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Mechanically driven syntheses of carbides and silicides

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Most metal carbides or silicides may be synthesized at room temperature, by ball milling mixtures of elemental powders for some tens of hours with a vibratory mill. Both stable and metastable compounds containing a high density of defects can be obtained. In general, phases stable at low temperatures are synthesized. This observation allows us to confirm recent estimations for the maximum temperature (~ 600 K) attained in these powders during mechanical alloying. Exceptions are found for some MSi_2 silicides with M = titanium, iron or molybdenum for which both low- and high-temperature phases are formed.

1. Introduction

The mechanical alloying (MA) process is being used more and more extensively in materials science both for technological and for scientific reasons. It is, for example, a means for producing complex oxide dispersion-strengthened alloys, composite metal powders, corrosion- and wear-resistant alloy powders for coating applications [1–3], etc. Moreover, since the discovery of amorphization by solid-state reactions [4, 5], the MA technique has been widely applied to the study of the amorphization of various alloys mainly in transition metal (TM)–TM and rare earth–TM binary systems [6, 7]. The amorphous alloys are produced either by ball milling of elemental powders or by grinding crystalline alloys. The often studied TM–metalloid amorphous alloys are more difficult to prepare by the MA technique and only a few results have been reported, such as in $(Fe_{0.75}Zr_{0.25})_{100-x}B_x$ alloys for $x \leqslant 0.15$ [6]. In general, the formation of stable or metastable crystalline phases competes with the formation of the amorphous phase. The question of the study of the direct synthesis of crystalline compounds with MA is therefore raised. Although still limited, recent trends also include such studies as [8–12] superconducting Nb_3Sn [2–3], hard magnets Fe-Nd-B (less than 10 at % B) [9] and high-temperature intermetallics such as aluminides [3, 12].

TM–C amorphous alloys [13] cannot be prepared over wide concentration ranges by liquid quenching. Moreover, they do not fulfil the conditions required for solid-state amorphization, with, for example, a slow diffusion of carbon in transition metals. All the previous arguments explain why, to our knowledge, amorphization of TM–C or the formation of carbides have not yet been systematically studied by MA. MA has been used, for example, to include already prepared carbides, such as SiC [3], in metallic matrices. Al_4C_3 has been observed to form during the elaboration of dispersion-strengthened aluminium alloys by MA of aluminium powders with TiC or carbon powders [8]. However, our results for the Fe–C system suggest that different mechanisms may occur if a carbide is formed by a precipitation reaction, as in the previous example, or if it is obtained by direct synthesis by grinding the elements in the stoichiometric or near stoichiometric proportions. Very recently [14], fresh Fe–1.2 wt % C martensite has been ball milled to obtain an upper limit to the temperatures attained during MA.

The present work was devoted to the study of the mechanochemical synthesis of carbides and of silicides [10], both of which are of technological significance. An independent study of MA in group V TM–Si systems has recently been published by Viswanadham *et al.* [11]. We have synthesized carbides and silicides by ball milling mixtures of elemental powders, with a composition denoted hereafter as p-A_xB_y. On the whole, more than thirty compounds have been prepared.

2. Experimental procedure

Elemental commercial powders of TM, with mean particle size varying between some micrometres and some tens of micrometres, and graphite (mean size 45 μm) from Strem Chemicals Inc. (USA) have been mixed in the required proportions. 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 p.p.m. range. Dry milling has been carried out in a Spex 8000 mixer/mill with a ball to powder weight ratio of about 10:1 to 5:1. In addition, hardened steel vial and balls have been used in some cases. MA samples have all been characterized by

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X-ray diffraction and also by Mössbauer spectroscopy for iron-containing systems. In general, X-ray diffraction patterns show that the processed powders are more or less polluted by the materials constituting the vial and the balls. Some experiments have also recently been performed with a Fritsch Pulverisette 7 planetary mill with WC or hardened steel vials and balls and a ball to powder weight ratio of about 40 : 1.

3. Carbides

We will first present the results obtained with the Fe–C system because the combination of the two previous techniques gives particularly valuable information, as has already been well established and shown in recent studies of MA amorphous $Fe_{1-x}Zr_x$ [15], or of the ball milling of p-FeV powders [16].

3.1. Cementite synthesis

As observed in many studies, the process of interatomic intermixing does not begin immediately. In p-FeV the change from dynamic interlamination of particles to alloying takes place after 3 to 6 h and similarly in Fe–C mixtures, for example for p-Fe_4C and p-Fe_3C. After about 4 h, the iron hyperfine field does not change and at most a slight broadening of the α-Fe peaks may be noticed while the X-ray peaks broaden due to particle size reduction. The carburization of iron is completed in about 18 h. Fig. 1 shows room-temperature Mössbauer spectra of products obtained after milling a mixture p-$Fe_{80}C_{20}$ for various times, t. For comparison, Fig. 1d also presents a spectrum of cementite, Fe_3C (Strem Chemicals Inc., USA), mechanically ground for 7 h. Any texture effect is excluded as identical spectra are obtained with and without the magic angle method [17] for samples 1c and 1d.

In addition to α-Fe, Fig. 1b shows the presence of cementite with hyperfine field $H = 205 \pm 2$ kG and isomer shift IS $= 0.19 \pm 0.01$ mm sec^{-1} with respect to α-Fe at room temperature (the cementite mean hyperfine field and mean isomer shift are independent of the grinding time), as compared to $H = 206 \pm 2$ kG and IS $= 0.18 \pm 0.01$ mm sec^{-1} for cementite extracted from heat-treated Fe–C alloys [18]. Moreover, the X-ray diffraction patterns (see Fig. 3a) are composed of broad peaks characteristic of Fe_3C. As proved by both methods, an hexagonal carbide of the disordered ε-L′3 type [19] has also been formed. It gives rise to a broad hyperfine field component (tails of the outer main peaks in Figs 1b to d) centred on 270 ± 4 kG, which is also independent of the grinding time. This mean hyperfine field is typical of iron atoms with two carbon neighbours [20], but the distribution may also include fields due to iron atoms with only one carbon neighbour. Its composition would therefore be between Fe_6C and Fe_3C, in agreement with the initial composition of the mixture. The spectrum in Fig. 1d also shows a similar hexagonal phase, which comes at least partly from a carbonitride (about 10% of the iron atoms) present at the beginning in this commercial cementite.

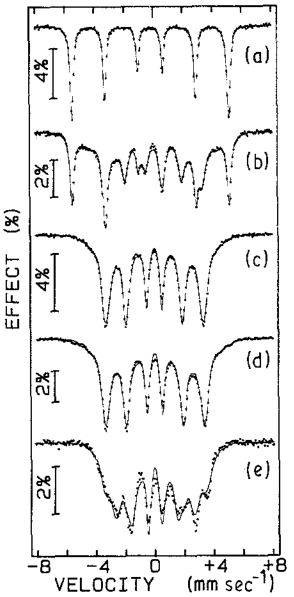

Figure 1 Room-temperature ^{57}Fe Mössbauer spectra of mixtures of powders of iron and graphite ball-milled for t h: p-Fe_4C for (a) $t = 0$ h, (b) $t = 12$ h, (c) $t = 24$ h; commercial Fe_3C for (d) $t = 7$ h; and p-FeC for (e) $t = 90$ h. (——) fits with sites for (a) and (b) and with hyperfine field distributions for (c), (d) and (e).

Once cementite (MA cementite) is formed, further grinding produces a broadening of the X-ray diffraction peaks (Figure 3a) and of the Mössbauer peaks. These two broadenings are correlated (Fig. 2). A characteristic dimension can be obtained from the Scherrer formula, which we have applied to the superimposed (2 3 0) and (0 4 0) X-ray diffraction peaks of cementite. For MA cementite which has been ground for about 6 h after its synthesis (∼ 18 h), we obtain a characteristic dimension of about 8 nm. This dimension steadily decreases when MA cementite is ground for times varying from 6 to 30 h. It would be interesting to know how it is related to defects, that is to the correlation length in the stacking of the triangular prismatic sheets which are the building elements of cementite [19, 20].

Superparamagnetism (related to size effects) cannot explain why a hyperfine field distribution (HFD) is observed, which becomes broader with increasing grinding times while keeping a constant average value. This results proves that a high density of defects exists in the MA samples. Various defects may, in fact, be easily introduced in such structures as is demonstrated by high-resolution electron microscopy [21] and, for some of these defects, as predicted by the chemical twinning model [22]. The MA cementite ($t = 24$ h) was heated at a rate of 0.05 K sec^{-1} to 750 K and cooled at the same rate either in vacuum or in an hydrogenated nitrogen atmosphere. The widths of both X-ray and Mössbauer lines strongly decrease, from 1.5° to 0.7° and from 0.71 to 0.42 mm sec^{-1} (lines 1 and 6), respectively, and the hexagonal carbide is no longer detected. The maximum temperature, T_{MA}, attained in the powders during MA has been estimated to be about 575 K in Fe–C martensite and in bismuth by Davis *et al.* [14]. The coexistence of hexagonal and orthorhombic iron carbides also agree with this estimation. Cementite and hexagonal carbides are also formed but at a faster rate with the planetary mill using WC vial and balls, as almost all iron atoms are combined to carbon atoms in about 7 h.

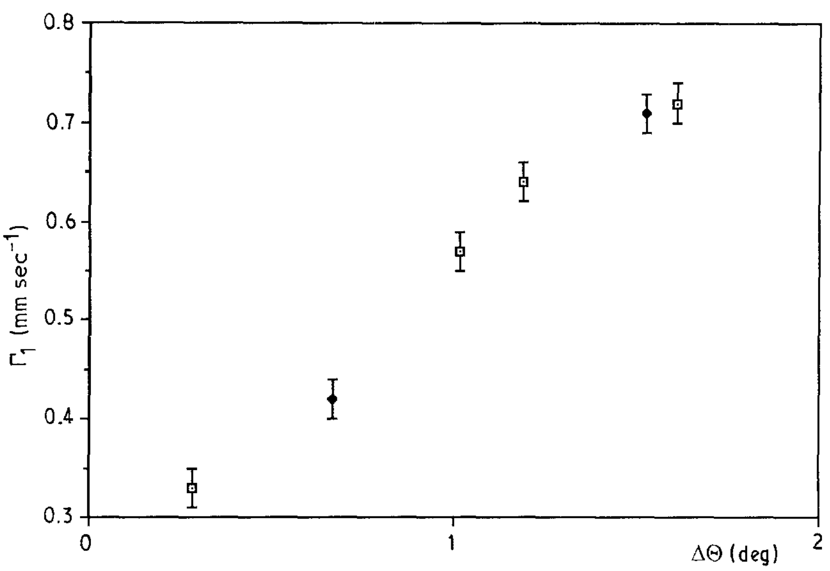

Figure 2 Full width at half maximum of Mössbauer lines 1 and 6 as a function of the width of the superimposed (2 3 0) and (0 4 0) X-ray diffraction lines (Co*K*α) (□) Fe_3C ground for times varying from 0 to 7 h (◆) p-Fe_4C annealed in vacuum (lower point) and ground for about 6 h after the formation of cementite (total alloying and grinding time of 24 h).

3.2. Fe_7C_3

Fig. 1e shows the Mössbauer spectrum of orthorhombic Fe_7C_3 carbide formed after milling a p-FeC mixture for 90 h. For shorter times (24 and 48 h), Mössbauer spectra show the subspectra of α-Fe, Fe_7C_3 and of an unknown paramagnetic compound at room temperature. This latter may correspond to a metastable NaCl-type $Fe_{(1-x)}C$ carbide but this question must be studied further. Usually the Fe_7C_3 carbide can only be directly synthesized at high temperature and pressure (1700 K and 8 GPa). It has otherwise been obtained as a by-product in hydrocarbon or diamond synthesis using iron-based catalysts or as a crystallization product of amorphous $Fe_{(1-x)}C_x$ alloys mainly for $x \geqslant 0.3$ [13]. The latter preparation method yields carbides containing many defects and consisting of microdomains of about 5 to 10 nm wide as shown by electron diffraction studies [23]. The spectrum in Fig. 1e is quite similar to that of Fe_7C_3 obtained from crystallized amorphous alloys (Fig. 12 of [13]). Both consist of broad sextets unlike the spectrum of Fe_7C_3 synthesized at high temperature and pressure with well-resolved magnetic sites [24]. These spectra are difficult to fit and have been calculated with a HFD in fig. 1e. We conclude that MA Fe_7C_3 also contains a high density of defects with a domain size which is quite similar to that quoted above for MA cementite.

Fe_7C_3 is formed over a wide concentration range (from about 29 to 50 at % C) but with a much faster kinetics (in ~ 1 h 30 min) with the WC planetary mill (in part due to the larger weight ratio). This concentration range includes the composition of epsilon or eta carbides [20, 21] which are therefore formed by MA in low-carbon Fe–C mixtures but cannot be synthesized directly in their composition ranges.

3.3. Other carbides

Fig. 3 summarizes our results. It shows the compositions of the initial mixtures that have been tried and which give rise to a total (T) or partial (P) combination of the element M with carbon or with silicon after 24 h milling. This does not mean that all carbon or silicon atoms are also combined with M. Cubic carbides TMC_x ($x \leqslant 1$), consistent with the already known structures [25, 26], are formed for titanium, vanadium, zirconium or niobium (Fig. 3b). For p-MoC milled for 24 h, the low-temperature hexagonal phase, γ′-MoC (space group P63/mmc), is observed while for p-Mo_2C, the X-ray pattern is indexed with an NaCl-type cubic structure (any possible ordering of the carbon atoms and vacancies would not be observed) with a lattice parameter of 0.427 nm. This structure differs from the structures of orthorhombic α-Mo_2C or hexagonal β-Mo_2C which may have been expected to form. The influence of the nitrogen atmosphere cannot be excluded. As tantalum is very ductile, the experiment performed with p-TaC failed. We have

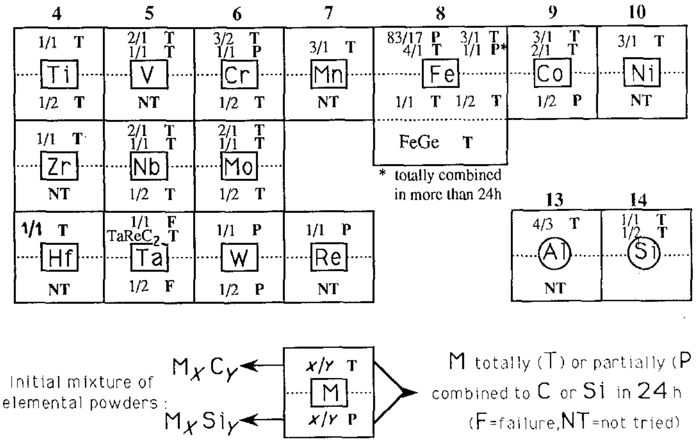

Figure 3 Summary of the results.

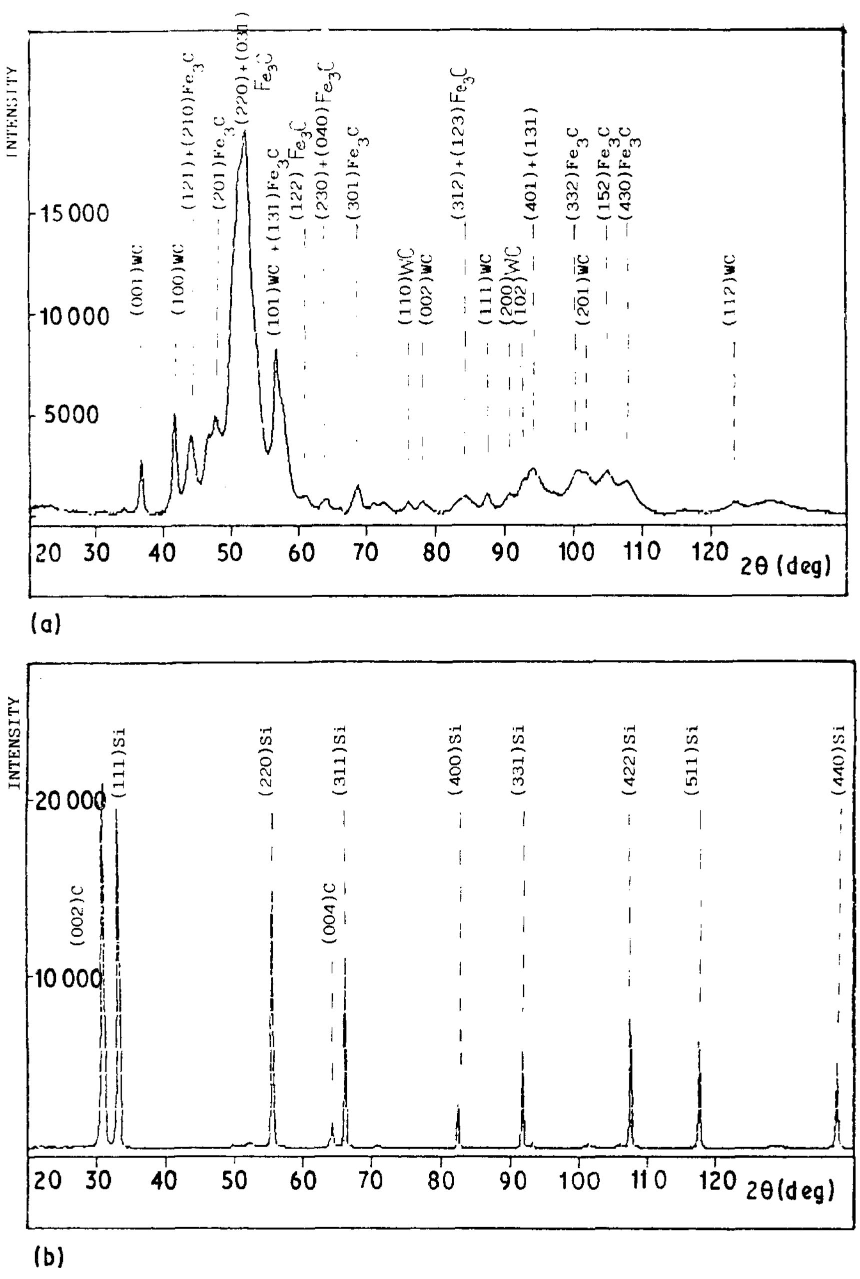

Figure 4 X-ray diffraction patterns (Co$K\alpha$, λ = 0.1789 nm) of various mixtures ball-milled for t = 24 h (except for c): (a) p-Fe_4C (WC vial and balls), (b) p-NbC (WC vial and balls), (c) p-SiC at t = 0 h, (d) p-SiC (steel vial and balls).

instead successfully milled a p-$(Ta_{0.5}Re_{0.5})C$ mixture as alloying with rhenium is known to decrease strongly the temperature of the ductile–brittle transition of tantalum. A cubic carbide is also formed.

The starting powders may contain more than two elements as well as already prepared alloys. For example, p-$(Nb_{0.25}Ta_{0.25}Mo_{0.25}Re_{0.25})C$ gives a mixture of two cubic carbides while p-(TiAlV)C, where (TiAlV) is a powder of a $Ti_{0.863}Al_{0.102}V_{0.035}$ alloy, gives a single cubic carbide. The values of x for the non-stoichiometric cubic carbides are not yet known, as chemical analyses remain to be done. Lattice parameters give good estimations of x, for example a = 0.444 nm for NbC_x giving $x \approx 0.75$ [25, 26]. However, the lattice parameters measured for the compounds in Fig. 3 are, in general, smaller by some 10^{-3} nm than the lattice parameters quoted in the ASTM files. A ball consumption of up to $\approx 2\%$ of their masses is measured for very hard carbides. Only a partial carburization is observed for tungsten and rhenium. In both cases, hexagonal carbides are formed, ReC being isotypic to γ'-MoC. For the 3d transition metals from chromium to nickel, hexagonal carbides (as Ni_3C) and/or carbides with carbon atoms in triangular prismatic interstices [20] are synthesized, such as Cr_3C_2, Mn_3C, Fe_3C, Co_3C (all with space group Pnma). It would be interesting to investigate if uranium or U–TM carbides [27] may also be synthesized by MA.

The milling of p-SiC for 24 h under various conditions (silicon purity, vial materials, atmosphere) gives a ZnS-type SiC carbide (a = 0.4354 ± 0.0002 nm, Figs 4c and d). The mean particle size is less than 1 μm. The carburization is incomplete for t = 12 h.

4. Silicides

The cases of disilicides of titanium, iron and molybdenum are of particular interest because they raise questions about the temperatures which may be reached. For p-$TiSi_2$, we obtain a mixture of $TiSi_2$ (space group Fddd) and of a phase which may be isotypic to γ-$CrSi_2$. Massalski *et al.* [28], suggested an allotropic transformation of $TiSi_2$ to take place at about 1500 K. For p-$FeSi_2$, the final powder is a mixture of semiconducting orthorhombic β-$FeSi_2$, of metallic tetragonal α-$FeSi_2$ and of cubic FeSi. In the

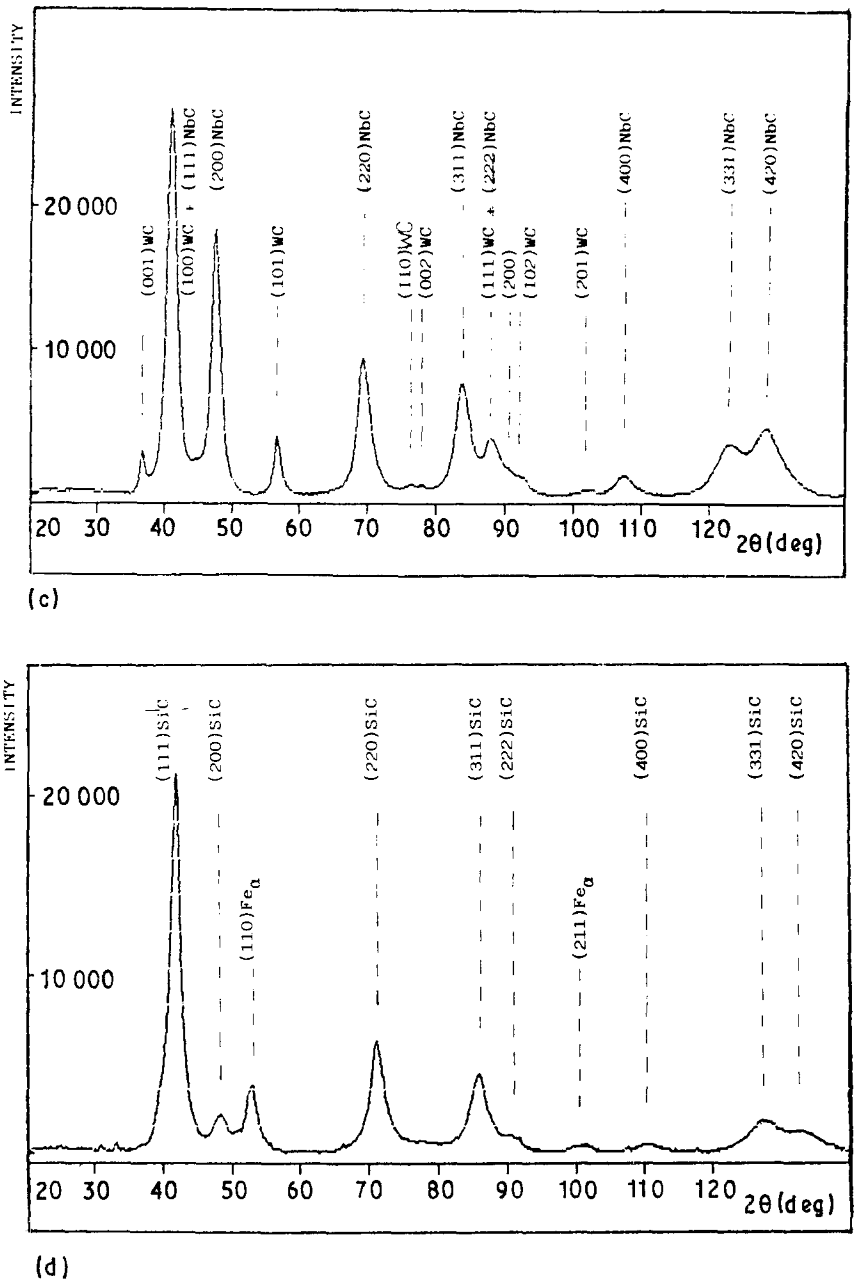

Figure 4 Continued

case of p-$MoSi_2$, the final powder is a mixture of tetragonal α-$MoSi_2$ and of hexagonal β-$MoSi_2$. The Fe–Si and Mo–Si phase diagrams [28] show that β-$FeSi_2$ is stable up to 1240 K where it decomposes into cubic FeSi and α-$FeSi_2$ and that the tetragonal phase, α-$MoSi_2$, transforms to hexagonal at 2173 K. For all other silicides, only single phases (Cr, Nb, FeSi) or mixtures (Co) expected from the respective phase diagrams are observed. Finally, a cubic monogermanide (B20 type, isotypic to FeSi) is produced by milling a p-FeGe powder. According to the Fe–Ge phase diagram, this germanide is stable up to 903 K where it transforms into a hexagonal monogermanide. This result does not contradict the estimation of T_{MA} by Davis *et al.* [14]. The different behaviours are not yet explained but transport properties as well as defects [29] and shear stresses [30] may play an important role.

5. Conclusion

The MA synthesis of stable or metastable carbides and silicides may be of practical and of fundamental interest. It provides the possibility to produce and study compounds containing high densities of defects. It may also throw light on the basic mechanisms involved in mechanical alloying. Studies of the synthesis of carbides with different mills such as planetary, vibratory [7] or fluid-energy mills are also being undertaken.

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