Time Dependent Magnetization of an Al-1.6%Mg_2Si Alloy

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Abstract

New observations of time dependent magnetization of an Al-1.6%Mg_2Si alloy over a range of constant temperatures between 250 K and 310 K are presented. The post solution heat treatment time variations of magnetization at 300 and 310 K increased with time out to about 1300 minutes, whereas those at 280 and 290 K showed minima around 150 and 50 minutes, respectively. The magnetization at 250 K initially decreased slightly and then became constant with time. The observed time variations of magnetization are explained in terms of clustering reactions of the Mg, Si and vacancies.

Keywords: time dependent magnetization, clustering reaction, vacancies, Al-Mg-Si alloy

1. Introduction

High mechanical strength to weight ratio is a common and important criteria for metals used in industry, particularly useful to improve energy efficiency of transportation systems. Al-Mg-Si (6xxx series) aluminum alloys are in high demand as a material for vehicles because of their low weight, excellent formability and age-hardenability. This alloy series has an attractive feature that only 1 % Mg + Si solute atoms increase the mechanical hardness by a factor of approximately 5 from the pure aluminum after appropriate heat treatment.[1,2] Previous investigations via electrical resistivity,[3,4] transmission electron microscope (TEM),[5,6] atom probe tomography (APT),[7-9] differential scanning calorimetry (DSC)[10-12] together with other methods, all point to a broadly accepted relationship that a large number of small size precipitations of solute elements result in a high strength, but a small number of large size precipitations lower the strength. Overall vacancy behavior is considered to play an important role in the process, stimulating diffusion of Mg and Si and nucleation of clusters. The Mg-Si-vacancy clusters can lead to initial precipitations of Mg and Si known as Guinier-Preston (GP) zones. Such vacancies and clusters are important, but they are too small to be observed directly. Positron annihilation spectroscopy (PAS)[13,14] and muon spin relaxation spectroscopy (μSR)[14-17] have been successfully used to investigate the vacancy and clustering behavior in Al-Mg-Si alloys. These techniques, however, are not widely accessible since they require special equipment and facilities to utilize radioactive materials.

In the previous work on Al-Mg-Si alloys using DSC, PAS and μSR, the clustering reactions were found to proceed intensively in early few hours after the solution heat treatment (SHT), even at room temperature (natural aging effect). We suspect that a rapid change in the densities of free vacancies and clusters resulting in an equally rapid change in the electronic structure of an alloy would be observable via changes in the magnetic susceptibility. This implies that the isothermal magnetization of the Al-Mg-Si alloys should change with time tracking the vacancy and clustering behavior.

We have carried out a series of magnetization measurements for an Al-1.6%Mg_2Si alloy at a number of constant temperatures between 250 and 310 K and over a time range from approximately 13 minutes to 1300 minutes after SHT. Additionally, the magnetization of a pure aluminum sample, of the same stock as used in preparing the Al-1.6%Mg_2Si alloy (referred as pure Al in text and figures) , was measured at 300 K. The

observed time variations of magnetization correlated well with those obtained via positron annihilation spectroscopy,[13,14] suggesting that, as with PAS, at least two kinds of clustering reactions exert an influence on the time variations of magnetization each manifesting via different magnitude changes and time constants.

2. Experimental Procedure

An ingot of an Al-1.6%Mg_2Si alloy was prepared by melting pure Al (99.99 % purity) with Mg and Si (purity 99.9%) in air. The ingot obtained was formed into 2.5 mm thick plates by hot and cold rolling. Several pieces of the Al-1.6%Mg_2Si sample to be used for magnetization measurements were cut out from the plate with the approximate dimensions of 2.5 × 2.5 × 5.0 mm^3. A sample of the pure Al was also prepared for a baseline comparison. Prior to the magnetization measurements, samples were treated as follows: 1) heated at 848 K for 1 hour, 2) quenched into ice-water, 3) mechanically polished on the surface with a 2000 emery paper for 1 minute to remove oxides, 4) washed in ethanol for 1 minute, 5) fixed on a polypropylene straw with a kapton tape and, 6) loaded into a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL7). The sample treatments 3) and 4) were carried out at approximately 280 K. An external magnetic field produced with a superconducting solenoid was set to 7 tesla (T) in a persistent mode, taking about 10 minutes at a measurement temperature. Typically, a magnetization measurement was started 13 minutes after the quenching. The resolution of the external field is 0.2 mT at 7 T and the temperature stability is about 0.05%. The temperature dependence of magnetization of an Al-1.6%Mg_2Si alloy and the pure Al were measured in the range from 20 to 300 K with the samples aged at room temperature for about one week.

3. Results and Discussions

The time variation of magnetization (M) of an Al-1.6%Mg_2Si alloy at 300 K and 7 T is shown in Fig. 1. The horizontal axis denotes the time (t) elapsed from the sample quench on a logarithmic scale. It is clear that M varies with time, firstly in an increasing rate (concave shape), then later tapering off to a constant value by around 10^3 minutes (convex shape). A similar measurement with the pure Al shows little

variation of M and can be seen in Fig. 2. This comparison clearly indicates that the variation of M with time in an Al-1.6%Mg_2Si alloy is caused through the presence of the solute Mg and Si and their behavior.

Isothermal magnetization measurements with an Al-1.6%Mg_2Si alloy were carried out at 250, 280, 290, 300 and 310 K in an external field of 7 T. The time variation of M were plotted in Fig. 3, where the data points are normalized using a M_0 that is the average of the first five data points in each data set, respectively. The normalization M_0 values for 250, 280, 290, 300 and 310 K are 4.071, 4.076, 3.845, 3.905 and 3.996 $\times$ 10^{-2} Am^2/kg. The data are also offset vertically to avoid overlapping. The offset values for 250 K, 280 K and 310 K are -0.002, -0.001 and 0.003 respectively, but there is no offset for the data at 290 K and 300 K. The M vs t curve at 280 K clearly shows a minimum at about 150 minutes (min). While the M minimum is shifted an earlier time around 50 min at 290 K. The shift of M minimum with a natural aging (NA) temperature is well correlated with those of the positron annihilation lifetime: e.g. figure 10 in reference 13. This shift phenomenon has been explained by two kinds of clustering reactions: cluster (type) 1 and cluster (type) 2.[10-13] From the DSC results, [10-12] the cluster 1 produces a smaller relative amplitude change when held at a lower temperature, while cluster 2 results in a larger amplitude change at a higher temperature. By comparison therefore it would appear that cluster 1 yields diamagnetic (i.e. a negative contribution to) magnetization, but that cluster 2 contributes paramagnetic (positive contribution to) magnetization. This interpretation explains the observed change in M vs t curves at 280, 290 and 300 K. While at higher NA temperatures the cluster 1 reaction occurs earlier. According to the PAS result at 310 K, the cluster 1 reaction was completed within 10 min of SHT and quenching.[13] This observation is in accord with our M vs t curve at 310 K, which has only a time dependence that rises towards an asymptote with a convex shape, i.e. exhibits behavior ascribed to type 2 clusters over measurement time scale.

The positron annihilation experiments with a 99.999% aluminum demonstrated that vacancies were frozen out below 250 K,[18] which is consistent with our M vs t result at 250 K, in which the curve decreases slightly in the early stages, but then becomes constant. Furthermore, after the M measurement at 250 K for 1022 min, the sample

temperature was raised to 300 K in about 10 min, then a *M* measurement was repeated at 300 K, these data are the solid circles in Fig. 3. (The starting time of this data set taken at 300 K, after the sample had already been through an NA at 250 K, was taken as the end point of the 250 K measurement; i.e. the 1022 min. For the *M* data at 300 K after 250K, the M_0 value is 3.931 × 10^{-2} Am^2/kg, and the offset value is 0.0005 in Fig. 3) The two observed *M* vs *t* curves at 300 K, post 250 K and measured at 300 K directly, almost overlap. A finding that also strongly supports the model of the different cluster types being active at different NA temperatures and resulting in different time dependences of *M*.

Temperature (*T*) dependent magnetization of Al-1.6%Mg_2Si and pure Al at 7 T between 20 and 300K are shown in Fig. 4. Both the data sets show increased *M* with decreasing *T* and run parallel to each other. It is therefore reasonable to assume that there are magnetic impurities, such Fe and Mn, which produce large contributions to *M* even though at ppm concentrations. It is not possible, however, that these magnetic impurities produce time dependent magnetizations as observed in Fig. 2. Smaller *M* values with Al-1.6%Mg_2Si than those of pure Al result from the solute Mg and Si.[19)]

Finally we note that the normalization M_0 values change a little between the data sets. There are three possible sources providing small variable contributions to *M* values: 1) a diamagnetic contribution from a straw and a kapton tape fixing the sample, 2) contaminations on the sample surface and/or 3) different concentrations of magnetic impurities. None of these, however, would result in time dependent contributions to the *M* values.

4. Conclusion

In this work time dependent magnetization of an Al-1.6%Mg_2Si alloy has been presented for the first time. The observed minimum on *M* vs *t* curves have a temperature dependence similar to the positron annihilation lifetime under equivalent conditions. The time variations of *M* at various temperatures can be interpreted in terms of clustering reactions. The present study, thus, points to a new way to study Mg, Si and vacancy clustering reactions via the use of the conventional technique of DC magnetization. Band structure calculations for an Al-Mg-Si alloy are in progress to

investigate the electronic structure.

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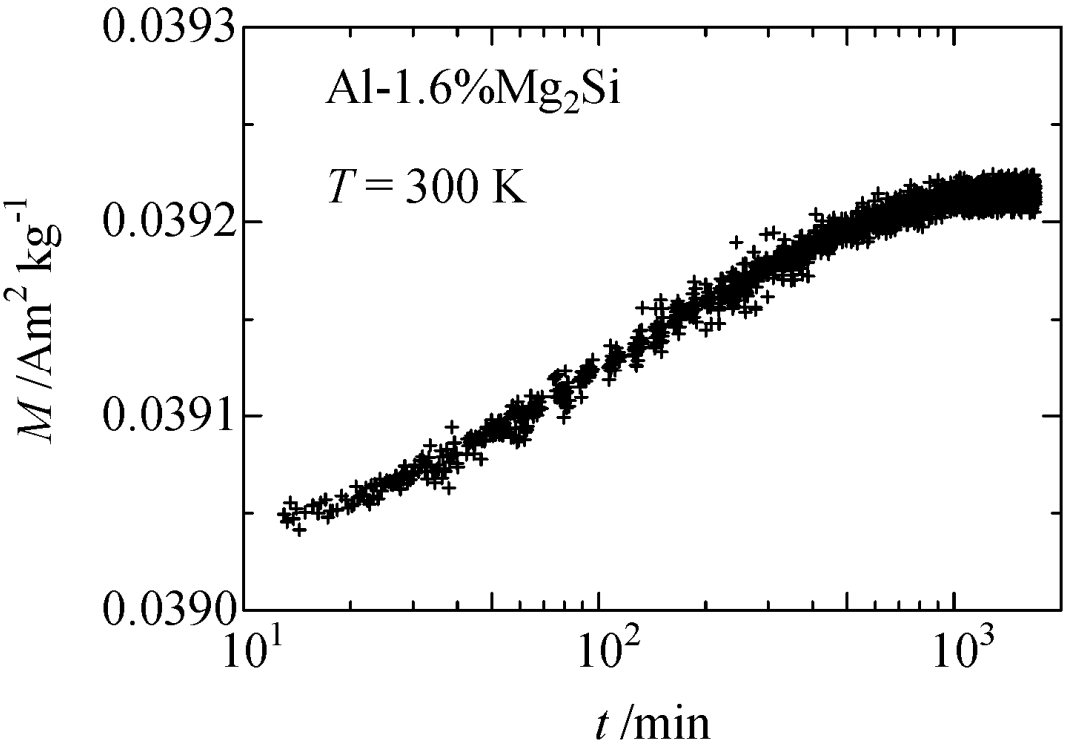
Captions List

Fig. 1 Time dependence of magnetization of an Al-1.6%Mg_2Si alloy at 300 K and 7 T.
Fig. 2 Time dependence of magnetization of pure Al at 300 K and 7 T.
Fig. 3 Time dependence of normalized magnetization of an Al-1.6%Mg_2Si alloy at a constant temperature between 250 and 310 K. The data points marked by solid circles (300 K after 250 K) are those data measured at 300 K on the sample post 250 K (see text).
Fig. 4 Temperature dependence of magnetization of pure Al and an Al-1.6%Mg_2Si alloy at 7 T.



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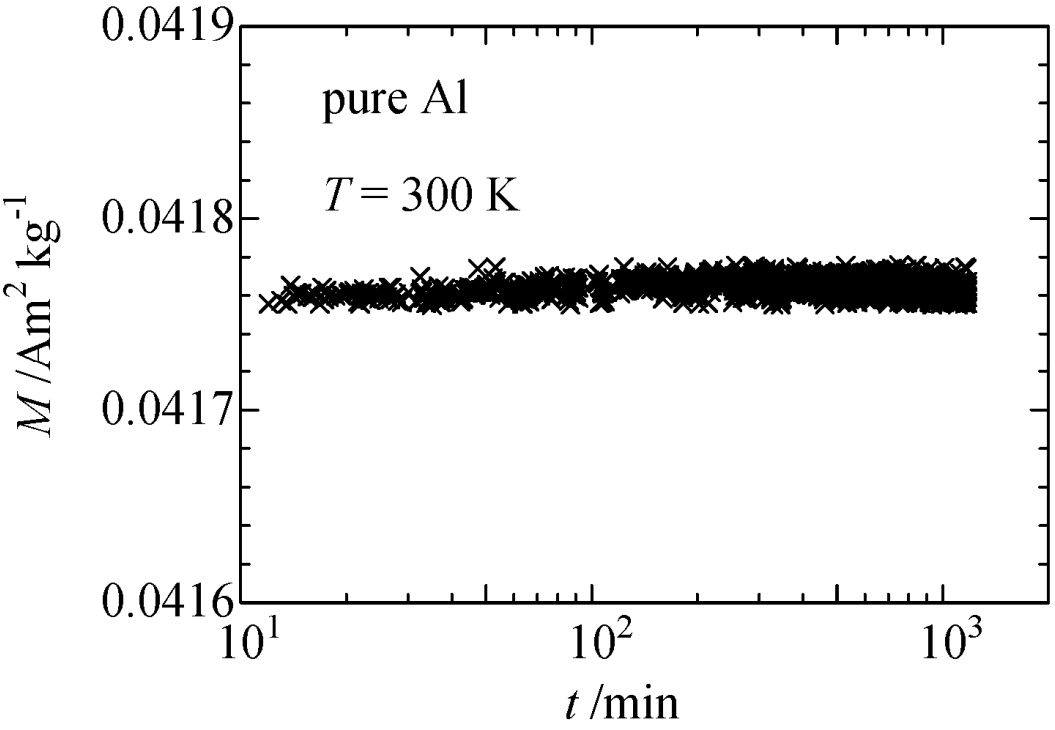


Fig. 2 Time dependence of magnetization of pure Al at 300 K and 7 T.

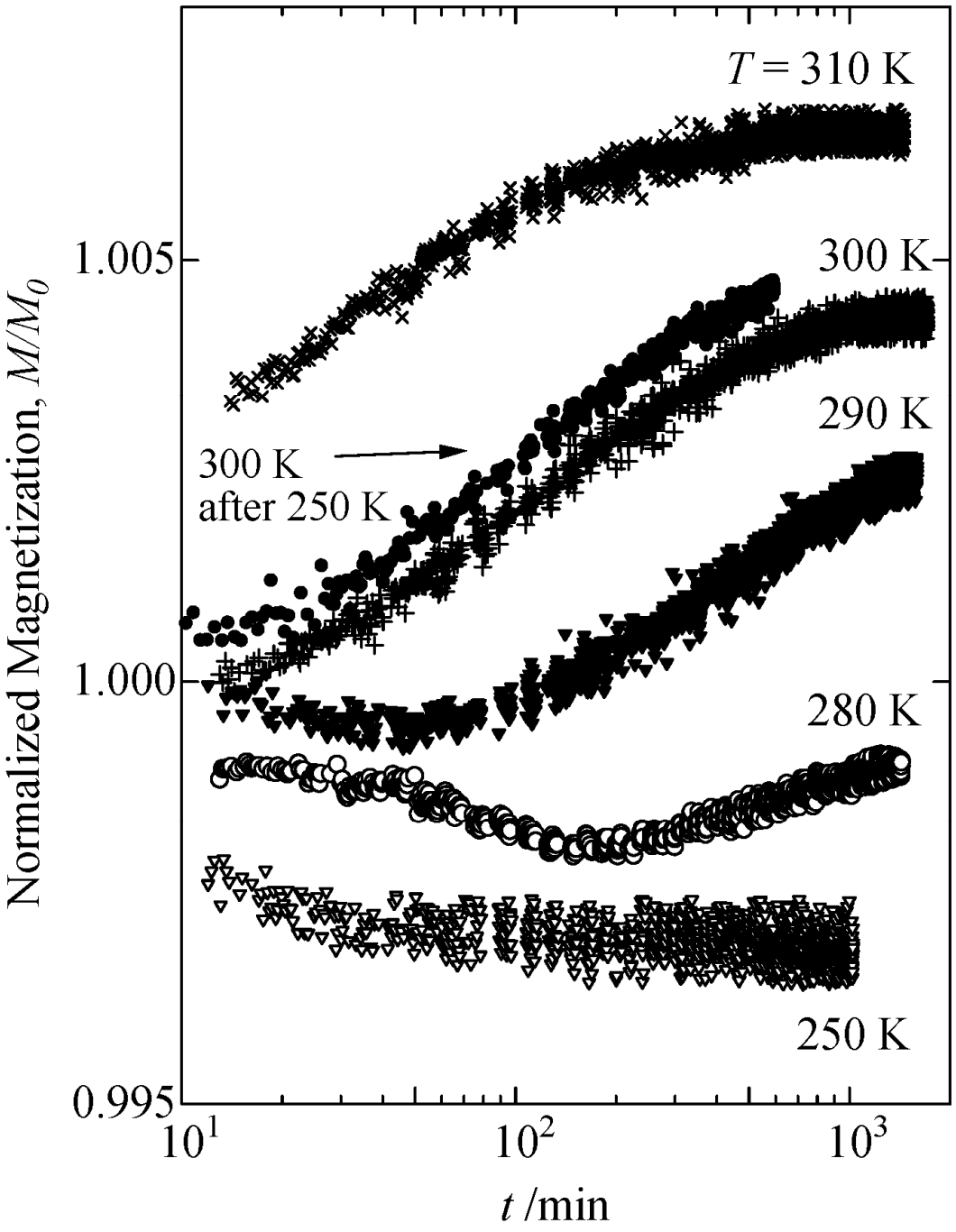
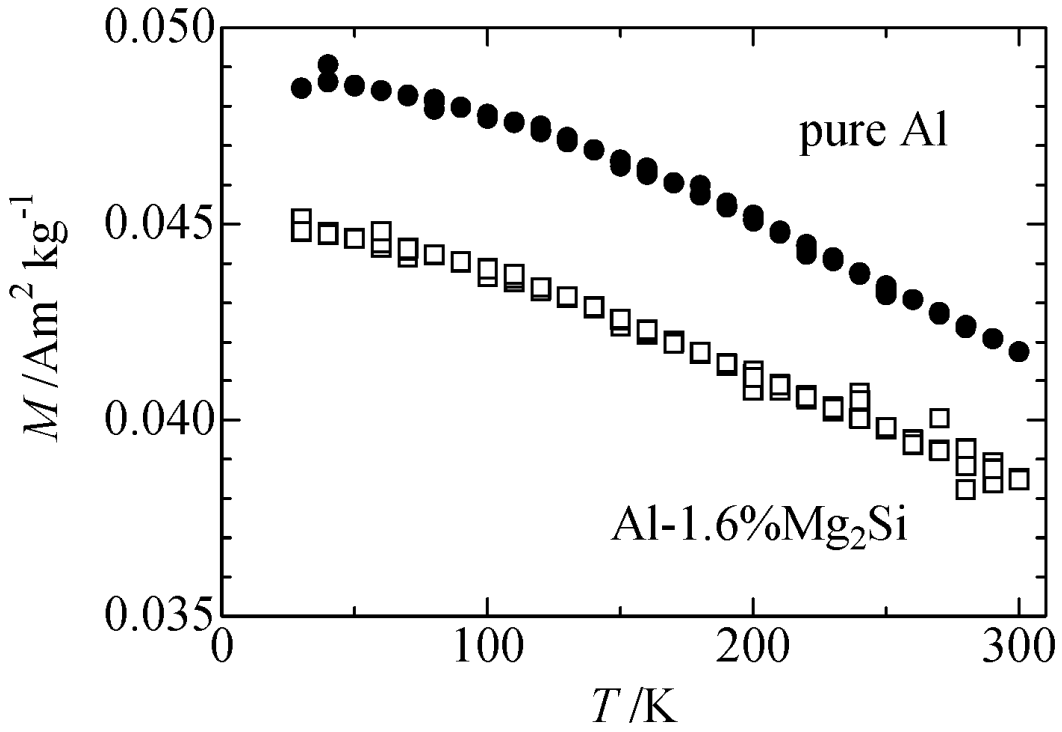


Fig. 3 Time dependence of normalized magnetization of an Al-1.6%Mg_2Si alloy at a constant temperature between 250 and 310 K. The data points marked by solid circles (300 K after 250 K) are those data measured at 300 K on the sample post 250 K (see text).



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