Ferromagnetic Glasses with Stable Supercooled Liquid in Gd-Al-(Cu,Ni,Co) Alloys

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ABSTRACT

Metallic glasses with ferromagnetism and stable supercooled liquid formed in melt-quenched $Gd_{55}Al_{25}TM_{20}$ (TM = Cu, Ni, and Co) alloys have been studied by means of vibrating-sample magnetometer (VSM) and differential scanning calorimeter (DSC). These glasses show a large temperature interval between glass transition temperature (T_g) and crystallization temperature (T_x) of about 60K which is comparable with typical metallic glasses. The glasses are predominantly ferromagnetic with curie temperature (T_c) from 90 K to 120 K and saturation magnetization (σ_s) between 160 emu/g and 200 emu/g.

A large amount of work in investigating the magnetic properties of metallic glasses has been done in several Fe and Co base systems. During the last decade, ferromagnetic glass ribbons revealing soft magnetic properties have been found to have practical application in different branches of electronics and electrical engineering. In the last few years, their soft magnetic properties have been further developed by the crystallization of the metallic glasses to a so-called nanocrystalline structure, e.g. Fimet /1/ and Fe-Zr-B /2/ which revealed great soft magnetic properties. On the other hand, recently a group of metallic glasses have been discovered in La-Al-TM /3/ or Zr-Al-TM /4/ (TM = transition metal) systems. These alloys are characterized by a wide temperature interval ($\Delta T_x = T_x - T_g$) between crystallization temperature (T_x) and glass transition temperature (T_g). Evidence of a large ΔT_x in an alloy represents excellent glass formation ability for the alloy, which raises the possibility of fabricating a bulky metallic glass.

T_g as determined by specific heat measurements for magnetic alloys was observed in a few Fe based glasses which revealed a ΔT_x of about ~20K /9/. However, to our knowledge, a large ΔT_x representing stable supercooled liquid has never been observed in a magnetic glass. "Do ferromagnetism and a large ΔT_x possibly coexist in a metallic glass?" is an open question, but it is crucial in material science. If a metallic glass could reveal both large ΔT_x and ferromagnetism, it would be possible to explore magnetic properties in a supercooled "liquid" state.

As mentioned above, metallic glasses with high formation ability and a larger ΔT_x have been found in the vicinity of $La_{55}Al_{25}Ni_{20}$ /3/. In the same sense, the metallic glass would also be formed in the alloy system when La is replaced by heavy rare-earth (RE) metals. We focus on the Gd-Al-TM system because the Gd is the only one of the heavier RE metals possessing simple ferromagnetism in the magnetically ordered state which formed ferromagnetic compounds with Al and TM. As a result, we have found that three metallic glasses, $Gd_{55}Al_{25}Co_{20}$, $Gd_{55}Al_{25}Ni_{20}$ and $Gd_{55}Al_{25}Cu_{20}$, reveal ferromagnetism at low temperature and stable supercooled liquid region at higher temperature. In this article we examine the structure, thermal stability and magnetic properties for the new style of glasses.

Ternary alloys used in the present study are Gd-Al-TM (TM = Fe, Co, Ni, Cu). Alloy ingots of Gd-Al-TM with the composition of $Gd_{55}Al_{25}TM_{20}$ were obtained by melting nominal amounts of high purity elements in an arc furnace under an argon atmosphere. Glass ribbons were made by single roller melt-spinning technique under an argon atmosphere. The diameter of the copper wheel is 20 cm. The ribbons obtained were 1-3 mm wide and the thickness was 20-40 μm. The structure of the rapidly solidified ribbons was verified using X-ray diffraction technique (CuK_α diffractometry). T_x and T_g were determined by a differential scanning calorimeter of Perkin Elmer DSC-2. T_g was defined as the point of inflection in the specific heat C_p versus temperature curve. The scanning rate was 40 K/min. Measurements of magnetization were performed by vibrating-sample magnetometer (VSM) at a fixed frequency of 80 Hz from 4.2 K to 300K in an applied field of 10 kOe. The values of the Curie temperature were derived from plots of the magnetization squares versus temperature.

As described in previous papers, the metallic glass having the largest ΔT_x in the La-Al-Ni system was $La_{55}Al_{25}TM_{20}$ which revealed a ΔT_x value as large as ~80 K. We replaced La by Gd and verified the formation of glass in $Gd_{55}Al_{25}Cu_{20}$ (a), $Gd_{55}Al_{25}Ni_{20}$ (b), $Gd_{55}Al_{25}Co_{20}$ (c) by x-ray diffraction, as shown in Figure 1. Because it is anticipated that the alloy containing Fe would raise interesting pictures in magnetic properties, we show $Gd_{55}Al_{25}Fe_{20}$ (d) for comparison although a weak peak was observed at Q = 2.0 A^{-1} in the diffraction pattern. Very similar to the La-Al-Ni alloys, three glasses exhibit a main diffuse halo close to Q = 2.33 A^{-1} (Q_1) and a sub-diffuse halo close to Q = 3.86 A^{-1} (Q_2) ($Q = 4\pi \sin\theta / \lambda$), where λ is the wavelength of X-ray and θ is the scattering angle. The ratio of Q_2/Q_1 is about 1.65, differing from that of Pd-Ni-P or Pt-Ni-P systems (1.82) /8/, implying differences in structure. The halo peaks show a symmetric distribution in intensity and broader peak width indicating that the present glasses have a highly disordered structure.

A typical thermogram for four glasses is exemplified in Fig. 2. The T_g rises in the order of Cu<Ni<Co for TM. ΔT_x was estimated to be 68K for $Gd_{55}Al_{25}Co_{20}$, 61K for $Gd_{55}Al_{25}Ni_{20}$, 52K for $Gd_{55}Al_{25}Cu_{20}$ and was not observed in $Gd_{55}Al_{25}Fe_{20}$. The glasses revealing manifest ΔT_x crystallize accompanied by a main and a few small exothermic peaks but $Gd_{55}Al_{25}Fe_{20}$ glasses crystallize via a complicated process where three crystallization peaks are shown. The crystallization of

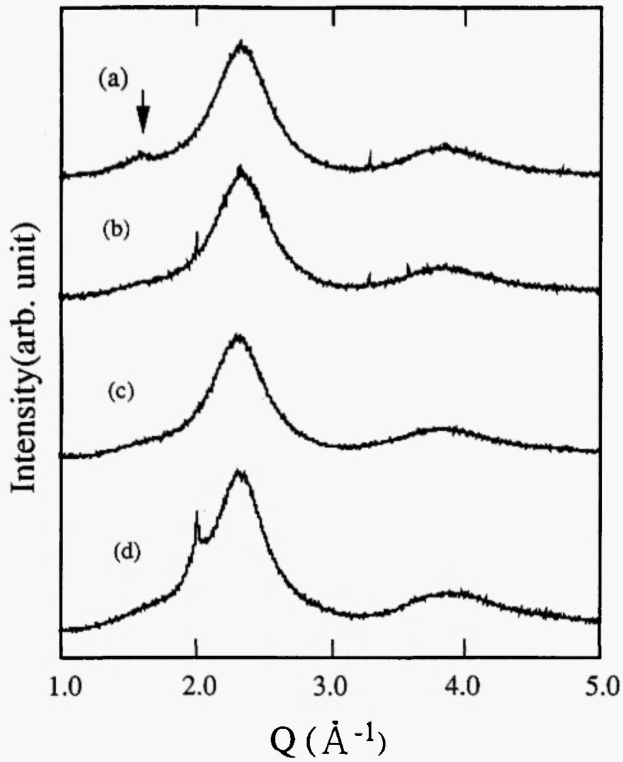

Fig. 1: X-ray diffraction (CuK_α) patterns of metallic glasses of $Gd_{55}Al_{25}TM_{20}$. TM = Cu (a), Ni (b), Co (c) and Fe (d).

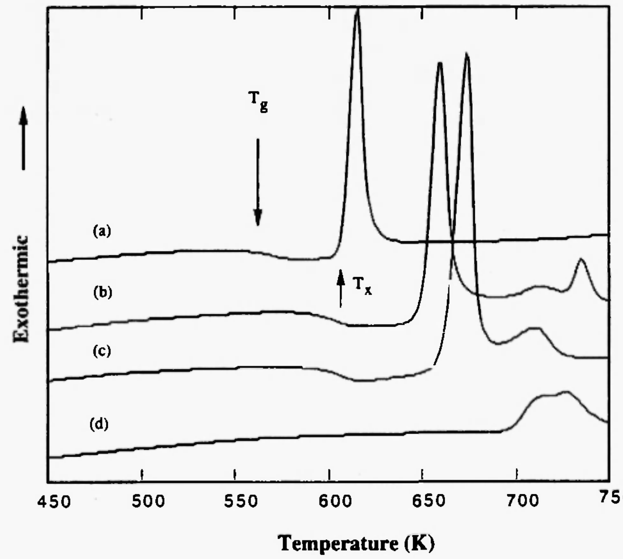

Fig. 2: DSC traces under a heating rate of 40 K/min for four metallic glasses: (a) $Gd_{55}Al_{25}Cu_{20}$, (b) $Gd_{55}Al_{25}Ni_{20}$, (c) $Gd_{55}Al_{25}Co_{20}$ and (d) $Gd_{55}Al_{25}Fe_{20}$.

glasses via an exothermic peak to form more than one product implies a eutectic crystallization which corresponds to the eutectic solidification of its melt. Such a glass, generally, possesses great glass formation ability and larger ΔT_x, as indicated in Fig. 2. For more details, apparent specific heat C_p was first scanned in the DSC to the T_g to obtain the specific heat of as-quenched state (solid line), then cooled to the room temperature for $Gd_{55}Al_{25}Cu_{20}$. The measurement was repeated *in situ* to obtain data for the reference sample (dashed line). The area surrounded by two lines is the enthalpy corresponding to the irreversible structural relaxation. The heat of enthalpy relaxation of the present alloys is about 1.5 kJ/mol, which is somewhat smaller than the usual metallic glasses.

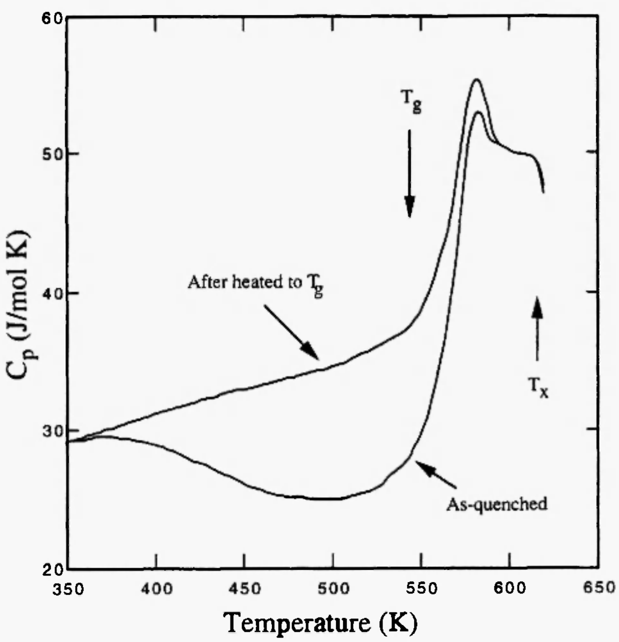

Fig. 3: Temperature dependence of apparent specific heats, C_p, measured at a heating rate of 40 K/min for $Gd_{55}Al_{25}Cu_{20}$ metallic glass.

From the results of the magnetic measurements we deduced that all alloys investigated are predominantly ferromagnetic in character. We show in Fig. 4 the temperature dependence of magnetization (σ_g) and reciprocal susceptibility (χ^{-1}) measured in four alloys. Although the T_g was not observed in $Gd_{55}Al_{25}Fe_{20}$ we measured its magnetic properties for comparison. Curie temperature (T_C) and paramagnetic Curie temperature

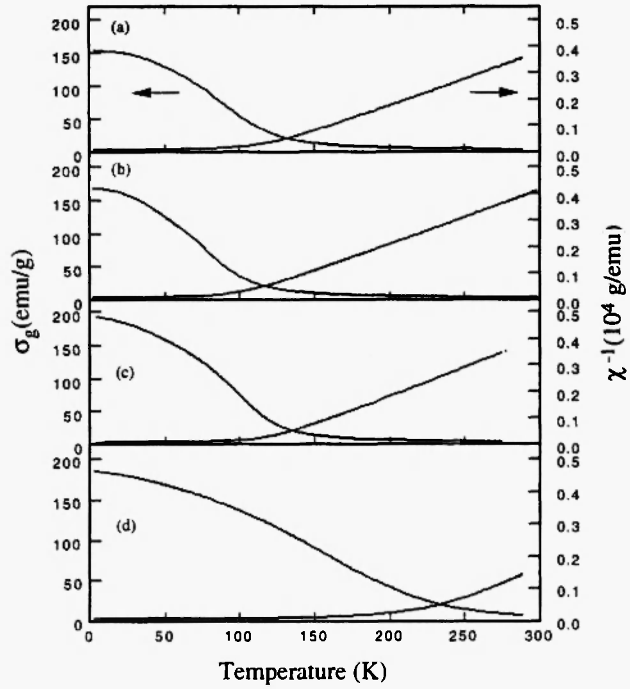

Fig. 4: Temperature dependence of magnetization (σ_g) under 10 kOe and the reciprocal susceptibility χ^{-1} in four glasses: (a) $Gd_{55}Al_{25}Cu_{20}$, (b) $Gd_{55}Al_{25}Ni_{20}$, (c) $Gd_{55}Al_{25}Co_{20}$ and (d) $Gd_{55}Al_{25}Fe_{20}$.

(θ_p) derived from the corresponding Curie-Weiss plots are shown in Table 1. The ferromagnetic nature of these Gd alloys investigated also follows from the behavior of their magnetization curves at 4.2 K. The curves show almost saturation at 18 kOe. Four glasses have a similar magnetization falling into 160 and 200 emu/g. We note a tendency that the values of saturation magnetization (σ_s) for the alloys containing magnetic

Table 1

Glass transition temperatures T_g, crystallization temperatures T_x, Curie temperatures T_C, paramagnetic Curie temperatures θ_p, and magnetization σ_s in a field of 18kOe, remanence σ_r, and coercive field H_c at 4.2K for $Gd_{55}Al_{25}TM_{20}$ metallic glasses

TM	T_g(K)	T_x(K)	T_C(K)	θ_p(K)	σ_s(emu/g)	σ_r(emu/g)	H_c(kOe)
Cu	555	607	108	112	166	49	0.53
Ni	590	651	90	95	180	28	0.39
Co	592	660	116	114	199	23	0.36
Fe	695	190	219	188	~0	~0	~0

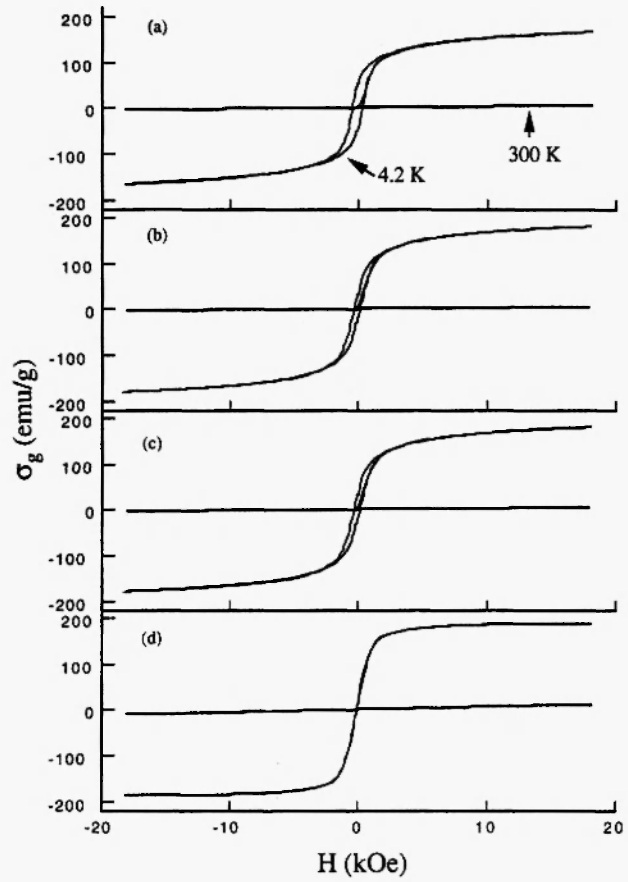

Fig. 5: Magnetization curves at 4.2 K for four glasses: (a) $Gd_{55}Al_{25}Cu_{20}$, (b) $Gd_{55}Al_{25}Ni_{20}$, (c) $Gd_{55}Al_{25}Co_{20}$ and (d) $Gd_{55}Al_{25}Fe_{20}$.

metal (Ni, Co) are higher than those containing non-magnetic metal (Cu). There is measurable hysteresis with remanence, σ_r, and coercive field (H_c) in $Gd_{55}Al_{25}Cu_{20}$, $Gd_{55}Al_{25}Ni_{20}$ and $Gd_{55}Al_{25}Co_{20}$. In general, the presence of hysteresis and a remanence in the magnetic isotherms of 4.2 K indicate that the coupling between the Gd spin is predominantly ferromagnetic. However, the hysteresis was not observed in $Gd_{55}Al_{25}Fe_{20}$. Values of σ_s, σ_r and H_c for four alloys are given in Table 1.

Formation of glasses and their magnetic properties have been reported in several RE-TM systems. For example, the magnetic properties of Gd-TM systems /5-7/ have been investigated in detail. T_c in the present system is closely similar to that in Gd-TM alloys reported by Buschow *et al.* /5/. Ferromagnetic order at low temperature of Gd based glasses can be expected if we assume that the indirect coupling between the Gd spins proceeds mainly via the mechanism involving the Gd 5d electrons. On the basis of the rather uniform behavior of various glasses of about 75 at.% of Gd, in which the nonmagnetic component was allowed to comprise elements differing widely in nature, it was concluded that the s-conduction electron mediated RKKY coupling is of minor importance in this concentration range. The concentration dependence of T_c in the binary Gd-Cu alloys with Gd at.% ranges from 66 to 76, where the T_c increases slightly with decreasing Gd concentration from 142K to 148K. On the other hand, in Gd-Ni alloys the Ni atoms do not carry a magnetic moment which was well reflected in the low T_c (90K) of $Gd_{55}Al_{25}Ni_{20}$. These two points may be able to explain higher T_c of $Gd_{55}Al_{25}Cu_{20}$ compared with that of $Gd_{55}Al_{25}Ni_{20}$. The glasses combined with Co or Fe are a special case. Although the Co and Fe moments in the composition of interest are much smaller than the Gd moments their mutual coupling is much stronger, which reflects on the higher T_c observed in the corresponding Gd-Fe and Gd-Co alloys. This seems to be valid in our ternary alloys. (T_c of $Gd_{55}Al_{25}Fe_{20}$ is 190K). On the whole, interpretations of magnetic properties in the Gd-Al-TM ternary alloys can be applied from binary system in ref. /5/. Addition of Al atoms to the Gd-TM glasses did not change the magnetic properties much, e.g., Curie temperature and magnetization, whereas it increased glass formation ability drastically. This raises an opportunity to fabricate such a magnetic glass even in slow solidification rates. We have also identified a group of metallic glasses in several RE-Al-Co alloys with various RE metals.

In conclusion, we have produced metallic glass of $Gd_{55}Al_{25}Co_{20}$, $Gd_{55}Al_{25}Ni_{20}$ and $Gd_{55}Al_{25}Cu_{20}$ with wide temperature interval of supercooled liquid between 50K and 70K and ferromagnetism at temperatures ranging from 120K to 150K. The magnetic properties of the ternary metallic glasses can be comprehensively interpreted by the argument given in binary Gd-TM glasses /5/.

REFERENCES

1. Y. Yoshizawa, S. Oguma and K. Yamauchi, *J. Appl. Phys.*, 64, 6044 (1988).
2. K. Suzuki, K. Kataoka, A. Inoue, A. Makino and T. Masumoto, *Mater. Trans. Jpn. Inst. Met.*, **31**, 743 (1990).
3. A. Inoue, T. Zhang and T. Masumoto, *Mater. Trans. Jpn. Inst. Met.*, 30, 965 (1989).
4. A. Inoue, T. Zhang and T. Masumoto, *Mater. Trans. Jpn. Inst. Met.*, **31**, 177 (1990).
5. K.H.J. Buschow, H.A. Algra and R.A. Henskens, *J. Appl. Phys.*, **51**, 561 (1980).
6. T.R. McGuire and R.J. Gambino, *IEEE Trans. MAG*-**14**, 838 (1978).
7. J. Durand and S.J. Poon, *IEEE Trans. MAG*-**13**, 1556 (1977).
8. K. Ashok and P. Duwez, *J. Phys. Chem. Solids*, **32**, 267 (1971).
9. H.S. Chen, R.C. Sherwood and E.M. Gyorgy, *IEEE Trans. MAG*-**13**, 1538 (1977).