Phase Transition and Magnetic Properties of Supercooled Al-Ge-TM (TM=Cr, Fe, Co) Alloys

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Formation criteria and magnetic properties of rapidly solidified Al-Ge-TM (TM=Cr, Fe and Co) alloys were examined. The phase changes from amorphous, icosahedral, and decagonal, to approximant crystalline, corresponding to TM as Cr (Ge rich), Cr, Fe and Co, respectively, in the rapidly solidified Al-Ge-TM alloys. Thermomagnetic curves indicate that for the systematically variation of the magnetic ordered phases, Al_{10}Ge_{60}Cr_{30} amorphous, Al_{10}Ge_{60}Cr_{30} icosahedral, Al_{10}Ge_{60}Fe_{30} decagonal and Al_{10}Ge_{60}Co_{30} approximant crystalline alloys were identified to be of ferromagnetism, micromagnetism, Curie-Weiss paramagnetism and Pauli paramagnetism, respectively.

(Received August 13, 1997; In Final Form January 6, 1998)

Keywords: icosahedral or decagonal quasicrystal, amorphous, aluminum-germanium-transition metal alloy system, Curie-Weiss paramagnetism, spin glass, ferromagnetism

I. Introduction

The study on intrinsic properties of quasicrystalline structure is attracting much attention, because of its unique atomic structure as quasi-periodicity, self similarity, etc. The findings of stable quasicrystals have enabled the study of structural analysis, e.g., the determination of atomic arrangements for various types of icosahedral and decagonal phases. Besides, some intrinsic properties of quasicrystals have been found in the stable quasicrystals and large single grained quasicrystals. As the features of stable icosahedral alloys, one can list high electrical resistivity(2), pseudo-gap at the Fermi energy level(3), high hardness(4) and high Young's modulus(5). On the other hand, it has been characterized that quasicrystals do not exhibit any distinct spontaneous magnetization, and their properties are similar to that of the spin-glass(6-7), inhomogeneous ferromagnetism(8) phenomena of dilute alloys. Since almost all quasicrystals contain 60 to 80 at% Al, it is difficult to expect the appearance of any magnetic ordered phase. However, the ferromagnetic quasicrystal becomes greatly attractive because of the influence of its unique atomic configuration, even though no homogeneous ferromagnetic phases have been found in quasicrystals. It has been previously reported(9) that an icosahedral Al_{10}Cu_{30}Mn_{30}Ge_{35} alloy prepared by rapid solidification shows a rather large coercivity at room temperature. The magnetic feature of this alloy has been determined as ferromagnetism(9-10). Subsequently, magnetic properties for some other quasicrystalline alloys have been examined in the temperature range from 4.2 K to room temperature (R.T.). In addition, icosahedral Al-Mn-Si alloys have been reported to exhibit ferromagnetic properties at low temperatures below 100 K(12). However, the magnetization values of these magnetic quasicrystalline alloys are very small even at low temperatures, in spite of their high Curie temperatures.

Recently, extensive studies are being carried out for the search of a new ferromagnetic quasicrystalline alloy with large magnetization and high Curie temperature. The Al-Ge-TM ternary alloy system is chosen instead of the Al-TM binary alloy system, because the great ability for quasicrystal formation even in TM-enriched composition with the added Ge element due to the larger outer electron valence of Ge(2+) than Al(3+). An excess or sort change of TM causes the deviation of the formation criteria of the quasicrystalline phase. That is, the average outer electron concentration (e/a) decreases (TM=Cr) or increases (TM=Fe, Co) from an optimum value of e/a = 1.75 and the strain field (phason strain) increases because of the difference in atomic size between TM and other constituent elements. The deviations in e/a and atomic size seem to be an origin of the change of quasicrystallinity from the quasicrystal to the approximant crystalline phase or amorphous phase. Ge is used to maintain the e/a value of about 1.75.

The aim of this paper is to clarify the magnetic properties of several Al-Ge-TM super-cooled phases, and the relation between the magnetic ordered phase and the atomic structure. The relation between the phase types and its magnetic order will also be discussed.

II. Experimental Procedure

The Al-Ge-TM (TM=Cr, Fe, Co) alloy ingots were prepared from the pure elements of Ge with 99.999 mass% purity, Al with 99.999 mass% purity and Cr, Fe and Co with 99.9 mass% purity. Mixtures of these pure elements were melted at a suitable alloy composition at 10-40 at% Ge and 10-30 at% Cr in the Al-Ge-Cr alloy system, 10-30 at% Ge and 20-40 at% Fe in the Al-Ge-Fe alloy system, and 5-40 at% Ge and 20-40 at% Co in the Al-Ge-Co alloy system, respectively, in an argon at-
mosphere using an arc furnace. Rapidly solidified ribbons of about 0.02 mm thickness and 1 mm width were prepared from the alloy ingots by a single roller melt spinning apparatus. The quasicrystallinity of the samples in rapidly solidified states was examined by X-ray diffractometry and transmission electron microscopy (TEM). Phase stability in the rapidly solidified states was examined by using a differential thermal analyzer (DTA). Magnetic properties were measured with a magnetic balance in the temperature range from 4.2 K to room temperature under externally applied fields up to 800 kA/m.

III. Results and Discussion

Figures 1 to 3 show the compositional ranges in which quasicrystalline phase with icosahedral or decagonal structure are formed in rapidly solidified Al–Ge–Cr, Al–Ge–Fe and Al–Ge–Co alloys, respectively. The icosahedral phase is formed only in the Al–Ge–Cr system in the composition range of 0 to 30 at% Ge and about 20 at% Cr with the satisfied criterion of $e/a \approx 1.75$. The decagonal phase is also formed in the Al–Ge–Fe system with the composition range deviating from the composition region of $e/a \approx 1.75$ to the Fe-enriched side. Neither icosahedral nor decagonal phase exists in the Al–Ge–Co system even at the composition of $e/a = 1.75$, though an approximant crystalline phase exists in the composition range of 25 to 30 at% Co and 5 to 10 at% Ge. Little is known about the formation of the decagonal phase in the Al–Ge–Fe system until now. The present result is believed to be the first evidence to the formation of the decagonal Al–Ge–Fe alloy.

Figure 4 shows the X-ray diffraction patterns of the icosahedral and amorphous phases for Al–Ge–Cr alloys, the decagonal phase for the Al–Ge–Fe alloy and the approximant crystalline phase for the Al–Ge–Co alloy. To confirm the absence of second phase and the microstructure, TEM is employed all the diffraction patterns are identified to be a single phase. The bright-field electron micrographs and selected-area electron diffraction patterns are shown in Fig. 5 for the icosahedral Al$_{60}$Ge$_{20}$Cr$_{20}$ alloy and in Fig. 6 for the decagonal Al$_{60}$Ge$_{20}$Fe$_{20}$ alloy. No appreciable second phase is seen even along the grain boundaries and the selected-area electron diffraction patterns can be identified to be of an icosahedral or a decagonal phase. Furthermore, Fig. 7 shows the bright-field electron micrograph and selected-area diffraction patterns of the approximant crystalline Al$_{60}$Ge$_{20}$Co$_{20}$ alloy. Though some of reflection spots split, Fig. 7(c), the diffraction patterns are basically identified to be of
an orthorhombic ($a=1.26$ nm, $b=1.48$ nm, $c=1.24$ nm) structure containing a small amount of different ordered regions similar to the Al$_x$Mn decagonal phase. The feature of the structure is analogous to that of the orthorhombic Al$_x$Mn phase. Even in the approximant crystalline phase, no appreciable second phase is observed.

The thermal stabilities of the these super-cooler Al-Ge-TM (TM=Cr, Fe, Co) alloy were examined. Figure 8 shows the DSC curves of the amorphous Al$_{60}$Ge$_{30}$Cr$_{10}$ alloy, icosahedral Al$_{60}$Ge$_{30}$Cr$_{10}$ alloy, decagonal Al$_{60}$Ge$_{20}$Fe$_{10}$ alloy and approximant crystalline Al$_{60}$Ge$_{20}$Co$_{10}$ alloy. Exothermic reactions appear along with on set temperature increasing when TM changes from Cr to Fe, implying the internal energy change which influenced by chemical order with sp-d interaction$^{(14)}$. So the structure changes from amorphous to crystalline with TM changing from Cr to Co because sp-d interaction between Al-TM changes. No distinct exothermic peaks can be observed for the approximant crystalline Al$_{60}$Ge$_{20}$Co$_{10}$ alloy in the temperature range from R.T. to 850 K.

The success of synthesizing the decagonal phase containing a large amount of Fe in the Al–Ge–Fe system allows us to expect the strong magnetization. Figure 9 shows the thermomagnetic curves of the amorphous Al$_{60}$Ge$_{30}$Cr$_{10}$ alloy, the icosahedral Al$_{60}$Ge$_{20}$Cr$_{10}$ alloy, the decagonal Al$_{60}$Ge$_{20}$Fe$_{10}$ alloy and the approximant crystalline Al$_{60}$Ge$_{20}$Co$_{10}$ alloy. It reveals that transition metals change significantly the magnetic structural order, i.e. the magnetic features of the amorphous Al$_{60}$Ge$_{20}$Cr$_{10}$.

Fig. 4 X-ray diffraction patterns of rapidly solidified amorphous Al$_{60}$Ge$_{40}$Cr$_{20}$, icosahedral Al$_{60}$Ge$_{50}$Cr$_{20}$, decagonal Al$_{60}$Ge$_{50}$Fe$_{20}$ and approximant crystalline Al$_{60}$Ge$_{50}$Co$_{20}$ alloys.

Fig. 5 Selected-area diffraction patterns and bright field image of icosahedral Al$_{60}$Ge$_{50}$Cr$_{20}$ alloy.
Fig. 6  Selected-area diffraction patterns and bright field electron micrograph of decagonal Al₆₅Ge₃₀Fe₁₀ alloy.

Fig. 7  Selected-area diffraction patterns and bright field electron micrograph of approximant crystalline Al₆₃Ge₉₀Co₁₀ alloy.
alloy, the icosahedral Al_{60}Ge_{20}Cr_{20} alloy, the decagonal Al_{50}Ge_{20}Fe_{30} alloy and the approximant crystalline Al_{60}Ge_{20}Co_{30} alloy show ferromagnetism, micromagnetism, Curie-Weiss paramagnetism and Pauli paramagnetism, respectively. The magnetic interaction between the TM elements becomes stronger with the TM change of Co→Fe→Cr. For TM=Co, the magnetization value about 0.126 μWb/m kg with no temperature dependence reveals Pauli paramagnetism. The inverse susceptibility versus temperature relation (not shown) indicates a superior liner relation with the Curie-Weiss paramagnetism region at low temperature. For the Curie constant: $C$ (μWb m K kg$^{-1}$) and asymptotic Curie temperature: $\Theta_C$ (K), Al$_{60}$Ge$_{20}$Cr$_{20}$ (amorphous) shows $C=20.72$ and $\Theta_C=8.97$; Al$_{50}$Ge$_{20}$Cr$_{20}$ (icosahedral), $C=14.29$ and $\Theta_C=-23.1$; Al$_{60}$Ge$_{20}$Fe$_{30}$ (decagonal), $C=3.87$ and $\Theta_C=-20.1$; Al$_{60}$Ge$_{20}$Co$_{30}$ (approximant crystal), Pauli paramagnetism, respectively. In the case of the TM=Cr icosahedral phase, the thermomagnetic curves is similar to that of a micromagnetic material even in field cooling (not shown) with the freezing temperature of about 25 K, and in the amorphous phase, the thermomagnetic curve shows a typical ferromagnetic feature with the Curie temperature of 34 K. The systematically magnetic characteristic transition reminds us that the chemical disorder cause the long range magnetic order because the possibility of formation TM pairs increases with a structural change to a more disordered one. In the case of such an Al-enriched system, the magnetic properties is very similar to that of a dilute alloy and the magnetic interaction between TM elements depends mainly on the TM–TM distance. Assuming that the Al–Ge–TM alloy has a chemical ordered periodic structure, the distance between the TM elements must be longer than the distance of third nearest neighborhood in majority because the TM elements are contained less than 30 at%. So, the Al–Ge–Co alloy with crystalline decagonal approximant structure indicates no magnetic interaction between the TM elements as shown in Fig.9. Figure 10 shows the Arrott plot magnetization data on $I^2$ of the TM=Cr amorphous alloy versus $H/I$ map at several temperatures. The superior linearity implies that the Al$_{60}$Ge$_{20}$Cr$_{20}$ amorphous alloy possess homogeneous ferromagnetic interactions in this alloy.
IV. Summary

We have searched a new quasicrystal with ferromagnetism at room temperature in rapidly solidified Al–Ge–TM (TM = Cr, Fe or Co) alloys. The results obtained are summarized as follows;

(1) The icosahedral phase was formed in the composition ranges of 0 to 30 at% Ge and about 20 at% Cr in the Al–Ge–Cr system. The icosahedral alloys have an average outer electron concentration ($e/a$) of about 1.75 and the empirical rule for the formation of the icosahedral phase is satisfied. And amorphous phase was formed in more Ge enriched area on Cr–20 at% compositional line.

(2) The decagonal phase was found to form in the composition range of 20 at% Ge and 30 at% Fe in the Al–Ge–Fe system. The composition range is limited to the $e/a$ value of about 1.75 and the decagonal structure is similar to that of Al–Fe binary super-cooled alloy with 4 layers in 0.8 nm.

(3) The as-quenched phases in the Al–Ge–Co with $e/a = 1.75$ consist of an approximant crystalline phase, and neither icosahedral nor decagonal phase is formed in the Al–Ge–Co system.

(4) The amorphous Al$_{60}$Ge$_{40}$Cr$_{30}$ alloy, the icosahedral Al$_{60}$Ge$_{30}$Cr$_{20}$ alloy, the decagonal Al$_{50}$Ge$_{30}$Fe$_{20}$ alloy and the approximant crystalline Al$_{60}$Ge$_{10}$Co$_{30}$ alloy are identified to be of ferromagnetism, micromagnetism, Curie-Weiss paramagnetism and Pauli paramagnetism, respectively.

Acknowledgment

The authors express their sincere thanks to Prof. A. Inoue (IMR Tohoku Univ.) and Dr. An Pang Tsai (National Research Institute for Metals) for instrumentation support and useful discussion for this paper.

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