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Mechanical alloying and characterization of $Ni_{50}Al_{25}Ti_{25}$

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Abstract

An amorphous-like phase, the mixture of amorphous phase and microcrystalline β-Ni(Al,Ti) compound, has been synthesized by mechanically alloying the $Ni_{50}Al_{25}Ti_{25}$ elemental powder mixtures in a high energy ball mill. It has been found that titanium plays a dominant role in this process. There exist two types of transformations of amorphous-like $Ni_{50}Al_{25}Ti_{25}$ upon heating: first, the amorphous-like alloy transforms into a disordered Ni_2AlTi compound (b.c.c. structure) at 345–445°C, and then into an ordered Ni_2AlTi compound at 554–626°C. It is suggested that at the low-temperature transition, the Ni atoms locate in the corners of the b.c.c. lattice, but the cubic centers are occupied randomly by Al and Ti atoms. When the temperature rises to 554°C, a long-range ordering transition occurs, resulting in the formation of ordered Ni_2AlTi. The ordering energy of Ni_2AlTi has been measured as 4.35 kJ mol^{-1}.

Keywords: Mechanical alloying; Phase transition; Ni–Al–Ti alloys

1. Introduction

The solid state powder processing technique for mechanical alloying (MA), a dry high-energy ball milling process [1], has been employed to synthesize a variety of alloy phases starting from either elemental powder mixtures or prealloyed powders [2–5], such as oxide-dispersion strengthened (ODS) superalloys, supersaturated solid solutions, nanocrystalline phases and amorphous phases. However, up to now most of the investigations have concentrated mainly on binary alloy systems, and only a few reports on the ternary alloy systems are available, partly because of the complicated interactions of the components.

Today, with the increasing interest in the ternary Ni–Al–Ti system for structural intermetallic compound applications [6–8], this system is naturally being subjected to MA study. Fortunately, much more comprehensive MA investigations of the binary systems Ni–Al, Ni–Ti and Al–Ti (e.g. Refs. [9–14]) give us a chance to study MA of the Ni–Al–Ti system intensively, and some preliminary studies on mechanical alloying of the ternary Ni–Al–Ti system have been carried out [15–17].

In the present work, $Ni_{50}Al_{25}Ti_{25}$ elemental powder mixtures have been subjected to mechanical alloying. Characterization of the alloying process, and investigation of the products and their properties have been performed experimentally in detail.

2. Experimental details

Mechanical alloying was carried out in a high-energy SPEX 8000 mixer/mill. Nickel, aluminum and titanium powders with particle sizes of 15, 15 and 60 μm, and purities of 99.95, 99.5% and 99%, respectively, were introduced into a hardened steel container after mixing in an agate mortar at a composition of $Ni_{50}Al_{25}Ti_{25}$. The weight ratio of ball-to-powder was 10:1. A pure argon atmosphere was employed to protect the powders from oxidation. In situ thermal analysis throughout the whole mechanical alloying process was carried out by the thermocouple attached directly to the outer bottom of the container and was recorded using an X–Y recorder. The structural evolution of the powders with the milling time was detected by X-ray diffraction in a RIGAKU D/max-rA X-ray diffractometer equipped with a graphite monochromator, using Cu-Kα radiation. The morphology

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and distribution of the elemental powders after different milling times were characterized using a Shimadzu EPM-810Q electron probe microanalyzer equipped with a scanning electron microscope. The microhardness (Hv) measurement of the powder particles was carried out using a Buehler Micromet II digital microhardness tester. The thermal analysis of the as-milled product was conducted with a Perkin-Elmer 7 differential scanning calorimeter at a heating rate of 20 K min^{-1} up to 700°C under the protection of a pure argon atmosphere. To determine the resultant products after heating at different characteristic temperature, the samples were annealed at the temperature just after the end of that reaction for 10 min to complete the transformation, and transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD) were used to characterize the specific products.

3. Results and discussion

3.1. Mechanical alloying of $Ni_{50}Al_{25}Ti_{25}$

Figs. 1(a)–1(e) show the XRD patterns of $Ni_{50}Al_{25}Ti_{25}$ powders after different milling time. It was found that the initial stage of milling up to 3 h resulted in a decrease in the intensities and broadening of the width of all the diffraction peaks of nickel, aluminum and titanium, which indicates grain size reduction. No evidence of diffusion and phase formation was observed. Upon milling for 5 h, there were traces of the β-Ni(Al,Ti) compound, which was derived from the appearance of the (100) reflection of β-Ni(Al,Ti) compound at $2\theta = 31°$. The small shift of the Ni peak positions to a lower angle reveals that the diffusion of aluminum and/or titanium atoms into the nickel matrix has taken place. However, the dissolution of the Ti into Ni matrix seemed to be more difficult than for Al, as proved by the fact that the Ti peaks were stronger than those of Al. When milling for 10 h, the amount of the β-Ni(Al, Ti) compound became reduced. Because this occurred together with a reduction of the elemental diffraction peaks and a shift of the main peak of the β-Ni(Al,Ti) compound to low angle, it indicates the diffusion of Ti and Al into the Ni matrix to form a new phase. After milling for 30 h, an amorphous-like phase formed with a diffuse peak at $2\theta = 44.4°$ accompanied by diffraction spots. This indicates that large amounts of microcrystalline materials are present. Further milling just stabilized this situation. It can be concluded that the occurrence of intermediate β-Ni(Al,Ti) compound is a dominant factor in this whole process. Throughout the MA process, no abrupt exo- or endothermal effects were detected by in situ thermal analysis, indicating a gradual process.

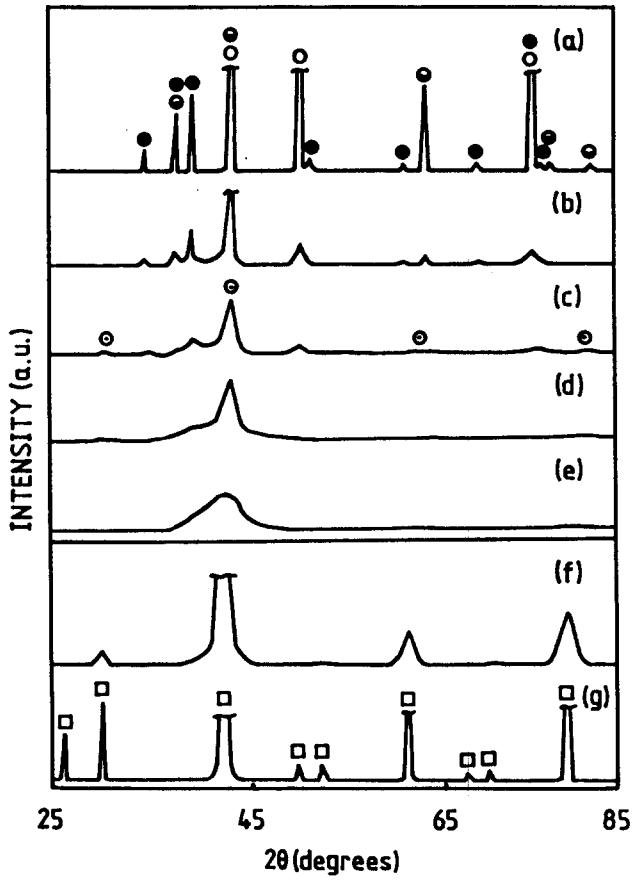

Fig. 1. XRD patterns of $Ni_{50}Al_{25}Ti_{25}$ after milling for: (a) 0 h; (b) 3 h; (c) 5 h; (d) 10 h; (e) 30 h; (f) after the low-temperature transition; and (g) after the high-temperature transition. ○ Ni; ◒ Al; ● Ti; ⊙ β-Ni(Al,Ti) compound; □ Ni_2AlTi.

Fig. 2 shows the microstructure and the distribution of elemental Ni, Al and Ti after milling for 1 h. It clearly shows the plate-like structure of Ni, Al and Ti fabricated by repeated cold welding and fracture, the thickness of the plate is about 1–5 μm. The distribution of the elements reveals that Ni and Al have mixed well without formation of a solid solution, but there is no distribution of Ni and Al in the Ti flakes. This might be due to the relatively fine initial particles of Al and Ni and their good ductility, as well as the relatively large particles and higher hardness of Ti. This phenomenon is in agreement with the XRD results, Ti playing a dominant role in this alloying process. The microhardness was measured to be about 610 after milling for 30 h.

Previous work has shown that it is very difficult to form an amorphous phase in the Ni–Al system by mechanical alloying [9,18]. The end products are ordered intermetallic compounds and/or supersaturated solid solutions with various compositions. In particular, mechanically alloying the equiatomic nickel and aluminum under these conditions resulted in the abrupt explosive formation of NiAl. Before this,

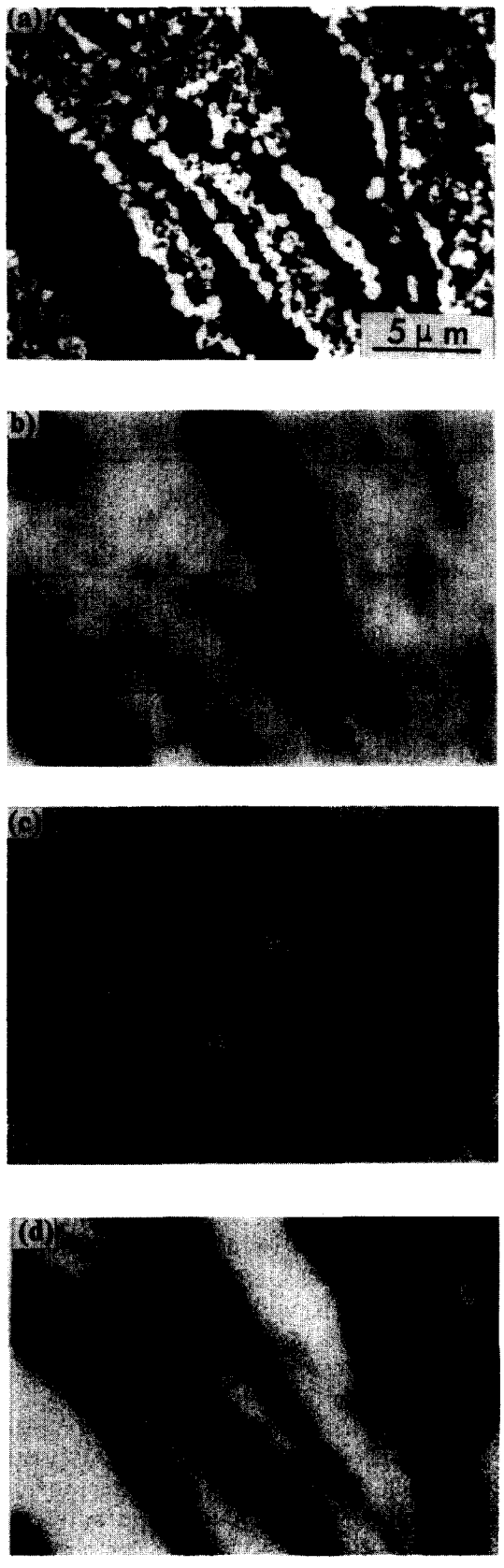

Fig. 2. SEM images and distribution of elements (a) Ni, (b) Al and (c) Ti of etched samples of $Ni_{50}Al_{25}Ti_{25}$ after milling for 1 h.

although the Ni and Al elements had been mixed homogeneously, no interdiffusion of Ni and Al occured. The NiAl compound could not be disordered by long-term milling, even for 80 h under the same conditions. By contrast, the Ni–Ti system is much more easily "amorphized" [11,12]. It has been found that the equiatomic Ni–Ti alloy can be directly amorphized during mechanical alloying by interdiffusion without formation of intermediate intermetallic phases [12], and the amorphous phase can be obtained in a wide range of compositions. The substitution of 25 at.% Ti for Al in the equiatomic Ni–Al alloy undoubtedly enhances the amorphous phase formation ability, of which the diffusion of Ti into Ni hinders the abrupt formation of the NiAl compound and facilitates the gradual diffusion of Al into the Ni matrix. The diffusion of titanium and aluminum into nickel first produces the β-Ni(Al,Ti) compound; further milling amorphizes this compound. Thus, the 25 at.% Ti atoms play an important role in the gradual formation of the β-Ni(Al,Ti) compound and consequently the amorphous-like phase.

3.2. Thermal measurement of the milled powders

The thermal behavior of the as-milled amorphous-like $Ni_{50}Al_{25}Ti_{25}$ powder was studied by differential scanning calorimetry (DSC). Fig. 3 shows the DSC curve of the amorphous-like phase. There are two apparent exothermic reactions during heating (P1, P2), one of which occurs at 345–445°C, and the other at 554–626°C. In order to examine these two exothermic reactions, the resultant powders were annealed at 450 and 650°C, respectively, for 10 min under the protection of an argon atmosphere, and the products were studied by X-ray diffraction analysis (XRD), and transmission electron microscopy (TEM). Fig. 1(f) shows that the product after annealing at 450°C for 10 min is a new b.c.c. phase. Fig. 4 shows the TEM

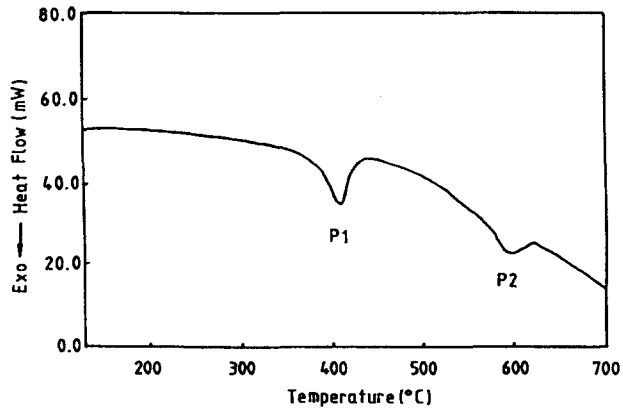

Fig. 3. DSC curve of quasi-amorphous $Ni_{50}Al_{25}Ti_{25}$ at a heating rate of 20 K min^{-1}.

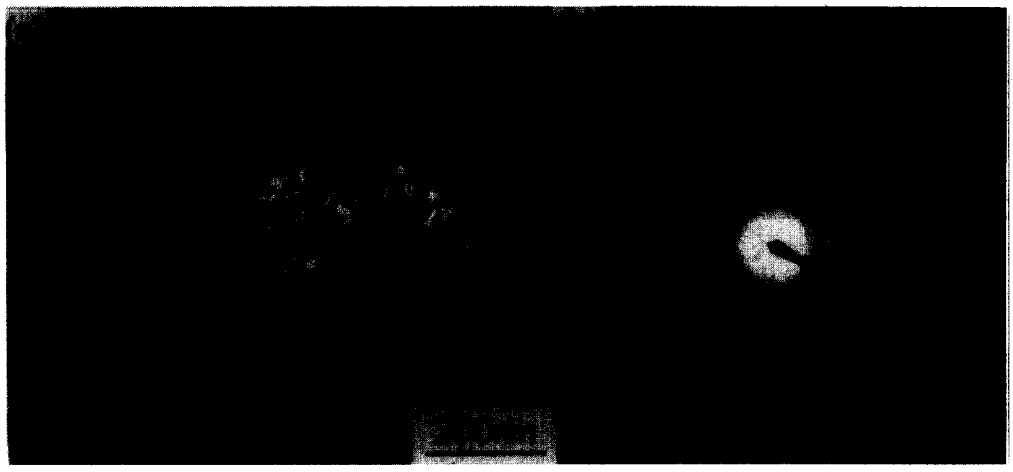

Fig. 4. TEM observation (dark field image) (a) and electron diffraction pattern (b) of crystalline disordered Ni_2AlTi.

observation and the electron diffraction pattern of the b.c.c. phase, which indicates that the b.c.c. phase is present as particles of nanometer size. After annealing at 650°C for 10 min, the b.c.c. phase transformed into ordered Ni_2AlTi, and all the diffraction peaks of the ordered Ni_2AlTi compound became visible (Fig. 1(g)).

The observed phenomena indicate that the crystallization of the as-milled $Ni_{50}Al_{25}Ti_{25}$ powders is comprised of two steps, as seen below.

3.2.1. The formation of disordered crystallites

Heating the amorphous-like phase to 345°C promotes the transformation to the crystalline phase. It is suggested that the atoms begin to move by thermal activation. Because of the lower temperature and the interactions of the three kinds of atoms, the long-distance migration of atoms to create long-range order is impossible, so it is difficult to form the complicated ordered crystalline Ni_2AlTi with $L2_1$ structure. The atoms migrate and arrange as a simple b.c.c. lattice when heating up to 445°C. It is considered that the short distance migration of atoms only results in a rearrangement of atoms in a relatively small region to form very small crystals. The size of the resultant crystallite can be calculated by Scherrer equation:

$$d = 0.91\lambda / B \cos\theta$$

where λ is the X-ray wavelength, B is the full width at half height after correction and θ is the position of the selected Bragg angle. It shows that the average crystallite size is about 6.5 nm.

The microhardness measurement shows an increase from 609 for the as-milled powders to 1120 for the disordered Ni_2AlTi. The later value is very close to that of the ordered Ni_2AlTi compound (1121, see Table 1), which will be discussed later. It indicates again that the b.c.c. phase should be the disordered Ni_2AlTi compound. The lattice parameters of the NiAl and NiTi compounds are 0.2880 nm and 0.2998 nm, respectively. The lattice parameter of this b.c.c. crystalline phase has been measured as 0.2935 nm (see Table 1), which is very close to the average of those two values (0.2939 nm). It is concluded, therefore, that the measured lattice parameter is evidence of the coexistence of these two kinds of crystal unit cell of NiAl and NiTi, which are arranged randomly.

3.2.2. The disorder–order transition

Figs. 1(f) and 1(g) present a disorder–order transition of $Ni_{50}Al_{25}Ti_{25}$ sample after annealing at 650°C. The b.c.c. crystalline phase, disordered Ni_2AlTi, transforms into ordered Ni_2AlTi, which is indicated by the appearance of the superlattice peaks ({111}, {311}) of the Ni_2AlTi compound.

Fig. 5 shows schematically the crystal structure of ordered $L2_1$ Ni_2AlTi. Clearly, atoms A occupy the corner sites of the cube, and the B and C atoms are located at alternate cube centers. In the Ni_2AlTi compound, the Ni, Al and Ti atoms act as A, B and C, respectively. When the disordered Ni_2AlTi compound forms, it is likely that the corners of the cubic cell are occupied by Ni atoms, but the cube centers are occupied by Al and Ti atoms at random. In the high temperature disorder–order transition, the rearrange-

Table 1
Microhardness and measured lattice parameters of different samples

Sample	Microhardness (Hv)	Measured lattice parameter a_m (nm)
Amorphous-like	609 (575–644)	—
Disordered Ni_2AlTi	1120 (1072–1145)	0.2935
Ordered Ni_2AlTi	1121 (1072–1170)	0.5885

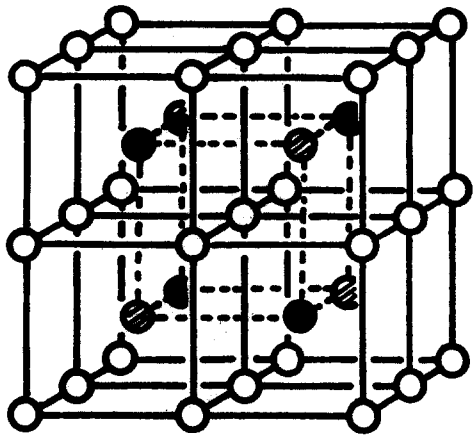

Fig. 5. Schematic $L2_1$ crystal structure (A_2BC intermetallics), ○ A, ⊘ B, ● C.

ment of the atoms concerns mainly these two kinds of atoms. After the high temperature transition, the Ti and Al atoms are arranged in an ordered state, and the sample is transformed into ordered Ni_2AlTi. The microhardness remains constant during this transition, indicating that this is just a disorder–order transition of the Ni_2AlTi compound, not a ordering transition from a solid solution, for which the microhardness would increase owing to the change of the bonding type of the atoms. The measured lattice parameter of the ordered Ni_2AlTi compound is 0.5886 nm, which is close to, but a little larger (0.61%) than the reference value of 0.5850 nm.

The exothermicity of the higher temperature disorder–order transition was measured to be 4.35 kJ mol^{-1}. The exothermicity of the lower temperature transition has been measured as about twice the value of the high temperature reaction. It is suggested that at the lower temperature, when the disordered Ni_2AlTi compound formed, a much larger heat release than at the higher temperature is observed, owing to the release of mechanically stored energy combined with the crystallization heat. Previous work [19] on the reordering of mechanically driven disordered CsCl-type intermetallic compounds gave a heat release of 5–10 kJ mol^{-1} for several compounds, which is stored by incorporation of lattice defects, chemical disorder and grain boundaries. Considering the other two effects and the degree of long range order of the compounds (0.65–0.9), the ordering energy of Ni_2AlTi is of the same order of magnitude.

4. Conclusions

$Ni_{50}Al_{25}Ti_{25}$ has been synthesized by mechanical alloying of the elemental powder mixtures in a high-energy ball mill. A mixture of a quasi-amorphous phase partly composed of microcrystalline Ni(Al,Ti) was obtained. This reaction is controlled by the grain size reduction and titanium diffusion. The intermediate β-Ni(Al,Ti) compound plays a dominant role in this process. The phase transition of the as-milled $Ni_{50}Al_{25}Ti_{25}$ upon heating consists of two steps: the formation of a disordered Ni_2AlTi compound at 345–445°C, and subsequently the formation of the ordered $Ni_{50}Al_{25}Ti_{25}$ compound at 554–626°C. It is suggested that at the low temperature transition, the Ni atoms occupy the corners of the b.c.c. lattice, but the cube centers are randomly occupied by Al and Ti atoms. The grain size is about 6.5 nm. When the temperature rises to 554°C, long-range ordering occurs, resulting in the formation of ordered Ni_2AlTi. These phenomena are strongly supported by measurements of the change of the microhardness and the lattice parameters of the phases. Both solid state reaction are exothermic. The ordering energy of Ni_2AlTi was measured as 4.35 kJ mol^{-1}, and the heat release of the low temperature transition is about twice of that of the ordering energy of the Ni_2AlTi compound at higher temperature.

References

[1] J.S. Benjamin and T.E. Volin, *Metall. Trans. 5* (1974) 1930.
[2] J.S. Benjamin, *Metall. Trans., 1* (1970) 2943.
[3] P.S. Gilman and J.S. Benjamin, *Ann. Rev. Mater. Sci., 13* (1983) 279.
[4] C.C. Koch, *Nanostruct. Mater., 2* (1993) 109.
[5] A.W. Weeber and H. Bakker, *Physica B, 153* (1988) 93.
[6] K.S. Kumer, *Int. Mater. Rev., 35* (1990) 293.
[7] S. Naka, M. Thomas and T. Khan, *Mater. Sci. Tech. 8* (1992) 291.
[8] R. Yang, J.A. Leake and R.W. Cahn, *J. Mater. Res., 6* (1991) 343.
[9] E. Ivanov, T. Gregorieva, G. Golubkova, V. Boldyran, A.B. Fasman, S.D. Mikhailenko and O.T. Kalinina, *Mater. Lett., 7* (1988) 51.
[10] M. Atzmon, *Phys. Rev. Lett., 64* (1990) 487.
[11] R.B. Schwarz, R.R. Petrich and C.K. Saw, *J. Non-Cryst. Solids, 76* (1985) 281.
[12] T. Itzukaichi, S. Ohara, J.G. Cabanas-Moreno, M. Umemoto and I. Okane, *J. Mater. Sci., 29* (1994) 1481.
[13] W. Guo, S. Martelli, N. Burgio, M. Magini, F. Padella, E. Paradisco and I. Soletta, *J. Mater. Sci. 24* (1991) 6190.
[14] C. Suryanarayana, G.H. Chan, A. Frefer and F.H. Froes, *Mater. Sci. Eng., A158* (1992) 93.
[15] T. Itzukaichi, M. Umemoto and J.G. Cabanas-Moreno, *Scripta Metall. Mater., 29* (1993) 583.
[16] M. Umemoto, T. Itzukaichi, J. Cabanas-Moreno and I. Okane, in J.J. de Barbadillo, F.H. Froes and R. Schwarz (eds.), *Mechanical Alloying for Structural Applications*, 1993 p. 245.
[17] Z.G. Liu, J.T. Guo and Z.Q. Hu, *Mater. Sci. Eng. A192/A193* (1995) 577.
[18] Z.G. Liu, J.T. Guo, L.L. He and Z.Q. Hu, *Nanostruct. Mater., 4* (1994) 787.
[19] E. Hellstern, H.J. Fecht, Z. Fu and W.L. Johnson, *J. Mater. Res., 4* (1989) 1292.