STRUCTURE AND MAGNETIC PROPERTIES OF SINTERED ALLOYS BASED ON MECHANICALLY ACTIVATED Fe-Ga POWDER

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Abstract

Results of the investigation into the effect of preliminary mechanical treatment of Fe-20%Ga powders on the structure of alloys obtained under high pressure and temperature are presented. It is demonstrated that the alloys mainly inherit the phase composition of powder mechanocomposites and are nano-structured. Magnetizing curves of the alloys within the temperature range 4-300°K are recorded.

Introduction

Mechanochemical method is one of relatively simple and efficient technique for metal grinding, activation and also for synthesis of chemical compounds [1]. Powders obtained under the conditions of intense mechanical treatment are characterized by the formation of various metastable and stable nanocrystalline and/or amorphous phases including mechanocomposites, intermetallic compounds and supersaturated solid solutions [2]. The structural and phase state of mechanocomposites is controlled by intensity and duration of milling, which allows one to obtain powders with required properties. One of the most important technological problems is the possibility to prepare functional materials starting with mechanically activated powders, a structural state of which provides the high level of performance characteristics [2]. In this connection, the most promising method to prepare nanostructured bulk materials is high pressure assisted sintering which allows one to decrease the temperature of alloy formation, slow down recrystallization processes and conserve the nanostructure in the resulting material [3].

At present, a growing attention to investigations of (Fe₁₋ₓGaₓ) alloys is observed due to their high mechanical and magnetic properties, including a huge magnetostriction effect [4-5], which makes these materials promising for to use in magnetoelastic elements of sensors, magnetic-field transducers, vibrogenerators. Both structural characteristics and preparation methods of such materials are subjects for intense investigations [6, 7].

The previous studies [8] of the evolution of structural phase transformations during mechanical activation (MA) in the system Fe-20% mass Ga demonstrated the formation of the composite structure of powders at all the stages of MA. The phase sequence for powders in the course of activation is described by the following reactions:

\[
\text{Fe} + \text{Ga} \rightarrow \text{Fe} + \text{FeGa}_3 \rightarrow \text{Fe} + \text{Fe(Ga)}_{\text{disord.}} \rightarrow \text{Fe} + \text{Fe(Ga)}_{\text{disord.}} + \text{Fe}_3\text{Ga}(D0_1 \text{ and L1}_2).
\]
The goal of our investigation was to study the effect of the time of mechanical treatment of Fe-Ga system powders on the structure and magnetic properties of alloys obtained from these powders through sintering under high pressure and temperature.

**Experimental procedure**

The Fe-20%Ga powders used as initial substances for mechanical activation were carbonyl-grade iron PZhK and gallium according to the State Standard (GOST) 12797–77. The AGO-2 high-energy planetary ball mill with water cooling and argon atmosphere protection was used for samples treatment at different time intervals. Powder sintering under high pressure and temperature was carried out in a press set-up DO–138 B under the pressing force of 630 t in a high-pressure apparatus «anvil with well» at a pressure of 2.5 GPa and temperature 973°K. Isothermal exposure at this pressure and temperature was 15 s. A container made of lithographic stone served as a pressure-transferring medium; a tubular graphite heater with the material under investigation was placed inside. To estimate the pressure in the synthesis chamber, we used the method of calibration at room temperature, based on the comparison between press force and the pressure of polymorphous transformation in a reference substance; Bi was used in our experiments. Temperature control was performed with a chromel-alumel thermocouple. To control the required sintering parameters (duration and power of heating, as well as loading power), we used a controller developed on the basis of a PC-compatible workstation. The diameter of cylindrical samples under investigation after sintering was 5 mm, and their height was 3 mm.

The X-ray diffraction measurements of the resulting alloys were carried out with the help of the D8 Advance diffractometer (Germany) using the characteristic radiation of the copper anode of X-ray tube CuKα1 (λ = 1,5406 Å) in Bragg-Brentano's configuration Θ-2Θ. Scanning was performed at room temperature over points within the angle range 2Θ from 20 to 120° with a step of 0.05° and the time of X-ray quanta integration in point 3 s. The phase analysis of the samples was carried out with the help of EVA software using the database of X-ray standards ICDD PDF2. Calculation and refining of the profile and structural parameters were carried out through the least squares procedure with the full-profile analysis of diffraction patterns in TOPAS software using Pawley's iteration procedure. Investigation of the microstructural characteristics (crystallite size <L> and micro-strain) was carried out using the double Voight method [9, 10] in which the profiles of diffraction on crystallite size and on micro-distortions are described in the generalized form with Voight's functions. To separate the contributions into the peak broadening from L and microstrains, the Lorentz function and the Gauss function were applied respectively. The morphology of alloys under investigation was studied by means of atomic force microscopy (AFM) with the NT-206 instrument. The qualitative estimation of porosity was made in the image analyzing software Surface View on the basis of the color contrast. The structure of the samples was examined using the optical microscope Mikro 200 and a high-resolution scanning electron microscope (SEM) MIRA\TESCAN with an attachment for micro X-ray spectral analysis. The diameter of the electron probe was 5.2 nm, the excitation region was 100 nm. Magnetic characteristics were examined with the help of vibration magnetometer of Cryogenic company (England). Magnetization was determined in the magnetic field up to 10 tesla within the temperature range 4–300 K.
Experimental results and discussion

Sintering powder particles after MA have mainly scaly and splintered shapes: the average size of agglomerates is 1.5-2 \( \mu \text{m} \) and does not change remarkably during activation. However, for powders activated mechanically for rather long time (90-150 min), the average size \( \langle L \rangle \) of \( \alpha \)-iron crystallites decreases substantially (from 35 to 8 nm), which was conserved at all the stages of mechanical alloying. In this situation, after MA for 120 min we observed local ordering of the solid solution of gallium in iron according to the Fe\(_3\)Ga type (\( D0_3 \) and \( L1_2 \)) [8]. An increase in activation time to 150 min causes a substantial formation of planar defects. Powders used for hot pressing had the following phase and quantitative composition:

- MA for 2 min – Fe(76%) + Fe\(_{\text{disordered}}\) (21%) + Fe\(_3\)Ga\(_3\) (3%),
- MA for 12 min – Fe(68%) + Fe\(_{\text{disord.}}\) (25%) + Fe\(_3\)Ga\(_3\) (7%),
- MA for 150 min – Fe(15%) + Fe(Ga)\(_{\text{disord.}}\) (20%) + Fe\(_3\)Ga\(_2\)(\( D0_3 \) + \( L1_2 \)) (65%).

The diffraction patterns of alloys sintered at high pressure and temperature in comparison with the initial powders after MA for different time intervals are presented in Figure 1.
Figure 1 – Diffraction patterns of the compact material (2) based on the powder precursor Fe-20%Ga (1) activated for: a – 2 min; b – 12 min; c – 150 min. Results of the X-ray structural analysis of initial powders and sintered materials based on them are shown in Table 1.

Table 1 – Microstructural parameters of (Fe) after MA and sintering under conditions of high pressure and temperature.

<table>
<thead>
<tr>
<th>Time of MA, min</th>
<th>(a_{(Fe)}), nm</th>
<th>(&lt;L&gt;), nm</th>
<th>(\varepsilon_g), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>powder</td>
<td>alloy</td>
<td>powder</td>
</tr>
<tr>
<td>2</td>
<td>2,867 (1)</td>
<td>2,867 (0)</td>
<td>30</td>
</tr>
<tr>
<td>12</td>
<td>2,871 (3)</td>
<td>2,878 (2)</td>
<td>20</td>
</tr>
<tr>
<td>150</td>
<td>2,905 (6)</td>
<td>2,918 (2)</td>
<td>5</td>
</tr>
</tbody>
</table>

Calculation of microstructural parameters was carried out taking into account the phase composition and the data of Moessbauer spectroscopy [8]. After sintering the mechanically activated Fe-20%Ga powder at high pressure and temperature, we observed a decrease in crystallite size in the resulting alloys in comparison with mechanocomposites, which is accompanied by the relaxation of internal strain. According to the data of X-ray phase analysis, no substantial changes occur in the phase composition, that is, the phase composition of precursors is conserved in the alloys. The microstructure of sintered samples is shown in Figure 1b. The grained structure is formed in Fe-20%massGa mechanocomposites during sintering. In the alloy based on powders after 2 min of MA, the grains and pores are close to round shaped, which is characteristic for liquid-phase sintering, with the dissolution of the solid phase in the liquid one (Figure 2 (a)).
The average size of iron grains was 3-8 μm. Dispersed particles of the intermetallic compound FeGa₃, with a size of ~500 nm, are located along the boundaries of coarse iron grains. These particles are clearly observed with the AFM (Figure 3).

**Figure 2** – Microstructure of compact materials based on Fe-20%Ga powders after MA for: a – 2 min; b – 12 min; c - 150 min.

**Figure 3** – AFM images of the alloys obtained by sintering the mechanically activated precursors Fe-20%Ga under pressure after MA for 2 min: a – topography, b – lateral contrast.
It may be assumed that gallium or Ga(Fe) is present in disordered layers after MA for 2 min; it is not recorded in X-ray studies but it promotes the formation of the melt during sintering at high pressure and temperature.

After sintering the powder activated mechanically for 12 min, the grain size in the alloy decreases to 1-6 μm. The X-ray phase analysis (Figure 1b) and X-ray spectral analysis (Figure 4) revealed the formation of additional intermediate intermetallide compounds Fe₃Ga₄ and Fe₆Ga₅.

Figure 4 – Microstructure of the alloy based on mechanocomposite after MA for 12 min: a – SEM image and micro X-ray phase analysis, b – AFM image in α-Fe grain.

According to the data of X-ray spectral analysis, the formation of subsurface diffusion layer of gallium in iron with nearly 4 mass % content on the particles of α-iron is observed. So, the phase composition of the alloy based on precursors mechanically activated for 12 min is α-Fe + FeGa₃ + Fe₃Ga₄ + Fe₆Ga₅.

Glide lines are observed in α-Fe grains (Figure 4b), which may be evidence of deformation processes. With an increase in MA time to 12 min, the surface porosity (which is equal to the ratio of pore area of the section to the total area of the section) decreases from 17% (in the case of sintering the powder mechanically activated for 2 min) to 3%, the mean pore size decreases to 1 μm.

Both for mechanocomposites mechanically activated for 2 min and for 12 min, the porosity in alloys has mainly the intergrain character. Sintering, at high pressure and temperature, of powders after MA for 150 min proceeds according to the type of solid-phase reactions. In this case, grained structure with grain size within the ranges 1-3 μm and 8-13 μm is formed. Small grains are arranged as local regions. The grains have polygonal shape and possess developed internal substructure. As micro X-ray structural analysis showed, the concentration of gallium and iron in coarse and small grains is the same (Figure 5).
Figure 5 – Scanning electron microscopic image in back-scattered electrons and AFM image of the grain structure in the alloy based on mechanocomposites after MA for 150 min.

The presence of intragranular porosity is characteristic of the alloys; an increase in the surface porosity up to 8% is observed, with the average pore size about 1.5μm.

The microhardness of compacts obtained under the same conditions is strongly dependent on the structural and phase state of initial mechanically activated Fe+20%Ga powders. For example, the microhardness of the alloy obtained from the mechanocomposite mechanically activated for 2 min is 360 HV$_{200}$. For the alloy based on mechanocomposite that was mechanically activated for 12 min, microhardness increases to 700 HV$_{200}$, while microhardness of the alloy based on powders after MA for 150 min reaches 780 HV$_{200}$. A substantial increase in hardness is likely to be due to the formation of harder phases and to the formation of block-type nanocrystalline substructure.

Investigation of the magnetization of resulting alloys showed that the alloys exhibit ferromagnetic properties within the studied temperature range 4-300 K. The ferromagnetic character of the magnetic properties of alloys is confirmed by the
hysteresis loop with clearly pronounced saturation of magnetization in the fields above 1.0T, 1.5 tesla (Figure 6).

Figure 6 – Magnetization curves of: (a) – alloys based on powders after MA for different time intervals at $T=4\,K$; (b) – alloy based on the precursor after mechanical activation for 150min at different temperatures.

The hysteresis loop of all samples within measured temperature range is characterized by the small coercive force ($H_c$). Specific saturation magnetization of all the alloys decreases by $\sim 7\%$ with an increase in temperature from 4 to 300 K.

Comparing the parameters of hysteresis loops for the samples we may conclude that the time of activation of the initial powder affects also the magnetic characteristics. In particular, one can see (Table 2) that an increase in the time of MA to 12 min causes a decrease in residual magnetization ($M_{\text{resid}}$) of the sample almost without any change of saturation magnetization ($M_{\text{sat}}$) and coercitivity force in the sample. Further increase in the time of MA causes a decrease in magnetization and substantial increase in coercitivity force.

Table 2 – Magnetic parameters of Fe+20%Ga alloys based on powders after MA for different time intervals

<table>
<thead>
<tr>
<th>Time of MA of powder</th>
<th>$H_c$, Oe</th>
<th>$B_{\text{sat}}$, tesla</th>
<th>$M_{\text{resid}}$, A·m$^2$/kg</th>
<th>$M_{\text{sat}}$, A·m$^2$/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 min (4K/300 K)</td>
<td>35</td>
<td>1</td>
<td>2.8</td>
<td>162</td>
</tr>
<tr>
<td>12 min (4K/300 K)</td>
<td>40/50</td>
<td>1/1</td>
<td>1.9/1.8</td>
<td>161/152</td>
</tr>
<tr>
<td>150 min (4 K/300 K)</td>
<td>77/70</td>
<td>1.5/1.5</td>
<td>2.1/1.91</td>
<td>131/120</td>
</tr>
</tbody>
</table>

This behaviour of the magnetic properties of alloys corresponds to the changes in the crystal structure during the formation of alloys. In particular, at the initial stage of MA, the concentration of initial metal iron decreases thus affecting the residual magnetization $M_{\text{resid}}$. a decrease in the size of crystallites and their defectiveness arising during MA start to affect coercive force $H_c$ of the sample. Further substantial increase in the time of MA leads to the expected increase in coercitivity force and decrease in specific magnetization. A decrease in specific saturation magnetization is
connected both with the process of Fe(Ga) phase formation leading to the magnetic dilution of the initial metal iron and with an increase in sample defectness, which affects the regular magnetic order. At the same time, the large amount of defects in the sample and the small size of crystallites cause an increase in coercivity force hindering the movement of domain walls on structural defects and grain boundaries.

Conclusions

The structure of alloys obtained by high-pressure and high-temperature sintering of mechanically activated Fe+20%Ga powders is determined by the time of mechanical action on the powders and by the resulting structural phase state of the mechanocomposites. After MA for a short time, an easy melting gallium phase is likely to be present in the structure of mechanocomposite; the presence of this phase promotes the formation of the melt. Sintering has the liquid-phase character. Sintering of mechanocomposites obtained after MA for 12 min leads to the formation of additional hard intermetallic phases Fe₃Ga₄ and Fe₆Ga₅, which causes an increase in microhardness of the resulting material. High-pressure sintering of mechanocomposites causes a decrease in the size of crystallites. The phase composition of the alloy based on the mechanocomposites of ordered solid solutions obtained after MA for 150 min is conserved. The alloys are magnetically soft within the temperature range 4-300 K. The change of the structure of mechanocomposites during MA of Fe+20%Ga powders affects the magnetic characteristics. An increase in the duration of MA to 150 min causes an increase in the coercive force of the material by a factor of 2, while its residual magnetization remains almost the same.

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References


