Journal of Alloys and Compounds, 187 (1992) L1–L6
JALCOM 329

Letter

Nanoscale quasi-amorphous nickel produced by leaching sputter-deposited $Ni_{25}Al_{75}$ alloy

Salah A. Makhlouf, E. Ivanov*, K. Sumiyama and K. Suzuki
Institute for Materials Research, Tohoku University, Sendai 980 (Japan)

(Received April 3, 1992, in final form April 13, 1992)

Abstract

In this letter, we report the formation of amorphous-like nickel by leaching aluminium atoms from amorphous $Ni_{25}Al_{75}$ alloys obtained by d.c. sputtering. X-ray diffraction, transmission electron microscopy with energy-dispersive X-ray analysis facilities and magnetization measurements reveal the following features: (i) the leached specimens have a nanoscale quasi-amorphous structure; (ii) the amorphous-like phase is paramagnetic at room temperature and transforms to a ferromagnetic f.c.c. phase at about 450 K.

1. Introduction

The precursor technology of using topotactic solid state reactions has been developed in solid state chemistry to make new materials with metastable structure, composition or crystal habits [1]. Mechanically alloyed metastable $Ni_{35}Al_{65}$ alloy with the B2-type structure can be topotactically transformed into metastable b.c.c. nickel after leaching aluminium in basic solution [2, 3]. A large increase in the surface area induces high catalytic activity of amorphous Cu–Zr and Ni–Zr alloys by partially extracting zirconium [4, 5]. Similarly, an amorphous $Ni_{77}Si_{13}B_{10}$ alloy covered by a zinc surface layer can be treated with basic solution for selective dissolution of doped zinc [6]. In this work we have attempted, for the first time, to obtain amorphous metals by leaching the major portion of aluminium from sputter-deposited amorphous Ni–Al alloys.

2. Experimental details

A facing target type of d.c. sputtering has been employed to prepare approximately 10 μm thick Ni–75at.%Al alloy on liquid nitrogen cooled

*On leave from Institute of Solid State Chemistry, 630091 Novosibirsk 91, Derzhavina 18, Russian Federation. Present address: TOSOH SMD, 3515 Grove City Road, Grove City, Ohio 43123, USA.

0925-8388/92/$5.00

polyimide films. The alloy specimens were crushed and treated in basic solution to leach aluminium by the conventional method for obtaining Raney nickel catalysts [7].

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the sputter-deposited $Ni_{25}Al_{75}$ alloy and the leached alloy before and after annealing at 770 K. The as-deposited $Ni_{25}Al_{75}$ alloy exhibits a very broad halo pattern characterizing an amorphous structure (Fig. 1, spectrum a). After leaching of aluminium atoms, a narrower halo-like pattern is detected without any clear Bragg peak although most of the aluminium atoms have been removed (Fig. 1, spectrum b). The apparent crystalline size t in the leached specimens is about 2 nm as estimated from the broad peak at $2\theta=44°$ using the Scherrer method [8]. After the leached alloy had been annealed at 770 K for 45 min the structure transformed to the f.c.c. phase with a lattice constant of about 0.354 nm and an apparent crystallite size of about 6 nm (Fig. 1, spectrum c). On the basis of the concentration dependence of the lattice constant of bulk and sputter-deposited f.c.c. Ni–Al alloys [9], the estimated aluminium content in the leached alloy is about 5 at.%. Moreover, the aluminium content in the leached samples was determined by energy-dispersive X-ray spectra taken for 20 randomly selected particles with different sizes. This did not exceed 6 at.%, being consistent with the result obtained from the lattice constant value of the annealed sample.

In order to study the details of the microstructure, transmission electron microscopy (TEM) observations were carried out. Figure 2 shows the results

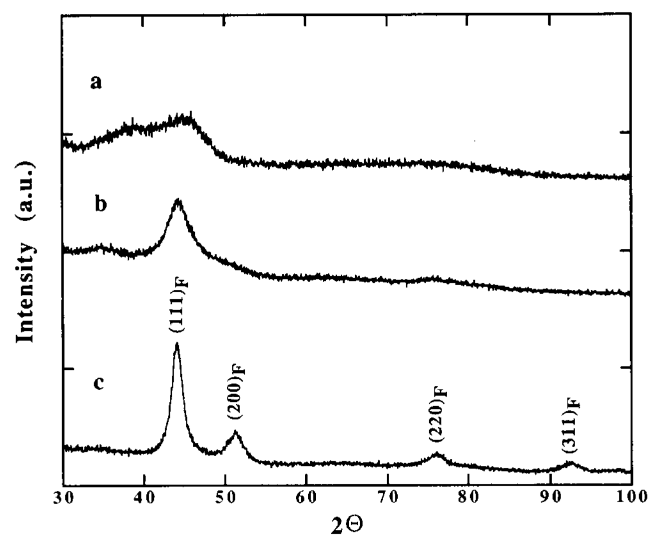

Fig. 1. X-ray diffraction patterns of as-deposited $Ni_{25}Al_{75}$ (spectrum a), a leached specimen (spectrum b) and a leached and annealed specimen (spectrum c).

Fig. 2. (a) TEM micrograph and (b) selected area diffraction (SAD) pattern of as-deposited $Ni_{25}Al_{75}$ alloy.

Fig. 3. (a) TEM micrograph and (b) SAD pattern of a leached specimen.

for the as-deposited $Ni_{25}Al_{75}$ alloy. A featureless uniform image and a halo diffraction ring are observed, indicating the formation of an amorphous structure. As shown in Fig. 3, the leached alloy is composed of nanoscale particles, and the SAD pattern is characterized by broad diffraction rings whose widths are narrower than those of the as-deposited alloy. These results indicate that nanoscale crystallites are produced by the aluminium leaching and their structures are still amorphous like, probably because of a large number of defects and a substantial amount of strain. After the observation of Fig. 3, the same particle was annealed in the electron beam. As shown in Fig. 4, the TEM image reveals crystallization of the amorphous-like particle, revealing the formation of crystallites 10 ~ 50 nm in size. The electron diffraction pattern of the annealed particle exhibits many clear diffraction rings and spots which are attributed to an f.c.c. nickel structure.

The differential scanning calorimetry curve of the leached sample reveals an endothermic effect due to desorption of hydrogen from the sample surface

Fig. 4. (a) TEM micrograph and SAD pattern of a leached specimen after *in situ* annealing by an electron beam.

and an exothermic effect at around 450 K corresponding to the crystallization of the amorphous phase.

Figure 5(a) shows the magnetization (σ *vs.* H) curves at room temperature (RT) for the leached sample before and after heating to 770 K over a period of 45 min. At room temperature the σ value of the leached sample is small and does not saturate even in a magnetic field $H = 16$ kOe, indicating a paramagnetic character for this material. σ for the annealed specimens technically saturates at a relatively low field, indicating a ferromagnetic character. Figure 5(b) shows the variation in σ at $H = 10$ kOe during the temperature cycle (RT $\rightarrow$ 770 K $\rightarrow$ RT). This figure reveals the following features.

(i) The leached sample has been transformed to a ferromagnetic f.c.c. phase at high temperature, which is consistent with X-ray diffraction and TEM measurements.

(ii) The Curie temperature T_c of the ferromagnetic phase is about 570 K, which is lower than the 630 K value for pure nickel and ascribable to the formation of Ni–Al solid solution. From the concentration dependence of T_c for bulk and sputter-deposited Ni–Al alloys [9], the aluminium content of the leached specimen is about 5 at.%.

4. Conclusion

We have succeeded in producing nanoscale amorphous-like nickel particles containing only about 5 at.% Al by leaching the major portion of the aluminium atoms from the sputter-deposited amorphous $Ni_{25}Al_{75}$. The paramagnetic amorphous-like phase transforms to the ferromagnetic f.c.c. phase at high temperature. It should be emphasized that the present technique is unique for obtaining amorphous-like nickel containing only 5 at.% Al. Moreover, we expect that controlling the reaction temperature and/or leaching solution may lead to almost complete removal of aluminium atoms and the formation

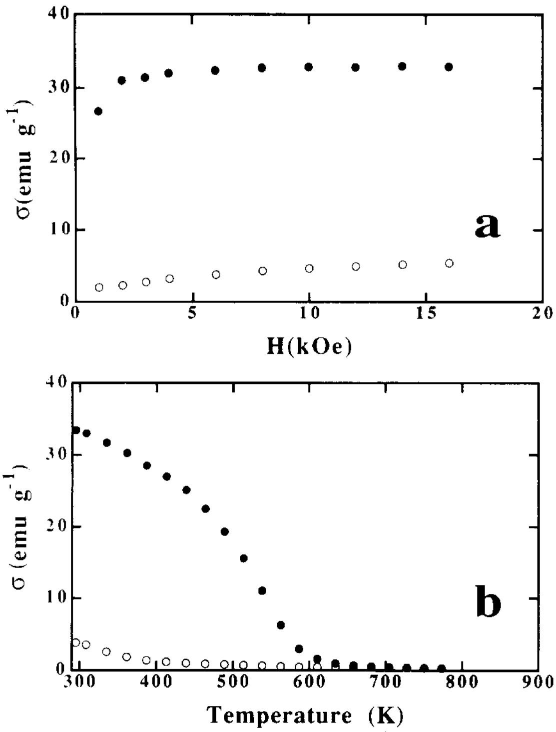

Fig. 5. (a) Magnetization (σ *vs.* H) curves of leached specimen: ○, as-leached; ●, heated to 770 K over a period of 45 min. (b) Temperature dependence of the magnetization σ of leached nickel: ○, measured during the heating stage; ●, measured during the cooling stage from 770 K.

of non-equilibrium pure metal particles having structure, magnetic and catalytic properties completely different from the equilibrium properties.

Acknowledgments

We wish to thank Miss. S. Morita for her kind help in the TEM observations. In particular, S. A. Makhlouf appreciates financial support from Egyptian Ministry of Higher Education and E.I. that from the Japan Society for Promotion of Science (JSPS).

References

1 A. R. West, *Solid State Chemistry and its Applications*, Wiley, Chichester, 1984, p. 793.
2 E. Ivanov, G. Golubkova and T. Grigorieva, *React. Solids, 8* (1990) 73.
3 E. Ivanov, S. A. Makhlouf, K. Sumiyama, H. Yamauchi, K. Suzuki and G. Golubkova, *J. Alloys Comp.*, in the press.
4 H. Yamashita, M. Yoshikawa, T. Kaminiade, T. Funabiki and S. Yoshida, *J. Chem. Soc., Faraday Trans. 1, 82* (1986) 707.

5 H. Yamashita, M. Yoshikawa, T. Funabiki and S. Yoshida, *J. Chem. Soc., Faraday Trans. 1*, *83* (1987) 2883.
6 H. Yamashita, T. Kaminiade, T. Funabiki and S. Yoshida, *J. Mater. Sci. Lett.*, *10* (1991) 532.
7 P. Fouilloux, *Appl. Catal.*, *8* (1983) 1.
8 H. Lipson and H. Steeple, *Interpretation of X-ray Powder Diffraction Patterns*, Macmillan, London, 1970, p. 261.
9 K. Sumiyama, Y. Hirose and Y. Nakamura, *Phys. Status Solidi A*, *114* (1989) 693, and references cited therein.