state is non self healing material, as expected, providing important first state result in the research of self healing Al alloys.

INTRODUCTION

The concept of self healing is a new and novel way to bestow a valuable functional property to a structural material and to obtain substantial improvements in reliability and durability. By incorporating a micro-encapsulated healing agent into the matrix even solid materials like polymers were shown to have acquired a self-healing ability [4]. In this application an approaching micro-crack will break the embedded micro-capsules releasing the healing agent into the crack by capillary action. This yields as much as 75% recovery in toughness and will increase the service life and reliability of such material in a wide variety of applications substantially. Besides this engineering approach to self healing, in which the healing functionality is concentrated in special entities in the material structure, other attempts to create self healing behaviour in polymers have focussed on a more integral and molecular appraoch involving reversible bond formation via hygdrogen bonding, ionomers or phase separation effects [1-3]. All these appraoches have in common that the natural mobility of molecules is employed to bring the molecules from their 'rest' position to the damaged site. This mobility of reactive species turns out to be a key ingredient in designing self healing behaviour.

In cementitious materials spontaneous crack closure and therefor self healing has been demonstrated promoting the redeposition of insoluable compounds in the cracks. This was achieved by slightly adjusting the cement chemistry and restricting the crack opening distance to less than 40 micron due to the presence of PVA microfibres [12]. A further improvement in self healing behaviour of cementitious materials was recently obtained by storing dedicated bacteria in the concrete which promote the formation of $CaCO_3$ deposits in cracks [13].

In solid metals self healing behaviour will be difficult to arrange as in general the atoms are insufficiently mobile to travel substantial distances to do their repairing action. However, there are two metal systems which maybe more promising: supersaturated aluminium alloys, which age harden naturally, and high temperature metals used close to their melting point. In this work we concentrate on a hardenable aluminium alloy.

We are using positron annihilation methods in order to study the native defects in Al alloy. A positron is the antiparticle of an electron, and it can get trapped by defects without positive charge, i.e. by vacancies or other open volume defects. Positrons can also get trapped by negative ions or by solute aggregates with higher positron affinity than the host atoms. A measurable positron signal is arising from the annihilation of positron-electron pair where the mass of both particles is converted to two 511 keV γ-quanta. The broadening of 511 keV annihilation photo peak is often characterized by S and W parameters [5], where the S parameter describes annihilations with low momentum electrons and the W parameter is sensitive to annihilations with high momentum electrons.

Using radioactive sources like ^{22}Na one can measure the lifetime of a positron. In the decay of ^{22}Na one 1.28 MeV photon is emitted almost simultaneously with the positron. By measuring the time interval between the birth and an annihilation photon the positron lifetime can be monitored. Open volume defects cause an increase in the positron average lifetime t_{ave} and S parameter and a decrease in W parameter because the electron density is locally reduced in the vacancies and less annihilations with high momentum electrons are occurring.

The purpose of this work is to study with positron annihilation spectroscopy the possibilities to manipulate solute atoms in the way that they can be tailored to the areas where initial cracking has begun. By applying mechanical load local forces in the neighborhood of nano-crack are increasing and could act as attractive centers for solute atoms, which diffuse easily with the help of vacancies, automatically healing the damage caused by load. The intention is to study the potential self healing Al alloy by generating damage with controlled stress and strain levels. Laboratory Al alloys exhibit positron lifetime changes during aging in room temperature indicating vacancy diffusion, which is essential for the self healing concept. In this work we present the damage development in AA2024 in its fully hardened and most frequently used state. It provides the reference behaviour from which to judge future alloy modifications aimed at inducing self healing behaviour.

EXPERIMENTAL

For determining basic stress-strain curves for aluminum we cut samples parallel to the direction of rolling from rolled commercial 1 mm thick AA2024 sheet in the hardened (T3) state. Used Al alloy contains Cu (3.8-4.9 at.%), Mg (1.2-1.8 at.%), Mn (0.3-0.9 at.%), Fe (0.5 at.% max.), Si (0.5 at.%), Zn (0.25 at.%) and other constituents with concentrations of 0.15 at. % at maximum. The sample shape and tension test were done according to ASTM B557 standard. In order to perform aging measurement samples were put in furnace with circulating N_2 gas (492 °C for 10 min) and quenched into water (20 °C) and stored in LN_2 before test. All measurements were done at room temperature with a ^{22}Na source between the samples. To prevent slipping during tension test sandpaper was placed between the samples at the position of the clamps of Instron tensile testing machine. Source was sealed in between two kapton foils with a thickness of 8 μm.

Lifetime detectors were placed as close as possible to the sample surface to maximize the counting rate. For lifetime measurements we use plastic scintillators and photomultiplier tubes, which were coupled to a fast digitizer (2 GS/s). The triggering of the digitizer was

acchieved by an external circuit, which was fed with the splitted signals from the anodes of the start and stop detectors [8]. The time window for the coincidence detection of the start and stop in the external triggering box was established by a simple cable delay (~ 5 m) [8]. The activity of used ^{22}Na source was 3 MBq and it gave ~ 200 counts per second for lifetime measurements. After background reduction and source correction the spectra were analyzed with posfit-program [9] using a single Gaussian resolution function with a FWHM = 260 ps. Collected data included 1 million counts in order to achieve good statistics. For the Doppler broadening spectroscopy we use two HPGe detectors for detecting both annihilation photons in coincidence. Compared to single detector Doppler broadening measurement this gives a much better peak-to-background ratio ($\sim 10^5$) with an energy resolution of 1 keV [10].

RESULTS AND DISCUSSION

Fig. 1 shows the average positron lifetime in the AA2024 (T3) sample during aging at RT after a heat treatment at 492 °C and a quench into water. In contrast to the other samples in this work, the material was not mechanically loaded. The solid line in Fig. 1 is a fit to the function ($? \; \boldsymbol{t}_0 + (\boldsymbol{t}_{inf} - \boldsymbol{t}_0) exp((-t/t_0)^{\boldsymbol{b}})$) with similar parameters as described in Ref. [7]. The fit gives an initial lifetime $\boldsymbol{t}_0$ of 205 ± 1 ps and a final value of $\boldsymbol{t}_{inf} = 188 \pm 1$ ps with a time constant t_0 of $1.4 \pm 0.1 \times 10^5$ s and $\boldsymbol{b} = 0.41$. The more detailed analysis is beyond the scope of this work, but we emphasize that this is important indication of vacancy and atom diffusion at room temperature, which holds promise for achieving self healing behaviour in this alloy.
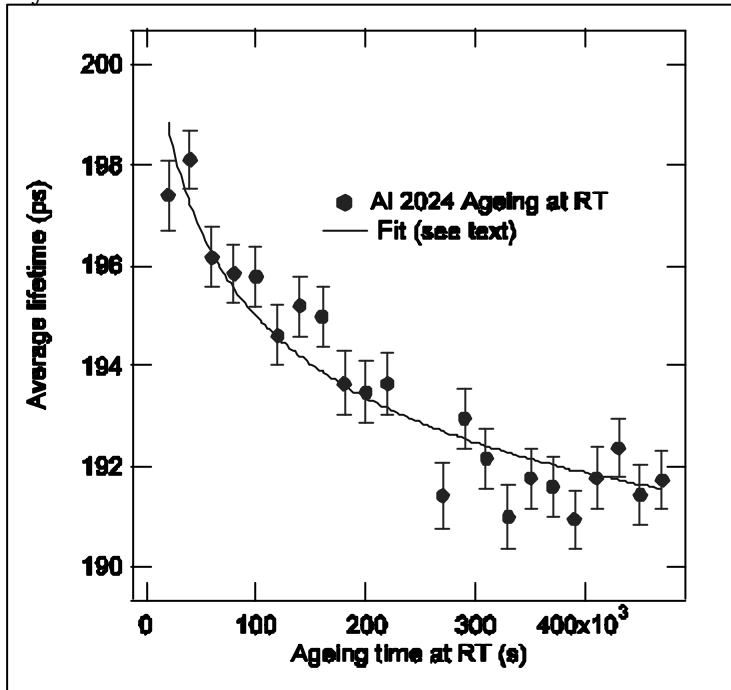

Fig. 1. Average positron lifetime during aging at room temperature after a solution treatment (492 °C for 10 min) and quench. The solid line is a fit.

Fig. 2 shows in a compact way the loading cycles of the sample. In the experiment the strain was increased stepwise (initially 1%, at higher strain levels bigger steps) and

subsequently unloaded to a constant stress level. The measurement at full load reveals the damage development with increasing deformation, which includes the elastic and plastic component of the strain. The measurements at constant stress level reveal the damage at fixed level of elastic straining and provides a better indication of the damage density development because the contribution of elastic deformation is minor in relation to full load condition.
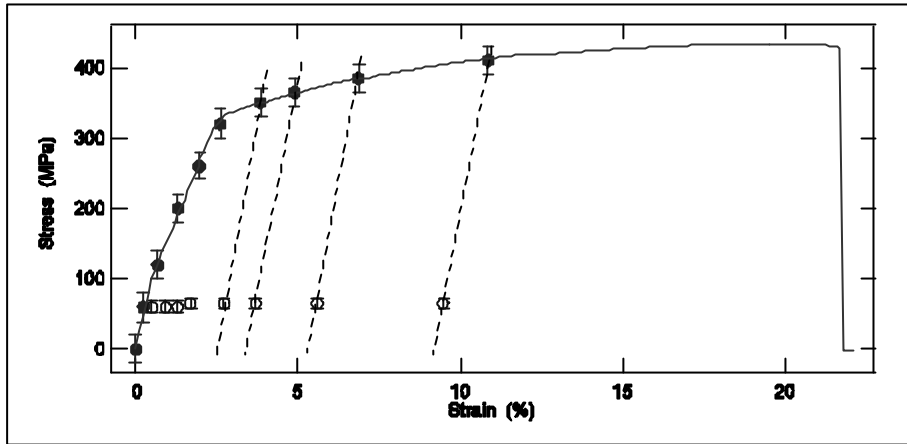

Fig. 2.   Basic stress-strain curve of used Al2024 alloy (solid line). Symbols (filled and opened) denote points where positron signal of Fig. 3 have been measured. Dashed lines connect the points where the sample has been unloaded from high stress value to the lower constant level.

Fig. 3 shows the evolution of the positron annihilation parameters during an applied load. The points are divided into two groups, where one denote measured positron signal during full load (filled circles) and another the signal during unloading the sample (open circles). The intention is to describe the variation in the positron signal between different loading states of the sample (see Fig. 2). The free volume generation during mechanical load is clearly seen in Fig. 3. Both S parameter and average positron lifetime increase with increasing total strain of the sample, while the corresponding W parameter decreases. The parameters seem to be unaffected for strain values below ~ 2.3 %. Referring again to Fig. 2, there is indeed a pronounced difference in the stress-strain curve at this strain value. This is due to the bigger yield of the material in the region where more dislocations are formed. This effect is best observed in the W parameter, which is constant on the strains below 2.3 % and starts to decrease at higher strain values. It can also be seen on average lifetime and S parameter. The plateau is less pronounced in the S parameter and the average lifetime for strains below 2.3 %, but this is probably due to a small increase in dislocation density, seen by the changing slope of the stress-strain curve in Fig. 2 around the stress values of 100-150 MPa. The fraction of positrons annihilating in dislocations is increasing with increasing plastic deformation having a positron lifetime of ~ 235 ps at the saturation [11].

There is also an interesting behavior of the parameters according to the plastic and elastic deformation of the samples. On the basis of Fig. 3 it can be said that releasing the load has no effect on the positron parameters whereas the increased plastic load will increase S parameter and positron lifetime and decrease the W parameter. This effect is the most pronounced in the S parameter; open and filled circles increase side by side indicating that plastic deformation has generated damage, which does not recover even if the load has been removed. This shows that positrons are sensitive only to plastic deformation i.e. generation of dislocations and other open volume defects, while the detection of the elastic deformation is obscured not only by a small increase in dislocation density at low strain

values (< 2.3%), but also by experimental scattering and stability of set up. However, recognizing the plastic deformation in a controlled stress-strain test by positron annihilation technique is an important step to perform the detailed study of self healing in metal alloys.
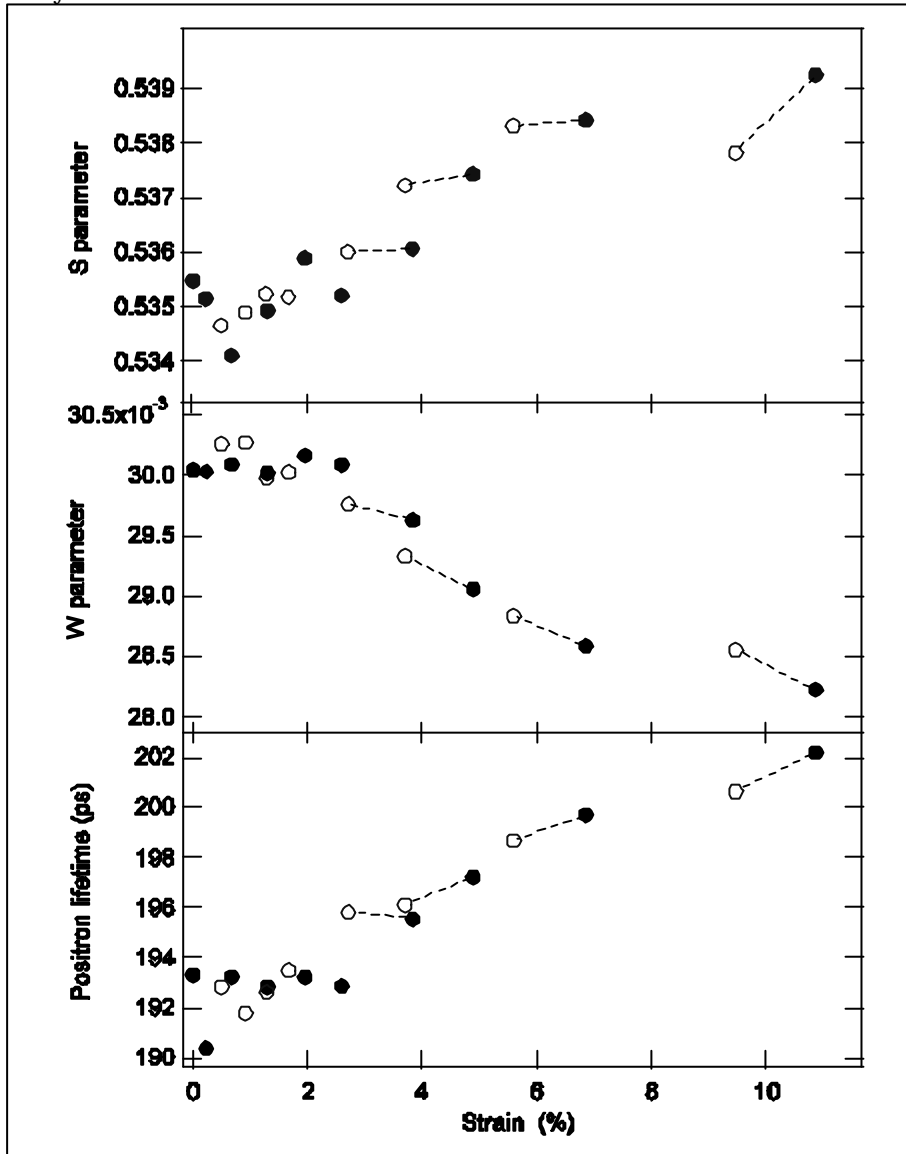

Fig. 3 Positron lifetime, S and W parameter as a function of the total strain of the AA2024 sample in T3 state. The S parameter is calculated from the momentum values between 0-$3 \times 10^{-3}\, m_0 c$ and the W parameter from values between 10-$30 \times 10^{-3}\, m_0 c$. Dashed lines connect the points of full load state and constant elastic strain (compare to Fig. 2).

Applied stress over the yield point increases the dislocation density, which has its characteristic effects on the average lifetime and Doppler annihilation parameters. The stress above yield point produces non recovering defects to the lattice. The introduced damage is sustained and remains constant after plastic deformation regardless of the level of elastic deformation. Interestingly, the positron parameters, both Doppler and average lifetime, are quite insensitive to the unloading, but react to loading of the sample. The present sample is a clear example of a system which does not auto repair itself, i.e. it is not

self healing.

CONCLUSIONS

The effects of aging and mechanical load on a commercial AA2024 (T3) aluminium alloy have been studied by positron annihilation spectroscopy in order to investigate self healing of metal systems. Aging at room temperature after solutionizing and quenching decreases the average lifetime from initial value of 205 ps to 188 ps with a complex exponential decay scheme. This is related to the diffusion of vacancy defects during aging and shows that the material is possibly active in terms of self healing.

Instead of using heat treatments to trigger the precipitation mechanism we study the possibilities to control solute atom clustering by applying mechanical load. The studied AA2024 (T3) alloy exhibits normal stress-strain behavior with regions of elastic and plastic deformation. The results of the combined tension test and the positron measurements during mechanical load can be summarized as follows: i) The stress-strain curve exhibits yield point at stress level of 100-150 MPa ii) The positron lifetime increases with increasing plastic deformation iii) The positron signal is more sensitive to the increase in dislocation density than the stretching of the lattice iv) There is no difference in positron signal in the elastic region of the sample after plastic deformation. This means that the damage introduced by loading the sample mechanically does not repair automatically, i.e. the material is non self healing. This is, of course, an expected result as the material is an untreated fully precipitated Al alloy, but is, nevertheless, an important result because it provides information about nano-scale damage generation in metal alloys with carefully controlled stress and strain levels.

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