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Preliminary characterization of the intermetallic 'YNi' obtained by both mechanical grinding and alloying

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Abstract

The intermetallic compound YNi and the (Y+Ni) mixture were submitted to a high-energy milling process under argon atmosphere. X-ray powder diffraction and microprobe analysis revealed in both cases the formation of a new phase 'YNi'. Its structural properties were different from those of the YNi as-cast sample (orthorhombic FeB type) and presented some similarities with GdNi (orthorhombic CrB type) milled under the same conditions. The application of isostatic pressure on the YNi as-cast sample gives a comparable result. This non-equilibrium material 'YNi' still exists even after annealing treatments performed up to 873 K. The presence of air during milling leads to the formation of a mixture of (oxy)nitride Y(O,N) and Ni metal and the new phase 'YNi' is not synthesized under such conditions. Also, the influence of the milling process on the magnetic properties of similar compounds such as GdNi and ErNi is discussed.

Keywords: Mechanical alloying and grinding; Yttrium–nickel system; Structural transition; SEM examination; Magnetic properties

1. Introduction

The milling performed at high-energy allows mainly: (i) the amorphisation of crystalline compounds prepared conventionally by solid state reaction, by melting of pure elements. (ii) The synthesis of compounds from the mixture of the elemental constituents. These applications can be illustrated considering for instance the numerous studies devoted to the intermetallic ZrNi. This compound which crystallizes in the orthorhombic CrB type, is obtained as amorphous phase after mechanical grinding (MG) under an argon atmosphere [1–3]. A similar amorphous phase is obtained after mechanical alloying (MA) of a (Zr+Ni) mixture of equiatomic composition [1]. Amorphous ZrNi reacts easily with nitrogen or hydrogen producing ZrN or $ZrNiH_3$ and ZrH_2.

In order to determine the hydrogen absorption properties of YNi, we have performed MG and MA experiments. We present here the characterization of the resulting products using X-ray powder diffraction, microprobe analysis, scanning electron microscopy and magnetization measurements. The results are discussed considering those obtained on similar compounds such as GdNi and ErNi.

2. Experimental

The intermetallics YNi, GdNi and ErNi (as-cast samples) were prepared by arc melting of stoichiometric amounts of the constituent elements in purified argon atmosphere. The purity of the starting materials was as follows: Y, Gd and Er 99.9% and Ni 99.99%. The alloy ingots were turned and remelted several times to ensure homogeneity. The weight loss of ingots during melting was negligible.

Y and Ni powders with, respectively, initial grain size of 420 and 4 μm were used as starting materials for MA experiments. A 4-g amount of the (Y+Ni) mixture was sealed under 0.1 MPa of purified argon gas, in a stainless steel container (80 cm^3 in volume) with 48 g of steel balls (10 mm in diameter). Milling was performed using a Fritsch pulverisette 5 high-energy instrument. The rotation speed of the plateau was fixed at 200 rpm for various

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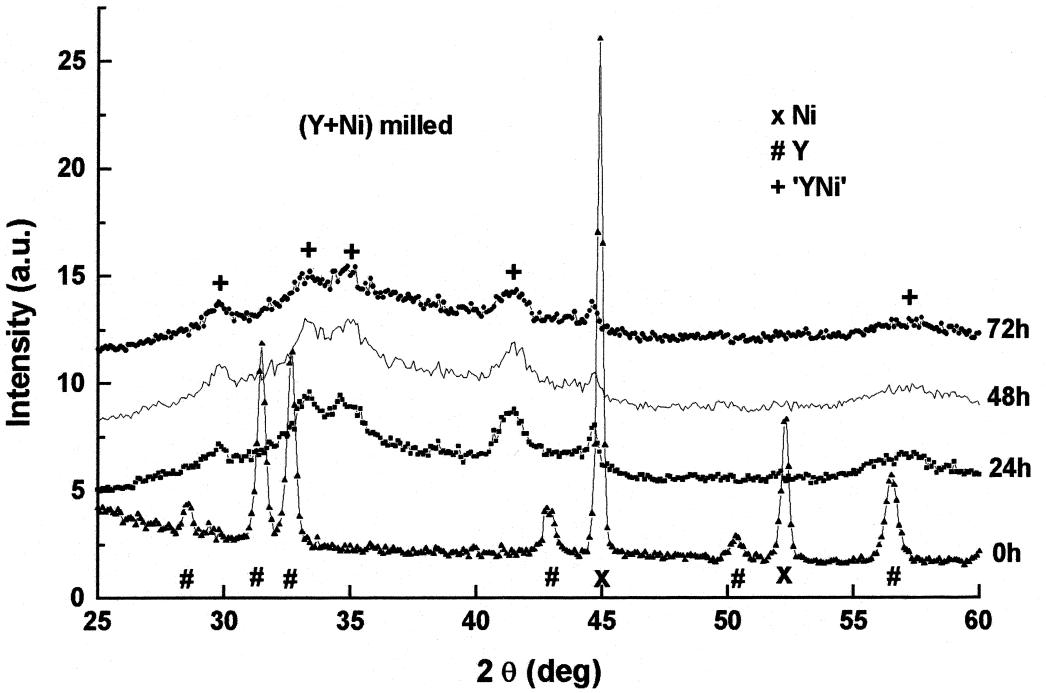

Fig. 1. X-ray powder patterns of the initial (Y + Ni) mixture alloyed for various times (+ indicates the peak position relative to the new phase 'YNi').

duration times. Similar experimental conditions were used for MG experiments performed on YNi, GdNi and ErNi as-cast samples.

Microprobe examination was carried out in a Cameca SX-100 scanning electron microscope. The analysis of the samples containing Y and Ni was based on the measurements of Y–$L_{\alpha 1}$ and Ni–$K_{\alpha 1}$ X-ray radiations, which were compared to those obtained for YNi used as reference. The particle size and morphology were investigated using a Jeol 840 microscope.

The samples were checked by conventional X-ray powder diffraction using a Philips 1050-diffractometer (Cu-Kα radiation). Typical crystallite sizes L for various samples were calculated before and after grinding from the Scherrer formula $L = 0.91\lambda_{Cu}/\beta\cos\theta$ where λ_{Cu} is the Cu-Kα radiation, β the peak width (in radian) at half-maximum peak and θ is the diffraction angle. Magnetization measurements were carried out between 2 and 300 K using a SQUID (superconducting quantum interference device) magnetometer.

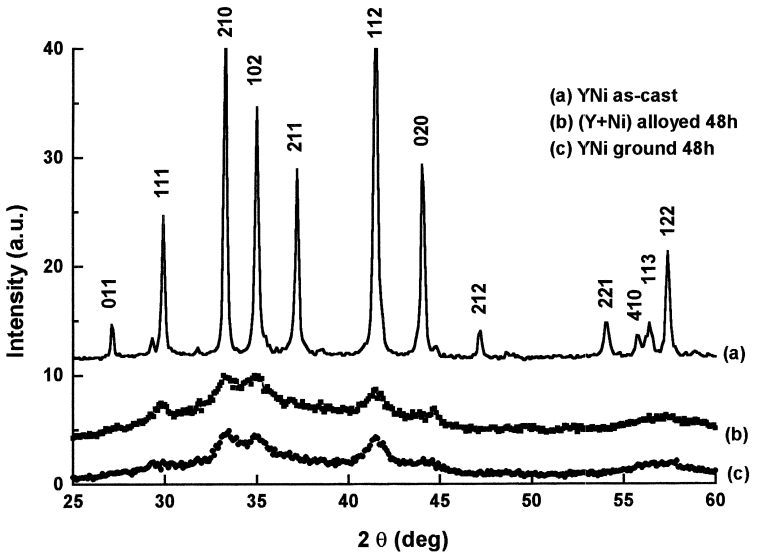

Fig. 2. Comparison between the X-ray powder patterns of YNi obtained by: (a) melting (Miller indices *hkl* are given), (b) alloying of the (Y + Ni) mixture for 48 h and (c) grinding of as-cast sample for 48 h.

3. Results and discussion

The X-ray powder patterns of the (Y+Ni) mixture mechanically alloyed for various times are presented in Fig. 1. The pattern of the unmilled sample (bottom curve), clearly shows the peaks characteristics of Y and Ni metals (initial product). The influence of MA is: (i) the peak characteristic of Ni metal ($2\theta \cong 44.5°$) is reduced as the milling duration increases but is still always detected. (ii) On the contrary, the peaks of the Y metal disappear rapidly with increasing MA duration; its presence cannot be detected by X-ray powder analysis. (iii) Moreover, the peaks at $2\theta \cong 29.8°$, 33.4°, 35.0°, 41.4° and 57.2° appear with this treatment. (iv) Finally, a very broad and diffuse peak is observed in the $2\theta \cong 25–45°$ range suggesting a lack of structural order. The microprobe analysis of the product alloyed for 72 h indicates that the main phase ($\cong$96% in volume) has the chemical composition Y: 50.4±0.3%, Ni: 49.6±0.3% (in atomic percent) and it reveals the presence of amounts of Ni metal.

Fig. 2 compares the X-ray powder patterns of the YNi as-cast sample (a) after grinding for 48 h (c). For the discussion, the pattern of the product resulting from MA of the (Y+Ni) mixture is also presented (b). As logically expected, the pattern of the as-cast sample can be completely indexed on the basis of an orthorhombic cell having the FeB-type structure [4]. Drastic changes can be observed under MG (c). All the peaks have decreased significantly and even some of them as (0 1 1), (1 1 1) and (2 1 1) have completely or almost disappeared. Moreover, an important broadening of the peaks is visible. These observations suggest a reduction of the crystalline size. The corresponding values of L derived from the broadening of diffraction peaks were calculated using the Scherrer equation. They are equal to $L = 50 \pm 5$ nm before grinding and $L = 10 \pm 3$ nm after grinding and the development of microstrain in the ground YNi sample. We note that this last product has an X-ray powder pattern similar to those observed for the product obtained by MA (b). The complete or almost complete disappearance of the (0 1 1), (1 1 1) and (2 1 1) peaks after milling suggests the occurrence of a structural transition.

Fig. 3 shows SEM micrographs for the 'YNi' phase obtained by MA and MG. The morphology and the size of the particles resulting from the two treatments, presents obvious differences. After 48 h of MA (Fig. 3a) the particles are basically spherical in shape and appear to be made up of layers of material and have an average size of about 10 μm. On the contrary, the particles prepared by MG (Fig. 3b) are much smaller in size ($\cong$5 μm) and seem to be fragmentary and flattened. This reflects the dominating effect of fracturing of the material. The appearance of significant amounts of debris on the particles in the first case is due to the interdiffusion between Y and Ni during the MA treatment and also due to the cold-welding process. A similar observation was previously made during the synthesis of Mg_2Ni [5].

It is well known that the equiatomic binary compounds RNi (R=rare earth) crystallize with two different orthorhombic structures types depending on the size of R element: (i) For R=La→Gd the intermetallics adopt preferentially the CrB structure type. (ii) For R=Dy→Lu the FeB type is observed [6]. In both structures the Ni atoms are inside characteristic trigonal prisms [R_6]. These prisms are stacked differently in the two structures. The structural transition between CrB and FeB types was explained considering unit-cell twining [6,7]. Under these conditions, it is interesting to study the influence of MG treatment on RNi compounds that adopt either one of these two structure types.

Fig. 4 presents the X-ray powder pattern of an GdNi

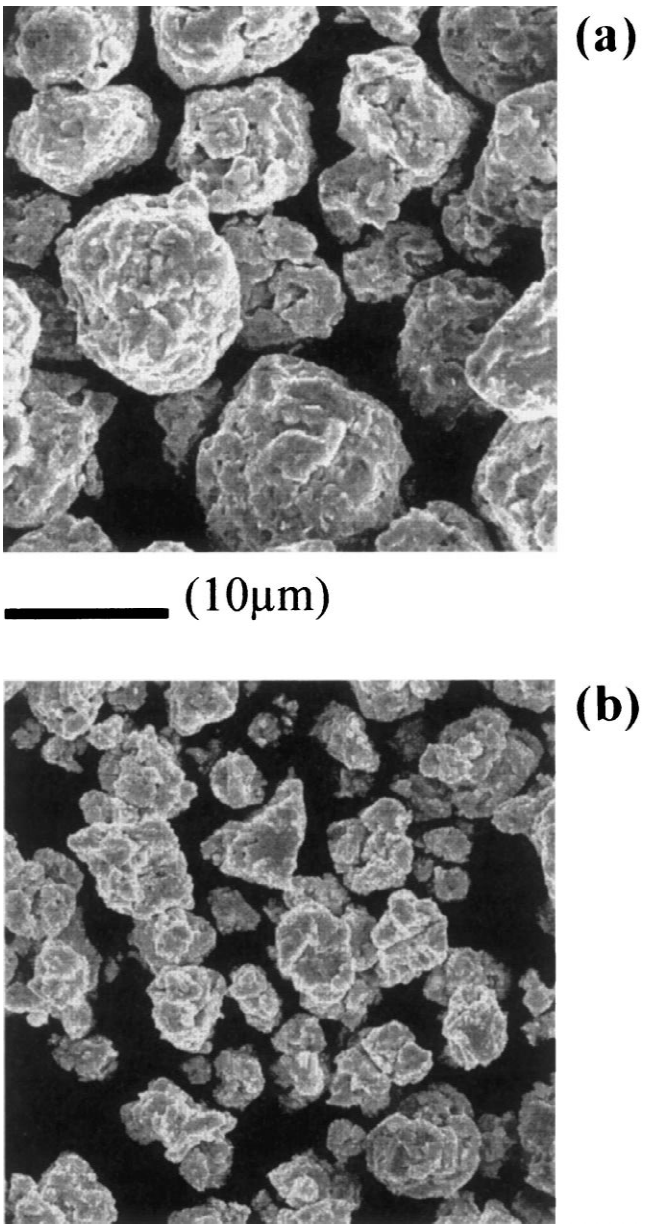

Fig. 3. SEM micrographs of the new phase 'YNi' obtained by: (a) MA of (Y+Ni) mixture and (b) MG of YNi as-cast sample (magnification, ×2000).

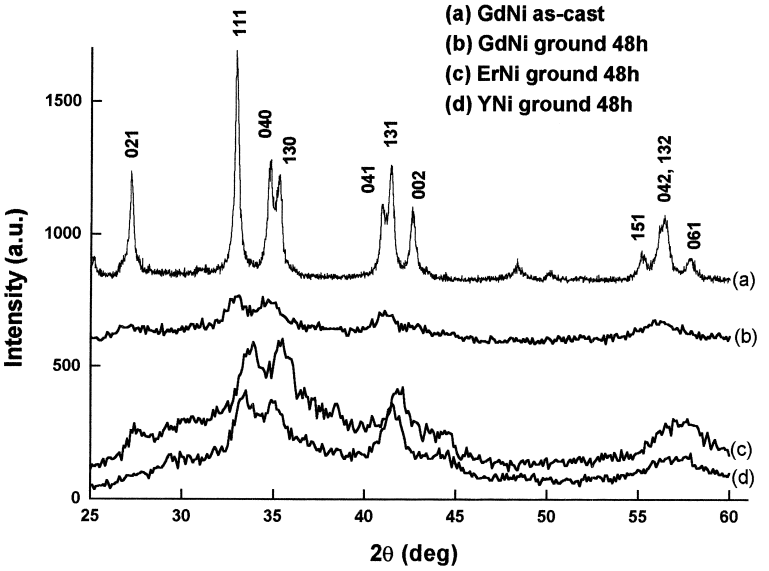

Fig. 4. Comparison between the X-ray powder patterns of GdNi obtained by melting (a) (Miller indices *hkl* are given) and GdNi (b), ErNi (c) and YNi (d) ground for 48 h.

as-cast sample (CrB type) after grinding for 48 h. After MG, only a decrease of the peak intensity is observed. The crystallite size L decreases strongly from 60 ± 5 to 15 ± 3 nm. The grinding performed on GdNi and YNi leads to products having X-ray powder patterns showing many similarities. The same observation can be made for an ErNi as-cast sample (FeB type) ground for 48 h (Fig. 4c). This result suggests that the compounds GdNi, YNi and ErNi present after grinding the same structural properties.

We have investigated at room temperature the effect of the pressure on the structural properties of the YNi as-cast sample. Fig. 5 exhibits the X-ray powder pattern of this intermetallic at two pressures: 0.1 MPa (room pressure) and 8.4 GPa. A decrease of some peak intensities is observed under pressure. For instance, the Bragg reflections (1 1 1) and (2 1 1) are less visible. This behaviour is similar to that observed at the time of the milling of YNi (Fig. 2). These two effects (pressure or grinding) seem to produce the same change in the structural properties of YNi.

An investigation by high temperature X-ray powder diffraction was performed up to 873 K under vacuum, in order to study the thermal stability of the new phase 'YNi'. The temperature was increased from 323 to 873 K in gradual steps of 50 K, the time required for acquiring data being around 3 h. The X-ray powder patterns obtained, respectively at room temperature, 573 and 873 K are given in Fig. 6. No drastic change appears at this last temperature, only a decrease of the peak width is observed. No reflection centered around $2\theta = 37.1°$ (corresponding to the

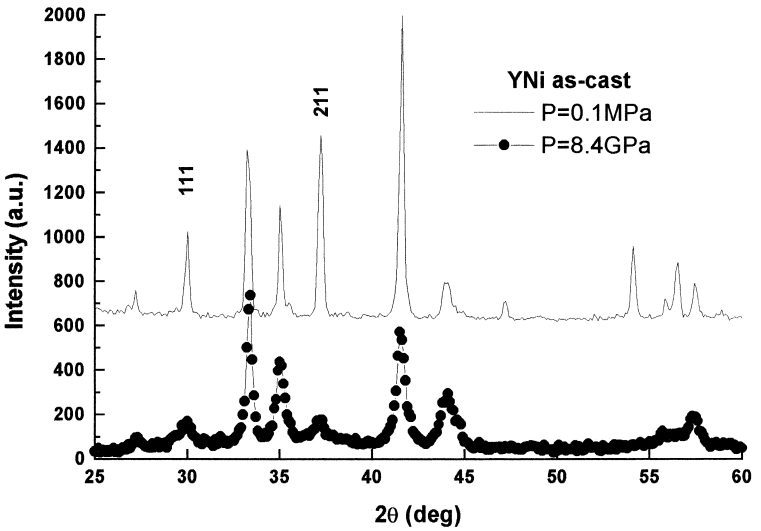

Fig. 5. X-ray powder patterns of YNi as-cast sample under a pressure of 0.1 MPa and 8.4 GPa.

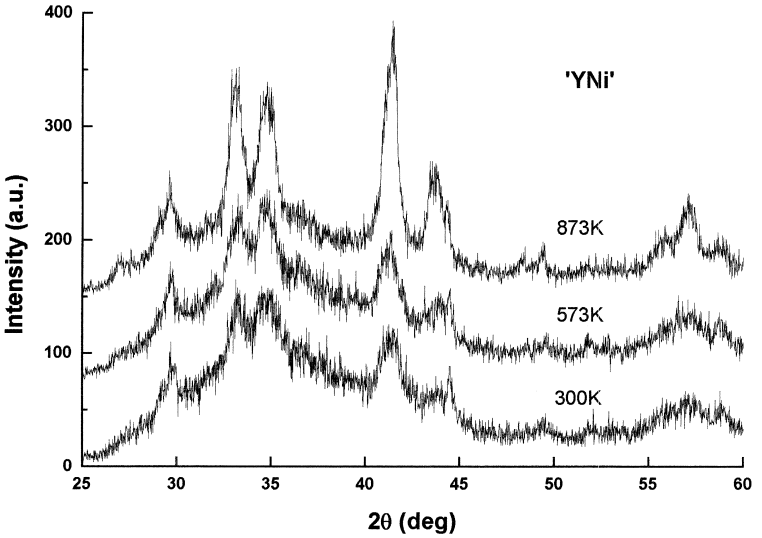

Fig. 6. X-ray powder patterns of the new phase 'YNi' at three temperatures 300, 573 and 873 K.

(2 1 1) peak of the as-cast sample; see Fig. 2) is noted. The new phase 'YNi' is thermally stable at least up to 873 K. An annealing of this phase under vacuum at 1173 K for 1 day is necessary in order to restore YNi having the FeB type but some traces of oxide Y_2O_3 and intermetallic YNi_2 are observed after this thermal treatment. The occurrence of these impurities is certainly linked to the contamination by oxygen during the milling process.

The synthesis by MA or MG of the new phase 'YNi' should be performed under argon atmosphere. The X-ray analysis of the resulting product obtained by MG under air reveals the coexistence of two phases (Fig. 7): (i) Ni metal giving a broad peak around $2\theta = 41–44°$. (ii) The second phase is characterized by the reflections appearing at $2\theta = 31–32°$, 36–37° and 52–53°. They were indexed with a fcc cubic unit cell having as parameter $a = 0.49 \pm 2$ nm. The structural properties of this second phase indicate the occurrence of yttrium (oxy)nitride during the MG process under air (YN crystallizes with the cubic NaCl type with $a = 0.4877$ nm [8]). In this MG experiment, YNi is decomposed into a mixture of Y(O, N) + Ni.

As high-energy ball milling changes the structural properties of the well-crystallized compounds, modifications of their magnetic properties are expected. Therefore, magnetization measurements of ground GdNi and ErNi are of prime interest.

The temperature dependence of the magnetization of the GdNi as-cast sample is characteristic of ferromagnetic behaviour (Fig. 8). The Curie temperature T_C estimated from the inflection point of the magnetization curve is equal to 71.5 ± 0.5 K. This value agrees with that reported previously $T_C = 73$ K [9]. After 48 h of grinding, GdNi remains a ferromagnet but its Curie temperature $T_C = 77.5 \pm 0.5$ K is observed to shift to higher temperature (Fig.

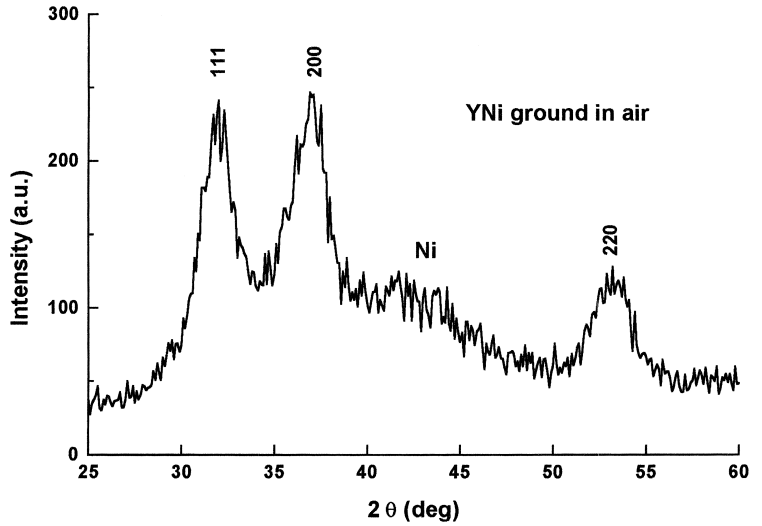

Fig. 7. X-ray powder pattern of YNi as-cast sample ground for 48 h under air (Miller indices are relative to the fcc phase).

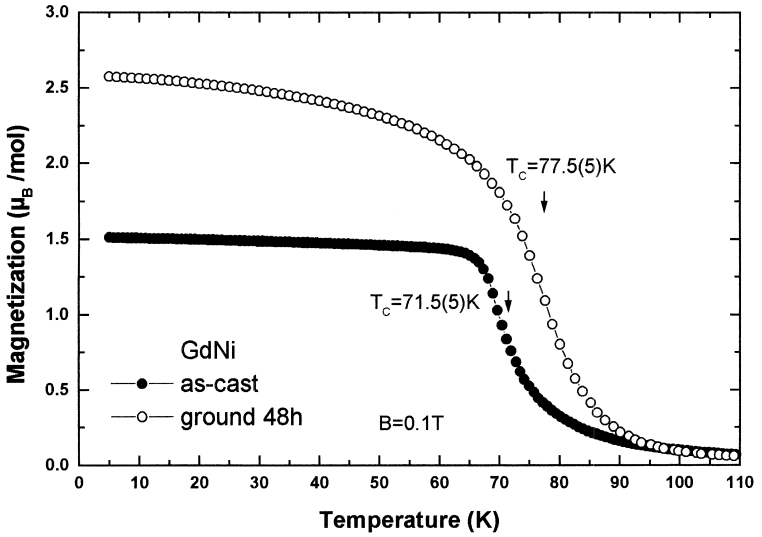

Fig. 8. Temperature dependence, measured in an applied field of 0.1 T, of the magnetization of GdNi before and after grinding for 48 h.

8). Similar effects were claimed recently during the milling of $GdPt_2$, $GdIr_2$ and $GdRh_2$ [10] and this was ascribed to the decrease of the unit cell volume which increases the ferromagnetic RKKY interactions. We also note that amorphous a GdNi film sample prepared by sputtering has a Curie temperature $T_C = 78$ K, close to that determined for ground GdNi [11]. Finally, the examination of the magnetization curves of GdNi unmilled and milled for 48 h (Fig. 8) shows that the second sample presents the greater magnetization at low temperature. This result can be ascribed to the change of particle size during the grinding process. A SEM experiment shows a reduction of the average size from 70–60 to 10 μm. The small particles orientate more easily in the applied low magnetic field of 0.1T inducing an increase of the measured magnetization.

Fig. 9 presents the temperature dependence of magnetization for ErNi before and after the grinding process. It is to be noted that the ErNi as-cast sample orders ferromagnetically below $T_C = 10.7 \pm 0.5$ K. This temperature agrees well with the literature value of $T_C = 10$ K [9,12]. On the contrary, no clear anomaly can be distinguished in the magnetization curve relative to the ground sample. In order to obtain more information on this sample, we have performed ac-magnetic susceptibility measurements without external magnetic field. Fig. 10 shows for ground ErNi the thermal dependence of the real χ' and imaginary χ'' parts of the ac-susceptibility at different frequencies ν in the temperature range 2–15 K. The $\chi' = f(T)$ curve for $\nu = 1.25$ Hz exhibits two anomalies: an inflection point at $T_C = 11.0 \pm 0.5$ K and a peak around $T_1 = 4.4 \pm 0.5$ K.

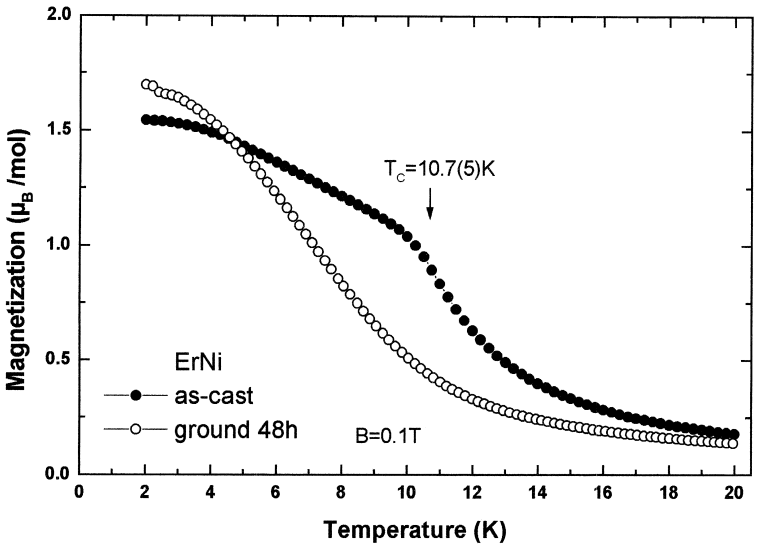

Fig. 9. Temperature dependence, measured in an applied field of 0.1T, of the magnetization of ErNi before and after grinding for 48 h.

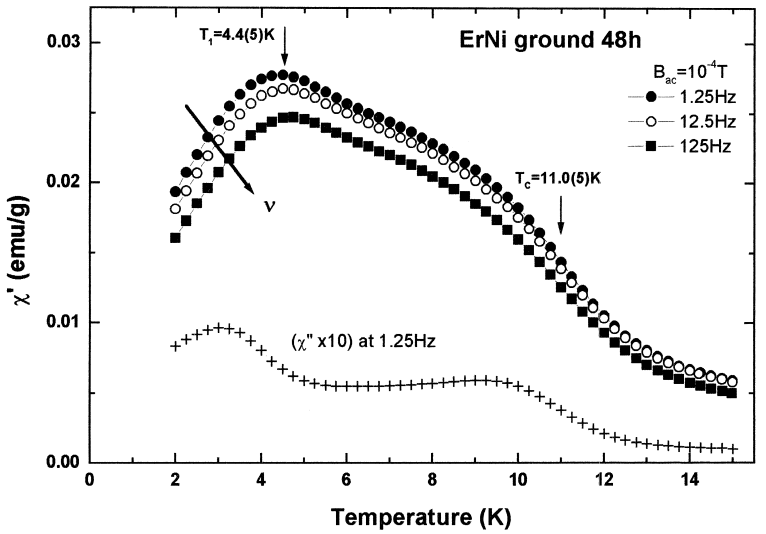

Fig. 10. Frequency dependence of the real (χ') and imaginary (χ'') part of the ac-magnetic susceptibility of ErNi ground for 48 h (ac-field of 0.1 mT, dc-field of 0T and $\nu = 1.25$, 12.5 and 125 Hz).

These two transitions are associated with similar anomalies on the $\chi'' = f(T)$ curve. This reflects important energy losses in the magnetically ordered state, presumably connected with domain effects appearing for instance in ferromagnetic, ferrimagnetic, canted or spin-glass systems. In Fig. 10, we can observe that both anomalies occurring at T_C and T_1 are frequency dependent. They shift to higher temperatures with increasing ν. For instance, for $\nu = 125$ Hz the values of T_C and T_1 are 11.4 ± 0.5 K and 4.8 ± 0.5 K, respectively. This behaviour is typical for a metallic spin-glass [13]. We note that the transition temperature T_C of the ground sample is close to that observed for the as-cast one (Fig. 9). Our study indicates that the grinding process has a drastic effect on the magnetic properties of ErNi. The measurements suggest a strong disorder (very broad magnetic transition, spin-glass behaviour) appearing in the ground sample. We recall that this process induces a structural change for this intermetallic and perhaps this change is not complete.

In conclusion, the mechanical grinding of YNi obtained by casting or the mechanical alloying of a (Y + Ni) mixture under argon atmosphere produces a similar new phase 'YNi' having structural properties different from those adopted by the well-crystallized compound (orthorhombic FeB type). This phase which still exists after annealing at 873 K under vacuum, exhibits an X-ray powder pattern resembling that of GdNi synthetized by melting and subsequent grinding (orthorhombic CrB type). Our study suggests a structural transition induced by high-energy ball milling of YNi. Further investigations (TEM examination) concerning the structure of this new phase 'YNi' are now in progress.

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References

[1] K. Aoki, A. Memezawa, T. Masumoto, J. Mater. Res. 8 (1993) 307.
[2] E. Gaffet, Mater. Sci. Eng. A 119 (1989) 185.
[3] S. Orimo, H. Fujii, T. Yoshino, J. Alloys Compd. 217 (1995) 287.
[4] K. Klepp, E. Parthé, Acta Cryst. B 36 (1980) 3093.
[5] J. Chen, S.X. Dou, H.K. Liu, J. Alloys Compd. 244 (1996) 184.
[6] E. Parthé, J.M. Moreau, J. Less-Common Met. 53 (1977) 1.
[7] K. Klepp, E. Parthé, J. Less-Common Met. 85 (1982) 181.
[8] C.P. Kempter, N.H. Krikorian, J.C. McGuire, J. Phys. Chem. 61 (1957) 1237.
[9] S.C. Abrahams, J.L. Bernstein, R.C. Sherwood, J.B. Wernick, H.J. Williams, J. Phys. Chem. Solids 23 (1964) 1069.
[10] I.W. Modder, H. Bakker, G.F. Zhou, Physica B 262 (1999) 141.
[11] T.R. McGuire, R.J. Gambino, IEEE Trans. Mag., MAG 14 (1978) 838.
[12] K. Sato, Y. Yosida, Y. Isikawa, K. Mori, J. Magn. Magn. Mat. 54–57 (1986) 467.
[13] S. Süllow, G.J. Nieuwenhuys, A.A. Menovsky, J.A. Mydosh, S.A.M. Mentink, T.E. Mason, W.J.L. Buyers, Phys. Rev. Lett. 78 (1997) 354.