MECHANICAL GRINDING OF TFe$_2$ (T= Hf, Zr) COMPOUNDS

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Abstract

The structural changes produced during the mechanical grinding of the crystalline compounds ZrFe$_2$ and HfFe$_2$ (Laves phases) were analyzed by means of Mössbauer effect spectroscopy on ^{57}Fe, perturbed angular correlations of gamma rays on ^{181}Hf and X-ray diffraction.

For the starting crystalline compounds the hyperfine interaction at both sites (T and Fe) is mainly magnetic with a weak electric quadrupole perturbation. The Mösssbauer spectra in both systems rapidly evolves with grinding time showing an increasing fraction of nuclei experiencing a pure quadrupole interaction. On the other hand, the nuclear spin precession curve changes monotonically and the fitted hyperfine parameters show that while the quadrupole perturbation increases the magnetic one remains nearly unchanged at Hf sites. The results show that after a severe grain size reduction partial amorphization and Fe segregation occurs probably as a consecuence of the surface energy accumulation and/or ambient contamination.

Introduction

Early and late transition metal alloys T$_{1-x}$T'$_x$ are known to amorphize in a wide composition range by vapour- or melt- quenching and by solid state amorphization reactions. The mechanical grinding (MG) of intermetallics T$_m$T'$_n$ has been succesfully applied in some of these systems to produce amorphous alloys through a crystalline-to-amorphous transition induced by the continuous mechanical impact [1-3].

On the other hand there exist a great number of TT'$_2$ compounds that crystallize in the topologically compact *C14*, *C15* and *C36* structures (Laves phases) [4]. Previous results on the amorphization by MG in these compounds are rather controversial and do not match amorphization criteria based on the accumulation of elastic energy during grinding [3]. Several authors have reported the amorphization by MG of Laves phases like: ScFe$_2$, YFe$_2$, ZrV$_2$, TaFe$_2$, ZrFe$_2$ [5,6].On the contrary, a decomposition process with partial segregation of the metallic elements or diluted alloys has been reported for ZrV$_2$ [7], YFe$_2$ [8], HfFe$_2$ [9] and GdFe$_2$, GdCo$_2$, and YCo$_2$ [10,11].

The atomistic processes involved in these solid state reactions assisted by mechanical work are not yet well understood. Hyperfine techniques like Mössbauer Effect (ME) spectroscopy and Perturbed Angular Correlations of gamma rays (PAC), which are sensitive to changes to the local atomic configurations, may make important contributions in this direction.

We present here results on the evolution of the short range order during the grinding of the crystalline compounds HfFe$_2$ and ZrFe$_2$ obtained with ME spectroscopy on ^{57}Fe and PAC technique on ^{181}Hf, probing both sites in the structure. Additional characterization was obtained by X ray diffraction (XRD).

Experimental

The starting intermetallic compounds (HfFe$_2$ and ZrFe$_2$) were prepared by melting stoichiometric quantities of the elemental powders and remelting several times. Afterwards, HfFe$_2$ ingots were annealed at 1300 K for a few days and ZrFe$_2$ ones at 1700 K for 3 h. The samples were ground under Ar atmosphere (9ppm N impurity) in cylindrical steel vials (5 cm^3) with one steel ball (ϕ = 9 mm), using a vibratory mixer mill (Retsch MM2) operating at 25-30 Hz. The milling was interrupted at several steps in order to carry on the PAC and ME experiments and to obtain X ray diffractograms. Since in each step, some material was removed from the initial quantity in the vial (about 300 mg), the results are analized in terms of milling time per unit weight (s/mg).

ME experiments were carried out with a conventional spectrometer under transmission geometry, employing a ^{57}CoRh source. The quoted isomer shifts are relative to α-Fe. The ^{181}Hf activity suited for the PAC experiments was obtained by irradiating part of the HfFe$_2$ material with thermal neutrons. PAC measurements were made in a conventional apparatus with two CsF detectors giving a time resolution of 0.8 ns (FWHM). XRD patterns were obtained in reflection geometry using a Philips PW1710 diffractometer with Cu $K\alpha$ radiation. All measurements were performed at room temperature.

Results

The XRD patterns are shown in Fig. 1 and 2 , respectively. For the starting materials, they are consistent with the reported corresponding crystalline structures, the cubic C15 structure for ZrFe$_2$ and the hexagonal C36 [12] Laves phase for HfFe$_2$. For the latter, the presence of a small sample fraction with the cubic C15 structure may not be discarded due to the coincidence of the corresponding reflections with some of those of the C36 structure. Furthermore, the existence of some stacking faults along the c direction may be inferred from the peakshape of some (h-k = 3n±1) reflections.
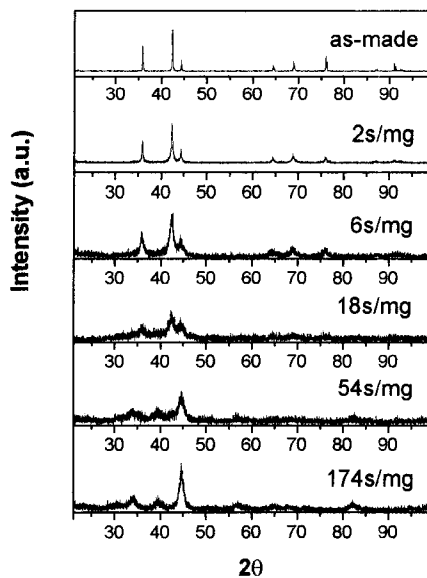
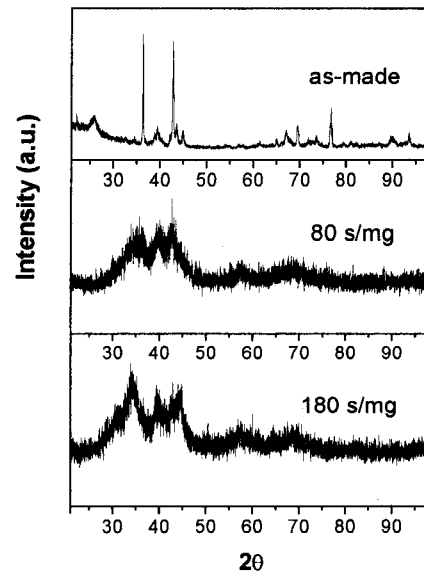

Fig. 1: XRD patterns of ZrFe$_2$ for different milling times.

Fig. 2: XRD patterns of HfFe$_2$ for different milling times.

As milling proceeds a broadening of the peaks is observed as a result of the grain size reduction. For $ZrFe_2$ after 18s/mg of milling, the diffraction peaks corresponding to the Laves phases are still present, superimposed to a wide bump characteristic of an amorphous phase. With further mechanical work, some Fe segregation and the formation of a new phase with Zr as main component is observed. These extra peaks may be indexed as those of ZrN. A similar behaviour was observed for $HfFe_2$ (see Fig. 2).

Before grinding, the hyperfine interaction at Hf and Fe sites in both compounds (see Figs.3, 4 and 5) is mainly magnetic with a weak electric quadrupole perturbation. The ME spectrum of $ZrFe_2$ shows two magnetic interactions corresponding to two different angles between the principal component of the electric quadrupole perturbation and the orientation of the magnetization [13]. For $HfFe_2$, two inequivalent sites for Fe and one for Hf may be distinguished, as expected from the crystalline structure.

The fitted hyperfine parameters: hyperfine magnetic field H_{hf}, isomer shift δ, quadrupole shift $\epsilon = eQV_{zz}(1+\eta^2/3)^{1/2}/4$ and quadrupole frequency $\omega_Q = eQV_{zz}/40h$ are:

$ZrFe_2$:

Fe-sites: $H_{hf} = 20.05_4$ T $\delta = -.181_4$ mm/s $\epsilon = +.076_5$ mm/s

    $H_{hf} = 18.76_1$ T $\delta = -.166_7$ mm/s $\epsilon = -.080_1$ mm/s

$HfFe_2$:

Fe-sites: $H_{hf} = 18.98_4$ T $\delta = -.183_4$ mm/s $\epsilon = +.066_7$ mm/s

    $H_{hf} = 16.99_7$ T $\delta = -.181_6$ mm/s $\epsilon = -.062_5$ mm/s

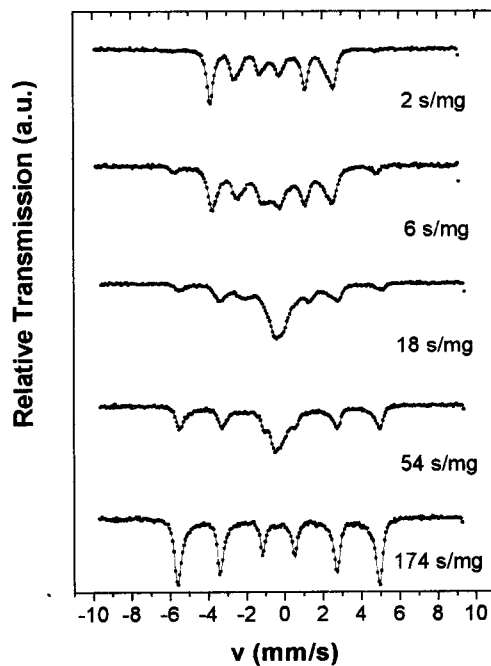Hf-site: $H_{hf} = 14.1_{1.2}$ T $\omega_Q = 7.0_1$ Mrad/s

Fig.3: ME spectra of $ZrFe_2$ for different milling times.

The PAC spectrum of $HfFe_2$ is better fitted by allowing for an additional component at about 7.2 T. Akselrod et al [14] in a comprehensive study of this system have found a similar second component in some samples whose XRD pattern also suggested anomalies in the stacking sequence along the c direction. It seems then that this component arises from probes in regions affected by these faults. Correspondingly, the addition of one or two extra components in the fit of the ME spectrum increases its quality.

The ME spectra evolve rapidly with grinding time showing an increasing fraction of nuclei experiencing a paramagnetic interaction (see Fig. 3 and 4). After 80 s/mg the signal from ferromagnetic $HfFe_2$ reduces to 16% of Fe probes; the remaining absorption may be due to superparamagnetic $HfFe_2$ and/or amorphous HfFe. With further grinding (180 s/mg), a new ferromagnetic interaction appears which may be easily assigned to metallic Fe with some impurity (Hf) content. $ZrFe_2$ displays a similar behaviour under grinding with the Fe signal

appearing earlier and developing faster.

On the other hand, the PAC spectra of $HfFe_2$ change monotonically with grinding time (see Fig. 5) and the fitted hyperfine parameters show: i) a gradual disappearance of the second component; ii) an increase in the quadrupole perturbation of the main component and iii) an increasingly broader distribution of the magnetic hyperfine field of this component, centered at a slightly decreasing H_{hf}. With further grinding the PAC spectra show an increasing fraction of probes experiencing a broadly distributed quadrupole perturbation which may be assigned to an amorphous phase. After the last grinding step the fraction of Hf probes in this amorphous phase amounts to $\approx 62\%$.

The ME spectrum of the same sample shows that the fraction of Fe probes in Fe-like environments has considerably increased and confirms the presence of diluted impurities (probably Hf atoms) in the Fe matrix. Indeed the PAC spectra may be fitted with 9% of probes experiencing a magnetic interaction with $H_{hf} \approx 42$ T which approaches the observed value of 60T for Hf probes highly diluted in a Fe matrix.

Fig.4: ^{57}Fe ME spectra of HfFe$_2$ for different grinding times.

Discussion

All the above results are consistent with a drastic reduction in the mean grain size with milling, as shown in Fig. 6 for $ZrFe_2$. This behaviour is not surprising given the extreme fragility of the Laves phases as a result of their topological compact structure. Although the small crystallite size may lead to superparamagnetic ^{57}Fe ME spectra, this dynamical effect would not necessarily affect the PAC spectra which sense a smaller time window.

After that, an amorphization process presumably starts which competes with the segregation of α-Fe probably alloyed with a few atomic percent Zr or Hf. The resulting amorphous phase would be poorer in Fe than the starting material: combining the ME and PAC results an average composition $Hf_{55}Fe_{45}$ may be estimated for the Hf case.

On the other hand, together with Fe segregation the formation of Zr- or Hf- rich phases occurs and XRD patterns indicate that they may presumably be ZrN and HfN. This is rather unexpected given the care taken in handling the samples during the milling processes.
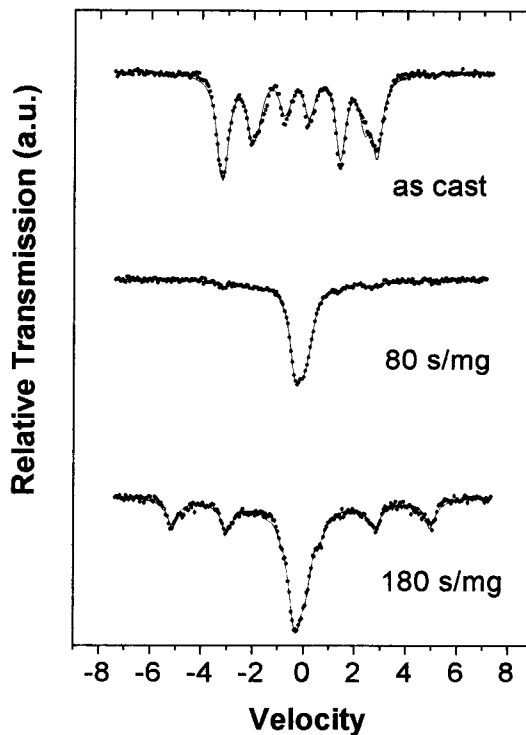
The needed N_2 molecules largely exceeds those contained as impurities in Ar gas and only a bad insulation of the vials, allowing the exchange with the open atmosphere, would justify the formation of nitrides.

Generally the amorphization of intermetallic compounds by MG has been interpreted as a result of the competence between the tendency of the system to evolve towards the stable state and the enthalpy increase caused by the energy transferred in the repeated mechanical impacts. In most cases it has been assumed that this excess enthalpy is mainly stored as elastic energy as a result of the atomic (chemical) disorder (antisite defects) induced by the mechanical work. Thus, when this energy exceeds the topological excess energy of the amorphous phase a non-equilibrium transition to the metastable amorphous phase would occur Under this hypothesis an amorphization criterium was established [14] which states that amorphization by MG will not be possible when $T_c < T_m$ (order-disorder transition and melting temperatures, respectively). Most of the reported systems satisfy this criterium but it seems to fail in the case of Laves phases. Indeed, most of the studied Laves phases have been amorphized by MG while the criterium predicts no amorphization.
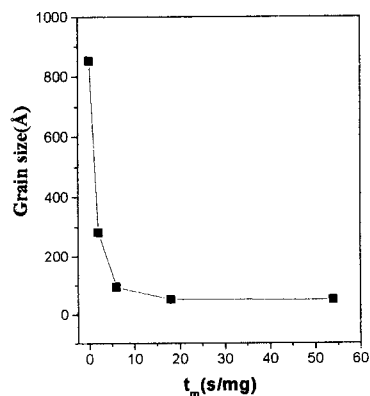
Fig.5: PAC spectra (left) and their Fourier transforms (right) of HfFe₂ for various grinding times. The solid line shows the fitted curve.

Recently, Serebryakov [15] has proposed the increase in the surface energy in finely divided systems as an alternative mechanism for the accumulation of excess energy during MG. Under appropriate conditions a wetting transition may occur giving rise to the amorphous phase formation.

Our results suggest that the amorphization is preceded by a severe grain size reduction associated with the fragility of Laves phases. At this stage, decomposition (Fe segregation) would be favourable and the observed amorphization [5,6] would be the result of the mechanical alloying with the remaining powder. In our case the formation of nitrides would inhibit this second process, obscuring the net result of grinding.

Fig.6: Evolution of the grain size for ZrFe₂.

Conclusion

The observed evolution of local order during the MG of $ZrFe_2$ and $HfFe_2$ supports a description of the amorphization process in Laves phases in terms of the accumulation of surface energy. Further insight in the proposed mechanism is needed to justify the observed Fe segregation and additional experiments aimed to elucidate the probable nitrogen contamination are in course.
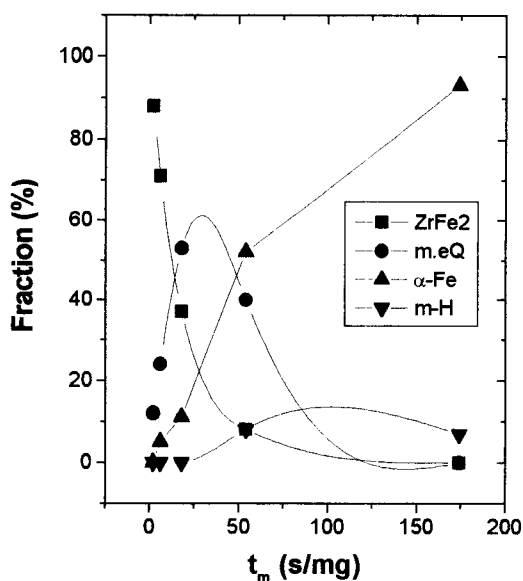

Fig. 7: **Evolution of the different fraction of ME components.**

References

[1] C.C.Koch, Mat. Sci. Forum 88-90 (1992), p.243.

[2] R.E.Watson and L.H.Bennett, Acta Metall 32 (1984), p. 447 and 491.

[3] A.W.Weeber and H.Bakker, Physica B 153 (1988), p. 93.

[4] D.L.Beke, H.Bakker and P.I.Loeff, J.Physique 51 (1990), C4-63.

[5] E.C.Passamani, V.A.Peña Rodríguez, S.K.Xia, M.Ghafari, S.L.Bud'ko, E.Baggio-Saitovitch, J.Mag.Mag.Mat. 140-144 (1995).

[6] S.K.Xia, C.Larica, V.A.Rodriguez, F.C. Rizzo Assunçao and E.Baggio-Saitovich, Mat.Sc.Forum 225-227 (1996), p.389.

[7] U.Herr and K.Samwer, Mat. Sci. Forum 179-181 (1995), p.85.

[8] H.Wada and M. Shiga, Nuc. Instr. Methods in Phys. Res. B76 (1993), p. 301.

[9] L.Mendoza-Zélis, S. Grigera and F.H. Sánchez, Latinamerican Conference on Mössbauer Spectroscopy, Santiago de Chile, Chile, (1994).

[10] C.Larica, A. Biondo, C.V.B.Tribuzy, K.M.B.Alves, E.Baggio-Saitovitch and A.P.Guimaraes, Latinamerican Conference on Mössbauer Spectroscopy (LACAME'96), Cuzco, Perú, (1996).

[11] C.Larica, K.M.B.Alves, A. Biondo, E.Baggio-Saitovitch, A.P.Guimaraes and C.V.B.Tribuzy, International Symposium on Metastable, Mechanically Alloyed and Nanocrystalline Materials, (ISMANAM'96), Roma, Italy, (1996).

[12] Elliot, Trans.Am.Soc.Met., 53 (1961)p.321.

[13] F.Aubertin, U.Gonser, S.J.Campbell and H.G.Wagner, Z.Metallkde.76 (1985)p.237.

[14] Z.Z.Akselrod, M.Budzynski, T.Khazratov, B.A.Komissarova, L.N.Kryukova, S.I.Reiman, G.K.Ryasny and A.A.Sorokin, Hyp. Int. 14 (1983), p. 7.

[15] A.Serebryakov, Mat. Sci. Forum 88-90 (1992), p.243.