Magnetic susceptibility of glass-forming Al-Co-Ce alloys at high temperatures

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Abstract. In this work magnetic susceptibility of Al$_{91-x}$Co$_9$Ce$_x$ (1<x<11 at.%) and Al$_{91-x}$Co$_x$Ce$_7$ (1<x<11 at.%) alloys was investigated by Faraday’s method in the wide temperature (T=300-2000 K) and field (B=0.6-1.2 T) ranges. The abnormal behavior of susceptibility above melting point of Al$_2$R compound is discovered. The magnetic susceptibility vs concentration curves for quasybinary systems Al-Ce (X$\text{Co}=9$ at.%) and Al-Co (X$\text{Ce}=7$ at.%) were plotted. It was found that $\chi=f(\text{Ce})$ dependences have oscillating form similar both in solid and liquid states; while for $\chi=f(\text{Co})$ susceptibility practically does not depend on Co content.

Some parameters of electron structure in Al-Co-Ce alloys are calculated from experimental results. The effective magnetic moment per cerium atom was found to be at a level of 1.1 $\mu_B$ and does not depend on alloy composition, while cobalt atoms exist in non-magnetic state in these alloys. The existence of Al$_2$R quasimolecules is highly probable in these alloys and their destruction starts only near melting point of Al$_2$R compound.

1. Introduction

Considerable interest in Al-rich alloys containing transition metals (TM) and rare earth (RE) has been generated in the last two decades, particularly because of their high glass forming ability at reducing cooling rates ($10^4-10^5$ K/s [1]) and the large range of amorphous forming compositions. The kinetic of amorphization for these alloys differs from those for alloys with deep eutectic mainly because they have rather high-melted intermetallic compounds [2]. In addition, these amorphous alloys exhibit very superior mechanical properties of high strength and good ductility, also suitable for high temperatures applications.

DSC investigations showed that crystallization in Al-TM-REM amorphous alloys goes in two steps (crystallization of intermetallic compounds and crystallization of aluminum matrix) [2]. X-ray analyses of crystal phases formed during crystallization identified them as $\alpha$-Al, Al$_3$REM$_3$ and Al$_3$TM. The quantity of ternary compounds was found to be very small [1].

Viscosity studies of Al-Ni-La melts demonstrated that Al-TM-REM systems preserve inhomogeneous state in liquid phase for a long time and the transformation into homogeneous stable state takes place at high overheatings above liquidus only [3].

Magnetic investigations performed at low temperatures showed that electronic structure of Al-TM-REM alloys is very complicated [4], however their magnetic properties at high temperatures are practically unknown.

Thus the main aim of this work was the investigation of magnetic susceptibility of Al$_{91-x}$Co$_9$Ce$_x$ (1<x<11 at.%) and Al$_{91-x}$Co$_x$Ce$_7$ (1<x<11 at.%) alloys in wide temperature and field ranges including solid and liquid states.
2. Experimental
The crystal samples for susceptibility investigation were prepared from pure aluminum (99.999%), Al$_{11}$Ce$_3$ and AlCo compounds by re-melting in helium atmosphere at 1900 K for half an hour. Phase control was made by X-rays and chemical composition was analyzed using atom adsorption spectrometer Spectrum Flame Modula S. Oxygen content before and after experiments was determined also.

Magnetic susceptibility $\chi$ was measured by Faraday’s method in BeO crucibles at the equipment described in [5]. The chamber was firstly de-gazed to $10^{-3}$ Pa and then filled in with helium of high purity up to $1.1 \times 10^5$ Pa. The experiment was made during heating and subsequent cooling in the temperature range 300 to 2000 K and fields $B = 0.6 – 1.2$ 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 crystalline and liquid phases were studied with an accuracy of 1.5 %.

3. Results
Magnetic susceptibility temperature and concentration dependences for Al$_{91-x}$Co$_x$Ce$_x$ (1<x<11 at.%) and Al$_{91-x}$Co$_x$Ce$_7$ (1<x<11 at.%) alloys are presented in figures 1-4.

![Figure 1. Magnetic susceptibility as a function of temperature for quasybinary Al-Ce (X$_{Co}=9$ at.%) alloys: 1 at.% Ce (● – heating, ○ – cooling); 2 at.% Ce (▲ – heating, △ – cooling); 3 at.% Ce (● – heating, ◇ – cooling). (+3;+1.5 - curves shift along vertical axis).](image1)

![Figure 2. Magnetic susceptibility as a function of temperature for quasybinary Al-Co (X$_{Ce}=7$ at.%) alloys: 0 at.% Co (● – heating, ○ – cooling); 1 at.% Co (▲ – heating, △ – cooling); 2 at.% Co (● – heating, ◇ – cooling). (+2;+4 - curves shift along vertical axis).](image2)

In the interval $T = 300-800$ K susceptibility decreases following Curie-Weiss law, after that it becomes practically temperature independent up to 1450 K. The significant increase of susceptibility was found out above 1550 K for quasybinary Al-Ce (X$_{Co}=9$ at.%) alloys and 1650 K for quasybinary Al-Co (X$_{Ce}=7$ at.%) alloys. No hysteresis of property, i.e. noncoincidence of heating and cooling curves, was fixed for all investigated compositions.

The shape of magnetic susceptibility concentration curves was found to be identical both in solid and liquid states. However, cerium and cobalt influence on susceptibility in different ways: $\chi=f(Ce)$ dependences have oscillating form, more pronounced in liquid states; while for $\chi=f(Co)$ susceptibility practically does not depend on Co content. From the late it comes that cobalt atoms exist in non-magnetic states in Al-Co-Ce alloys. The similar non-magnetic behavior of 3d-transition atoms in liquid aluminum was fixed earlier in [6].
Figure 3. The influence of cerium on magnetic susceptibility of quasybinary Al-Ce \((X_{\text{Ce}}=9 \text{ at.\%})\) alloys: “∆” – \((T = 300 \text{ K})\); “ж” – \((T = 500 \text{ K})\); “+” – \((T=1100\text{ K})\); “○” – \((T=1500\text{ K})\).

Figure 4. The influence of cobalt on magnetic susceptibility of quasybinary Al-Co \((X_{\text{Co}}=7 \text{ at.\%})\) alloys: “∆” – \((T = 300 \text{ K})\); “ж” – \((T = 700 \text{ K})\); “-” – \((T=1100\text{ K})\); “○” – \((T=1500\text{ K})\).

4. Discussion

In order to understand the obtained results we fitted susceptibility temperature curves below 800 K by the so-called “generalized” Curie-Weiss law

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

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

As aluminum is weak magnetic material and cobalt exists in non-magnetic state in these alloys, the effective magnetic moment was calculated for rare earth atoms only by the equation

\[
\mu = \sqrt{\frac{3kCM}{\alpha N_A (\mu_B)^2}}
\]

where: \(k\) – Boltzman constant, \(C\) - Curie constant, \(M\) – molar mass, \(N_A\) – Avogadro constant, \(\mu_B\) - Bohr magneton, \(\alpha\) – atomic fraction of cerium in the alloys. The results of electronic parameters (density of electron states at Fermi level – \(N(E_F)\), paramagnetic Curie temperature – \(\Theta\), effective magnetic moment per cerium atom - \(\mu_{\text{eff}}\)) calculation for Al-Co-Ce alloys are given in tables 1 and 2.

**Table 1.** Parameters of electron structure for quasybinary Al-Ce \((X_{\text{Ce}}=9 \text{ at.\%})\) alloys:

| Cerium content (at.\%) | \(\chi_0 \times 10^6\), emu/g | \(N(E_F)\), eV\(^{-1}\) | \(\Theta\), K | \(C \times 10^5\), emuK/g | \(\mu_{\text{eff}}\), μB | \(\mu_B\) |
|------------------------|-------------------------------|--------------------------|----------|---------------------------|----------------|---------|
| 1                      | 0.708                         | 1.02                     | 110      | 9.100                     | 1.01          |         |
| 2                      | 0.903                         | 1.30                     | 105      | 19.297                    | 1.04          |         |
| 3                      | 1.146                         | 1.65                     | 100      | 28.945                    | 1.04          |         |
| 4                      | 1.167                         | 1.68                     | 95       | 36.400                    | 1.01          |         |
| 5                      | 1.313                         | 1.89                     | 90       | 55.950                    | 1.12          |         |
| 6                      | 1.333                         | 1.92                     | 80       | 55.686                    | 1.02          |         |
| 7                      | 1.361                         | 1.96                     | 75       | 67.540                    | 1.04          |         |
| 8                      | 1.396                         | 2.01                     | 70       | 83.240                    | 1.08          |         |
| 9                      | 1.417                         | 2.04                     | 65       | 100.711                   | 1.12          |         |
| 10                     | 1.403                         | 2.02                     | 55       | 91.000                    | 1.01          |         |
| 11                     | 1.493                         | 2.15                     | 52       | 118.734                   | 1.1           |         |
Table 2. Parameters of electron structure for quasybinary Al-Co (X_{Ce}=7 at.%) alloys:

| Cobalt content (at.%) | $\chi_0 \times 10^5$, emu/g | N(E_F), eV$^{-1}$ | $\theta$, K | $C \times 10^5$, emu*K/g | $\mu_{\text{eff}}$, $\mu_B$ |
|-----------------------|-----------------------------|------------------|-----------|--------------------------|-----------------|
| 0                     | 1.445                       | 2.08             | 105       | 68,845                   | 1.05            |
| 1                     | 1.507                       | 2.17             | 100       | 74,190                   | 1.09            |
| 2                     | 1.493                       | 2.15             | 98        | 74,190                   | 1.09            |
| 3                     | 1.493                       | 2.15             | 95        | 72,835                   | 1.08            |
| 4                     | 1.479                       | 2.13             | 90        | 70,163                   | 1.06            |
| 5                     | 1.472                       | 2.12             | 85        | 67,540                   | 1.04            |
| 6                     | 1.514                       | 2.18             | 82        | 76,938                   | 1.11            |
| 7                     | 1.514                       | 2.18             | 80        | 75,558                   | 1.10            |
| 8                     | 1.507                       | 2.17             | 78        | 64,967                   | 1.02            |
| 9                     | 1.493                       | 2.15             | 75        | 64,967                   | 1.02            |
| 10                    | 1.493                       | 2.15             | 70        | 67,540                   | 1.04            |
| 11                    | 1.493                       | 2.15             | 65        | 72,835                   | 1.08            |
| 12                    | 1.493                       | 2.15             | 60        | 72,835                   | 1.08            |
| 13                    | 1.445                       | 2.08             | 55        | 63,700                   | 1.01            |

As one can see from tables 1 and 2, density of states at Fermi level increases from 1.02 to 2.15 eV$^{-1}$ with the increase of cerium content from 1 to 10 at. % in quasybinary Al-Ce alloys and remains practically constant at the level of 2.15 eV$^{-1}$ for quasybinary Al-Co alloys. The paramagnetic Curie temperature decreases from 110 to 55 K with doped element content growth both in quasybinary Al-Ce and Al-Co alloys.

The most attractive fact is rather small and constant value of effective magnetic moment per cerium atom at the level of 1.0 – 1.1 $\mu_B$ for all the investigated alloys. This fact is in contradiction with well-known idea about $R^{3+}$ state of REM atoms in aluminum and other similar alloys [7], but it was confirmed in our previous works [8,9]. Our current and previous results 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. The existence of Al$_2$R quasimoleculars is highly probable in these alloys. If we suppose that above melting point of Al$_2$R compound (or close to it) the destruction of such quasimoleculars takes place, than those 4f-electrons that were involved into bonds formation begin to localize back at cerium atoms; as a result magnetic moment per REM atom begins to increase and susceptibility of the sample grows up, as it was fixed in the experiments (see figures 1 and 2). The existence of Al$_2$R quasimoleculars and their interaction can explain the nonmonotonous increase of susceptibility with cerium content growth (see figure 3).

5. Conclusions
Magnetic susceptibility of Al$_{91-x}$Co$_x$Ce$_x$ (1<x<11 at.%) and Al$_{91-x}$Co$_x$C$_7$ (1<x<11 at.%) alloys was investigated in the wide temperature (T=300-2000 K) and field (B=0.6-1.2 T) ranges. The abnormal behavior of susceptibility above melting point of Al$_2$R compound is discovered. The magnetic susceptibility vs concentration curves for quasybinary systems Al-Ce (X_{Co} = 9 at.%) and Al-Co (X_{Ce} = 7 at.%) were plotted. It was found that $\chi=f(Ce)$ dependences have oscillating form similar both in solid and liquid states; while for $\chi=f(Co)$ susceptibility practically does not depend on Co content. Some parameters of electron structure (density of electron states at Fermi level – N(E_F), paramagnetic Curie temperature – $\Theta$, effective magnetic moment per cerium atom - $\mu_{\text{eff}}$) in Al-Co-Ce alloys are calculated from experimental results. The effective magnetic moment per cerium atom was found to be at a level
of 1.1 $\mu_B$ and does not depend on alloy composition, while cobalt atoms exist in non-magnetic state in these alloys. We think that the existence of Al$_2$R quasimoleculars is highly probable in these alloys and their destruction starts only near melting point of Al$_2$R compound.

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