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MÖSSBAUER STUDY OF MECHANICAL ALLOYING IN Fe-V AND Fe-C ALLOYS

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Résumé : La spectrométrie Mössbauer et la diffraction des rayons X ont été utilisées pour caractériser les changements microstructuraux qui se produisent pendant le broyage de mélanges de poudres de fer et de Vanadium d'une part, de fer et de graphite d'autre part. Des hétérogénéités persistantes de compositions chimiques sont observées dans les deux cas. La synthèse de presque tous les carbures et siliciures par broyage est brièvement décrite.

Abstract : Mössbauer spectroscopy and X-ray diffraction have been used to characterize the microstructural changes which occur during ball milling of mixtures of iron and vanadium on the one hand and of iron and graphite on the other hand. The chemical compositions of the alloys are inhomogeneous during a large fraction of time of the synthesis. Almost all carbides and silicides may be synthesized by mechanical alloying.

1 - Introduction

Many unanswered questions remain about how mechanical alloying (MA) occurs and particularly about the transition from the comminution of the original particles to interatomic intermixing. Mössbauer spectroscopy is a technique which is particularly suited for that purpose as it is sensitive to phenomena occurring at the nanometer scale. This technique has already been used in mechanochemistry by Lefelshtel et al. /1/ to characterize the formation of zinc ferrite by prolonged dry grinding of stoichiometric powder mixtures of zinc oxide and hematite. Mössbauer spectroscopy was also used to explore the composition range of amorphous phase formation of Fe-Zr alloys /2/. In the present study, we follow the evolution of the local compositions during the mechanical alloying of Fe and V powders on the one hand and of Fe and C powders on the other hand that is for substitutional and interstitial elements respectively. More detailed results /3/ and synthesis of almost all carbides by mechanical alloying are described elsewhere /4/.

2 - Experimental Methods

Elemental powders of Fe having a purity of 99.0 % and a particule size of 60 μm , of V having a purity of 99.7 % and a particule size of 44 μm and of graphite (45 μm) from Strem Chemicals Inc. (USA) have been mixed in the required proportions, that is $\text{Fe}_{50}\text{V}_{50}$, Fe_{80}

C_{20} , $\text{Fe}_{75}\text{C}_{25}$, $\text{Fe}_{50}\text{C}_{50}$. The powders were sealed in tungsten carbide vials with tungsten carbide balls in a glove box having a pure nitrogen or argon atmosphere with oxygen and water concentrations in the ppm range. Dry milling has been carried out in a Spex 8000 vibratory mill with a ball to powder weight ratio of about 10:1 to 5:1. For the Fe-C system, some experiments have been performed with a Fritsch Pulverisette 7 planetary mill with a ball to powder weight ratio of about 40:1.

Mössbauer spectra were recorded in transmission geometry at 77 K and 290 K and analyzed with a method which extracts an hyperfine field distribution (HFD) $P(H)$ from an experimental spectrum /5/. MA samples have all been characterized by X-ray diffraction either with $\text{CoK}\alpha$ or with $\text{Cr K}\alpha$ radiation.

3 - Results

3.1 - Fe-V system : $\text{Fe}_{50}\text{V}_{50}$

For milling times less or equal to 3 h, only broadening of some lines of the X-ray diffraction patterns was observed. After 6 h of milling, the interplanary spacings of Fe and V came closer together. The (110) peaks from Fe and V merged into a single broad peak after 12 h of milling time. After 24 h of milling, a broad, gradual peak was observed.

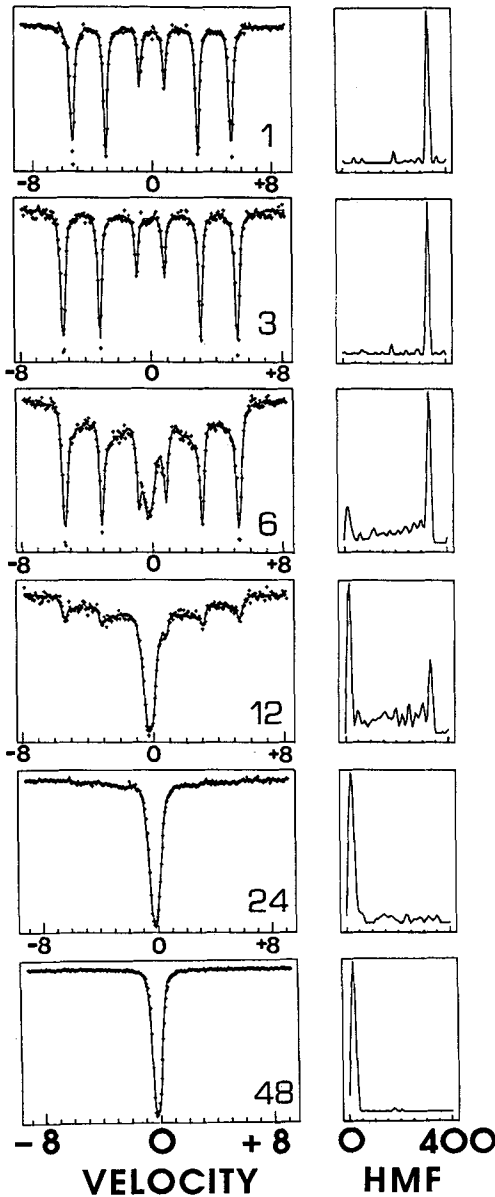


Figure 1 : room temperature Mössbauer spectra from Fe-V powders as a function of ball milling time and corresponding HFD.

The fractional amounts of these three components as a function of milling time is shown in figure 2. Transmission electron microscopy of the powder milled for 48 h has shown the presence of amorphous and nanocrystalline regions of about 3 nm for samples ground in a mortar and transferred to a holey carbon grid /3/. On the contrary, powders embedded in epoxy and microtomed only showed nanocrystalline material. The amorphous phase is therefore rather unstable against transformation to nanocrystalline material.

3.2 - Fe-C system

For $\text{Fe}_{80}\text{C}_{20}$ or $\text{Fe}_{75}\text{C}_{25}$ alloys, the ^{57}Fe Mössbauer spectra were identical to spectra from

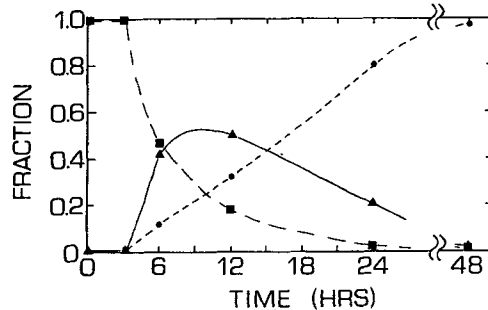


Figure 2 : Fractional amounts of Fe as a function of milling time in the broad ferromagnetic component (solid line), in the non-magnetic component (short dashed line) and in pure Fe (long dashed line).

For milling times of 10 min, 30 min, 1 h, 2 h and 3 h, the ^{57}Fe Mössbauer spectra at room temperature were identical to spectra from pure Fe. A significant change was observed after 6 h of milling time (figure 1) with the appearance of a non-magnetic environment. The non-magnetic subspectrum steadily increased and was the only observed contribution after 48 h of milling. The latter spectrum corresponds to an amorphous phase as both ordered and disordered solid solutions are magnetic at room temperature for $\text{Fe}_{50}\text{V}_{50}/6/$. Moreover the amorphous phase is in fact nonmagnetic for that composition /6/. The hyperfine field distributions show three components (figure 1) :

- 1) a sharp peak at $H = 330$ kG characteristic of pure α -Fe at room temperature with in any case less than 1 % V. The intensity of this peak decreases with time but its position does not change.
- 2) a broad distribution (from ~ 50 kG to ~ 300 kG) characteristic of Fe-V alloys with appreciable V concentrations but less than about 60 at % at which the Curie temperature is below room temperature.
- 3) a sharp non-magnetic peak (centered here at ~ 20 kG) which may be due to Fe-V alloys with a V content greater than about 60 % or (and) amorphous Fe-V alloys with nearly equiatomic compositions /6/.

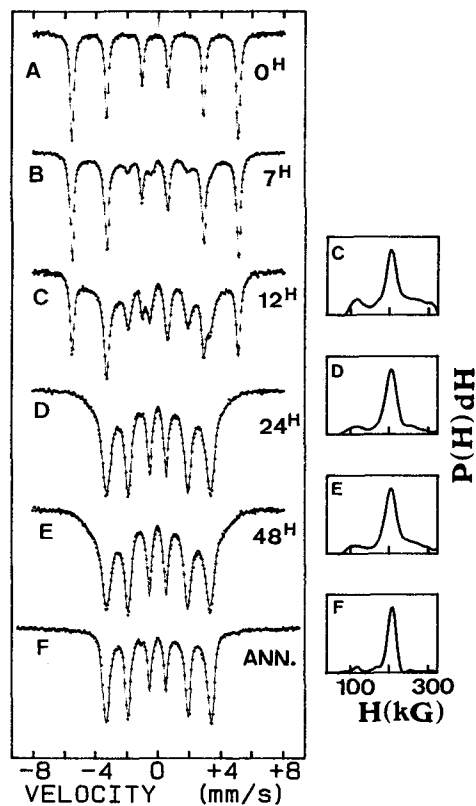


Figure 3 : Room temperature Mössbauer spectra from $\text{Fe}_{80}\text{C}_{20}$ powders as a function of milling time and corresponding HFD (ann. = annealed, see text).

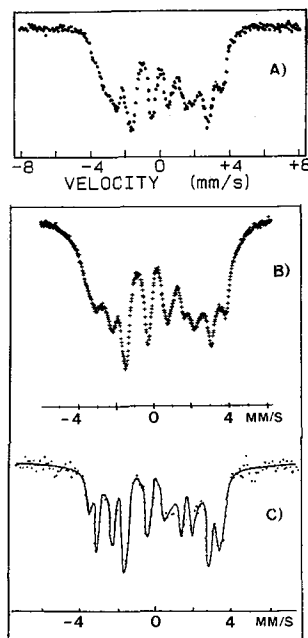


Figure 4 : Room temperature Mössbauer spectra from Fe_7C_3 formed a) by ball milling a $\text{Fe}_{50}\text{C}_{50}$ powder during 90 h b) by crystallization of amorphous Fe-C alloys /8/ c) at high temperature and high pressure /10/.

α -Fe for milling times less or equal to 4 h. After 7 h, figure 3b shows the presence of cementite Fe_3C with an hyperfine field $H = 205 \pm 2$ kG, independent of time and an isomer shift $IS = 0.19 \pm 0.01$ mm/s with respect to α -Fe at room temperature in perfect agreement with the literature values. Moreover, the X-ray diffraction patterns /4/ are composed of broad peaks characteristic of Fe_3C . As proved by both methods, an hexagonal carbide of the disordered ϵ -L'3 type /7/ has also been formed. It gives rise to a broad hyperfine field component whose outer part is clearly seen in figure 3 and centered on 270 ± 4 kG which is also independent of the grinding time. The carburization of iron was completed in about 18 h. Once cementite was formed, further grinding produced a broadening of the X-ray diffraction peaks and of the Mössbauer peaks (figure 3d,e). Both results prove that a high density of defects exist in cementite. For $t = 24$ h, a characteristic dimension of about 8 nm has been obtained from the widths of X-ray diffraction lines. This dimension is likely related to a correlation length in the stacking of the triangular prismatic sheets which are the building elements of cementite /7/. Cementite obtained after 24 h milling has been heated at a rate of 0.05 K/s up to 750 K and cooled at the same rate in vacuum or in an hydrogenated nitrogen atmosphere (figure 3f). The widths of both X-ray and Mössbauer lines strongly decrease and the hexagonal carbide is no longer detected (figure 3f, HFD). Cementite and hexagonal carbides are also formed with the planetary mill, but at a faster rate, that is in about seven hours, with a larger ball to powder weight ratio (section 2). Figure 4a shows the Mössbauer spectrum of orthorhombic Fe_7C_3 carbide formed after milling a $\text{Fe}_{50}\text{C}_{50}$ mixture during 90 hours with a vibratory mill. This spectrum is quite similar

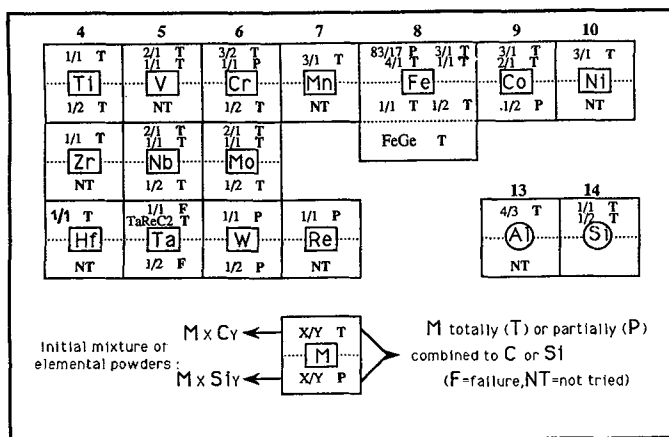


Figure 5 : Summary of the results obtained in the mechanosynthesis study of carbides and silicides.

to that of Fe_7C_3 obtained from crystallized amorphous alloys /8/ (figure 4b). The latter preparation method yields carbides consisting of microdomains of about 5 to 10 nm wide as shown by electron diffraction studies /9/, a domain size also consistent with the previous evaluation done for Fe_3C .

Both Mössbauer spectra differ from the spectrum of Fe_7C_3 (figure 4c) synthesized at 1200°C and 80 kbars /10/ which is expected to be essentially free of defects. As Fe_3C , Fe_7C_3 is formed with a much faster kinetics ($\sim 1 \text{ h } 30$) with the planetary mill than with the vibratory mill but at least a part of the one order of magnitude difference is related to the change of the ball to powder weight ratio.

4 - Discussion

A continuous enrichment of V with Fe and of Fe with V is not consistent with the results of Mössbauer spectroscopy. For instance the HFD of material milled for 6 h shows that about 50 % of the iron atoms are still in essentially pure Fe. As no distinct X-ray diffraction can be associated with regions of pure Fe, we suggest that these composition inhomogeneities are of the order of 10 nm or less in size. Qualitatively similar results have been obtained recently by de Araujo Pontes et al. (to be published) in the study of mechanical alloying of $\text{Fe}_{50}\text{Si}_{50}$ and $\text{Fe}_{33}\text{Si}_{67}$ powder mixtures which form cubic FeSi and cubic FeSi , α and β - FeSi_2 crystalline compounds respectively. Using optical microscopy the latter authors observe the classical structure respectively with composite particles consisting of parallel lamellae /11/ during the first milling stage while Mössbauer spectroscopy shows essentially pure iron. In a latter stage, particles which look homogeneous are observed while they are inhomogeneous at an atomic scale. For $\text{Fe}_{50}\text{V}_{50}$, a simulation of the hyperfine field distribution has also proved that only a broad composition distribution with Fe-rich and V-rich peaks is consistent with experiment /3/.

As the main peak of the HFD in the case of Fe-C alloys is the one characteristic of cementite, one can exclude a broad composition distribution although such carbides built from triangular prismatic sheets may exist from Fe_3C to Fe_2C , as observed in the crystallization products of amorphous Fe-C alloys /13/. Iron carbides with carbon atoms in octahedral sites also exist between Fe_6C and Fe_2C /12/. Such carbides are responsible for the broad part of the hyperfine field distribution with $H \geq 220 \text{ kG}$ and may also contribute to the cementite peak. A transformation mechanism from hexagonal carbides to triangular prismatic sheet carbides is chemical twinning (/12,13/ and references therein). It is

therefore reasonable to assume that the close-packed hexagonal (or slightly distorted) carbides play a role similar to the heterogeneous solid solution in the Fe-V case. We finally emphasize that almost all carbides may be synthesized by ball milling mixtures of elemental powders and graphite (/14/, figure 5).

5 - Conclusion

In spite of their differences, Fe-V and Fe-C have some similarities in their behaviour during mechanical alloying :

- 1 - The powders do not chemically mix during an initial period of some hours and an almost pure Fe component is observed not only during that stage but also in later stages. The decrease of that component is similar in both cases (figure 2).
- 2 - There exist chemical inhomogeneities with a broad composition distribution which persist during the synthesis.

This is also observed for Fe-Si alloys (de Araujo Pontes et al., to be published). Carbides and silicides may be synthesized at room temperature by grinding the elemental powders.

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