Steady state products in the Fe–Ge system produced by mechanical alloying

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Abstract

Prolonged mechanical alloying of elemental blends and mechanical milling of individual intermetallics of the same chemical composition in the Fe–Ge system lead to the same steady state. The phase composition of this steady state was investigated in the entire composition range using a conventional XRD technique. A map reflecting the steady-state phase composition for the different chemical composition was constructed. Mechanical alloying and grinding form products of the following composition (in sequence of increasing Ge content): α (α_1) bcc solid solution, $\alpha + \beta$-phase ($Fe_{2-x}Ge$), β-phase, β+FeGe(B20), FeGe(B20), FeGe(B20)+$FeGe_2$, $FeGe_2$, $FeGe_2$+Ge, Ge. The incongruently melting intermetallics Fe_6Ge_5 and Fe_2Ge_3 decompose on milling. Fe_6Ge_5 produces a mixture of the β-phase and FeGe(B20) while Fe_2Ge_3 produces a mixture of the FeGe(B20) and $FeGe_2$ phases. These facts are in good agreement with a model that implies local melting as mechanism for new phase formation during mechanical alloying. The stability of the FeGe(B20) phase, which is also an incongruently melting compound, is explained as a result of the highest density of this phase in the Fe–Ge system.
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1. Introduction

Although the technique of mechanical alloying (MA) has progressed to the industrial level, research efforts to elucidate the operative mechanisms underlying MA have been limited, and it is only recently that the science of this processing technology has begun to be investigated [1,2]. Expanding the scope of practical application of MA gives rise to demand for a model that is able to predict results of MA for a given system and particular operation conditions and to give ideas on how the conditions are to be changed to reach a desired result. The physical background of MA is rather sophisticated. A set of concurrent processes of different nature contribute it, so that existing 'ab initio' models rely strongly on given parameters. When the number of parameters grows a given model quickly loses its predicting ability.

In our opinion, a satisfactory model of MA may be obtained from investigating results of MA in some model

system rather than attempting to understand MA from separate actions. Such an approach would reveal integral principles that characterize MA. One of such principles is the hypothesis of local melting. In the context of MA this hypothesis is usually ascribed to Ermakov et al. [3]. In mechanochemistry it has been long known to be derived from Tissen's 'magma–plasma' model [4]. We believe that this hypothesis is a fruitful approach for describing and understanding MA in many cases. However, some investigators query the possibility of a temperature rise high enough for melting. Such conclusions follow from estimations of a temperature rise caused by mechanical energy dissipation during ball collisions [5]. A problem with these estimations is that the same amount of energy dissipated in a sufficiently small volume may produce an arbitrary high temperature rise. While the energy may be estimated in a relatively credible way, assumptions on the involved volume are inconclusive. So only experimental investigations may justify a conclusion on the possibility of local melting.

To investigate MA we need a model system that satisfies several criteria. First, the system needs to be rich in intermediate phases. In that case, results of MA may be

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analyzed by investigating the phase composition of the products. The system should not exhibit a tendency to form amorphous products, as they can hardly be assigned to a particular phase starting from X-ray diffraction patterns. Hence the atomic radii of the components of the system should not differ substantially. From the viewpoint of experiment, the system should preferably have iron as a constituent. In this case any iron contamination, inevitable when milling in steel vials with steel balls, would result in a shift in composition but not convert the binary system into a ternary one. The system Fe–Ge satisfies these criteria and has been selected by us as a model system.

2. Experimental

As a contamination by non-metal impurities may substantially distort the resulting phase composition, special care was taken to minimize the amount of oxygen found in the specimens being investigated. The main channels by means of which oxygen gets into the MA product are surface oxides and oxygen caught from the atmosphere during the treatment in the mill.

To reduce contamination associated with the surface, we have not used fine dispersed powders. Coarse powders of Fe (99.9% purity) and Ge (semiconductor grade) were used instead.

To avoid contamination during mechanical alloying, the mechanical treatment was carried out in an inert atmosphere. An AGO-2 planetary ball mill was used for the treatment. This mill has two vials cooled during operation by running water. The vials have 150 cm^3 capacity and an inner radius of 3.0 cm. The design of the vials allowed pumping and subsequent filling with gases up to pressure of 1.0 MPa. Hydrogen or argon with a pressure of 0.5 MPa was used as atmosphere in the vials in this study. The hardened steel balls used for the experiments were 5.5 and 7.5 mm in diameter. The ball charge was approximately 200 g and the mass of the powders being treated was 10 g in each vial. The operation mode of the mill was as follows: the planet carrier radius (distance from the mill axes to vial axes) was 5.2 cm, the rotation frequency of planet carrier was 630 rpm, the centrifugal acceleration was 226.3 m/s^2 (23 g) and the rotation frequency of the vials was 1290 rpm.

For the preparation of the intermetallic compounds, powder blends with the corresponding compositions were initially milled for 30 min and after that annealed in inert atmosphere for several days. The samples were examined by powder X-ray diffraction (XRD) using Co Kα radiation (λ=1.7902A) and by differential scanning calorimetry (DSC).

Despite special precautions against oxygen contamination, some amount of it may appear in the specimens investigated due to oxygen dissolved in the original components and absorbed on the surface. Besides, any

treatment in steel vials inevitably leads to contamination by the material of the balls and vials, mainly of iron. In our case the wear of ball and vial does not change the system (it remains binary) but may cause a shift in composition. To verify that level of contamination is small enough, all products of alloying were subjected to long annealing (4 h at 600 °C). The product of annealing was then examined by X-ray diffraction. If any contamination by oxygen would be high, the reflections of phases not belonging to the Fe–Ge system would be observed in the XRD patterns. Again, if the amount of iron worn from balls and vial would be large, the XRD patterns would correspond to compositions richer in iron than the nominal one. Any of these indications means an unacceptable level of contamination.

3. Results and discussion

The viewpoint on MA as an inherently low-temperature solid-state process [2] is likely to be common. In contrast, the model of local melting considers that phase formation during MA takes place in small regions of high temperature originating from local plastic deformation as a result of the colliding milling bodies. This model is now much less popular. Nevertheless some results concerning MA may be explained in a much more obvious way just by a model of local melting. The system investigated in this work considers several such cases.

If MA or mechanical grinding (MG) is carried out for a sufficiently long time, the material being milled must reach a state in which the phase composition does not change upon further treatment. If this steady state does not depend on the initial state of the product but is a function of the element composition and the milling conditions only, it represents an equilibrium state resulting from a dynamic balance of processes taking place at the mechanical treatment. Indeed, it was observed in [6,7] that at the steady state the composition and the structure of the products obtained by MA of the metallic blends or by mechanical milling of the individual intermetallics of the same chemical composition is identical. Study of the steady states observed during MA and MG may give important information about the nature of MA. From the viewpoint of the model of local melting, the corresponding dynamic equilibrium is the result of a concurrency of melting at the points of impact (which means decomposition of a solid compound) and phase formation in the molten regions. If a given material is being treated for a long time, each particle of it has a chance to be melted. Hence the steady state should correspond to phase compositions resulting from cooling of a melt of the corresponding composition. The steady state should not depend on the initial state of the material, as phase formation occurs from the liquid state. On the contrary, if MA is only a solid-state diffusion enhancement by its nature, its

driving force is the difference in thermodynamic potential between the material in the starting and steady states. Changing the initial state obviously influences the value of the driving force. In the particular case that the starting phase composition corresponds to thermodynamic equilibrium, the driving force seems to vanish. By choosing compositions that would produce different results according to these models (usually this is related to the existence of the low-temperature phase) evidence in favor of one of the two models can be obtained.

When investigating steady states one should obtain evidence that the composition observed really represents the equilibrium state but does not follow from the low rate of processing taking place on MA. Using an apparatus that provides a high milling power ensures that the steady state will be reached in a reasonable time. For many compositions investigated in this paper different initial states (elemental blends and intermetallics) were used. Results indicate that in all cases 2 h of treatment were enough to reach the steady state. The phase composition of the products at the steady state is presented in the upper part of Fig. 1 together with the equilibrium diagram for the Fe–Ge system.

3.1. Iron-rich compositions

The MA of Fe–Ge blends of iron contents less than 27at% and the milling of the hexagonal ε-Fe$_3$Ge and the cubic ε'-Fe$_3$Ge intermetallics lead to the formation of bcc structures (Fig. 2a). The lattice parameter increased with germanium concentration from 2.8664 Å for pure iron to
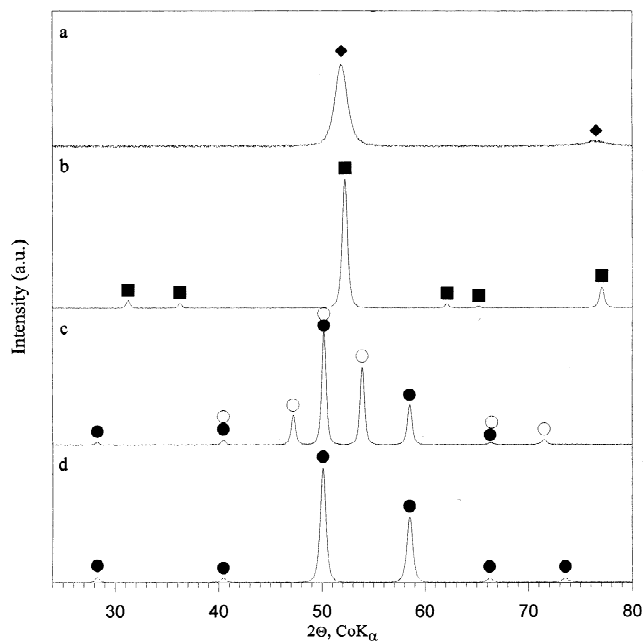
Fig. 2. XRD-patterns for Fe$_{75}$Ge$_{25}$ mechanical alloy: (a) steady state after milling; (b) after annealing at 500 °C for 5 min; (c) after annealing at 500 °C for 1 h; (d) after annealing at 500 °C for 10 h. Reflections (♦) of α-phase, (■) of DO$_3$, (●) of cubic Fe$_3$Ge, (○) of hexagonal Fe$_3$Ge.

2.898 Å for the Fe$_{75}$Ge$_{25}$ composition. The latter value is in good agreement with the value 2.90 Å observed in [8] for the bcc phase obtained by mechanical milling of the Fe$_3$Ge intermetallic. As several phases in this part of the phase diagram are based on the bcc lattice and hence are distinguished from each other by weak superlattice reflections, it is difficult to reveal the phase composition of the product using only XRD patterns of the mechanical alloy. Short time annealing may enhance the crystalline structure without substantial change of the phase composition, opening the possibility to see superlattice reflections in the XRD patterns. Fig. 2b shows XRD pattern of a mechanical alloy annealed for a very short time at 773 K. The formation of transient DO$_3$ order is seen. More prolonged annealing leads to a mixture of the high temperature hexagonal phase and the equilibrium cubic phase (Fig. 2c). Finally single equilibrium ε'-Fe$_3$Ge is observed after long annealing. The absence of decomposition of ε'-Fe$_3$Ge during cooling obviously follows from kinetic difficulties.

If MA is a low-temperature process, MA of powders of Fe$_{75}$Ge$_{25}$ composition should produce a mixture of the α_1 and β phase or of ε'-Fe$_3$Ge (as its temperature of formation is low enough and may be present as average temperature during the treatment). Nevertheless, ε'-Fe$_3$Ge appears only after long annealing. Instead, a sequence of high-temperature phases is observed in the mechanical alloy. If phase formation takes place during cooling of the melted regions, the first phase that would precipitate from the melt of Fe$_{75}$Ge$_{25}$ composition is α_2. This conclusion is more close to the experimental data.
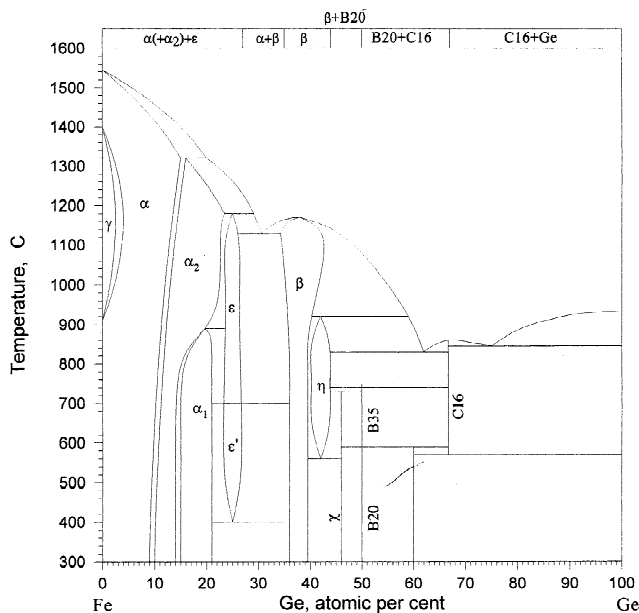

Fig. 1. Equilibrium phase diagram for Fe–Ge system. The map in the upper part reflects phase composition of the steady-state product for different chemical compositions.

3.2. Compositions with Ge contents of 30–40%

The compositions $Fe_{70}Ge_{30}$, $Fe_{65}Ge_{35}$ and $Fe_{60}Ge_{40}$ were investigated. MA of a $Fe_{70}Ge_{30}$ blend produces a two-phase mixture of the bcc phase and the β-phase as a steady state product (Fig. 3). The bcc phase is similar to that observed as a product of MA of the $Fe_{75}Ge_{25}$ composition and it undergoes the same changes during annealing as the latter composition. For the $Fe_{65}Ge_{35}$ and $Fe_{60}Ge_{40}$ compositions, a single β-phase was observed.

The β-phase is stable at low and high temperatures and melts congruently. So it is expected as a product in both models. However, the models differ as to the second phase observed on MA of powders of the $Fe_{70}Ge_{30}$ composition in the same manner as in the case of the $Fe_{75}Ge_{25}$ composition.

3.3. Composition corresponding to χ-Fe_6Ge_5

The χ-Fe_6Ge_5 is a phase stable at low temperatures. This composition is interesting from the viewpoint of model discrimination, as the predictions of the models differ substantially. χ-Fe_6Ge_5 is expected as a result of MA by the model of solid-state diffusion enhancement, but it must decompose if the phases are formed during cooling of the melted regions.

Indeed, no trace of χ-Fe_6Ge_5 was detected in the steady state products of MA of elemental blends with Fe contents larger than 45at%. Milling of the single χ-phase leads to decomposition, the product consists of a mixture of the β-phase and the cubic FeGe (Fig. 4).
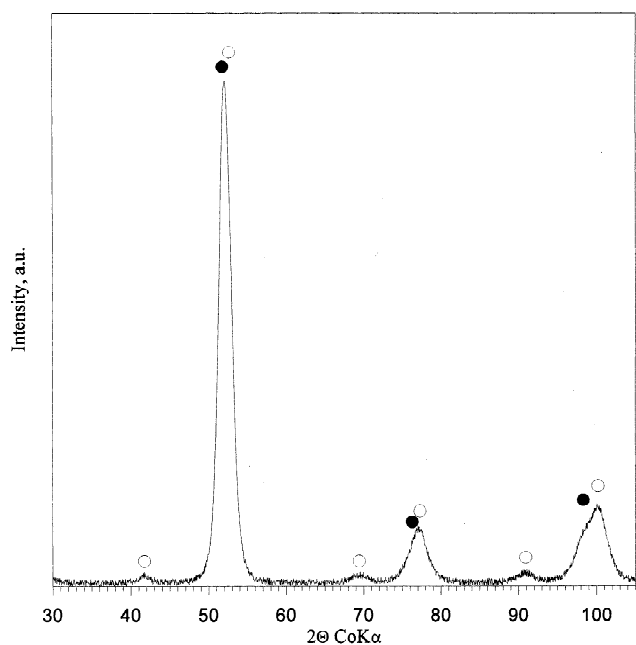

Fig. 3. XRD pattern for mechanical alloy $Fe_{70}Ge_{30}$: (●) α-phase, (○) β-phase.
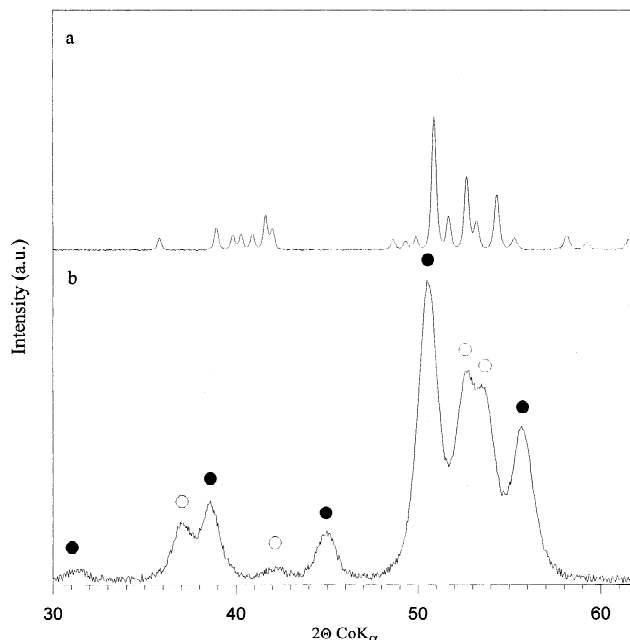

Fig. 4. XRD patterns for Fe_6Ge_5 intermetallic: (a) before milling, (b) after milling. Reflection (○) of β-phase, (●) of FeGe (B20).

3.4. Composition $Fe_{50}Ge_{50}$

An elemental blend, low-temperature (cubic B20) FeGe and high-temperature (hexadecimal B35) FeGe were used as initial states. In all cases the product of MA consisted of cubic FeGe only. This fact seems to be in contradiction with the model of local melting, as cubic FeGe should decompose at high temperature, hence cannot form during cooling of the melt. Nevertheless, this result also may be brought into accordance with the model of local melting. Indeed, a high local temperature results from plastic deformation, which in turn requires high local stress. The stress observed in materials during MA is of the order of 1 GPa and may cause transformations of solids in high pressure polymorphs [10]. Hence, the conditions of MA favor high-pressure modifications. Fig. 8 shows the density of the intermediate phases in the Fe–Ge system. The cubic modification of FeGe (B20) has the largest density of all phases in the system. Due to its high density, this phase is expected to be more preferable under high-pressure observed during MA.

3.5. Ge-rich compositions

Two intermediate phases exist in this region, $FeGe_2$ and Fe_2Ge_3 [9]. $FeGe_2$ melts congruently so it is expected to be a product of MA in the model of local melting. However, this compound is stable at high temperatures, hence a low-temperature process would produce a mixture of Fe_2Ge_3 with either Ge or FeGe, depending on composition. MA of $Fe_{33}Ge_{67}$ blends and mechanical milling of $FeGe_2$ compound lead to the same steady state. The XRD pattern of the as milled sample shown in Fig. 5a
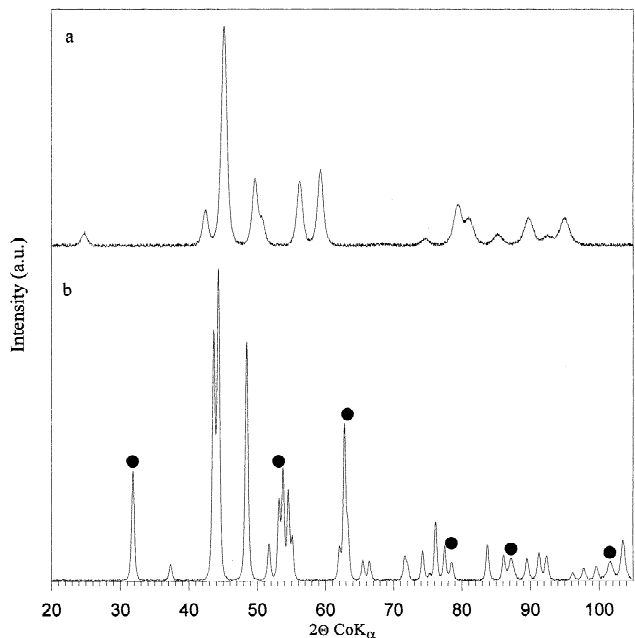
Fig. 5. XRD patterns of $Fe_{33}Ge_{67}$ mechanical alloy: (a) steady state after milling, (b) after milling and annealing at 450 °C for 1 h. (●) Reflections of Ge.

Fig. 7. XRD patterns of Fe_2Ge_3 intermetallic: (a) before milling, (b) after 6 min milling, (c) after 40 min milling. Reflections (○) of FeGe (B20) phase, (◆) of $FeGe_2$ phase.

contains only broadened reflections of $FeGe_2$ (C16). The DSC (Fig. 6) heating trace of this sample reveals an exothermic effect at temperatures between 200 and 300 °C and two endothermic peaks above 530 °C. XRD patterns of the samples annealed at temperatures (450 °C) between the exothermic effect and the low-temperature endothermic effect contain reflections from germanium and from the Fe_2Ge_3-phase [9] (Fig. 5b). In Ref. [9] it was shown that
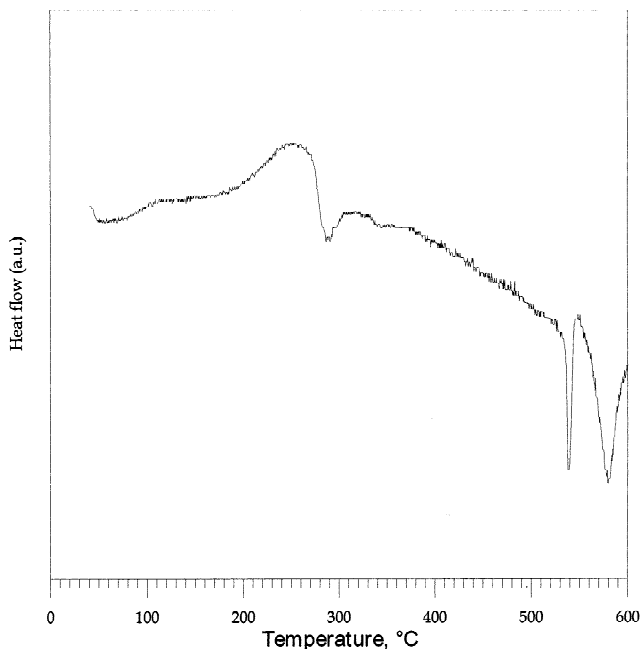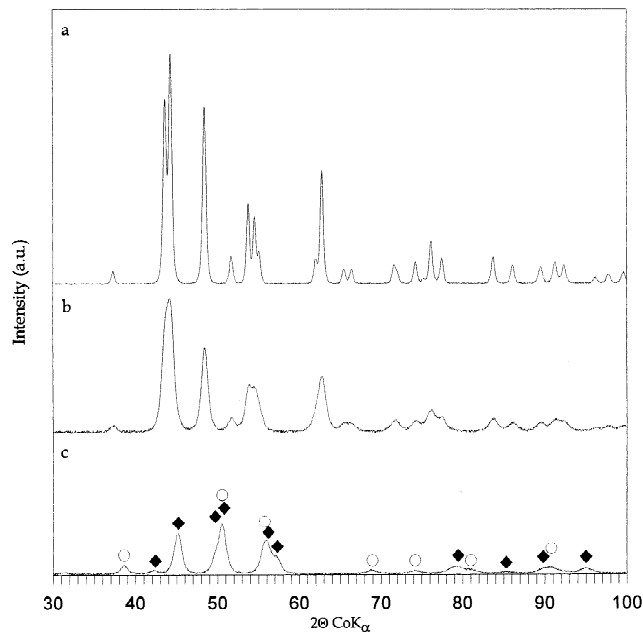
reflections from the Fe_2Ge_3-phase may be satisfactorily indexed, if this compound has a structure type of Ru_2Sn_3 with lattice parameters $a = 5.59$ Å, $c = 8.92$ Å. The first endothermic effect corresponds to the eutectoid transformation, when $FeGe_2$ begins to form. The XRD patterns of the samples annealed at temperatures between the endothermic effects reveals reflections of both the Fe_2Ge_3 and $FeGe_2$ phase, besides peaks from Ge. The second endothermic effect corresponds to the peritectoid transformation, in which Fe_2Ge_3 is completely decomposed.

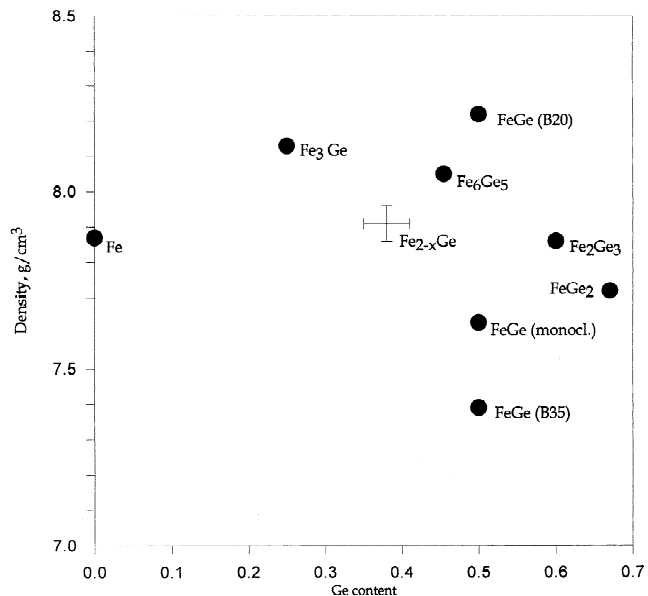Fig. 6. DSC trace for the $Fe_{33}Ge_{67}$ mechanical alloy.

Fig. 8. Density of phases in Fe–Ge system.

Fe_2Ge_3 is a low-temperature polymorph, according to the model of local melting it must decompose during grinding. On the contrary if MA were diffusion enhanced, Fe_2Ge_3 would be the preferred product. The steady state of mechanically alloyed $Fe_{40}Ge_{60}$ as well as that of mechanically ground Fe_2Ge_3 represents a mixture of $FeGe_2$ and the cubic modification of FeGe (Fig. 7). Hence Fe_2Ge_3 is unstable during mechanical treatment, the model of local melting again leading to a more realistic prediction.

4. Conclusion

(1) MA and mechanical milling in the Fe–Ge system leads to the formation of compounds melting congruently (β-$FeGe_{2-x}$ and $FeGe_2$) and to high-density phases (cubic FeGe).

(2) Incongruently melting Fe_6Ge_5 decomposes during MA into a mixture of β-$FeGe_{2-x}$ and cubic FeGe.

(3) Incongruently melting Fe_2Ge_3 decomposes during MA into a mixture of $FeGe_2$ and cubic FeGe.

(4) The formation of the incongruently melting FeGe (B20) phase as a steady state product can be accounted for by its high density and hence stability at high pressure.

(5) The composition of steady-state products of MA in the Fe–Ge system is in good accordance with the model of local melting.

References

[1] C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1.
[2] C. Suryanarayana, E. Ivanov, V.V. Boldyrev, Mater. Sci. Eng. A304 (2001) 151.
[3] A.E. Emakov, Y.Y. Yurchicov, V.A. Barinov, Phys. Met. Metall. 52 (1981) 50.
[4] P.A. Thiessen, Grundlagen der Tribochemie. Abh. Dtsch, Akad. Wiss., K1. Chem., Geol. u. Biol., No. 1 (1966) S.16.
[5] C.C. Koch, Int. J. Mechanochem. Mech. Alloying 1 (1994) 56.
[6] K.B. Gerasimov, A.A. Gusev, E.Y. Ivanov, V.V. Boldyrev, J. Mater. Sci. 26 (1991) 2495.
[7] K.B. Gerasimov, S.V. Pavlov, J. Alloys Comp. 242 (1996) 136.
[8] C. Bansal, Z.Q. Gao, L.B. Hong, B. Fultz, J. Appl. Phys. 76 (1994) 5961.
[9] K.B. Gerasimov, S.V. Pavlov, Intermetallics 8 (2000) 451.
[10] F. Dachille, R. Roy, Nature 186 (1960) 39.