Extended solubility and spin-glass behavior in a Ag-Gd solid solution prepared by mechanical alloying

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The effects of mechanical alloying on the solubility in a Ag-Gd solid solution have been investigated. The study shows that the solubility of Gd in Ag can be extended to about 5 at. % Gd by mechanical alloying from the equilibrium solubility of less than 0.95 at. % Gd. $Ag_{85}Gd_{15}$ prepared by mechanical alloying exhibits a spin-glass-type transition at ~5 K. A Curie-Weiss behavior at higher temperatures and x-ray patterns of the material indicate that Gd atoms are either dissolved in the Ag matrix or in the form of small clusters of diameters of a few nanometers.

I. INTRODUCTION

It has been demonstrated that extended solubility in two originally immiscible elements can be achieved by mechanical alloying in transition metals.[1–3] For example, a solubility of 60 at. % of Fe in fcc Cu was found in the as mechanically alloyed samples,[4] while Fe and Cu are virtually insoluble in each other at equilibrium. The study of metastable solid solution formation by mechanical alloying in intermetallic systems containing rare earths, however, has been scarce. Decomposition of La-Ni, La-Co, and La-Ag intermetallic compounds into the elements by ball milling was reported by Loeff, Bakker, and de Boer,[5] and no observable solid solution was found in the systems. On the other hand, ball milling of crystalline La-Au alloys resulted in an amorphous alloy.[6] In this paper, we report the observation of extended solid solution (~5 at. % Gd in Ag) induced by mechanical alloying of the starting powder elements. A spin-glass transition at ~5 K is observed in this binary Ag-Gd system.

II. EXPERIMENTAL DETAILS

Samples were prepared by mechanical alloying using a high-energy Spex 8000 mixer/mill. The starting materials were fine powders of silver and gadolinium of 99.9% purity. The starting composition of the Ag-Gd mixture was $Ag_{85}Gd_{15}$, which was sealed in a grinding vial made of hardened steel under argon atmosphere. Also sealed in the vial were hardened steel balls. The sticking of metal powders to the walls of vial and balls, which often occurs during milling, was avoided by the addition of small amount of ethanol to the initial mixture. Samples were obtained after 2.5, 15, and 35 h of mechanical alloying. They were dried under vacuum at room temperature. The vacuum dried samples contained no ethanol as indicated from the ir spectroscopy. The weight of the balls was measured before and after mechanical alloying, and there was no weight loss of the balls (less than 0.01 g), which indicated that the samples (~7 g) were essentially Fe free (less than 0.1 wt. % Fe). X-ray diffraction was conducted on a Rigaku x-ray powder diffractometer with Cu $K\alpha$ radiation. During the experiments, samples were sealed underneath an Al_2O_3 foil in order to prevent any possible oxidation of the samples. Magnetic susceptibility of the 35-h mechanically alloyed sample was measured as a function of temperature under both zero-field-cooled (ZFC) and field-cooled (FC) conditions using a Quantum Design superconducting quantum interference device susceptometer (model MPMS-5S).

III. RESULTS AND DISCUSSION

Shown in Fig. 1 are the x-ray-diffraction patterns of samples ground for 2.5, 15, and 35 h. Also shown in Fig. 1 is the x-ray pattern of the 35-h mechanically alloyed sample, which was subsequently heat treated at 550 °C for 10 min. The pattern for the 2.5-h mechanically alloyed sample was essentially that of a mixture of Ag and Gd. As the grinding

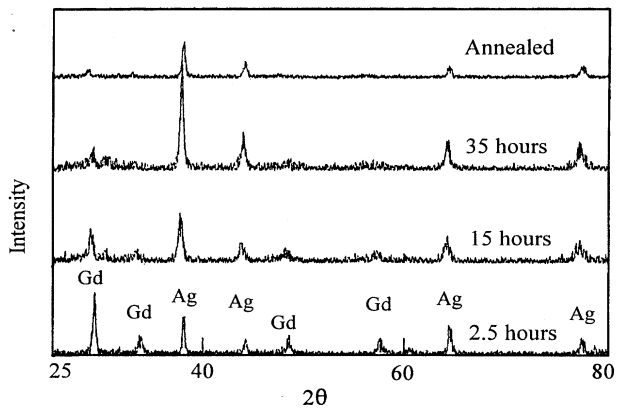

FIG. 1. X-ray-diffraction patterns of samples mechanically alloyed for 2.5, 15, and 35 h and that of the 35-h sample that was subsequently annealed at 550 °C. The intensity is in arbitrary units and 2θ in degrees.

time increased, the intensities of the Gd peaks decreased and became very broad at 35 h, and, at the same time, the intensities of the Ag peaks increased, which might be caused by the presence of heavier Gd atoms in the fcc Ag matrix. A more direct evidence for the formation of a solid solution of Gd in Ag was that the positions of the Ag peaks were shifted toward lower angles for the 15- and 35-h mechanically alloyed samples because of the substitution of the larger Gd atoms for Ag.

As a matter of fact one can estimate the number of Gd atoms dissolved in the Ag matrix by determining the lattice constants of the samples. The lattice constant of pure fcc Ag $a=4.086$ Å was determined from the Ag powders used in this study. The lattice constant of the 35-h mechanically alloyed sample had a lattice constant a of 4.100 Å. If one assumes that the linear relation between the lattice constant and Gd concentration in fcc Ag under equilibrium conditions for concentrations less than the maximum solubility of 0.95 at. % Gd[7] is valid in our case, a lattice constant $a=4.100$ Å of the mechanically alloyed sample corresponds to a solubility of ~5 at. % Gd in fcc Ag. This extended solubility was a direct result of mechanical alloying, in which intimate contacts between Gd and Ag and subsequent imbedding of Gd into Ag might have been brought by the high-energy ball-sample-container collisions.[1,8] It should be noted that the reported maximum equilibrium solubility of 0.95 at. % Gd is at a eutectic temperature of 805 °C, the equilibrium solubility at room temperature is even lower (~0.1 at. % Gd).[7] This is not hard to understand if one considers the fact that the metallic radius of Gd is 25% larger than that of Ag. The 15-h mechanically alloyed sample showed a lattice constant that is very close to the 35-h sample, which suggested that much of the 5 at. % of Gd atoms were already dissolved in the Ag matrix at 15 h and the solubility of Gd in fcc Ag may not be extended much further by simply extending the grinding time. The Gd atoms in the 35-h mechanically alloyed "$Ag_{85}Gd_{15}$" sample were either dissolved in the Ag-Gd solid solution (~5 at. % Gd), or in the form of small clusters of average diameter of 2–3 nm as determined from the broadening of Gd x-ray peaks using the Scherrer formula.[9]

After 10 min of annealing at 550 °C, the metastably dissolved Gd atoms in the 35-h sample precipitated out of the fcc lattice, and the fcc Ag peaks in the x-ray pattern returned to their original positions of pure Ag (Fig. 1).

Magnetic susceptibility of the 35-h mechanically alloyed sample was measured as a function of temperature under both ZFC and FC conditions. Shown in Fig. 2 is the ZFC and FC susceptibilities measured with magnetic fields of $H=20$, 100, 1000 G. The spin-glass transition at $T_f=5$ K is clearly seen in the ZFC and FC susceptibilities at a measuring field of $H=20$ G. T_f was reduced to 3.5 K for $H=100$ G and further reduced to below 2 K, which is the lowest temperature our instrument can reach, for $H=1000$ G. A spin glass transition was observed in a Ag-Gd solid solution.

The magnetic properties of Ag-Gd, mostly amorphous, have been studied extensively.[10–14] Amorphous Gd_xAg_{100-x} for $x>20$ were prepared and exhibited ferromagnetic ordering with a transition temperature proportional to the Gd concentration, although alloys for $x<30$ displayed some of the features normally associated with spin glass. The amorphous Ag-Gd system for smaller Gd concentration was difficult to

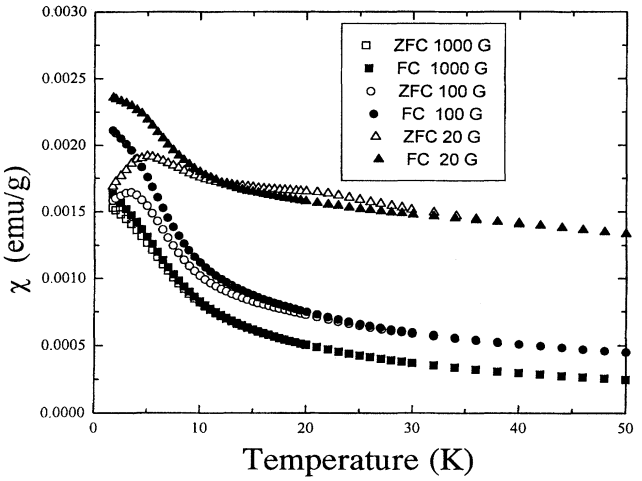

FIG. 2. Zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities of the 35-h sample measured with magnetic fields of $H=20$, 100, and 1000 G.

prepare, and Y was used to dilute the Gd concentration by Mohammed and Lanchester.[15] Their study indicated that amorphous $Gd_{10}Y_{20}Ag_{70}$ and $Gd_{20}Y_{10}Ag_{70}$ are spin glasses with freezing temperatures of ~6 and ~13 K, respectively. The spin-glass behavior observed in our study is of significance in that the Ag-rich fcc Ag-Gd (5 at. %) system is a true binary alloy and is crystalline rather than amorphous. As far as we know, the only other study on the crystalline fcc Ag-Gd alloy was that of Sugawara *et al.*, where a sharp maximum in resistivity and change of slope in magnetic susceptibility were found at about 3 K in quenched dilute Ag-Gd alloys between 0.3 and 0.5 at. % Gd.[16] However, no anomaly was found in the heat capacity of these alloys, which was expected for either a spin glass or for other magnetic phase transitions.[17] The extended solubility of ~5 at. % Gd in Ag achieved by mechanical alloying has made possible the direct observation of the spin-glass behavior in this true binary system. Experiments are being planned to prepare samples with varying initial Gd concentration near 5 at. % to obtain complete alloying. Magnetic study on such a pure solid solution sample will shed more light on the nature of the spin-glass transition and Ruderman-Kittel-Kasuya-Yosida interaction.

In the 35-h mechanically alloyed sample, about one-third of the Gd atoms were dissolved in the Ag-Gd solid solution (5 at. % Gd) and two-thirds of the Gd atoms were in the form of nanoparticles 2–3 nm in size. It should be pointed out that superparamagnetism arising from these Gd nanoparticles cannot be accountable for the peak in susceptibility at 5 K. The blocking temperature T_B of superparamagnetic particles is proportional to KV, where K is anisotropy constant and V the particle volume.[18] The anisotropy constants K are $\sim 5\times 10^5$ and $\sim 1\times 10^6$ erg/cm^3 for Fe and Gd, respectively.[19] The blocking temperatures of systems containing Fe particles of a few nanometers have been found to have a typical value of $T_B>10$ K, which suggests that the T_B of the Gd nanoparticles of similar size should be at least twice that (>20 K). In addition, a recent study on small Gd clusters has suggested that the blocking temperature of Gd

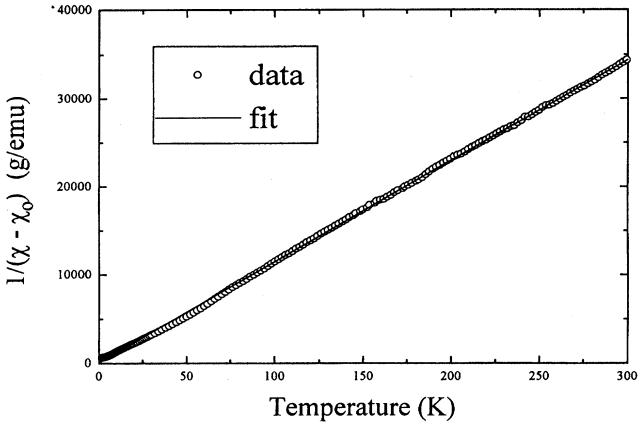

FIG. 3. Inverse susceptibility $1/(\chi-\chi_0)$ of the 35-h sample measured at 1000 G, where $\chi_0=0.000\,058$ emu/g.

clusters containing 10–35 atoms has typical values between 100 K and room temperature.[20] Thus the peak at ~5 K could not be associated with the blocking temperature of Gd nanoparticles. However a broad maximum between 15 and 30 K in low-field susceptibility (ZFC and $H=20$ G) might be related to the blocking of the Gd superparamagnetic nanoparticles. Compared to the nanoparticles of transition metals (Fe, Co, and Ni), the magnetic behavior of Gd nanoparticles is far less understood and needs to be further investigated. Additional experiments will be conducted in order to study the superparamagnetic properties of Gd nanoparticles produced by mechanical milling.

Figure 3 shows the inverse susceptibility $1/(\chi-\chi_0)$ measured at 1000 G, where constant $\chi_0=0.0000\,58$ emu/g. It follows the Curie-Weiss law, with a small and negative $\theta=-0.5$ K. If one assumes that the Gd atoms dissolved in the Ag-Gd solid solution have effective moment $\mu_{\text{eff}}=7.9\mu_B$ (expected for a free-Gd ion), the saturation magnetization M_s of the Gd nanoparticles can be calculated from $\chi=M_s^2V/3k_B(T-\theta)$, where V is the average Gd particle volume. $\theta=-0.5$ K and $V=(4-14)\times10^{-27}$ m^3 (particle diameter $d=2-3$ nm) were used in the calculation. Such a calculation resulted in an average saturation magnetization of M_s between 3 and $5\mu_B$ per Gd atom for Gd particles. The reduced magnetization (compared to $7\mu_B$) in small Gd particles has been observed in a few cases and may be attributed to the possible presence of antiferromagnetic coupling within the particle.[13,20] The reduced moment can also be seen in the magnetization curve (Fig. 4), which shows that the magnetization does not saturate at 2 K and a field of 5 T. The highest value obtained was $4.9\mu_B$/Gd. The inset of Fig. 4 shows the hysteresis normally associated with spin glass or superparamagnetic particles below the critical temperature. The low-field susceptibilities ($H=20$ and 100 G) could not be fitted into a Curie-Weiss law, which is attributed to the enhanced effect at low fields by residual ferromagnetic Gd existing in the sample. This is also seen as the difference in susceptibilities between different measuring fields (Fig. 2) at high temperatures.

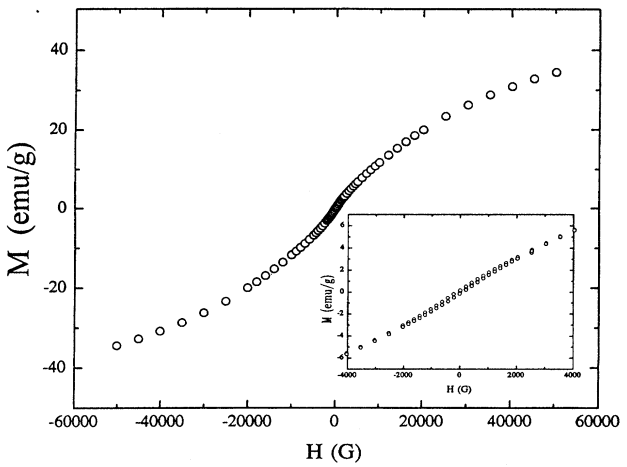

FIG. 4. Magnetization and hysteresis loop for the 35-h sample. The inset shows the region of smaller fields ($H<4000$ G).

IV. CONCLUSIONS

An extended solubility (5 at. % Gd) was induced by mechanical alloying in an Ag-rich fcc solid solution. A spin-glass freezing temperature of 5 K was observed in this system. A Curie-Weiss behavior at higher temperatures and x-ray patterns of the material indicate that Gd atoms are either dissolved in the Ag matrix or in the form of small clusters of diameters of a few nanometers.

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[1] A. R. Yavari, P. J. Desré, and T. Benameur, Phys. Rev. Lett. **68**, 2235 (1992).
[2] J. Eckert, J. C. Holzer, C. E. Krill III, and W. L. Johnson, J. Appl. Phys. **73**, 2794 (1993).
[3] R. Brüningk, K. Samwer, C. Kuhrt, and L. Schultz, J. Appl. Phys. **72**, 2978 (1992).
[4] E. Ma, M. Atzmon, and F. E. Pinkerton, J. Appl. Phys. **74**, 955 (1993).
[5] P. I. Loeff, H. Bakker, and F. R. de Boer, *New Materials by Mechanical Alloying Techniques*, edited by E. Arzt and L. Schultz (DGM, Oberursel, Germany, 1989), p. 119.
[6] P. I. Loeff and H. Bakker, Scr. Metall. **22**, 401 (1988).
[7] K. A. Gschneidner, Jr., O. D. McMasters, D. G. Alexander, and R. F. Venteicher, Metall. Trans. **1**, 1961 (1970).
[8] C. C. Koch, Annu. Rev. Mater. Sci. **19**, 121 (1989).
[9] A. Guinier, *Théorie et Technique de la Radiocristallographie* (Dunod, Paris, 1964).
[10] J. J. Hauser, Phys. Rev. B **12**, 5160 (1975).

[11] K. H. J. Buschow, Solid State Commun. **27**, 275 (1978).
[12] S. W. Charles, J. Popplewell, and P. A. Bates, J. Phys. F **3**, 664 (1973).
[13] R. J. Begum, C. A. Cornelius, E. W. Lee, and V. Samadian, J. Phys. F **14**, 2739 (1984).
[14] C. D. Fuerst, J. F. Herbst, R. K. Mishra, and R. D. McMichael, J. Appl. Phys. **76**, 6301 (1994).
[15] K. A. Mohammed and P. C. Lanchester, Solid State Commun. **70**, 367 (1989).
[16] T. Sugawara, R. Soga, and I. Yamase, J. Phys. Soc. Jpn. **19**, 780 (1964).
[17] G. R. Pickett, Phys. Lett. **21**, 618 (1966).
[18] E. M. Logothetis, W. J. Kaiser, H. K. Pluammer, and S. S. Shinozaki, J. Appl. Phys. **60**, 2548 (1986).
[19] E. P. Wohlfarth, *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North-Holland, New York, 1980), Vol. 1, p. 1; S. Legvold, *ibid.*, Vol. 1, p. 183.
[20] D. C. Douglass, A. J. Cox, J. P. Bucher, and L. A. Bloomfield, Phys. Rev. B **47**, 12 874 (1993).