

Determination of Fatigue Damage at Precipitate Level in 2024-T3 using Positron Annihilation and Nuclear Magnetic Resonance.

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Abstract

During service, aircraft wing panels have to endure a wide spectrum of mechanical and thermal loads. With the increase in average aircraft lifespan there is a clear need to increase our understanding of the fine details of fatigue damage. An aspect hitherto not addressed is the fatigue damage to the precipitates themselves, ranging from precipitate shearing and dissolution on the one hand and the defect volume at the precipitate-matrix interface on the other hand. Such information can be obtained by combining Positron annihilation and Nuclear Magnetic Resonance measurements. Preliminary measurements on a 30 year old aircraft wing section made out of AA2024-T3 alloy revealed shifts in the positron annihilation curves suggesting a change in the free volume at the precipitate matrix interface. The NMR data indicates that the type and fraction of precipitates had not changed substantially during service. The observations warrant more detailed research on samples fatigued under controlled laboratory conditions.

1. Introduction

Aluminium aircraft alloys, such as AA2024, derive their excellent mechanical properties from the presence of nano-sized precipitates of well-tailored composition and dimension. It is the interaction of dislocations with these precipitates that is responsible for the high yield and tensile strengths values. The precipitate-dislocation interaction is also a key metallurgical parameter for the fatigue strength. While the development of dislocation networks in aluminium alloys during cyclic loading and the successive growth into microcracks (the accumulation of fatigue damage) has attracted a lot of attention in the literature, no studies have been performed on the fatigue damage of the actual precipitates themselves because of the enormous experimental challenges.

Based on existing dislocation-precipitate theories, it can be postulated that at least two potential precipitate fatigue mechanisms can occur: precipitate dissolution and loss of interfacial coherency. Precipitate dissolution is a real option for small precipitates as a result of successive precipitate shearing. The mechanism will lead to an increase in solute concentration and a very local loss of dislocation pinning force and a loss of strength at nanometer scale level.

Alternatively a repeated interaction of dislocations with larger sized precipitates may lead to an atomic restructuring of the semi-coherent precipitate-matrix interface. There are two options: the interface dislocation interaction increases the free volume at the interface via a deformation process or the amount of free volume decreases at the interface due to time dependent and possibly stress accelerated recovery. As with precipitate dissolution, the mechanism will lead to a reduction of precipitate pinning force and a reduction of local static and fatigue strength.

As the fatigue damage in precipitates occurs at the nanometer and sub-nanometer length scale, it will be clear that its experimental determination is extremely difficult. Even the most common technique for revealing the fine detail of precipitate and their interface structure, high resolution Transmission Electron Microscopy, is not very suitable, as the minimal amount of material probed does not easily provide representative information. It is only due to the recent advent of new physical characterisation techniques that we can now attempt to study this damage. The two techniques we used in combination in this project are solid state Nuclear Magnetic Resonance (NMR) and Positron Annihilation (PA). At a later stage we will attempt to use HREM to confirm the information obtained with PA and NMR and to make the link to the dislocation structure.

The Positron Annihilation technique is the most suitable technique to determine free volume or nano-porosity in a all sorts of materials such as metals [1] polymers [2] and ceramics [3]. The technique has also been used successfully to determine the changes in free volume at the AlN –ferrite interface as a function of the internal nitriding conditions [4].

Bastow recently pioneered the NMR technique for characterising Cu containing precipitates in dilute Al(Cu) alloys and related alloys [5,6]. The Al(Cu) alloy system is particularly interesting in that five clearly resolved ^{63}Cu lines are observed which distinguish Cu in solid solution (α -phase), Guinier-Preston zones, θ'' -, θ' - and θ -phase (where the latter two phases are Al_2Cu variants). The spectra observed in low temperature aging in which Cu is transferring between random substitutional sites (α -phase) and GP zones yield clear and novel information about clustering. This spectroscopy has been extended to industrial alloys such as AA 2024 Al(Cu,Mg) to further detect Cu in GPB zones and Cu in S-phase precipitates. Very recent work at CSIRO has shown that, in addition to the Al_2Cu variants listed above, Mg- and Zn-containing intermetallic precipitates in 2000, 5000, and 7000 series aluminium alloys are also observable via ^{25}Mg and ^{67}Zn NMR yielding the detection of S-phase (Al_2CuMg), β -phase (Mg_2Si) and η -phase (MgZn_2) precipitates [7]. No other techniques exist which yield such quantitative and discriminating detail.

2. Experimental

The material to be used in this preliminary study comes from the wing section of a 30-year-old passenger aircraft, which had been in regular use. The original material was in the 2024-T3 condition and had received the usual surface treatments to protect the material against corrosion.

The sample thickness was 1.0 mm. Prior to the NMR and PA measurements the protective surface layer was removed mechanically at low rates and low force levels to avoid the introduction of additional damage to the surface.

As the reference material we used a piece of AA2024-T3 selected randomly from a recently acquired batch of this material. Although no surface treatment had been applied

to the reference material, it received the same mild mechanical grinding treatment to generate a similar amount of surface damage (if any). Two samples from neighbouring places at the wing section were taken and separately prepared for the measurements.

The positron annihilation Lifetime (PAL) and Doppler Broadening (PADB) measurements were performed at the Positron Centre at the Interfaculty Reactor Institute at Delft (The Netherlands). In a PAL measurement a ^{22}Na source (activity typically 2 MBq) encapsulated by two thin kapton foils is sandwiched between two identical samples. ^{22}Na decays to the groundstate of ^{22}Ne by the ejection of a positron immediately followed by the emission of a 1.74 MeV gamma. Two fast scintillation detectors placed around the source/sample assembly are tuned to either detect the 1.74 MeV gamma (start) or one of the two 511 keV annihilation gamma's (stop). These start and stop signals are fed into the timing electronics (with a resolution of 180 ps) coupled to a Time to Amplitude converter, ADC and Multi-Channel-Analyser. By collecting typically 1 million delayed coincidences a so-called lifetime spectrum is obtained. The next step is to analyse the spectrum in terms of (in this study) two lifetime components and their corresponding intensities.

The PADB technique utilises a beam of mono energetic positrons with energies tuneable between 100 eV and 25 keV. After implantation and thermalization the positron diffuses through the matrix until it annihilates with an electron as a free positron or after it has become trapped at an open volume defect. In case of small vacancy type defects both annihilation channels result in the emission of two annihilation gamma's. The energy of the gamma's is found to deviate from the expected value of 511 keV due to the momentum of the annihilating electron (Doppler effect). The two-gamma annihilation events are detected with a high resolution Ge detector and are accumulated in a pulse height analyzed annihilation spectrum. In general, the annihilation of positrons with valence electrons causes less broadening as compared to annihilation with core electrons. The broadening due to core annihilations is to some extent elemental specific as can be observed when both annihilation gammas are detected in coincidence. The broadening of the 511 keV peak is characterized by two parameters. The S-parameter is defined as the relative contribution of the central part of the peak and is related to the annihilation with low momentum valence or conduction electrons. The W(ing) parameter is defined as the relative contribution with high momentum core electrons. Since in this study effects are expected to be depth independent, the S and W data presented are taken at maximum positron implantation energy to avoid surface contributions.

The NMR measurements were performed at CSIRO. The reference (as received) material was sealed in a glass tube under argon, solution treated at a temperature of 490°C and then quenched into an ice/water bath. The NMR specimens (aged from 30-year-old aircraft and as received) were prepared by filing and sieving to 160µm. The 'as received' reference sample was allowed to age at room temperature for 30 days following the quench. NMR spectra for ^{63}Cu were obtained using a Bruker Avance 400 spectrometer operating in a nominal 9.395T field at around 106.0 MHz for ^{63}Cu . The spectra were collected using a phase cycled solid echo sequence: $p_{1,x}-\tau_1-p_{1,y}-\tau_2$ -acq, with pulses of width $p_1=3\mu\text{s}$, $\tau_1 = 250\mu\text{s}$ and $\tau_2= 20\mu\text{s}$. The whole echo was recorded and Fourier transformed to give the absorption lineshape. The reference Knight shift zero for the spectra was obtained from solid CuCl.

3. Results and Discussion

In figure 1 we show the first results obtained by the positron annihilation Doppler broadening technique. In the left panel the Doppler Broadening parameter W is plotted as

a function of S . The axes are scaled in such a way that for crystalline copper and aluminium the coordinates of the S - W cluster points are (0,1) and (1,0), respectively (see inset of figure 1). For points on the line connecting the Cu and Al cluster points the left vertical axis gives the fraction of positrons annihilating at Cu. The data measured on the Al 2024 T3 samples are close to the aluminium cluster point. This part of the figure is plotted on a larger scale in the left panel.

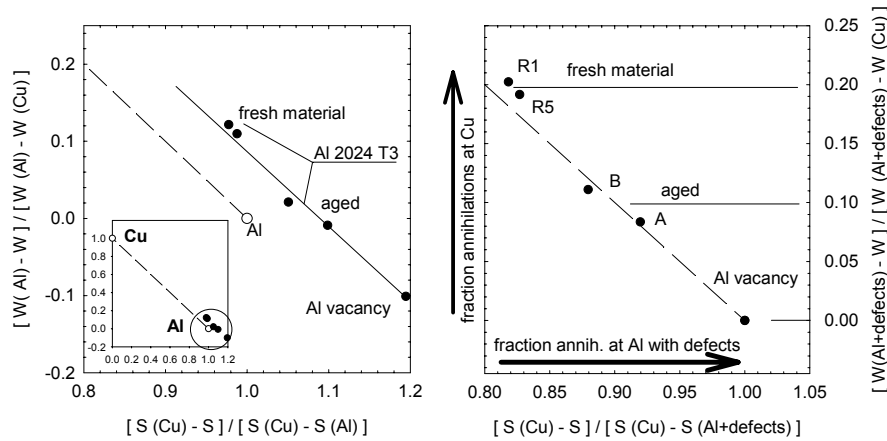


Figure 1: The results of positron Doppler broadening measurements on different Al 2024 T3 samples. The right panel shows the reduction of annihilation at the copper precipitates after aging.

Clearly, the samples can be distinguished in the S - W map according to their history (fresh versus aged material). A second observation is that the points are shifted from the line connecting the Cu and Al cluster points. On this line also the cluster point associated with thermally generated vacancies in an Al single crystal can be found. This invites to rescale the data between the cluster points of Al containing vacancy type defects and that of Cu. The result is shown in the right panel of the figure. The vertical axis now gives the fraction of positrons annihilating at copper (precipitates) as compared to the fraction annihilating in Al containing defects.

An important conclusion following from this is that for the fresh samples R1 and R5 the fraction annihilating at Cu of 20% is obtained, while for the two aged samples (A and B) this fraction has reduced to 10%. In a separate measurement with higher resolution using two detectors in coincidence similar results are obtained.

The results of positron lifetime measurements on these sets of samples show a decrease of the lifetime associated with trapping from 260 ps for the fresh samples to 240 ps for the aged samples. Furthermore, the intensities of this lifetime component increases from 20 to 33%. The lifetime of 240 ps is typical for positron annihilating in vacancies or dislocations in Al and is about 70 ps longer than the observed 166 ps for annihilation in Al. The fact that for the fresh samples the fraction of annihilations at Cu is higher and the long lifetime component is longer than that for Al vacancies indicates that in the fresh state the trapping of positrons likely occurs at the Al-Cu interface accompanied with relative large open volume.

Summarising the positron results, it appears that the aging and/or mechanical loading reduces the size of the vacancy-type defects associated with the precipitate matrix interface but increases the relative amount of these defects. The Doppler broadening results indicate that the amount of Cu observed by the positrons trapped at these sites is less in the aged samples.

Solid state ^{63}Cu NMR can be used to directly probe the Cu environments in the aged and as-received samples. Previous work by Bastow [2] has established the peak assignments in AA2024 as shown in Table 1, and these spectra are reproduced in figure 2a for illustrative purposes. The progressive diminution of the α -phase line on aging, shown in figure 2a, represents the depletion of Cu from the random substitutional sites in the α -phase Al fcc lattice. The α -phase peak position gradually moves to higher ppm shift as the Cu concentration decreases and reaches an upper limit when Cu is in extreme dilution. The position of the peak can be used to provide an independent measurement of the Cu concentration in the α -phase at any stage in the phase evolution. More directly, quantitative integration under the component lines in the spectrum can be used to determine the fraction of Cu atoms in each phase.

Table 1. The alloy and intermetallic phase ^{63}Cu line shifts (± 10 ppm) in AA2024.

Peak position	Phase	Sample Heat Treatment
~3460 ppm	depleted Cu in α -phase	As-quenched, ~ 0.1 at% Cu in random substitutional sites
~3300 ppm	Cu in α -phase	As-quenched, 1.8 at% Cu in random substitutional sites
~2890 ppm	GPB zones	Developed on aging at 177C for 2 hr
~1740/1420 ppm doublet	S phase $\equiv \text{Al}_2\text{CuMg}$	177C for 2 days (and/or stoichiometric Al_2CuMg)

Figure 2b shows the ^{63}Cu NMR spectra for the aged aircraft material and the as received reference material. The spectra are very similar exhibiting an asymmetric peak at 3250 ppm and a broad low intensity peak with centre at approximately 1780 ppm. In the ^{63}Cu spectra shown in figure 2b the asymmetric line peaked at 3250 ppm characterises a state in which there is no clear distinction between Cu in α -phase and GPB zones. The position of the peak at 3250 ppm does not change for as received reference material and aircraft material that has undergone the service loading of 30 years. This result indicates that there is not an appreciable (or measurable) amount of Cu atoms moving to or from the α -phase or GPB zones as a result of the fatigue history. The broad featureless ^{63}Cu peak at ~1780 ppm possibly indicates the formation of a precursor S-phase (Al_2CuMg). This peak is slightly more developed in the aged aircraft sample, beginning to show the doublet peak associated with S-phase. These changes are minor and do not indicate appreciable change in phase content due to fatigue history.

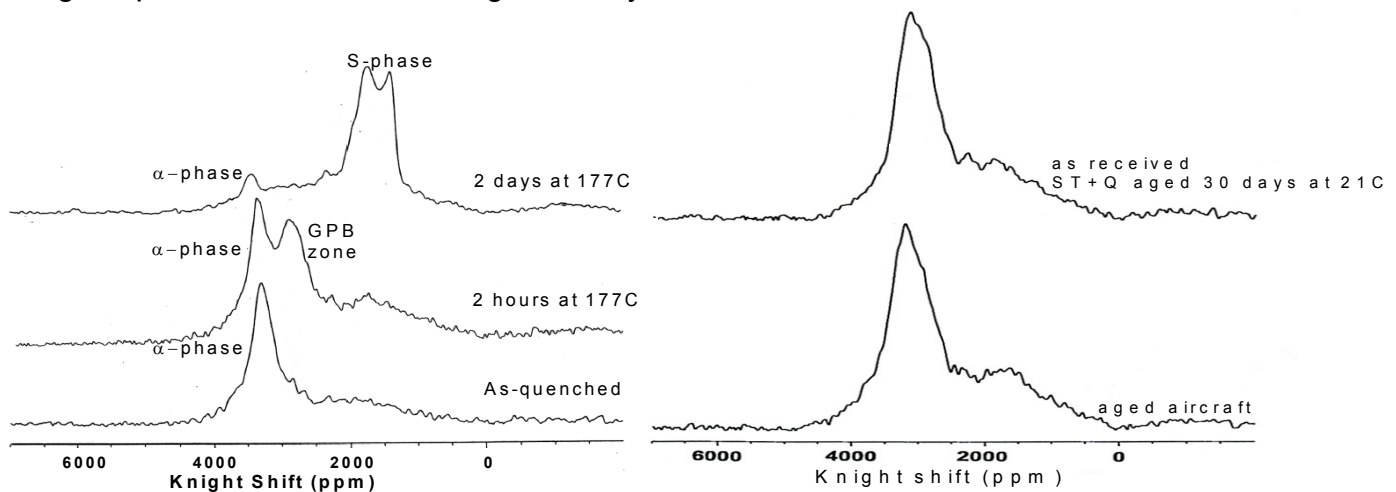


Figure 2: (a) The results of ^{63}Cu solid state NMR measurements on commercial alloy AA2024 illustrating the peak assignments for α -phase, GPB zones and S-phase [Adapted from reference 2]. (b) The results of ^{63}Cu solid state NMR measurements on AA2024-T3 as received and aged samples.

4. Conclusions

In this preliminary study on the fatigue damage of precipitates in a fatigue loaded 30 year old AA2024-T3 sample using Positron Annihilation and solid state NMR we observed changes in the amount of free volume at the precipitate-matrix interface, while the precipitate populations and solute level remained constant. Such a change in interfacial coherency might affect the corrosion and deformation behaviour.

More research using samples with a better-controlled history is required to establish in full the relation between the fatigue history and the interfacial coherency.

Acknowledgement

It is with great sadness that we have to report the death of one of the authors, professor Tom van Veen, during the preparation of the manuscript. Dr. van Veen was the founder and head of the Positron Centre at the Technische Universiteit Delft and a distinguished scientist with a wide international reputation and an excellent colleague. He will be missed by all of us.

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