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Formation of nominal Ni amorphous phase by mechanical milling and leaching

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Abstract

A nominal Ni amorphous phase was obtained by leaching Al atoms from mechanically alloyed $Ni_{40}Al_{60}$ amorphous alloy. X-ray diffraction, transmission electron microscopy and magnetization measurements were utilized to characterize the as-milled and leached specimens. The Ni amorphous phase is a strong paramagnet and transforms to a ferromagnetic f.c.c. phase above 500 K.

1. Introduction

In the last decade there has been a rapidly increasing interest in the mechanical alloying (MA) process, because a large number of amorphous alloys can be formed by this technique [1]. Moreover, a substantial possibility of making new materials whose structural, magnetic and catalytic properties are quite different from the original materials has emerged on combining MA with topotactic chemical reactions [2].

Recently we have developed a combination technique of mechanical alloying and chemical leaching as follows. Mechanically alloyed metastable $Ni_{35}Al_{65}$ alloy with the B2 structure can be topotactically transformed into nanocrystalline b.c.c. Ni after leaching Al in basic solution [3, 4]. Similarly, a nanocrystalline b.c.c. Co phase was obtained by leaching out Al atoms from mechanically alloyed b.c.c. $Co_{40}Al_{60}$ [5]. The b.c.c. Ni exhibits a paramagnetic character, whereas the b.c.c. Co is ferromagnetic. These results are consistent with other experimental and theoretical results [6–9]. More recently, the present authors have attempted, for the first time, to obtain an Ni amorphous phase by leaching the major portion of Al from sputter-deposited amorphous Ni–Al alloy [10].

In this work, we apply the same leaching technique to a mechanically alloyed $Ni_{40}Al_{60}$ amorphous alloy to obtain Ni amorphous phase and study its structural and magnetic properties through X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and magnetization measurements.

2. Experimental details

A conventional low energy vibrating ball mill was utilized to obtain $Ni_{40}Al_{60}$ amorphous alloy from pure elemental Ni and Al powders. The mechanically alloyed samples were leached in 25 wt.% KOH solution at 375 K to remove Al atoms. This process is the same as a conventional method for obtaining Raney Ni catalysts [11]. The XRD was performed at 290 K by using Cu Kα radiation and a graphite monochromator. The heat treatment up to crystallization was monitored by DSC at a heating rate of 40 K min^{-1}. The microstructures of the as-milled and the leached specimens were characterized by TEM at 200 kV. The composition of the alloys was determined using energy-dispersive X-ray (EDX) analysis with a detector connected to the electron microscope. Magnetization was measured between 77 and 800 K in magnetic fields up to 16 kOe by using a conventional vibrating sample magnetometer.

3. Results and discussion

3.1. Structure and thermal stability

Figure 1 shows the XRD patterns of the as-milled $Ni_{40}Al_{60}$ alloy and the leached alloy. The as-milled $Ni_{40}Al_{60}$ alloy exhibits a very broad halo pattern characterizing an amorphous structure. The position and the width of the halos do not change significantly, indicating the persistence of the amorphous phase,

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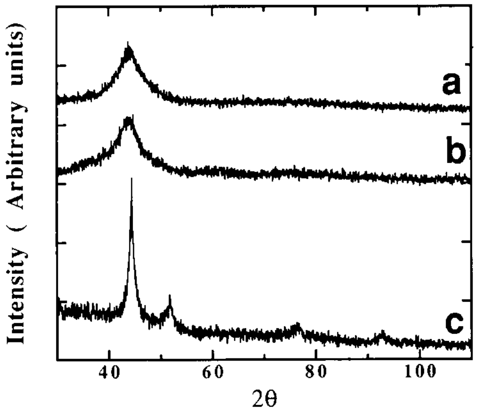

Fig. 1. XRD patterns of as-milled $Ni_{40}Al_{60}$ (spectrum (a)), leached nominal Ni amorphous (spectrum (b)) and crystallized nominal Ni (spectrum (c)) specimens.

although most Al atoms have been removed. It should be emphasized that no f.c.c. Ni peaks appear after the leaching process, whereas after leaching of the sputter-deposited $Ni_{25}Al_{75}$ amorphous alloy the width of the halos becomes narrower because of the formation of nanocrystals with an apparent size of about 2 nm [10]. This result suggests that the mechanically alloyed Ni–Al amorphous alloy is structurally more stable than the sputter-deposited alloy against leaching. As shown in Fig. 1, spectrum c, after annealing at 770 K for 45 min, the leached specimen transforms to the f.c.c. structure with a lattice constant of about 0.352 ± 0.002 nm. This lattice constant is slightly larger than that of elemental f.c.c. Ni, suggesting that about 3 at.% of Al atoms are still included in f.c.c. Ni lattice.

In order to observe the microstructure and to identify the chemical composition on a microscopic scale, TEM equipment with EDX facilities was employed. The chemical composition of the as-milled sample is close to the nominal composition, whereas most of the Al atoms are removed after leaching in the basic solution. About 2 at.% of Fe impurities was found to be introduced into the mother alloy from the stainless steel vial during the MA process. Figure 2(a) shows the TEM micrograph and the specific area diffraction (SAD) pattern of the as-milled $Ni_{40}Al_{60}$ amorphous alloy. A featureless uniform TEM image and a broad halo diffraction pattern are observed, indicating the amorphous structure of this alloy. As shown in Fig. 2(b), the leached alloy is also characterized by an almost uniform featureless TEM image and a broad halo SAD pattern, these being attributed to the amorphous phase. Thus, leaching of the Al atoms does not induce a significant change in the diffraction pattern and the amorphous structure is safely preserved in the leached specimens. A micrograph of the same particle in Fig. 2(b) after *in situ* annealing in the electron beam column is shown in Fig. 2(c). The image manifests the crystallization of the amorphous particle, exhibiting the formation of 10–30 nm Ni crystals. The electron diffraction pattern of the annealed particle has several Debye rings with spots which are attributed to the f.c.c. structure. TEM observation combined with EDX analysis has also been carried out on a leached sample after *ex situ* annealing at 800 K for 45 min. The result is displayed in Fig. 3. Most of the observations reveal a crystalline f.c.c. Ni structure containing about 5 at.% Al as illustrated by the TEM micrograph and SAD pattern of Fig. 3(a). However, some particles of Al oxide compounds can be observed in the TEM micrograph and SAD pattern as shown in Fig. 3(b), with a probability of less than 10%.

In summary of this part, TEM observations reveal that the structures of the as-milled and the leached specimens are amorphous. The crystallization of the leached specimens could be observed distinctly. Some Al oxide compounds were physically included in the leached specimens. It must be emphasized that the presence of such non-magnetic Al oxides in the leached sample affects the saturation magnetization of the annealed leached Ni specimen.

Figure 4 illustrates the DSC curve of the leached sample. Two broad but distinct exothermic peaks are observed. The first peak at about 500 K can be attributed to the crystallization of the nominal Ni amorphous phase. It is worth noting that the second peak at about 630 K is quite close from the Curie point of f.c.c. Ni and can be attributed to the magnetic transformation.

3.2. Magnetic Properties

Figure 5 illustrates the temperature dependence of the magnetization σ of leached Ni specimens between 290 and 820 K in an applied magnetic field H of about 10 kOe. It can be seen that σ is very small (0.8 emu g^{-1}) at 290 K and slightly decreases with increasing temperature up to 550 K. σ increases above 550 K and decreases again above 630 K. On cooling the specimen from 820 K, σ sharply increases at about 630 K and attains a value of about 42 emu g^{-1} at 290 K. The following features can be understood from this figure.

(1) The nominal Ni amorphous phase obtained by leaching is paramagnetic and gradually transforms to a ferromagnetic f.c.c. phase when heated above 500 K.

(2) Although the saturation magnetization at room temperature of the nominal Ni crystallized phase is still lower than the 54 emu g^{-1} of f.c.c. pure Ni, the Curie temperature T_c of this phase matches that of f.c.c. pure nickel, indicating that most of the retained Al atoms do not form a dilute solid solution with Ni but are chemically isolated from Ni. This result is consistent with the TEM observation which reveals Al oxide particles in this sample.

Figures 6(a) and 6(b) show the magnetization curves σ (H) at room temperature (RT) and 77 K for the as-

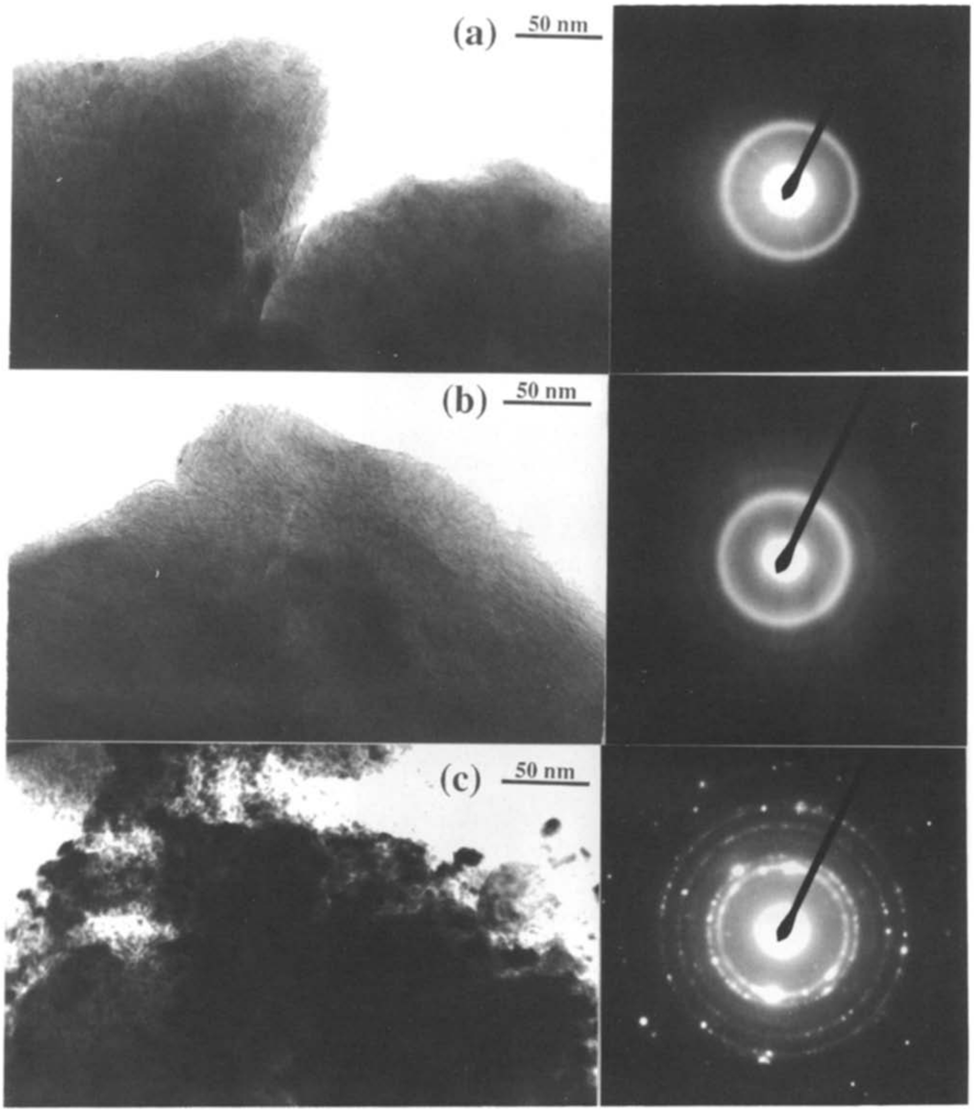

Fig. 2. TEM images and SAD patterns of (a) as-milled $Ni_{40}Al_{60}$, (b) leached nominal Ni amorphous and (c) leached nominal Ni specimens after *in situ* annealing by electron beam.

milled and leached specimens. The general features of these curves are as follows.

(1) The magnetization does not saturate up to $H = 16$ kOe at RT and 77 K, and the high field susceptibility becomes larger at 77 K: σ increases almost linearly with increasing magnetic field between 5 and 16 kOe.

(2) The characteristic change in $\sigma(H)$ is slightly different from that of a simple paramagnet. Here, the magnetization σ (H, T) at an applied field H and temperature T can be described by the following formula:

$$\sigma(H,T) = \sigma_0(H,T) + \chi(H,T)H \quad (1)$$

where $\sigma_0(H,T)$ is attributed to the ferromagnetic impurities of Fe and f.c.c. Ni present in both alloys and $\sigma_0(H,T)$ is roughly independent of temperature. The value of $\sigma_0(H, 290\ K)$ was found to be 0.2–0.3 emu g^{-1} for the as-milled and the leached specimens. Here, $\sigma_0(H, 290\ K)$ of the leached specimen is 1 order of magnitude smaller than that observed after leaching of the sputter-deposited alloy [10] where Ni nanocrystallites were partially formed. Such a very small value confirms the structural homogeneity of both alloys, indicating no f.c.c. Ni phase formation in the leaching process. This result also supports the structural data obtained by XRD and TEM. The increase in $\sigma(H,T)$ of the leached specimen with decreasing temperature and the pronounced high field susceptibility at 77 K are attributable to the paramagnetic Ni amorphous phase.

Figure 7 illustrates the temperature dependence of the corrected magnetization σ and the inverse susceptibility χ^{-1} for the as-milled and the leached Ni specimens measured in an applied field of 10 kOe. Although

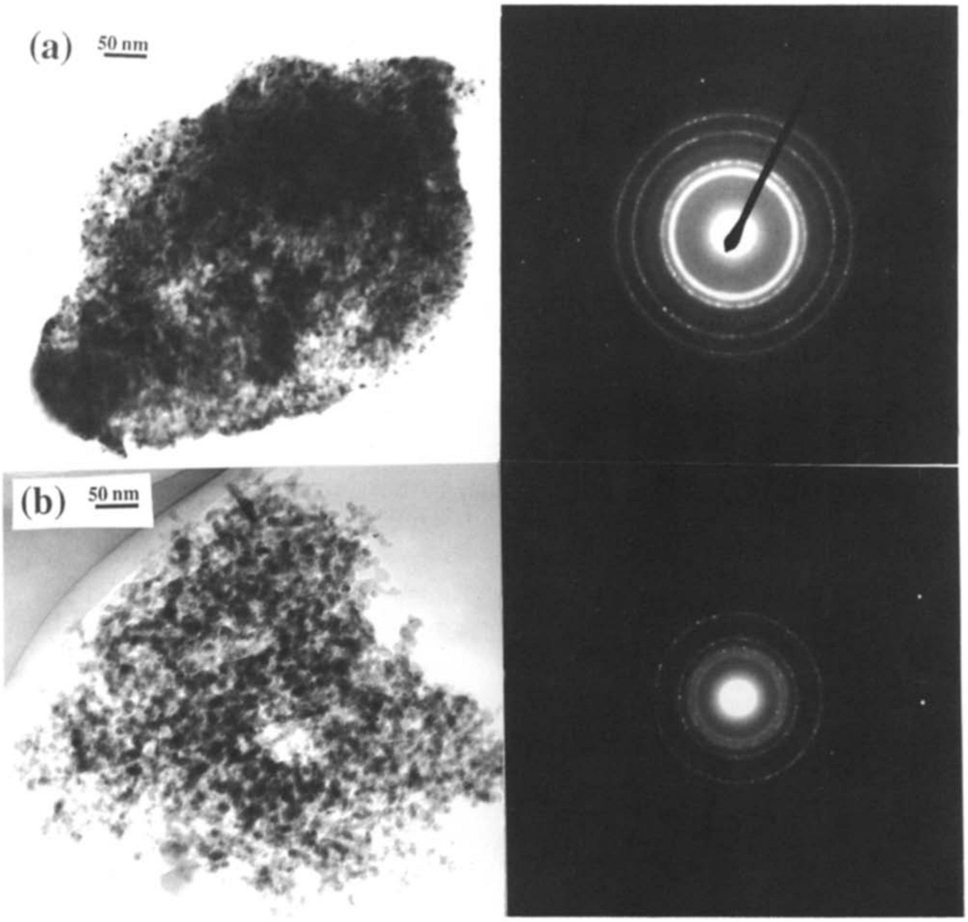

Fig. 3. TEM images and SAD patterns of crystallized nominal Ni phase obtained by leaching: (a) crystalline f.c.c. Ni; (b) Al oxides.

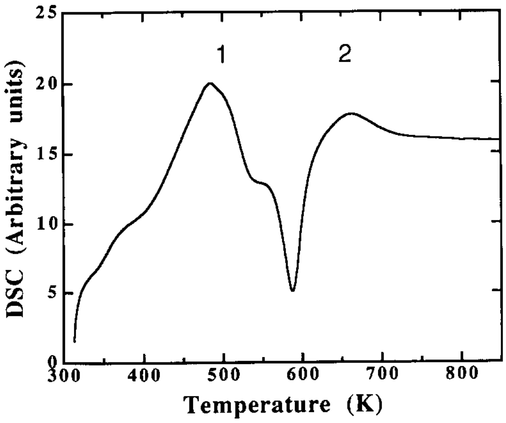

Fig. 4. DSC trace of the leached nominal Ni amorphous specimen.

the Curie–Weiss law is satisfied in the entire temperature range (T = 77–290 K), the presence of non-magnetic Al oxide, of uncertain amount, makes it difficult to estimate the effective magnetic moment per Ni atom for the Ni amorphous phase. However, the value of the Curie constant is noted and it is considered that the fraction of retained Al in the leached specimen is

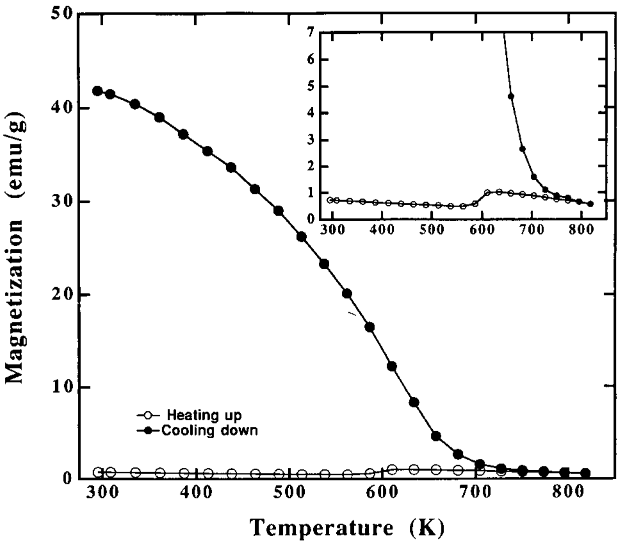

Fig. 5. Temperature dependence of the magnetization σ of the leached nominal Ni amorphous specimen in the temperature cycle 290 K→820 K→290 K.

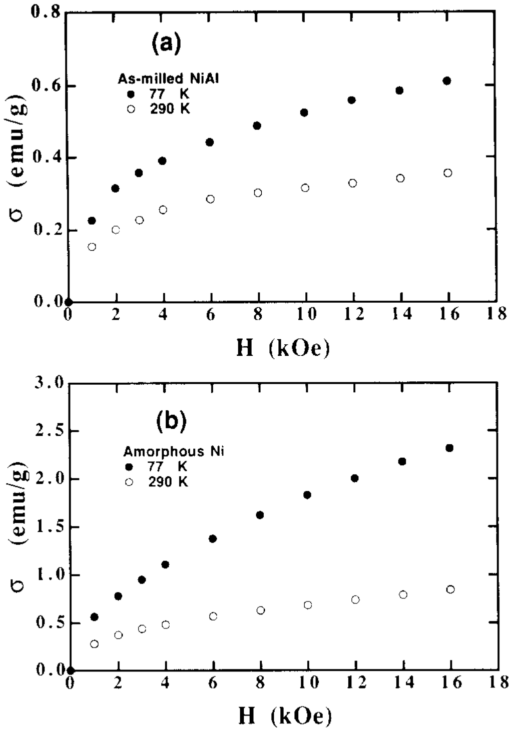

Fig. 6. Magnetization (σ *vs.* H) curves at 290 K and 77 K for (a) as-milled $Ni_{40}Al_{60}$ and (b) leached nominal Ni amorphous specimens.

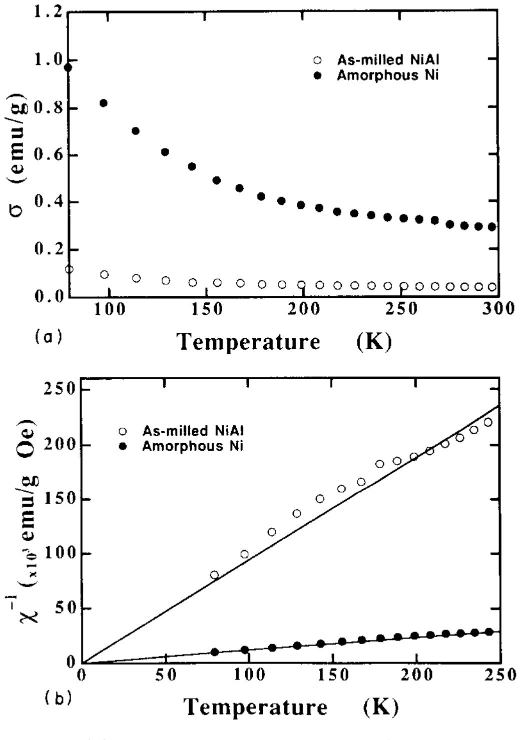

Fig. 7. (a) Thermomagnetic (σ *vs.* T) curves and (b) thermal variation of the inverse susceptibility χ^{-1} for the as-milled $Ni_{40}Al_{60}$ and the leached nominal Ni amorphous specimens obtained at an applied field of 10 kOe.

less than 10 at.%. It can be concluded that the effective magnetic moment per Ni atom in the leached specimen is three times larger than that in the as-milled specimen.

Finally, our experimental results [4, 5] show that b.c.c. phases of Ni and Co can be formed by leaching Al from their B2-type ordered aluminides obtained by MA. The b.c.c. Ni was found to be a strong paramagnet whereas the b.c.c. Co phase displayed a ferromagnetic character. These results are in good agreement with the magnetic properties of those phases obtained by epitaxial growth [6, 7] and also are in accordance with theoretical predictions based on band structure calculations of 3d metals [8, 9]. However, there have been no data on the magnetic properties of the amorphous Ni phase. Thus further experimental work as well as additional theoretical treatments are needed to explain the magnetic properties of the amorphous Ni phase. The low temperature physical properties of the phase described here will be presented elsewhere [12].

4. Conclusion

In conclusion, we have succeeded in producing nominal Ni amorphous phase by leaching most of the Al atoms from the mechanically alloyed $Ni_{40}Al_{60}$ amorphous alloy where less than 10 at.% Al is retained in the oxide state. The Ni amorphous phase transforms to the ferromagnetic f.c.c. phase above 500 K. It should be emphasized that the present technique is unique for obtaining amorphous Ni. Controlling the reaction temperature and/or the leaching solution may lead to the complete removal of the Al atoms and form non-equilibrium pure metal phases having structural and magnetic properties different from the equilibrium phases.

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