Magnetic properties of dilute Al-REM alloys in liquid and amorphous states

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Abstract. Magnetic susceptibility of dilute Al-Ce and Al-Dy alloys is investigated in wide temperature and field ranges including liquid and amorphous phases. The abnormal behavior of susceptibility above melting point of Al₂R compound is discovered. The concentration curves (χ vs %REM) have oscillating shape similar in solid and liquid states. The existence of Al₂R quasimoleculars is highly probable in these alloys and their destruction starts only above melting point of Al₂R compound. Magnetic properties of the alloys depend on behavior of such quasimoleculars – creation of chains, nets etc. The estimation of some parameters for such chains and nets is given.

1. Introduction

Al-REM alloys are of permanent interest due to their physical properties in crystal and amorphous states. It is a common place for many works that rare-earth elements exist in R³⁺ or R²⁺ states at high temperatures in Al-based alloys (see, for example [1]). It means that magnetic moment per R-atom in the alloys is the same as for pure REM. However, experimental data for Al₁R₂ (Al₁₁R₃) compounds obtained at low temperatures show the big difference between measured values of μₑff and theoretical predictions [2-5]. Our recent results for these compounds confirmed the conclusion that even at high temperatures effective magnetic moment per R-atom is rather lower than for ions R³⁺ [6]. Moreover, in liquid phase the existence of Al₂R quasimoleculars is highly probable and their reversible disintegration takes place above melting point of Al₂R compound only.

As for dilute Al-REM alloys in liquid state the results of viscosity, electroresistivity and surface tension also can be well explained in supposition of Al₂R clusters formation [7,8]. But magnetic properties of these alloys at high temperatures are not studied yet. Since aluminum is a very weak paramagnetic just magnetic studies can answer the question of rare-earth metals states in aluminum melts.

That is why the aim of this work was experimental investigation of magnetic susceptibility temperature and field dependences of dilute Al-R (R = Ce, Dy) alloys in crystal, liquid and amorphous states.
2. Experimental
The crystal samples for susceptibility investigation were prepared from pure aluminum (99.999%) and AlCe (Al:Dy) compounds by re-melting in vacuum at 1900 K for half an hour. Phase control was made by X-rays and chemical composition was analyzed using atom adsorption spectrometer. Oxygen content before and after experiments was determined also.

Amorphous ribbons (width - 4 mm, thickness – 30-35 μm) of Al-8at.%Ce composition were produced by standard planar flow method in the controlled atmosphere of inert gas (the chamber was preliminary de-gazed).

Magnetic susceptibility $\chi$ was measured by Faraday’s method in BeO crucibles at the equipment described in [9]. The chamber was firstly de-gazed to $10^{-3}$ Pa and then filled in with helium of high purity up to $1.1*10^5$ Pa. The experiment was made during heating and subsequent cooling in the temperature range 300 to 1900 K and fields $B = 0.4 – 1.2$ T. The temperature was changed in steps of 10 to 15 degrees and with an isothermal exposition during 5-10 min at each temperature. Both the amorphous and crystalline phases were studied with an accuracy of 1.5 %.

3. Results
Temperature and concentration dependences of magnetic susceptibility for dilute Al-Ce and Al-Dy alloys are presented in figures 1-4.

Figure 1. Magnetic susceptibility as a function of temperature for Al-Ce alloys: 1 – 3 at.% Ce (● – heating, ○ – cooling); 2 – 2 at.% Ce (■ – heating, □ – cooling); 3 – 1 at.% Ce (♦ – heating, ◇ – cooling).

Figure 2. Magnetic susceptibility as a function of temperature for Al-Dy alloys: 1 – 0.6 at.% Dy (▲ – heating, △ – cooling); 2 – 0.4 at.% Dy (■ – heating, □ – cooling); 3 – 0.2 at.% Dy (● – heating, ○ – cooling).

The main features of the curves are:
- in the interval $T = 300-800$K susceptibility decreases following Curie-Weiss law, after that it becomes practically temperature independent;
- the shape of concentration curves is identical both in solid and liquid states;
- susceptibility does not show any abnormal behavior either at solidus, or at liquidus points;
- the increase of susceptibility was found out above melting point of Al$_2$R compound;
- no hysteresis of property was fixed for all investigated compositions.

For Al-8at.%Ce amorphous ribbon $\chi(T)$ curves are identical to crystal samples, but field dependence of susceptibility was also discovered (Figure 5).
Figure 3. The influence of cerium on magnetic susceptibility of aluminum:
1 – T = 300 K; 2 – T = 1100 K; 3 – calculated in additive approximation at T = 300 K.

Figure 4. The influence of dysprosium on magnetic susceptibility of aluminum:
1 – T = 300 K; 2 – calculated in additive approximation at T = 300 K; 3 – T = 1600 K.

Figure 5. Magnetic susceptibility vs applied field for Al-8 at.% Ce alloy at different temperatures.

4. Discussion
The results obtained mean that the mechanism of the formation of magnetic properties in Al-REM alloys should be universal and non-depending on matrix state (solid or liquid). Moreover, since aluminum is a very weak magnetic material the explanation of susceptibility curves should be found in rare-earth atoms behavior. Our current and previous results [6-8] allow us to develop the idea that in alloys with aluminum, especially in liquid state, rare-earth atoms exist not in R$^{3+}$ or R$^{2+}$ ions form but create directed bonds with aluminum atoms. 4f-electrons are involved into bonds formation and that is why effective magnetic moment per REM atom becomes lower than for ions. Moreover this idea is confirmed by the results of thermodynamic modeling [10]. It was shown that in Al-Ce melts Al$_{2}$Ce quasimolecules continue to “live” even at high overheating above liquidus. If we suppose that above
melting point of $\text{Al}_2\text{R}$ compound the destruction of such quasimolecules takes place, than those 4f-electrons that were used for bonds formation begin to localize back at cerium atoms; as a result magnetic moment per REM begins to increase and susceptibility of the sample grows up.

The introduction of first REM portions into aluminum leads to $\text{Al}_2\text{R}$ quasimolecules formation. Subsequently with the increase of REM content the number of quasimolecules grows up and some intermolecular bonds of hydrogen type can appear. These new bonds are saturated and directed (for example, for $\text{Al}_2\text{R}$ the maximum possible number of such bonds is 4 [11]). Due to these bonds different kinds of associates (in form of chains and nets) start to form. The theory and statistics of the melts having associates with hydrogen type of bonds is described in [12] and we shall not stop on it in this paper.

It is quite possible that such quasipolymer chains and nets can play a role of nucleation centers for $\text{Al}_2\text{R}$ ($\text{Al}_2\text{R}_3$) compounds formation during crystallization. For example, in [13] it was shown that in hypoeutectic Al-Ce alloys practically pure aluminum exists in primary and eutectic dendrites whereas $\text{Al}_{11}\text{Ce}_3$ compound has net-like structure occupying all the remain space. The presence of net-like associates in Al-Ce melts was confirmed by thermodynamics calculations also [11].

For rare-earth metals the indirect interaction of RKKY type is considered to be the main exchange between 4f-electrons shells. In case of dilute Al-REM alloys the indirect exchange between rare-earth atoms realizes through conductive electrons. In the chain consisting of two monomers ($\text{Al}_2\text{R}$ quasimolecules) the nonmagnetic aluminum atom settled between two rare-earth atoms fixes the distance between them sharply. RKKY exchange integrals have oscillating and weak decay on distance [14]:

$$J_{ij}^{\text{RKKY}} = \frac{9\pi n^2 l^2}{2g_s^2 E_F} F\left(2k_F|R_i - R_j|\right)$$

where $F(x)$ determines the space dependence of RKKY interaction.

Knowing the ionic radii of aluminum and rare-earth atoms one can calculate dimensionless parameter $x$ and plot $F(x)$ using eq. (1). The estimation for $\text{Al}_{12}\text{Ce}-\text{Al}_{12}\text{Ce}$ dimer gives the value $x = 10.4$ that leads to strong negative interaction. For $\text{Al}_{12}\text{Dy}-\text{Al}_{12}\text{Dy}$ dimer the value $x = 8.4$ and the exchange interaction is still negative and strong. Thus one can say that in dimers $\text{Al}_2\text{R}$-$\text{Al}_2\text{R}$ magnetic moments localized on rare-earth atoms always have antiparallel orientation.

At the first stage of Al-REM alloying when the concentration of rare-earth element in aluminum matrix is insignificant the probability of chains and nets formation is rather low. The main structural units of impurity here are separate $\text{Al}_2\text{R}$ monomers ($\text{Al}_2\text{R}$ quasimolecules). With the enlargement of REM content in the alloy the number of monomers increases and susceptibility grows up as well till the first maximum on concentration curves. In the interval from first maximum to first minimum the main part of impurities exists in the form of $\text{Al}_2\text{R}$-$\text{Al}_2\text{R}$ dimers. These associates have zero total magnetic moments because moments of individual $\text{Al}_2\text{R}$ quasimolecules have antiparallel orientation due to negative RKKY exchange. Their contribution into total susceptibility of the sample is zero also. The further increase of REM content leads to the appearance of trimers that give the similar contribution into total susceptibility as monomers and susceptibility begins to grow up again. Thus the oscillating behavior of magnetic susceptibility in Al-REM alloys we connect with the increase of mean length of chains and nets consisting of $\text{Al}_2\text{R}$ quasimolecules. Depending on mean length these associates give maximal or minimal contribution into total susceptibility.

As for amorphous ribbon of Al-8 at.% Ce composition the existence of strong field dependence of susceptibility allow one to suppose that during rapid quenching the melt the formation of $\text{Al}_{12}\text{Ce}_3$ compound is suppressed due to lack of time. The structure of the ribbon can be represented as paramagnetic aluminum matrix with the inclusions of chains and nets consisting of $\text{Al}_2\text{R}$ quasimolecules. Thus chains and nets are characterized by specific magnetic ordering the susceptibility of the ribbon can be approximated by
In eq. (2) \( N \) is the number of particles per mass unit and \( M_o \) is the average magnetic moment of one particle. The first term corresponds to superparamagnetic particles [15] and the second describes the susceptibility of the remaining paramagnetic amorphous phase. The so-called “generalized” Curie-Weiss law can be used for the second term

\[
\chi_p(T) = \chi_0 + \frac{C}{T - \Theta}
\]

here \( C \) is the Curie constant, \( \Theta \) the paramagnetic Curie temperature and \( \chi_0 \) - the temperature-independent susceptibility depending mainly on the density of electrons states at the Fermi level.

The function \( f(x) \) in eq. (2) is the derivative of Langevin function [15]:

\[
f(x) = \frac{1}{x} - 4(e^{x} - e^{-x})^{-2}, \quad f(0) = \frac{1}{3}
\]

From measurements at the fields \( B_1, B_2 \) and at two temperatures \( T_1, T_2 \) one can according to eq. (2) obtain the quantity

\[
\alpha \cdot a = \frac{f(x_1) - f(\beta x_1)}{f(\alpha x_1) - f(\alpha \beta x_1)}
\]

where

\[
a = \frac{\chi(T_1, B_1) - \chi(T_2, B_1)}{\chi(T_2, B_1) - \chi(T_2, B_2)}, \quad \alpha = \frac{T_1}{T_2}, \quad \beta = \frac{B_2}{B_1}, \quad x_1 = \frac{M_o B_1}{kT_1}
\]

Since the value of \( a \) is determined from the experimental data, \( x_1 \) can be deduced from eq. (5). For amorphous state the solution gives one stable root, \( x_1 = 1.73 \). The value of \( x_1 \) depends only slightly on \( T_2 \) and \( B_2 \). Supposing that the magnetic moment of \( \text{Al}_2\text{R} \) quasimolecular is close to \( \mu_{\text{eff}} \approx 2.5 \ \mu_B \), the effective number of “noncompensated” ends in the particle \( n \) can be determined from \( M_o = n \times 2.5 \ \mu_B \).

Using (6), one gets \( n \approx 310 \). However, without knowing the dimension of the net and structure of its core, it is not possible to estimate linear sizes of superparamagnetic particles correctly.

The stability of the solution (5) means that magnetic moment per particle \( M_o \) does not depend on temperature and field. Thus the mass density \( N(T) \) of superparamagnetic particles can be determined through

\[
\frac{1}{4\pi} N M_o^2 = kT \frac{\chi(T_1, B_1) - \chi(T_2, B_2)}{f(x_1) - f(x_2)}
\]

where \( x_i = \frac{M_o B_i}{kT} \). Using the \( M_o \) value from eq. (6) one obtains \( N = 7.3 \times 10^{14} \ \text{g}^{-1} \).

5. Summary

Magnetic susceptibility (by Faraday’s method) of dilute \( \text{Al-Ce} \) and \( \text{Al-Dy} \) alloys is investigated in wide temperature and field ranges including liquid and amorphous phases. The abnormal behavior of susceptibility above melting point of \( \text{Al}_2\text{R} \) compound is discovered. The concentration curves (\( \chi \) vs \%REM) have oscillating shape similar in solid and liquid states. Al-REM melts remain strongly microheterogeneous systems even at high overheating above liquidus. The existence of \( \text{Al}_2\text{R} \) quasimolecules is highly probable in these alloys and their destruction starts only above melting point of \( \text{Al}_2\text{R} \) compound. Magnetic properties of the alloys depend on behavior of such quasimolecules – creation of chains, nets etc. The estimation of some parameters for such chains and nets are given.
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