JOURNAL OF MATERIALS SCIENCE 39 (2004) 5407–5410

Mechanochemical synthesis of $B8_2$ phases by ball-milling of $Fe_{60-x}Co_xGe_{40}$ mixtures

L. M. KUBALOVA*
K. L. Khetagurov North-Ossetian State University, Vladikavkaz, Russia
E-mail: kubal@front.ru

V. I. FADEEVA, I. A. SVIRIDOV, A. YE. BOGDANOV
M. V. Lomonosov Moscow State University, Moscow, Russia

Powders of Fe, Co and Ge blended in mixtures of $Fe_{60}Ge_{40}$, $Co_{60}Ge_{40}$, $Fe_{30}Co_{30}Ge_{40}$ (at.%) were synthesized into alloys by milling in a high energy ball-mill. Only β-phases with hexagonal structure $B8_2$ are formed in all alloys after 2 h of mechanical alloying (MA). In $Fe_{60}Ge_{40}$ and $Fe_{30}Co_{30}Ge_{40}$ chemical interaction occurred with simultaneous formation of β-Fe_5Ge_3 and $FeGe_2$. In the system of Fe-Ge the $FeGe_2$ phase is characterized by the highest negative enthalpy of formation in comparison with other phases, therefore it is preferably formed at the initial stage of MA. In the $Co_{60}Ge_{40}$ alloy the β-Co_5Ge_3-phase is formed without intermediate reaction products. The obtained β-phases have a nanocrystalline structure (13–18 nm) and are characterized by considerable local chemical heterogeneity.

Structural transformations during heating to 720°C of metastable β-Fe_5Ge_3 result in a stable $B8_2$ phase and consist of micro deformation relaxation and elimination of chemical heterogeneity. The heating of chemically heterogeneous β-Co_5Ge_3 results in its stratification and formation of metastable Co_2Ge with orthorhombic structure. At $T \geq$ 630°C, Co_2Ge redissolves in hexagonal β-Co_5Ge_3 and after heating to 720°C the β-phase becomes chemically homogeneous. © *2004 Kluwer Academic Publishers*

1. Introduction
The obtaining and investigation of mechanosynthesized alloys on the basis of Fe, Co, Ni, with sp-elements, such as Al and Si, are widely represented in the publications of recent years. The studies of alloys in the Fe-Ge and Co-Ge systems obtained by mechanical alloying (MA) are not so numerous [1–6].

In the conditions of dynamic deformation by ball-milling, the solid-state interaction between the mixture components takes place at low temperatures close to room temperature. The phases of various composition may be formed at early stages of milling, therefore, to interpret the phase composition of such powders is rather a problem. Besides, the number and structure of phases marked in the equilibrium diagrams of Fe-Ge and Co-Ge, are different in published variants of diagrams. Nevertheless, in both systems Fe-Ge and Co-Ge there are β-phases denoted as Fe_5Ge_3 and Co_5Ge_3 characterized by wide homogeneity regions [7]. These phases melt congruently at high temperature and have a hexagonal lattice of $B8_2$ (the structural type of Ni_2In). The components ratio in $B8_2$ lattice for the homogeneity region of β-phases is varied, but at the points of congruent melting it is β-$Fe_{1.7}Ge$ and β-$Co_{1.67}Ge$. In the Co-Ge system β-phase has a low-temperature polymorphous modification of a Co_5Ge_3, though the transition temperatures in the equilibrium diagram are marked conventionally and the structure of this phase has not been established.

This work includes mechanochemical synthesis of $Fe_{60-x}Co_xGe_{40}$ ($x = 0$–60) alloys by high energy ball-milling of the Fe, Co and Ge mixtures, the study of the structure of obtained alloys and of the structural transformations in mechanically alloyed phases during heating.

2. Experimental procedure
The starting materials were high-purity (99.98%) powders of Fe, Co and Ge from which the mixtures of the following compositions were made: $Fe_{60}Ge_{40}$, $Co_{60}Ge_{40}$ and $Fe_{30}Co_{30}Ge_{40}$ (at.%). The milling of the mixtures weighing 9 g was conducted in the water-cooled ball planetary mill with the use of protective argon atmosphere. The drum and the balls were made of hardened steel, the balls mass to the powder mass ratio was 6:1. The energy intensity of ball-milling was 10 W/g according to the calculations by the method described in [8], which takes into account the amplitude of the drum rotation and the mass of loaded powder.

*Author to whom all correspondence should be addressed.

The products of ball-milling were studied by X-ray diffraction analysis (DRON-4, monochromatic $Co_{K\alpha}$-radiation), differential-scanning calorimetry (Perkin-Elmer DSC-7), scanning electron microscopy (Camebax-Microbeam). The X-ray diffraction (XRD) analysis included phase analyses, the measurement of lattice parameters of hexagonal phase ($\Delta a = \pm 0.0002$ nm, $\Delta c = \pm 0.0001$ nm), the calculation of the coherent domain size ($\Delta D = \pm 2$–5 nm) and of the value of the average quadratic microdeformations of the crystalline lattice (the error of about 15%). The general and local chemical composition of powders after the final stage of milling was determined using LINK-860 detector and the program of quantative analysis ZAF-4. The error of the determination of element content was (mass%): ±0.30–0.45 for Fe, ±0.36–0.42 for Co, and ±0.43–0.71 for Ge.

3. Results and discussions

The sequence of phase composition variations in powder mixtures of $Fe_{60}Ge_{40}$ and $Co_{60}Ge_{40}$ at different milling time is represented in Figs 1 and 2. It is seen that in the $Fe_{60}Ge_{40}$ mixture mechanochemical reaction between Fe and Ge begins with the formation of $FeGe_2$ phase characterized by the highest negative enthalpy of formation ($\Delta_f H_0 = -18$ kJ/mol [9]) in comparison with other phases of the Fe-Ge system. However, already after an 1 h of MA the lines of β-Fe_5Ge_3 appear in the diffraction pattern and the further process results in the formation of an one-phase alloy with β-phase. After 2 h of MA, only very broad lines of β-phase related to the hexagonal $B8_2$ structure are shown in the diffraction pattern. The lattice parameters of the formed β-Fe_5Ge_3 calculated from the XRD data represent average values because the width of difraction peaks is determined not only by the small coherent domain size and the lattice microdeformation, but also by the apparent concentrational heterogeneity of the formed β-phase. The widening of homogeneity regions of phases is often observed at mechanochemical processes, e.g., in the Fe-Ge system [10]. It allows us to suppose that the formed nanocrystallites have different chemical compositions corresponding to any concentration of components in the interval of equilibrium region of β-phase and also at broadening β-phase region by MA.

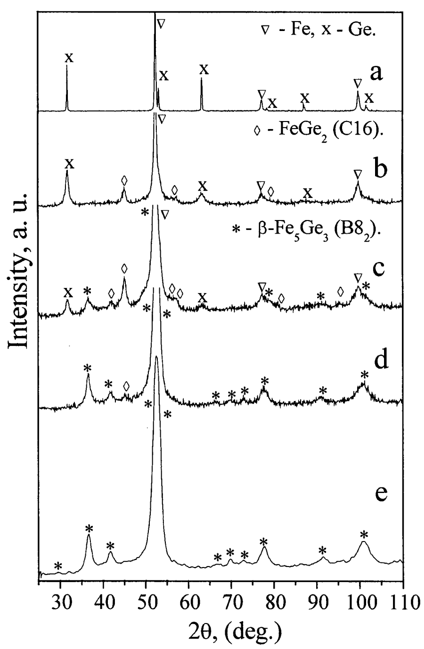

Figure 1 XRD patterns of $Fe_{60}Ge_{40}$ alloys after different time of MA: initial powder mixture (a), 0.5 h (b), 1 h (c), 1.5 h (d), 2 h (e).

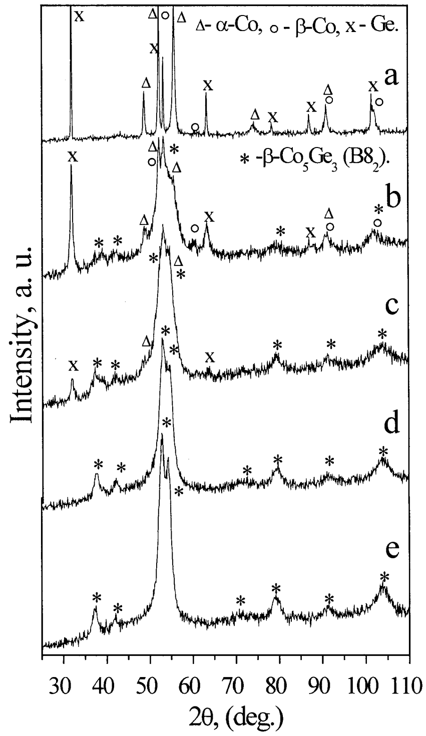

Figure 2 XRD patterns of $Co_{60}Ge_{40}$ alloys after different time of MA: initial powder mixture (a), 0.5 h (b), 1 h (c), 1.5 h (d), 2 h (e).

The solid-phase interaction between Co and Ge in the $Co_{60}Ge_{40}$ mixture at different stages results in the formation of β-Co_5Ge_3 only. The diffraction pattern taken already after 1.5 h of MA shows only the lines of hexagonal β-phase. Mechanochemical reaction in the mixture of three components of Fe, Co and Ge ($Fe_{30}Co_{30}Ge_{40}$) takes place with the competeting interaction of Fe and Ge separately, and Co and Ge separately, too. At the intermediate stages of milling, the $FeGe_2$ (C16) formation is observed and simultaneously the β-phase ($B8_2$) is formed which is likely to contain more Co than Fe. The solid-state reaction between $FeGe_2$ and β-$(Co, Fe)_5Ge_3$ is completed after 2 h of MA according to the X-ray diffraction analysis.

Table I presents the results of the X-ray diffraction and chemical analysis of the synthesized powders of β-phase. The content of the component of the final product of MA is close to the nominal composition of the initial mixture, however, it has been noted that the content of Fe increases from 0.90 to 1.30 at.%, that is connected with grinding out of the steel drum and balls. The local chemical analysis using 0.5 μm microzond has shown a considerable difference in the content of elements. Thus, the amount of Ge in the synthesized phase of β-Co_5Ge_3 in different points varied from 34.1 to 40.2 at.% with the corresponding variation of the Co-content. Nevertheless, the Co(Fe)/Ge component ratio

TABLE I Chemical composition and structural parameters of mechanically alloyed $B8_2$ phases

Alloy and formed phase after 2 h of MA	Chemical composition at.%	Lattice parameters a (nm)	Lattice parameters c (nm)	Substructure D (nm)	Substructure $\langle\varepsilon 2\rangle 1/2\%$
$Fe_{60}Ge_{40}$ β-$Fe_5Ge_3(B8_2)$	Fe–61.29 Ge–38.71	0.3992	0.5014	18	0.96
$Co_{60}Ge_{40}$ β-$Co_5Ge_3(B8_2)$	Fe–1.39 Co–60.50 Ge–38.11	0.3913	0.4997	13	1.07
$Fe_{30}Co_{30}Ge_{40}$ β-$(Fe,Co)_5Ge_3(B8_2)$	Fe–31.03 Co–60.51 Ge–39.46	0.3952	0.5001	14	0.77

testifies to the fact that the crystallite composition of the obtained phase is within the β-phase homogeneity region or lies on the phase boundary. Analogous heterogeneity of β-phase chemical composition is observed in the alloy of $Fe_{30}Co_{30}Ge_{40}$, whereas the local heterogeneity of $Fe_{60}Ge_{40}$ turned out to be minimal. This fact shows that the obtained alloys are metastable and for their homogenization it is necessary to develop the diffusion process.

Fig. 3 shows the DSC curves of the $Fe_{60}Ge_{40}$ and $Co_{60}Ge_{40}$ alloys after 2 h of MA. On the subtracted curves of both alloys there is an low temperature exothermal peak (130–270°C), often observed in alloys obtained by the MA method. The XRD analysis showed that the heating of both alloys in this temperature interval does not produce any essential changes of the β-phases structure with the exception of the relaxation of lattice microdeformation. Thus, the microdeformation $\langle\varepsilon 2\rangle\frac{1}{2}$ decreased from 0.96 to 0.50% for β-Fe_5Ge_3 phase after heating up to 320°C, and from 1.07 to 0.86% after heating β-Co_5Ge_3 phase up to 250°C. At the same time the domain size as well as lattice parameters of both phases did not change. On DSC curve of β-Fe_5Ge_3 there is a second more noticable exothermal peak in the range of 570–700°C, but it is caused by partial oxidation of Fe_5Ge_3 and FeO formation. Impurity with oxygen is a result of the used technology connected with the opening of vial after a certain milling times. The amount of oxygen in β-Fe_5Ge_3 was about 2 mass%, and during heating the dissolved oxygen formed a FeO phase. The temperature of the beginning of the second exothermal peak is 570°C (Fig. 3a) which according to the equilibrium diagram of Fe-O [7] corresponds to the temperature of FeO formation. A single very weak (200) line with intensity 100 is observed in the diffraction pattern of $Fe_{60}Ge_{40}$ alloy heated in the calorimeter to 720°C. After heating to 720°C the lattice parameters of β-Fe_5Ge_3 are $a = 0.3977$ nm, $c = 0.4998$ nm that corresponds to the table values for $Fe_{1.7}Ge$ ($B8_2$). The lattice microdeformation is very small $\langle\varepsilon 2\rangle\frac{1}{2} \approx 0.12\%$, the domain size increased to 45 nm, however this value corresponds to nanosize scale.

The subtracted DSC curve of $Co_{60}Ge_{40}$ alloy has a more complicated character (Fig. 3b). An endothermal peak in the 270–480°C range is observed after the low-temperature relaxation exoeffect. In the diffraction

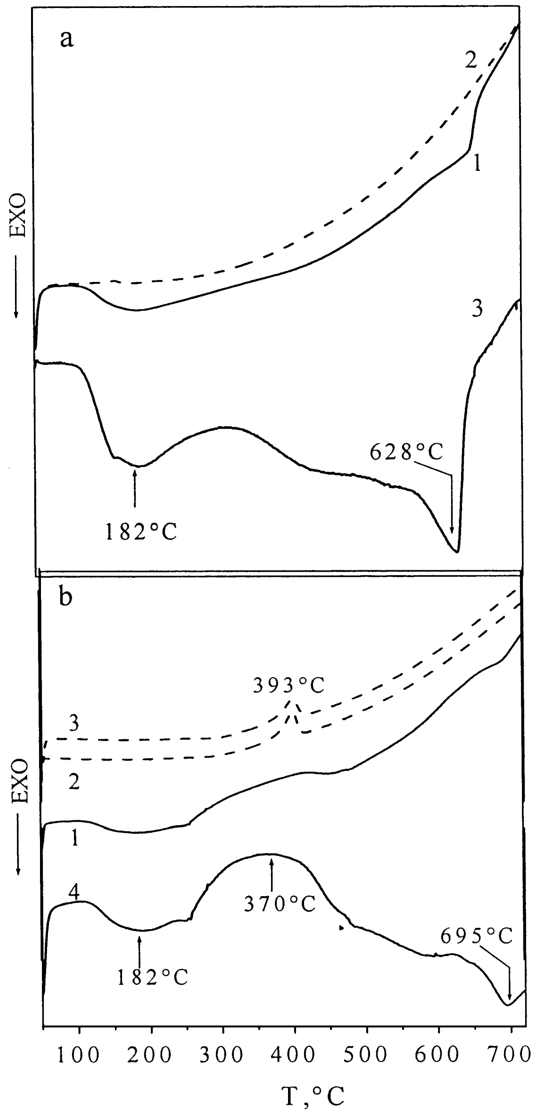

Figure 3 DSC curves of synthesized β-Fe_5Ge_3 (a) and β-Co_5Ge_3 (b) phases: in (a) 1,2–first and second heating, 3–subtracted curve; in (b) 1,2,3–first, second and third heating, 4–subtracted curve (heating rate: 20 K/min).

pattern of the samples annealed up to 480, 500 and 610°C there are weak peaks of the second phase that may be interpreted as the intensive lines of Co_2Ge phase with orthorhombic structure.

Fig. 4 presents the SEM images of β-Co_5Ge_3 after 2 h of MA and subsequent heating to 480°C. The alloy after milling consists of homogeneous particles of monophase product of MA (Fig. 2a). The chemical analysis of β-Co_5Ge_3 showed the presence of local composition close to Co_2Ge. During the heating of such metastable alloy it was possible to form a two-phase state consisting of Co_2Ge and Co_5Ge_3. The formation of Co_2Ge at heating is a reversed eutectoid reaction of $Co \leftrightarrow Co_2Ge \leftrightarrow Co_5Ge_3$, in such a case the birth and the growth of orthorhombic Co_2Ge phase must be accompanied by endothermal effect. A heteromorphous structure is seen (Fig. 4b) in the image of the $Co_{60}Ge_{40}$ sample after 2 h of MA and following heating in calorimeter to 480°C. According to the data of the local chemical analysis large crystals have a composition with the ratio of (Co, Fe)/Ge $\approx$ 1.5–1.6 and they can be related

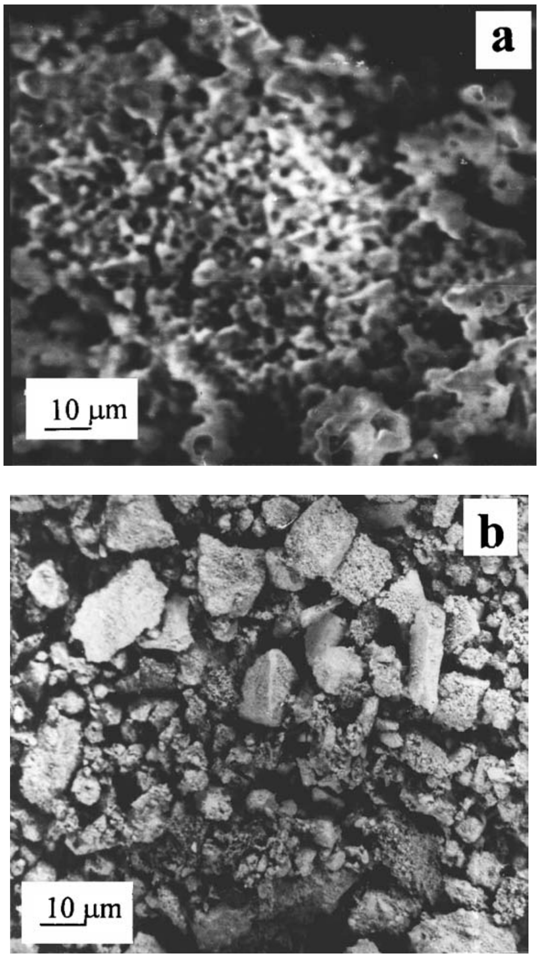

Figure 4 SEM image of β-Co_5Ge_3 after 2 h of MA (a) and subsequent heating up to 480°C (b).

to the β-phase whereas fine-disperse scale-like secretions on the surface of these crystals have a composition close to the Co_2Ge phase because of the ratio of (Co, Fe)/Ge ≈ 1.85–1.95.

At the temperature ≥630°C the β-phase region begins to widen. Therefore, the Co_2Ge metastable phase dissolves again in the hexagonal lattice of $B8_2$. This process is related to the exoeffect with $T_{max} = 695$°C (Fig. 3b). After being heated to 720°C the alloy was completely transformed into a stable state and contained only one β-Co_5Ge_3-phase with parameters $a = 0.3880$ nm, $c = 0.4995$ nm. In an elementary cell of β-Co_5Ge_3 obtained by MA the ratio of lattice parameters is $c/a = 1.252$, whereas after annealing in the calorimeter and, also, after isothermal annealing at 800°C for 1 h the ratio of the lattice parameters is $c/a = 1.287$ which corresponds to the most dense packing in the equilibrium β-phase of the β-$Co_{1,67}Ge$ composition [7].

An λ-like endothermal peak at $T = 393 \pm 1$°C (at the heating rate of 10 and 20 K/min) is observed in DSC curves of the second and any other subsequent heatings. It may be supposed that this peak is connected with changes in the electronic structure of β-Co_5Ge_3. The measurement of temperature dependence of electroresistence of Co_5Ge_3 made in [11] showed the presence of the peak at $T = 385$°C on the curve, that indicates a sharp change of electronic state of the crystalline lattice.

4. Summary

1. Monophase alloys with hexagonal structure $B8_2$ were obtained after 2 h of high-energy ball milling of elementary powder component mixtures corresponding to compositions $Fe_{60}Ge_{40}$, $Co_{60}Ge_{40}$ and $Fe_{30}Co_{30}Ge_{40}$.

2. Mechanochemical reactions in each of the compositions took place in a different way. In the mixtures containing Fe at the intermediate stages of MA, two phases—$FeGe_2$ and β-Fe_5Ge_3 were formed and only at the final stage alloys became completely monophase. In the mixture of $Co_{60}Ge_{40}$, the formation of β-Co_5Ge_3 took place directly through chemical reaction of components.

3. The formed β-phases were characterized by nanosize (13–18 nm) and by considerable chemical heterogeneity. After being heated to 720°C the mechanically alloyed alloys transformed into a stable state preserving the $B8_2$ structure.

Acknowledgments

This research was supported by Russian Foundation for Basic Researches (project no. 03-02-16267).

References

1. F. ALBERTINI, A. PAOLUZI, L. PARETI, L. NASI, G. SALVATI and G. GAESTANI, *Mater. Sci. Forum* **195** (1995) 167.
2. Q. Z. CHEN, A. H. NGAN and B. J. DUGGAN, *J. Mater. Sci.* **33** (1998) 5405.
3. A. F. CABRERA, F. H. SÁNCHEZ and L. MENDOZA, *J. Metast. Nanocryst. Mater.* **2–6** (1999) 85.
4. K. V. GERASIMOV and S. V. PAVLOV, *Intermetallics* **8** (2000) 451.
5. E. P. ELSUKOV, G. A. DOROFEEV, A. L. ULYANOV and A. V. ZAGAINOV, *Fizika Metallov i Metallovedenie* **95** (2003) 1 (in Russian).
6. V. I. FADEEVA, I. A. SVIRIDOV and A. YE. BOGDANOV, *Izv. Acad. Nauk. Ser. Phys.* **67** (2003) 969 (in Russian).
7. P. VILLARS (ed.), Pauling File Binaries Edition, Version 1.0, Release 2002/1.
8. E. V. SHELEKHOV and T. A. SVIRIDOVA, *Materialovedenie* **10** (1999) 13 (in Russian).
9. J. S. LIMA, V. H. F. SANTOS, T. A. GRANDI, P. C. T. D'AJELLO and A. DMITRIEV, *Phys. Rev.* B. **62** (2000) 8871.
10. P. K. PANDAY and K. SCHUBERT, *J. Less-Comm. Met.* **18** (1969) 175.
11. P. V. GELD, E. S. LEVIN, V. L. ZAGRYAZHSKY and V. N. ZAMARAEV, *Inorganic Mater.* **15** (1979) 21 (in Russian).

Received 11 September 2003
and accepted 27 February 2004