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The influence of thermal annealing on structural order in the μ-Al_4Mn complex intermetallic

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Abstract. The influence of cooling rate on structural order in the complex hexagonal μ-Al_4Mn phase was investigated. As higher magnetizations are detected in more disordered samples, the short-scale disorder was studied indirectly by magnetic measurements. The magnetizations of as-grown samples and samples subjected to different thermal treatments were compared. It was found that water-quenching increases the disorder in the crystal structure regardless of previous thermal history. Qualitatively the same results were obtained for the quasicrystalline *i*-Al–Pd–Mn phase where the changes in magnetic properties and consequently in the degree of structural order for different thermal treatments were even more pronounced.

Introduction

The order in crystal structure can often be improved by thermal annealing procedures. The annealing temperatures must be high enough that the diffusion of atoms can relax the structure. The aim is to preserve this relaxed structure even after the crystal is cooled down to room temperature (RT). This can be done either by an almost sudden change in temperature by water-quenching (WQ) or by cooling the sample slowly to RT. In first case, the resulting structure is partially relaxed and contains a too large amount of frozen-in vacancies for the RT conditions. WQ also introduces large temperature gradients that result in quenched-in thermal strains. The problem of thermal strains can be overcome by employing slow cooling (SC) rates. However, this procedure can be used only when the alloy system does not contain additional low-temperature equilibrium phases for the particular chemical composition.

The discovery of quasicrystals and the renewed interest in complex intermetallics [1] have triggered intense research of their extraordinary crystallographic features and unconventional physical properties. Within the icosahedral family the *i*-Al–Pd–Mn phase, which can be currently grown to a high structural perfection, shows large scatter of the electrical resistivity values [2], magnetoresistance [3] and magnetic properties [4] of samples with the same or similar chemical compositions. This was also revealed in a detailed investigation of this icosahedral phase in [5]. Particularly, WQ was found to significantly increase its saturation magnetization in comparison to the as-grown state even for very short annealing times. The aim of the present research is to investigate the evolution of structural order of other Mn-containing intermetallics subjected to different thermal annealing sequences indirectly by magnetic measurements.

In this paper the results of the influence of cooling rates after short-term thermal annealing on the complex hexagonal μ-Al_4Mn phase ($P6_3/mmc$, $a = 1.998$ nm, $c = 2.467$ nm [6]) are presented. It is worth noting that in rapidly solidified alloys metastable Al–Mn icosahedral phase is formed very close to the Al_4Mn composition and that both phases exhibit structural similarities.

Sample preparation and thermal treatment

Four samples for magnetic measurements were cut from a central part of the same ingot grown by the Bridgman technique. Metallographic examinations using a scanning electron microscope with the application of point energy-dispersive analysis confirmed the homogeneity of the investigated parts of the ingot within ± 0.3 at%. The composition of the samples was measured on the rest of the material taken from the same part of the ingot by inductively coupled plasma optical emission spectroscopy with a precision of ± 0.4 at% (absolute). The composition of $Al_{79.3}Mn_{20.7}$ was obtained.

Two of the samples were studied as-grown (AG-samples) to verify that the differences in magnetizations are not due to slightly different compositions of the samples. The other two samples were inserted to a furnace heated to 800 °C, were held there up to 5 min in total and cooled down: one sample was water-quenched (WQ-sample) and the other was left in the furnace for slow cooling (SC-sample) at a

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rate of about 5 K/min between 800 °C and 500 °C. Before the samples were magnetically investigated their surfaces were mechanically polished in order to remove oxides.

Magnetic measurements

In order to study how different cooling rates influence the magnetic state of the μ-phase (and thus the structural order in the crystal), measurements of electronic magnetization versus external magnetic field, $M(H)$, and magnetic susceptibility versus temperature, $\chi(T)$, were carried out using a commercial Quantum Design MPMS XL-5 magnetometer.

The $M(H)$ curves were measured at $T = 5$ K by varying the magnetic field form 0 to 5 T. The curves were fitted with the expression

$$M = M_S B_J + kH \,, \tag{1}$$

where B_J is the Brillouin function describing the magnetization of localized paramagnetic moments with angular momentum J. Furthermore, M_S is the saturation magnetization and k is the magnetic susceptibility associated with contributions linear with the magnetic field H (Larmor diamagnetism and contributions due to the magnetism of conducting electrons). In the analysis we assumed the Mn atoms in the Mn^{2+} state and thus used $J = 5/2$ [7].

The comparison of $M(H)$ curves between the AG-sample and the thermally annealed samples (SC-sample and WQ-sample) is shown in Fig. 1. The parameters obtained by fitting the curves using Eq. (1) are listed in Table 1. WQ has increased the saturation magnetization in comparison to that of the AG-sample, whereas in the case of SC the saturation magnetization slightly decreased.

The $\chi(T)$ curves were measured in a magnetic field $H = 1$ T and in the temperature interval between 2 K and 300 K. The measured curves were fitted by the Curie-Weiss law including a temperature-independent term χ_0:

$$\chi = \chi_0 + \frac{C}{T - \theta} \,. \tag{2}$$

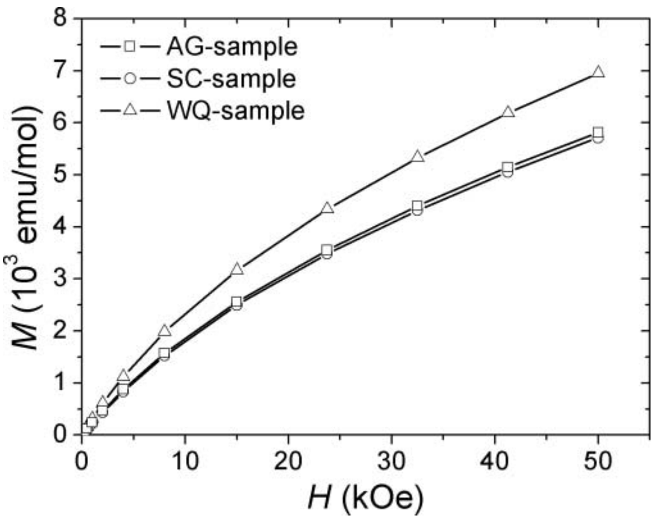

Fig. 1. Magnetization versus magnetic filed curves at $T = 5$ K for the AG-sample and the two thermally treated samples (SC- and WQ-sample). WQ significantly increases, whereas SC slightly decreases the saturation magnetization.

Table 1. The fitting parameters M_S and C, for the Brillouin (Eq. (1)) and Currie-Weiss (Eq. (2)) fit, respectively, the calculated mean effective Bohr magneton number per Mn atom $\bar{p}_{eff}$, and the normalized mean effective magnetic moment per Mn atom m. The value of C is given per mol of Mn atoms.

Sample	M_S (emu/mol)	C (emu K/mol Mn)	$\bar{p}_{eff}$	m
AG	4640	0.0872	0.836	0.142
SC	4450	0.0759	0.780	0.132
WQ	6160	0.119	0.976	0.165

The constants C and θ are the Curie constant and the Curie-Weiss temperature, respectively. The θ values for all samples where found to be slightly negative (see Table 1). As no other results suggested antiferromagnetic interactions θ should be considered only as an additional fitting parameter which slightly improves the fits. From the Curie constant C, the mean effective Bohr magneton number per Mn atom $\bar{p}_{eff}$ could be calculated using the formula $\bar{p}_{eff} = 2.83\sqrt{C}$ [8]. For the comparison of the electronic magnetizations after thermal treatment we used the normalized mean effective magnetic moment per Mn atom (for brevity called just *normalized moment* in the following) $m = \bar{p}_{eff}/p_{eff}$, where p_{eff} is the effective Bohr magneton number of bare Mn^{2+} with the value of $p_{eff} = 5.9$ [7].

In Fig. 2 the comparison of $\chi(T)$ curves for the AG-sample, the SC-sample and the WQ-sample is shown. The measured data was fitted with Eq. (2). The fits are shown as solid lines in Fig. 2 and the fitting parameters are listed in Table 1. The calculated normalized moment is higher in the case of WQ-sample in comparison to the AG-sample for 16%, whereas SC after short-term annealing slightly decreased the normalized moment for 7%.

Magnetic susceptibility measurements were also performed on a reference AG-sample. The difference in the normalized moment of the AG-samples is less than 1%, which confirms that the increasing and decreasing of the

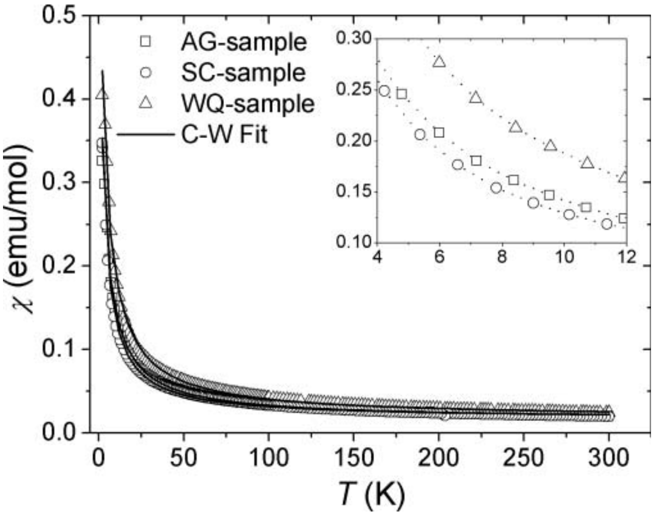

Fig. 2. Magnetic susceptibility versus temperature in a magnetic field of $H = 1$ T for the AG-sample, SC-sample and the WQ-sample. The solid lines show the Currie-Weiss fits of the measured data and the inset shows the magnification of the scale at lower temperatures with the dotted lines as guidance.

normalized moment in the case of WQ-sample and SC-sample, respectively, is indeed due to the thermal treatment.

Discussion and conclusions

The short scale disorder (up to about 5 to 10 Å) in μ-Al_4Mn and *i*-Al–Pd–Mn can be indirectly studied by measurements of the electronic magnetization as the magnetic state of Mn atoms in the μ-phase is highly dependent on their environment [9, 10, 11]. Already a small redistribution of atoms and vacancies near a Mn atom can induce the appearance or disappearance of magnetic moments at that site. The introduction of vacancies and thermal strains by thermal treatment can thus influence the magnetic moment of the sample. Higher magnetic moments are obtained in more disordered samples, possessing higher vacancy concentrations and more thermal strains.

Similar thermal treatments, magnetic measurements and their analysis as described here for μ-Al_4Mn phase were done on *i*-Al–Pd–Mn samples [5]. The changes in magnetic properties were significantly more pronounced in *i*-Al–Pd–Mn (up to factor of 30 for different thermal treatments). All magnetization measurements showed an increase in saturation magnetization and the normalized moment of the samples that were WQ after short- or long-term annealing in comparison to the as-grown samples. As higher magnetic moments are obtained in more disordered samples, the increase in saturation magnetization implies a higher degree of short-scale disorder in the WQ sample. On the contrary, the SC-samples showed a decrease in the saturation magnetization and the normalized moment that implies a more ordered structure than in the as-grown samples.

In conclusion, employing of water-quenching after thermal annealing of the hexagonal μ-Al_4Mn phase increases the magnetization, which can be related to the increased structural disorder.

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