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INFLUENCE OF MG AND SI ON CLUSTER FORMATION IN Al-Mg-Si ALLOYS STUDIED BY POSITRON ANNIHILATION LIFETIME SPECTROSCOPY

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Abstract

The change of positron lifetimes during natural ageing of binary Al-Mg and Al-Si alloys was characterized. The experiments show that for dilute alloys, the average lifetimes in Al-Si alloys decrease faster to a stable value during natural aging (NA) than in Al-Mg alloys and the vacancy-related lifetime components of Al-Si are also significantly higher than in Al-Mg alloys for equal solute content. For alloys with higher solute contents, the decrease of the lifetime becomes insignificant. This indicates that Si enhances the jump frequency of vacancy while Mg can trap vacancy and slow down the jump frequency of vacancy.

Introduction

Al-Mg-Si alloys are extensively used in the automotive industry due to their excellent mechanical properties, namely medium to high strength, low specific weight combined with good formability, which fulfills the requirement of use as car body panel. Age hardening is induced by the formation of precipitates. These precipitates are formed by diffusion during artificial aging and effectively hinder the movement of dislocations, thereby increasing the strength of the material. Due to the unavoidable storage at ‘room temperature’ before artificial aging (which is equivalent to natural ageing, NA), Al-Mg-Si alloys with various Mg and Si contents exhibit either “positive” or “negative” strength response, which is known to be caused by clusters of solutes formed during NA. Previous studies focused on cluster formation in Al-Mg-Si alloys by using different kinds of indirect methods (DSC, resistivity, etc.) demonstrated that clustering is rather complex. In particular, by using positron annihilation lifetime spectroscopy (which is uniquely sensitive to one of the major ingredients of all age-hardenable Al alloys, namely vacancies) it was found that at least 4 clustering stages exists. However, the exact interpretation of the underlying microscopic processes is still under dispute. In-situ positron lifetime experiments were carried out for pure binary Al-Mg and Al-Si alloys and also ternary Al-Mg-Si alloys in order to clarify the behaviour of Mg/Si atoms during the clustering formation process.

Experiments

Sample preparation

A series of binary Al-Mg and Al-Si alloys with solute contents ranging from 0.005 to 1%, and some ternary Al-Mg-Si alloys, all based on pure Al (5N), were cast by Hydro Aluminium Rolled Products GmbH (comcentrations in this paper are given in atomic percent). Chemical analyses showed that the impurity contents of all alloys are actually smaller than 0.001%, i.e. <1/5 of the smallest solute content. After homogenisation for 24 hours at 530ºC, the alloys were cold rolled to 1.2 mm-thick pieces. The samples used for positron lifetime measurement have a surface area of 10 mm×10 mm and are 1 mm thick, which ensures that most positrons annihilate in the sample material rather than in the surroundings. After mechanical grinding, all samples were ultrasonically cleaned in alcohol to reduce surface effects. The heat treatments of the samples included solutionizing at 545ºC for 1 hour and quenching into ice water. In the furnace, the samples were held in a nickel sample holder in an argon atmosphere. For quenching, the sample holder was first dropped and the sample then pulled out of the holder into the ice water automatically just shortly before reaching the water surface, thus preventing premature cooling and ensuring a high quenching rate. After quenching, the samples were immediately cleaned with alcohol, dried, assembled to a sandwich (consisting of two identical specimens and the ^{22}Na positron source) and placed between detectors. This handling usually takes 1-2 min. All measurements were carried out at 'room temperature' (20 ± 2ºC).

Positron Annihilation Spectroscopy (PAS)

Positron Annihilation Spectroscopy (PAS) is a non-destructive nuclear technique which is used in solid state physics, materials science, chemistry, etc. due to its unique sensitivity to open volume defects such as atom-sized vacancies. In general, the positron lifetime depends on electron density. Different defect components can be measured and distinguished by their corresponding lifetimes. The spectroscopic signals, which depend on defects and phase transitions, provide useful information about the microstructure in solids.

The applied positron source ^{22}Na has an activity of 22.5 μCi and is in the form of $^{22}Na_2CO_3$ salt enclosed by a thin Kapton foil. By performing the conventional "fast-fast" coincidence technique [8], the positron lifetime can be measured as the time difference between the 1.27 MeV γ quantum almost simultaneously emitted with the "birth" of a positron and one of the 0.511 MeV annihilation γ quanta which indicates the "death" of the positron. Two spectrometers were used. The count rate of the first was about 800 s^{-1} with a lifetime resolution of 255 ps. All measurements were repeated by using the second spectrometer equipped with a new detection system (Hamamatsu H3378-50 PMT and BaF_2 scintillator with improved geometry), which has a count rate of 1300 s^{-1} and a lifetime resolution of 220 ps.

For a reliable analysis, a PALS spectrum should contain at least $2{\cdot}10^6$ annihilation events, which would take approximately 30 min at the given count rate. However, the observation of the early kinetics of the quenched alloys during NA requires faster acquisition. This can be solved by interrupting NA and measuring the positron lifetime at a temperature around or below -50ºC where the microstructure is stable. Alternatively, shorter accumulation times can be applied: data sets were acquired sequentially every 60 seconds from the start of the measurement to 1000 min of NA. Four data sets were then binned into one new data set. Preliminary tests showed that this can provide sufficient statistics and we call this "low statistics method". After 3000 min of NA, no significant positron lifetime change was observed in all alloys, and therefore the "high statistics method" was applied. Data sets containing at least $2{\cdot}10^6$ counts were acquired for further analyses and to verify the "low statistics method".

The positron lifetime spectrum is a superposition of exponential decays corresponding to different lifetime components. For instance, fully annealed pure metal has only one bulk component. Due to the presence of an additional positron trap e.g. vacancy, a second lifetime component will appear, which gives us information on the corresponding defect type and possibly its concentration. Different lifetime components were identified mathematically by utilizing the fit program LT9 (in order to get a reasonable spectrum, contributions caused by undesired annihilation events in the source itself have to be subtracted). For the sample which contains two lifetime component, the average lifetime can be calculated as:

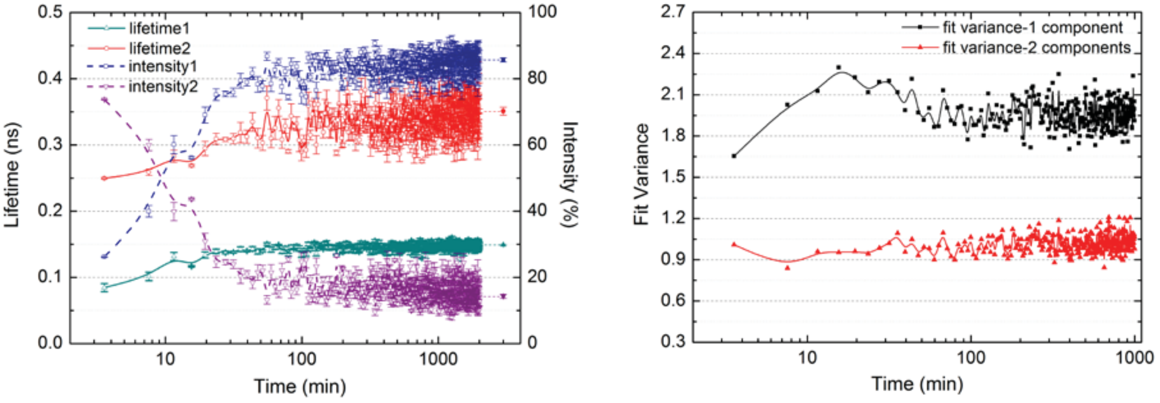
$$\tau = \tau_1 \cdot I_1 + \tau_2 \cdot I_2 \quad (1)$$

where τ_1 and τ_2 refer to bulk and defect-related lifetimes respectively, I_1 and I_2 are the corresponding intensities. Previous studies succeeded in using “low statistics method” for single lifetime component analyses in Al-Mg-Si alloys [6]. The presence of more lifetime components was difficult to prove. Therefore, it is of great interest to show whether this method could be applied for quenched binary alloys which should contain more lifetime components.

Results

Validation of the “Low Statistics Method”

Two lifetimes τ_1, τ_2 and their corresponding intensities I_1, I_2 can be clearly distinguished after decomposing the lifetime spectra of all Al-Mg and Al-Si alloys by using the “low statistics method”. For illustration, Figure 1(a) shows the results for Al-0.005%Si. All the fitted components change significantly during the first 1h of NA but then fluctuate within an acceptable range. The lifetimes and intensities obtained from the “high statistics method” for data collected after 3000 min of NA are also shown in Figure 1 (a), and lie within the scattered range of the “low statistics method”. The fit variances of the two component fits are all much smaller compared with those of the one component fits, Figure 1(b). This is different in ternary Al-Mg-Si alloys where the variances of 1 and 2 components are almost the same.



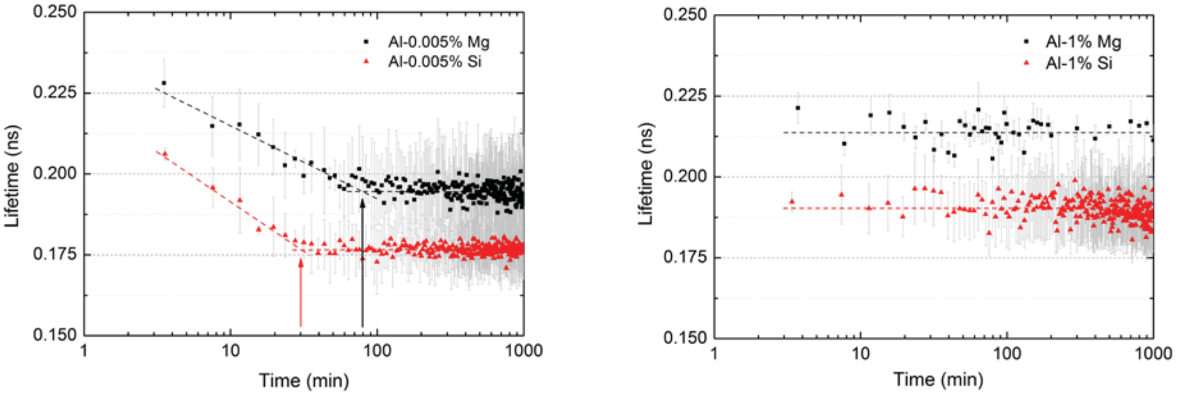
(a) (b)

Figure 1. (a) Decomposition of two lifetime components in Al-0.005%Si alloy by applying the “low statistics method”. For comparison, the components obtained from “high statistics method” are also shown as solid symbols. (b) Variances of one and two lifetime components fits, where the results of the latter are shown in (a).

In order to check the validity of the two component fits, the lifetime τ_1 was also calculated according to the 2-state trapping model [8] and it was found that the calculated and experimental values were nearly the same. Therefore, we conclude that apart from the fluctuations of data caused by low statistics, a reliable estimation of the individual lifetimes and the relevant intensities can be obtained by using a much faster acquisition, and the “low statistics method” of two component fits is applicable to the binary alloys for investigating the fast kinetics during NA.

Comparison of the Binary Al-Mg and Al-Si Alloys

The "low statistics method" shown above was applied to all the binary alloys and the evolution of the average lifetimes during NA was calculated by Eq. (1).

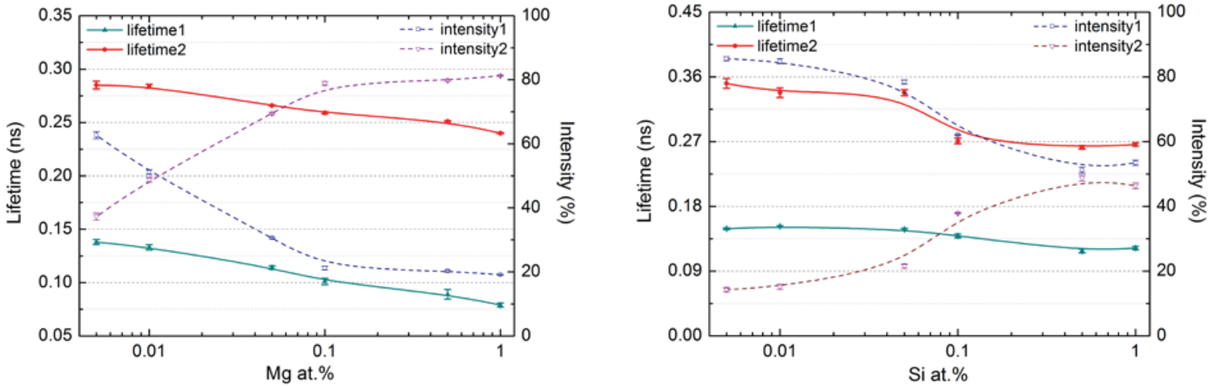


(a) (b)

Figure 2. Evolution of the average lifetime during NA in alloys containing (a) 0.005% Mg/Si and (b) 1% Mg/Si. Arrows indicate the NA time when lifetimes reach to stable values.

As examples, Figure 2(a) and 2(b) show the results for alloys containing 0.005% and 1% solutes, respectively. Three trends were observed: (1) after quenching, the average lifetimes for both of the alloy systems decrease with NA time and reach to a stable value. (2) the decrease gradually becomes inconspicuous for higher solute concentration, and almost disappears in Al-1%Mg and Al-1%Si alloys. (3) with equal solute content, the average lifetime in Al-Si alloys always evolves much faster (<30 min) than in Al-Mg alloys (>80 min). Also, the final lifetime is always higher in Mg containing alloys.

By using the "high statistics method", τ_1, τ_2 and their corresponding I_1, I_2 after 3000 min of NA are obtained for different alloys as given below.



(a) (b)

Figure 3. Dependence of positron lifetimes and intensities after 3000 min of NA on solute concentration in (a) Al-Mg alloys and (b) Al-Si alloys. Spline interpolations serve as guiding lines.

In both alloy systems, the bulk-related τ_1 and I_1 decrease with increasing solute content, while the defect-related τ_2 decreases and I_2 increases with solute content. In addition, Al-Si alloys always exhibit higher τ_1, τ_2 and I_1 values than Al-Mg alloys, while having smaller I_2 values.

Comparison of Pure Al, Binary Al-Mg, Al-Si and Ternary Al-Mg-Si Alloys

The average lifetime evolution of different alloy systems is plotted in Figure 4.

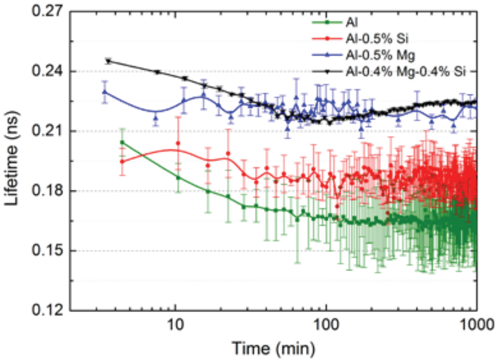


Figure 4. Average positron lifetime evolution during NA. For Al-0.4%Mg-0.4%Si, the spectrum was processed with single component fitting. For pure Al, Al-0.5%Mg and Al-0.5%Si alloys, 2 components were fitted.

Discussion

In pure Al (5N), the fraction of quenched-in vacancies after solution heat treatment at 545°C is around 0.009%. These vacancies will escape to the nearest sinks or in most cases, form vacancy clusters. This process is reflected by the decrease in the average lifetime (combined effect of τ_1/I_1 and τ_2/I_2 in Eq. (1)) during NA for pure Al, see Figure 4. The decomposed stable defect-related τ_2 is ~0.3ns with a corresponding I_2 ~13%, indicating that positrons are trapped in vacancy clusters. Since the lifetime in single vacancies should be ~0.25 ns.

It was shown that single Mg or Si atoms in Al will not trap positrons [4,5,7]. Therefore, the average lifetimes observed in all results are vacancy-related. For the most dilute alloys, i.e. alloys containing 0.005% solutes, the changes in average lifetime is different compared to pure Al, Figure 2 (a), indicating that solutes markedly influence the formation of vacancy clusters. If the binding energy of a vacancy (V) with Mg or Si is positive [3], some of the vacancies will temporarily bind with solute form a V-Si/V-Mg complex. On the other hand, from atomistic calculations, binding between Mg-Mg and Si-Si is not favourable. Also, no clustering reaction can be observed in Differential Scanning Calorimetry experiments [1,2] and therefore solute clustering in the binary alloys can be excluded. Whether a vacancy will detach from a pre-existing V-solute complex is still unknown, as this will depend on a complete set of comparable binding energies between vacancy, solute and Al, plus the vacancy/solute concentration. However, the jump frequency of a vacancy will definitely be affected by the presence of solutes. In recent Monte-Carlo simulations of clustering in a ternary Al-Mg-Si alloy the jump frequency of a vacancy is three times faster than in pure Al due to the presence of Si. The shorter time required to reach a stable average lifetime in Al-Si shown in Figure 2(a) could be explained by the above proposition. The difference between the defect lifetimes ($\tau_{2\text{-}Mg} \approx \tau_{2\text{-Al}} < \tau_{2\text{-}Si}$) and their intensities ($I_{2\text{-}Mg} > I_{2\text{-}Al} > I_{2\text{-}Si}$) is more complicated, as this might involve combinations of vacancy clusters with and without solutes. One possibility could be that Si can act as "inhomogeneous nucleation sites" for vacancy clusters and combining high jump frequency of vacancy with the help of Si, resulting in larger but less vacancy clusters containing at least 3 vacancies. Further experiments and analysis should be done to verify this point. With increasing solute content, the time for a vacancy to find the nearest solute will become shorter until to an extent that the fraction of solutes exceeds the fraction of vacancies in the alloy. This could results in similar behaviour for both alloys that the decrease of average lifetime becomes less obvious for increasing amount of solute, Figure 2(b), but the mechanism could be different. In Al-Si alloys, once a vacancy is attached to Si, the vacancy can still move with high jump frequency to other vacancies to form vacancy clusters (with/without Si), whereas in Al-Mg, the jump frequency of a vacancy is slowed down by attaching to Mg, and the formation of vacancy clusters could be difficult. As a result, $\tau_{2\text{-}Si}$ ~0.260 to 0.275 ns and τ_{2-Mg} ~0.240 to 0.260 ns were obtained which are close to the lifetime of vacancy pairs and mono-vacancy respectively [5].

In ternary alloys in which the concentration of solutes is higher than the concentration of vacancies, a first decrease in lifetime is observed [6], Figure 4. However, it is known that solute clusters are formed and therefore the decrease in lifetime could mean something different than in the binary alloys. What we could learn from the results so far is that both Si and Mg attract vacancies, but Si will move together with a vacancy while Mg could "trap" a vacancy and slow down its movement. This indicates that Si diffusion is the dominating mechanism in clustering in Al-Mg-Si alloys.

Conclusions

The evolution of positron lifetime during NA in quenched Al-Mg/Al-Si has been studied. Two lifetime components can be resolved using the "low statistics method" and it was found that:

1) The average lifetime decreases during NA and becomes stable after a certain NA time. Al-Si alloys reach a stable value faster than Al-Mg alloys due to the high jump frequency of vacancies related to Si.
2) With increasing solute content, the decrease in lifetime becomes less copious. Vacancies can bind with solutes much faster with increasing solute content, forming vacancy solute pairs.
3) The high jump frequency of vacancies with Si results in the formation of vacancy clusters in the final stable state of Al-1%Si alloys, whereas vacancies are "trapped" by Mg which leads to a dominance of the lifetime of mono-vacancies in the final stable state of such alloys.

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References

1. A.K. Gupta and D.J. Lloyd, " Study of Precipitation Kinetics in a Super Purity Al-0.8Pct Mg-0.9Pct Si Alloy Using Differential Scanning Calorimetry," Metallurgical and Materials Transactions A, 30A (1999), 879-890.
2. C.S.T. Chang and J. Banhart, "Low-Temperature Differential Scanning Calorimetry of an Al-Mg-Si Alloy," Metallurgical and Materials Transactions, A 42 (2011), 1960-1964.
3. C. Wolverton, "Solute-Vacancy Binding in Aluminium," Acta Materialia, 55 (2007), 5867.
4. G. Dlubek, o. Brümmer and B. Möser, "A Positron Annihilation Study of Quenched-in Defects in Diluted Al-Mg Alloys," Physica Status Solidi, 63 (a) (1981), 115.
5. G. Dlubek et al., "A Positron Study of Vacancies and their Clusters in Diluted Aluminium Alloys Quenched or Neutron-irradiated," Kristall und Technik, 15 (1980), 1409-1413.
6. J. Banhart et al., "Kinetics of Natural Aging in Al-Mg-Si Alloys Studied by Positron Annihilation Lifetime Spectroscopy," Physical Review, B 83, (2011), 014101.
7. M.J. Stott and P. Kubica, "New Approach to the Positron Distribution in Metals and Alloys," Physical Review, B 11, (1975) 1.

8. R. Krause. Rehberg, Positron Annihilation in Semiconductors (Springer, 1999), 11, 85-88.