Early stage clustering behavior in Al-Mg-Si alloys observed via time dependent magnetization

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Abstract

Time dependent magnetization of Al-0.67 at.%Mg-0.73 at.%Si, Al-1.07 at.%Mg-0.33 at.%Si and Al-1.07 at.%Mg-0.53 at.%Si alloys are presented over a range of constant temperatures between 250 and 320 K. The magnetization vs. time curves for the samples show minima for temperatures near 290 K. The observed times at which the magnetization minima occur were found to depend on both the solute concentrations and the measurement temperatures. From these results the activation energies from the Si-rich clustering stage to the Mg-Si co-clustering stage were extracted. The deduced activation energies were found to be comparable to those from the positron annihilation measurements, depending on the solute concentrations.

Keywords: time dependent magnetization, clustering reaction, activation energy

1. Introduction

Strong, light weight metals are essential to industry, especially for transport where high energy-efficiency is an important criterion. The Al-Mg-Si (6xxx series) aluminum alloys are in high demand as materials for vehicles because of their low weight, excellent formability and age hardenability.[1,2] The usual process for heat treatment is a solution heat treatment (SHT) at around 820 K followed by a quick quench to water, resulting in a supersaturated solid solution (SSSS). After inevitable storage at room temperature (called natural aging, NA), the alloy is given an artificial aging (AA) at around 420 K, leading to a precipitation sequence:[3,4]

SSSS $\rightarrow$ Mg/Si/vacancy cluster $\rightarrow$ Guinier Preston (GP) zone $\rightarrow$
$\beta' \rightarrow \beta'' \rightarrow \beta(Mg_2Si)$.

It is well known that the early stage of solute clustering of Si and Mg proceeds quite quickly and often is completed in less than an hour even at room temperature.[5-9] A long-standing problem for industry is that some periods of NA often result in a negative effect on the mechanical hardness in the following AA.[4,10-12] The microstructures of the precipitations have been studied intensively via transmission electron microscopy (TEM)[13,14] and atom probe tomography (APT)[3, 15-17] to reveal the age hardening mechanism. These techniques, however, require time consuming sample preparations, thus it is difficult to observe directly the early stage of clustering. Differential scanning calorimetry (DSC)[18-21] has been widely used to investigate the precipitation processes and cluster formations, but in principle this method cannot be used for isothermal measurements since peak positions in a heat follow spectrum depend on a heating rate. From the various studies with Al-Mg-Si alloys, vacancy behavior is considered to play an important role in the aging process, stimulating diffusion of solute Mg and Si atoms and nucleation of clusters. Positron annihilation spectroscopy (PAS)[6-9] and muon spin relaxation spectroscopy (μSR)[22-24] have been successfully used to investigate the vacancy and clustering behavior in Al-Mg-Si alloys. These methods, however, are not widely accessible as special facilities and equipment are required to handle radioactive materials. Quite recently we have found that conventional DC magnetization of Al-1.07 at.%Mg-0.53 at.%Si could provide similar information to the previous studies.[25)]

In this paper we expand the studies, confirming that DC magnetization can track time development of the early stage clustering of Mg- or/and Si-vacancy in Al-Mg-Si alloys with different solute Mg and Si concentrations. Magnetization measurements were carried out for Al-0.67 at.%Mg-0.73 at.%Si (noted as Al-7-7) and Al-1.07 at.%Mg-0.33 at.%Si (Al-10-3) at a number of constant temperatures between 250 and 320 K (NA temperature) and over a time range from approximately 12 to 1300 minutes after SHT. A measurement on the Al-1.07 at.%Mg-0.53 at.%Si (Al-10-5), additional to the previous work, was carried out at 270 K. The magnetization vs. time curves with these three samples showed minima at NA temperatures around 290 K. In addition, the times of the magnetization minima were found to depend on the solute concentrations, as well as the NA temperatures. These results enable us to extract the activation energies for the clustering process, which can be compared with values reported previously.

2. Experimental Procedure

The experimental procedure was the same as that in our previous work.[25)] Ingots of Al-7-7, Al-10-3 and Al-10-5 alloys were prepared by melting pure Al (99.99 % purity) with Si and Mg (purity 99.9 %) in air. The resulting ingots were formed into 2.5 mm thick plates by hot and cold rolling. Several pieces of the samples to be used for magnetization measurements were cut out from the plate with the approximate dimensions of 2.5 × 2.5 × 5.0 mm. Prior to the magnetization measurements, samples were annealed at 848 K for 1 hour and directly quenched into ice-water (SHTQ). It took about 12 minutes to load the sample into a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL7), then apply an external magnetic field of 7 tesla (T) produced with a superconducting solenoid in a persistent mode and started the measurements.

3. Results and Discussions

The time variation of magnetization (M) of the Al-7-7 sample at 290 K and 7 T is shown in Fig. 1. The horizontal axis denotes the time (t) from SHTQ on a logarithmic scale. It is clear that M varies with time with a minimum occurring at 55 minutes as marked by the arrow in Fig 1. This magnetization minimum was estimated from the intersection of the two lines as shown. These lines are least-square fits to two adjacent parts of the data (on the logarithmic time scale), before and after the minimum, respectively. The observed M vs. t curve closely resembles that of the positron lifetime vs. time at 291 K with a Al-Mg-Si alloy of similar Mg and Si concentrations (see FIG. 6 in ref.6)), which did not give exact concentrations of the solutes for the alloy F, but from their FIG. 16) we estimate Al-0.75 at.%Mg-0.78 at.%Si), in which the minimum of the lifetime was found at 50 minutes; this value is consistent with that extracted in Fig. 1.

Isothermal magnetization measurements with the Al-7-7 sample were carried out at 250, 270, 280, 290, 300 and 310 K in an external field of 7 T. The time variations of M were plotted in Fig. 2. Minima in M are apparent in 280, 290 and 300 K data (marked by the arrows). Also there is an NA temperature dependence in the minimum time; a higher NA temperature leads to an earlier M minimum time. This phenomenon is explained by the clustering processes of Mg- or/and Si-vacancies.5,6) The initial M values at each individual NA temperature scattered around 0.0403 $\mathrm{Am^2kg^{-1}}$ by about 1 % in magnitude, most likely due to the diamagnetism of a kapton tape used for fixing the sample. This diamagnetism, however, hardly makes time dependent contributions to the magnetization.

Isothermal M vs. t with the Al-10-3 sample were measured at 275, 280, 290, 295, 300 and 320 K as shown in Fig. 3. A comparison of the results for the (Mg rich) Al-10-3 sample with those for the (Si rich) Al-7-7 reveals two distinct contributions of the solute concentrations to the M variations with time. The M minimum times at 280 and 290 K with the Al-10-3 clearly occur later than those with the Al-7-7. The magnitudes of M

changes around 10^3 minutes for the Al-10-3 are about double of those for the Al-7-7 above 290 K; thus the solute Mg atoms seem to make positive contributions to magnetization in the clustering process in the later time ranges.

A measurement with the Al-10-5, additional to those of ref. 25), was performed at 270 K. The M vs. t curve is displayed in Fig. 4 together with our previous data sets at 280, 290 and 300 K. Again the shift of M minimum with NA temperature is obvious. The largest solute concentration of Mg + Si among the three samples is considered to result in the largest M value change of 1.6×10^{-4} Am^{2}kg^{-1} near 10^3 minutes at 300 K. The corresponding values for the Al-7-7 and Al-10-3 are 5.1×10^{-4} and 9.2×10^{-4} Am^{2}kg^{-1}, respectively.

The observed complex variations of M vs. t curves imply that the clustering processes of Mg, Si and vacancy involves several stages with different magnitudes and time constants depending on the solute concentrations and the NA temperatures. While it is not possible to clarify cluster types from the present data, we have made an attempt to estimate the activation energy of clustering (Q) following the methods used in the PAS study.6) Since the observed M minimum times (t_{min}) are well correlated to the transition times from stage II (C1, in which Si rich clusters form) to stage III (C2, Mg-Si co-clusters form) reported from the positron lifetime and resistivity studies under equivalent conditions,5,6) we assume that the t_{min} is related with the transition time from the stage II to III. In Fig. 5 we present Arrhenius plots of logarithmic t_{min} against reciprocal temperature of NA (T_{NA}), $\ln(t_{\mathrm{min}}) \sim Q/k_{\mathrm{B}}T_{\mathrm{NA}}$, based on the data of Figs. 2, 3 and 4. Least square fits of the data yields Q = 0.73 (+-0.04), 1.08 (+-0.08) and 0.91 (+-0.02) eV for the Al-7-7, Al-10-3 and Al-10-5, respectively. The resulting stage II to III Q values seem to be dependent on the sample Si concentrations; the Q values increase with decreasing Si concentrations as shown in the inset in Fig. 5. This finding is consistent with the conclusion of the DSC studies, in which the DSC peaks for the C1 reaction shifted to higher temperatures with decreasing the Si concentrations of Al-Mg-Si alloys.19,21) From this analysis it is apparent that the clustering process in the stage II is dominated by the action of the Si-vacancy clusters. The recent APT study by

Zandbergen et al.[17)] explains that relatively large size of Mg atoms favors formation of Si-rich clusters in an early time range due to relatively larger diffusivities of Si. The deduced Q value for the Al-7-7 agrees with that of 0.77 (+-0.05) eV for the sample F (Al-0.75 at.%Mg-0.78 at.%Si) in the PAS study.[6)] There are indeed several reports of Q values in the range 0.32 – 0.90 eV.[5,6,21)]

4. Conclusion

This work has confirmed that a conventional DC magnetization measurement can be utilized to study the early stage clustering reactions in Al-Mg-Si alloys in isothermal conditions. The isothermal time variations of M were found to depend on temperature as well as the solute Mg and Si concentrations. The observed t_{min} on M vs. t curve has temperature dependence similar to that of positron annihilation lifetime under equivalent conditions. Arrhenius plots of logarithmic t_{min} vs. reciprocal NA temperature provide activation energy from stage II to stage III, which are consistent with those in literature. In addition, the deduced values of the activation energy were found to depend on the solute Si concentrations, implying the predominant reactions of Si-vacancy in stage II. The present results of M vs. t curves would be useful to investigate forms of Mg/Si/vacancy clusters in Al-Mg-Si alloys since the magnetization is closely related with the electronic structure of clusters.

Acknowledgments

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Captions List

Fig. 1 Time dependence of magnetization of an Al-0.67 at.%Mg-0.73 at.%Si alloy at 290 K and 7 T. The time that the magnetization minimum occurs is marked by the arrow which in turn was determined as the intersection point of the two linear least-square fits.

Fig. 2 Time dependence of magnetization of an Al-0.67 at.%Mg-0.76 at.%Si alloy at a constant temperature between 250 and 310 K.

Fig. 3 Time dependence of magnetization of an Al-1.07 at.%Mg-0.33 at.%Si alloy at a constant temperature between 270 and 320 K.

Fig. 4 Time dependence of magnetization of an Al-1.07 at.%Mg-0.53 at.%Si alloy at a constant temperature between 270 and 300 K. (The data sets at 280, 290 and 300 K are quoted from ref. 25))

Fig. 5 Arrhenius plots for Al-0.67 at.%Mg-0.73 at.%Si, Al-1.07 at.%Mg-0.33 at.%Si and Al-1.07at.%Mg-0.53 at.%Si using the magnetization minimum time and a natural aging temperature. The inset shows a plot of activation energy vs. Si concentration.

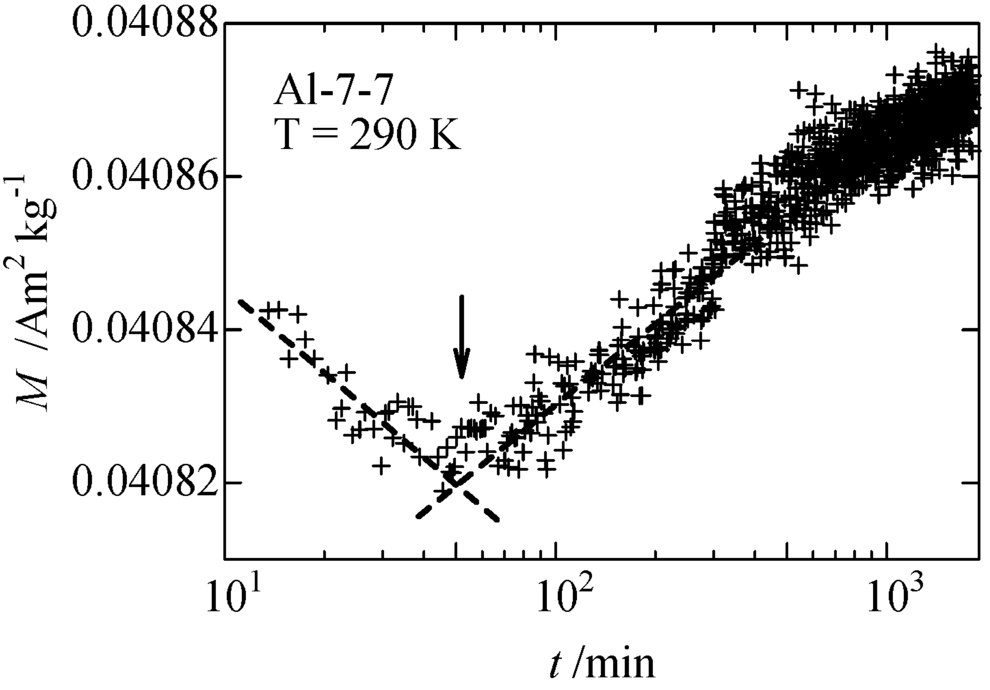


Fig. 1 Time dependence of magnetization of an Al-0.67 at.%Mg-0.73 at.%Si alloy at 290 K and 7 T. The time that the magnetization minimum occurs is marked by the arrow which in turn was determined as the intersection point of the two linear least-square fits.

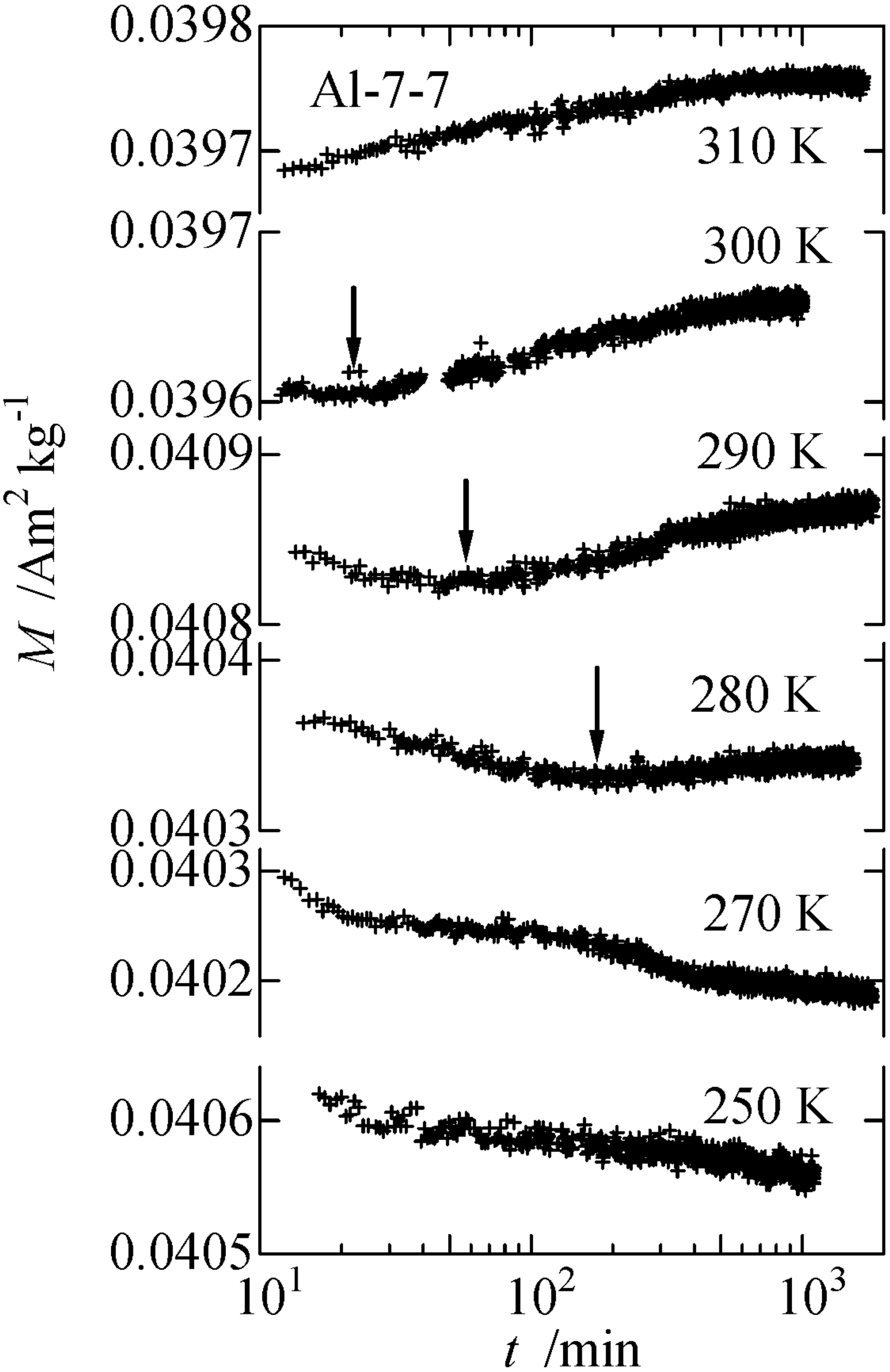


Fig. 2 Time dependence of magnetization of an Al-0.67 at.%Mg-0.76 at.%Si alloy at a constant temperature between 250 and 310 K.

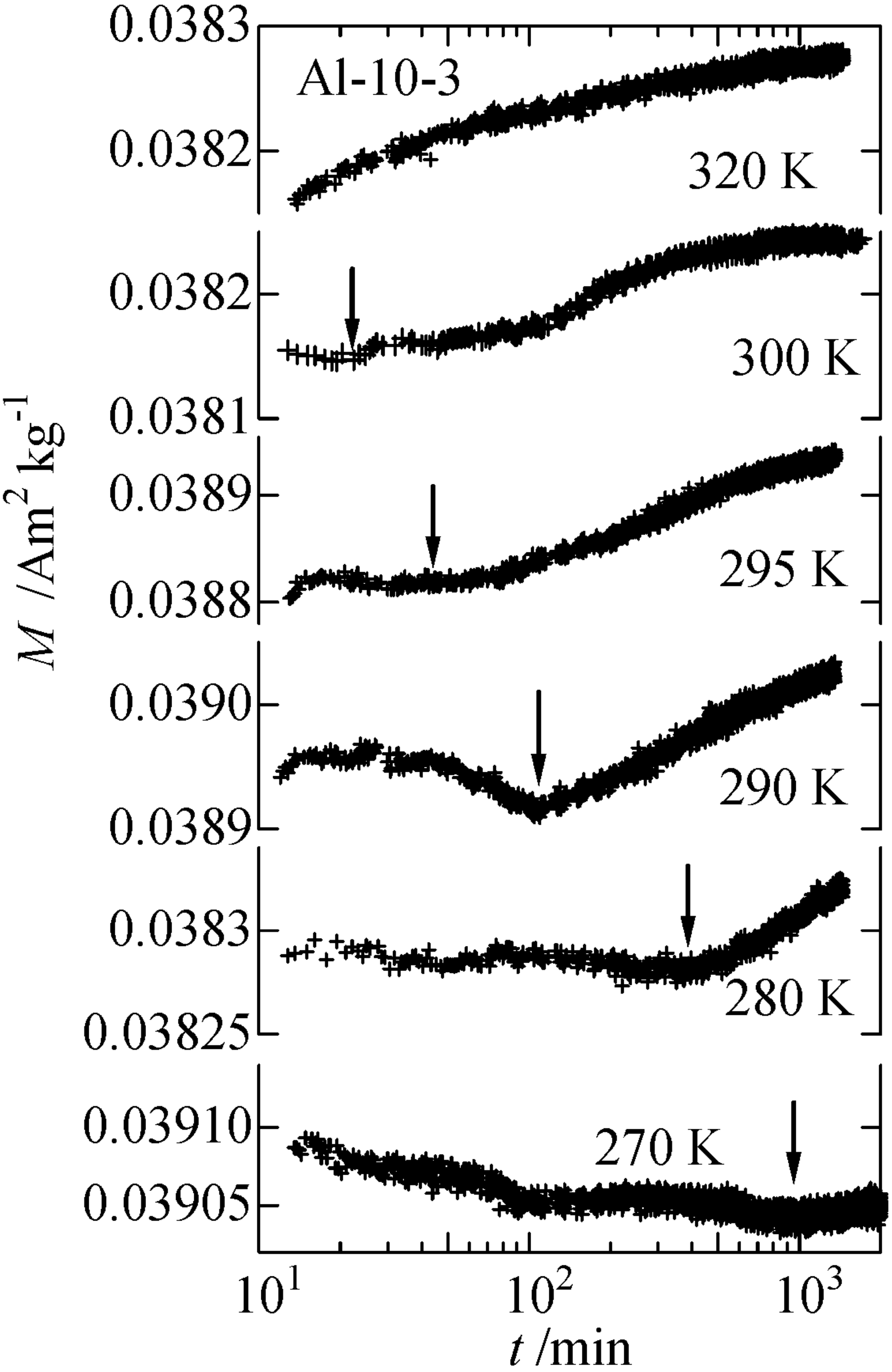


Fig. 3 Time dependence of magnetization of an Al-1.07 at.%Mg-0.33 at.%Si alloy at a constant temperature between 270 and 320 K.

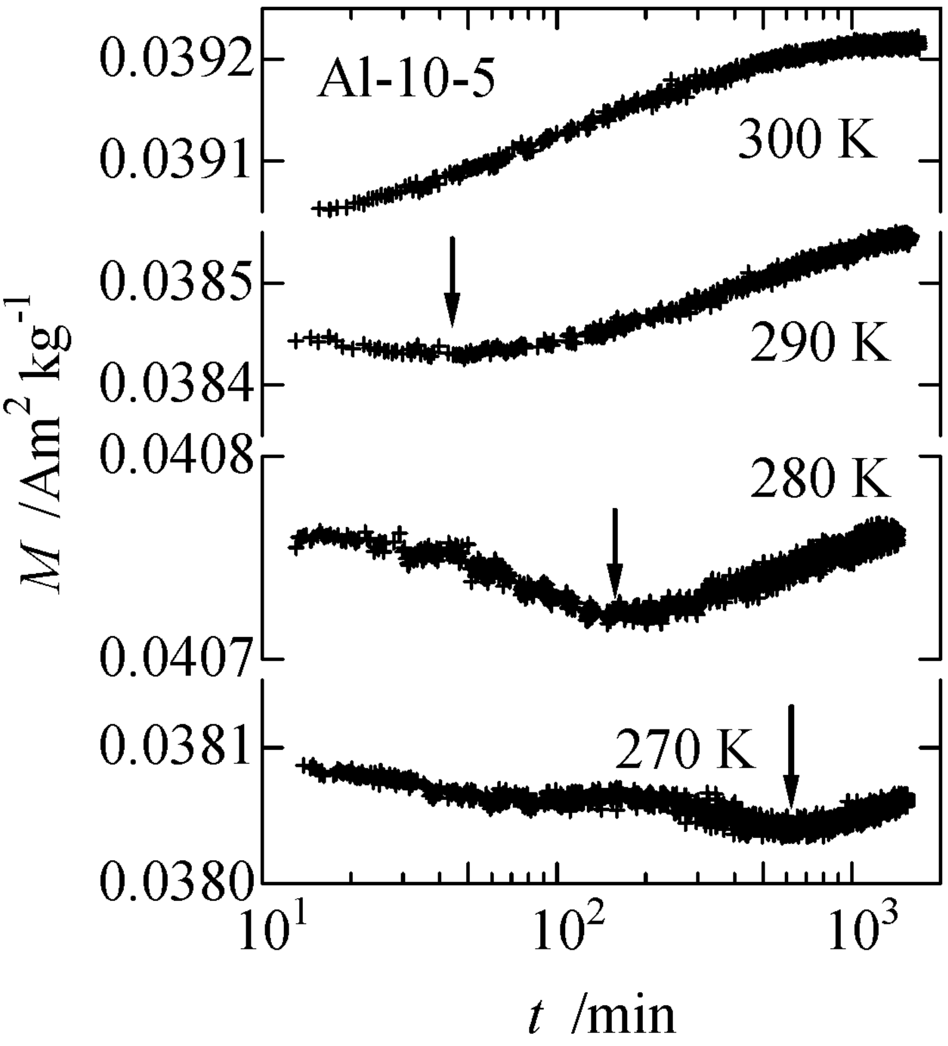
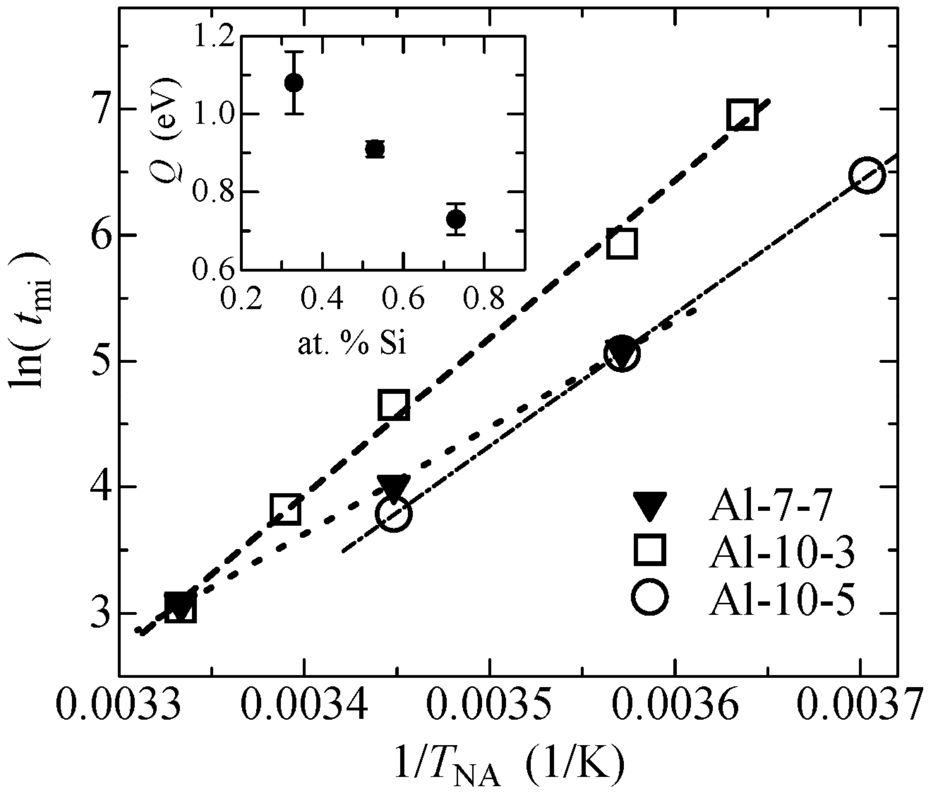


Fig. 4 Time dependence of magnetization of an Al-1.07 at.%Mg-0.53 at.%Si alloy at a constant temperature between 270 and 300 K. (The data sets at 280, 290 and 300 K are quoted from ref.[25])



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