IOP Conf. Series: Materials Science and Engineering **347** (2018) 012053 doi:10.1088/1757-899X/347/1/012053

Magnetic properties of powder hard magnetic Fe–27Cr–10Co–0.5Mo and Fe–27Cr–10Co–2Mo alloys

I M Milyaev[1], M I Alymov[1,2], I N Bouryakov[2], V S Yusupov[1] and D M Abashev[3]

[1]Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Leninskii 49, Moscow 119336, Russia
[2]Merzhanov Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Akademika Osipyana 8, Chernogolovka, Moscow Region 142432, Russia
[2]JCS Spetsmagnit, Dmitrovskoe 58, Moscow 127238, Russia

E-mail: imilyaev@mail.ru; yusupov@2000aport.ru; bouriakov@mail.ru

Abstract. Magnetic hysteresis properties of powder hard magnetic Fe–27Cr–10Co alloys with 0.5 and 2.0 wt % molybdenum were studied. For Fe–27Cr–10Co–0.5Mo alloy: B_r = 1.35 T, H_{cB} = 45.6 kA/m and $(BH)_{max}$ = 41 kJ/m^3. For Fe–27Cr–10Co–2Mo alloy: B_r = 1.29 T, H_{cB} = 41 kA/m, $(BH)_{max}$ = 34.8 kJ/m^3. It was shown that an alloying with 2 wt. % molybdenum of the low-cobalt powder hard magnetic Fe–27Cr–10Co alloy unlike high-cobalt hard magnetic FeCrCo alloys did not increase its magnetic hysteresis properties, reduced the camber of a demagnetization curve in a second quadrant.

1. Introduction

The problem of research of economically alloyed and effective hard magnetic materials (HMMs) with the use of new processes of their production is of undoubted interest in the context of the constant growth of raw material resources on the global market and requirements of reducing the labor and energy expenses for greater their competitiveness. Only deformable hard magnetic alloys based on the Fe–Cr–Co system combine high magnetic hysteresis properties with high mechanical (first of all strength) ones. The Russian metallurgical industry has mastered the mass production of sheet and rod from hard magnetic FeCrCo alloys containing a moderate amount of cobalt (15 wt. %). Further development of these alloys was aimed at the study of the alloys both with lower cobalt content with a view to reducing their cost and with its high content for greater magnetic hysteresis properties owing to an increase in the saturation magnetization.

Alloys containing more than 9–10% by weight of cobalt possess rather high values of residual induction B_r (above 1.3 *T*) and maximum energy product $(BH)_{max}$ (> 40 kJ/m^3) at relatively low values of coercive force H_{cB} (40–44 kA/m) [1].

To prepare the low-cobalt FeCrCo alloy with higher values of coercive force, the Fe–27Cr–10Co alloy was alloyed with 0.5 and 2 wt. % molybdenum. Molybdenum was chosen as the additional alloying element according to [2]. In [3, 4], it was shown that an additional alloying with molybdenum of high-cobalt FeCrCo alloys increases the value of H_{cB} to 80 kA/m.

In this work, the samples of the investigated alloys were prepared by powder metallurgy methods, which are cost-effective for manufacturing of permanent magnets.

IOP Conf. Series: Materials Science and Engineering **347** (2018) 012053 doi:10.1088/1757-899X/347/1/012053

2. Experimental

The alloys for the study were obtained by method of powder metallurgy using element powders of metals of industrial purity: carbonyl iron of the VS brand, PHS-1 chrome, PK-1 cobalt, powdered direct-reduction molybdenum with a size of particles less than 40 μm. Homogeneous powder mixtures were obtained in a C2.0 turbulent mixer. The powders were mixed in a glass vessel with capacity of 200 ml for 80 min without intermediate stops. The prepared powder mixes were refined using a Pulverizett-7 mill for 15 min with a rate of 600 rpm. In some cases, we added surfactants (stearin and oleic acids). The mixture was subjected to uniaxial pressing using a KNUTH-130042 manual press in demountable matrixes with a diameter of 13.6 mm under a pressure of 600 MPa. As a result, the cylindrical samples 20 mm in height were obtained. After molding, the samples were sintered in an SShV-1.2.3/25I1 mine vacuum electric furnace in vacuum no worse than 10^{-2} Pa. The heat treatment of the sintered powder samples was carried out in standard muffle furnaces in the container with a diameter of 60 mm, which was filled with metal ballast in order to simulate real operating conditions. The temperature and time were controlled using a TPM251 programmable PID-regulators. The thermomagnetic processing was carried out in a laboratory installation with the armor-clad electromagnet providing magnetic field intensity H = 320 kA/m (> 4000 Oe). Magnetic hysteresis properties were measured using a Permagraph L hysteresisgraph.

The magnetic hysteresis properties of the alloys were evaluated and the heat treatment regimes were optimized both by the method of one-factorial experiment and by the method of design of experiment with plotting central composite 2^4 designs + star points. The choice of the central composite (consecutive) designs applied to the description of almost stationary area, which cannot be described by means of linear approach, was caused by the fact that the preliminary experiments on evaluation of near-zero magnetic properties of the alloys with the use of heat treatment regimes did not show their sharp fluctuations. The chosen designs were rotatable (information contained in the regression equations is distributed uniformly over a sphere on which points of carrying out experiment get out, and the researcher do not know the area of the response surface where the optimum region of interest is located) and randomized (the order of carrying out experiments is defined in a random way).

Based on the existing concept on the mechanism of formation of a high-coercive state in hard magnetic Fe–Cr–Co alloys [5,6], we consider that generally the magnetic hysteresis properties (residual induction of B_r, coercive force H_c and maximum energy product $(BH)_{max}$) depend on the following: (1) tempering temperature of for α-solution; (2) temperature of isothermal thermomagnetic processing (ITMP); (3) time of ITMP; (4) cooling rate $V1$ in the temperature range from temperature of ITMP to 600–580°C; (5) tempering time at 600 (580°C), (6) cooling rate $V2$ in the temperature range of 600 (580)–500°C.

Other factors, such as, for example, a rate of heating to the temperature of ITMP, were stabilized as much as possible. In particular, the tempering of samples of the studied alloys was carried out from 1100°C in water with a holding at this temperature for 15 min; heating of the container to the temperature of ITMP was carried out for 40 min. The processing of experimental results was carried out using Statgraphics XVI and Statistica 10 software packages.

3. Results and discussion

The zero regime of the heat treatment of the hard magnetic Fe–27Cr–10Co–0.5Mo alloy involved the following: tempering at 1100°C (15 min) + heating to 670°C (10 min) + cooling in magnetic field to 580°C with a rate $V1$ = 12 °C/h + cooling without field to 500°C with $V2$ = 7 °C/h with variation of the temperature of the beginning of thermomagnetic processing (TMP) ± 10°C (factor A), cooling rates $V1$ ± 2°C/h (factor B) and cooling rates $V2$ ± 2°C/h (factor C). The experimental results and design matrix for anisotropic samples are given in table 1.

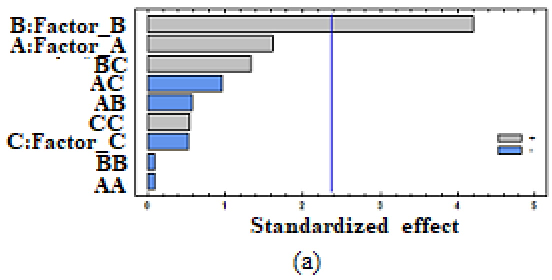
The statistical analysis of data in table 1 gives analytical dependences in the form of the regression equations for residual induction Br, coercive force Hc and maximum energy product (BH)max as a function of chosen variable factors.

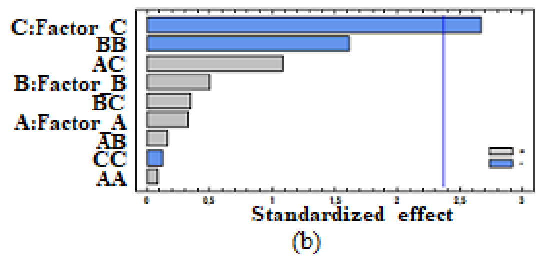
IOP Conf. Series: Materials Science and Engineering **347** (2018) 012053 doi:10.1088/1757-899X/347/1/012053

Table 1. Magnetic hysteresis properties of anisotropic samples of the Fe–27Cr–10Co–0.5Mo alloy.

	Temperature of the beginning of TMP, °C	Cooling rate *V*1 to 580°C, °C/h	Cooling rate *V*2 to 500°C, °C/h	B_r, T	H_{cB}, kA/m	$(BH)_{max}$, kJ/m^3
1	680 (1)	10 (–1)	9 (1)	1.34	44.75	40.3
2	670 (0)	12 (0)	10.4 (1.68)	1.36	45.4	42.2
3	687 (1.68)	12 (0)	7 (0)	1.35	45.7	42.1
4	660 (–1)	14 (1)	5 (–1)	1.35	45.9	43.9
5	680 (1)	14 (1)	5 (–1)	1.37	46.0	43.5
6	670 (0)	12 (0)	7 (0)	1.34	45.45	40.5
7	670 (0)	8.64(–1.68)	7 (0)	1.33	45.2	40.0
8	670 (0)	12 (0)	3.64 (–1.68)	1.35	46.0	43.1
9	660 (–1)	10 (–1)	5 (–1)	1.34	45.9	40.7
10	670 (0)	12 (0)	7 (0)	1.36	46.3	43.1
11	670 (0)	12 (0)	7 (0)	1.35	45.0	40.4
12	670 (0)	15.4 (1.68)	7 (0)	1.37	44.75	40.9
13	653 (–1.68)	12 (0)	7 (0)	1.35	45.9	42.9
14	680 (1)	10 (–1)	5 (–1)	1.36	45.4	42.1
15	660 (–1)	14 (1)	9 (1)	1.36	44.65	42.1
16	660 (–1)	10 (–1)	9 (1)	1.325	43.9	38.3
17	680 (1)	14 (1)	9 (1)	1.36	45.2	42.2

However, it can be seen in figure 1 from the standardized Pareto charts, which make it possible to estimate the statistical significance of the coefficients of the regression equations (coefficients are statistically significant when the vertical line on the chart crosses the column image of the corresponding coefficient), that it is reliably possible to speak only about average values of B_r, H_{cB} and $(BH)_{max}$, which are 1.35 T, 45.6 kA/m and 41 kJ/m^3, respectively.





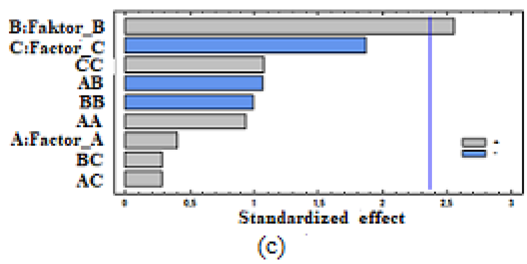


Figure 1. The standardized Pareto charts of alloy Fe-27Cr-10Co-0,5Mo for residual induction B_r (a), coercive force H_{cB} (b) and maximum energy product of $(BH)_{max}$ (c) in the anisotropic state.

According to the Statgraphics program, the following values can be obtained: B_r = 1.38 T, H_{cB} = 46.8 kA/m and $(BH)_{max}$ = 46 kJ/m^3.

Upon study of the magnetic hysteresis properties of powder Fe–27Cr–10Co–2Mo alloy after tempering from 1100°C, a zero (initial) point was the regime of ITMP at 640°C (40 min) + cooling with *V*1 = 15 °C/h to 580°C + cooling with *V*2 = 7 °C/h to 500°C. The variation was ± 10°C for ITMP temperature (factor *A*), ± 10 min for time of ITMP (factor *B*), ± 2 °C/h for cooling rates *V*1 (factor *C*) and ± 2 °C/h for cooling rates *V*2 (factor *D*). The results of the carried out experiments and design matrix for anisotropic samples are given in table 2.

Table 2. Magnetic hysteresis properties of anisotropic samples of the Fe–27Cr–10Co–2Mo alloy.

Temperature of ITMP, °C	Time of ITMP, min	Cooling rate *V*1, °C/h	Cooling rate *V*2, °C/h	B_r, T	H_{cB}, kA/m	H_{cM}, kA/m	$(BH)_{max}$, kJ/m^3
1 670	1 50	1 17	1 9	1.29	39.9	40.0	34.2
–1 650	–1 30	–1 13	1 9	1.29	40.1	40.3	33.5
–2 640	0 40	0 15	0 7	1.31	41.0	41.1	32.9
–1 650	–1 30	–1 13	–1 5	1.30	42.1	42.3	36.3
2 680	0 40	0 15	0 7	1.22	41.6	41.7	31.2
–1 650	1 50	–1 13	–1 5	1.30	42.1	42.3	35.4
0 660	0 40	0 15	0 7	1.29	40.2	40.3	33.6
1 670	–1 30	–1 13	–1 5	1.27	42.9	43.1	34.0
–1 650	1 50	1 17	–1 5	1.31	41.1	41.9	34.1
–1 650	–1 30	1 17	1 9	1.30	38.9	39.1	34.0
–1 650	1 50	–1 13	1 9	1.285	39.9	40.2	32.6
0 660	0 40	0 15	0 7	1.30	41.5	41.8	35.1
0 660	0 40	0 15	0 7	1.30	41.9	42.1	35.6
–1 650	1 50	1 17	1 9	1,30	39.2	39.4	34.0
0 660	0 40	–2 11	0 7	1.26	42.6	42.8	32.7
1 670	1 50	–1 13	–1 5	1.29	42.1	42.2	36.2
0 660	0 40	0 15	2 11	1.30	39.6	39.8	33.8
1 670	–1 30	–1 13	1 9	1.265	40.4	40.5	32.3
0 660	2 60	0 15	0 7	1.34	41.6	42.0	35.8
–1 650	–1 30	1 17	–1 5	1.29	46.8	41.0	34.8
1 670	–1 30	1 17	–1 5	1.30	42.1	42.2	36.2
0 660	0 40	2 19	0 7	1.26	40.35	40.6	32.4
1 670	–1 30	1 17	1 9	1.30	42.0	42.2	36.9
0 660	0 40	0 15	–2 3	1.29	41.3	41.6	36.2
0 660	0 40	0 15	0 7	1.26	40.85	41.1	35.2
1 670	1 50	–1 13	1 9	1.27	40.9	41.0	32.8
1 670	1 50	1 17	–1 5	1.30	41.05	41.3	36.0

The statistical analysis of data in table 2 gives analytical dependences in the form of the regression equations for residual induction B_r, coercive force H_c and maximum energy product of $(BH)_{max}$ as a function of chosen variable factors.

The standardized Pareto charts, which make it possible to estimate the statistical significance of coefficients of the regression equations, are presented in figure 2 (coefficients are statistically significant when the vertical line on the chart crosses the column image of the corresponding coefficient).

As can be seen from presented charts, the residual induction B_r is described by the nonlinear equation:

$$B_r = 1.29 + 0.007BB - 0.01A - 0.007CC \quad (1)$$

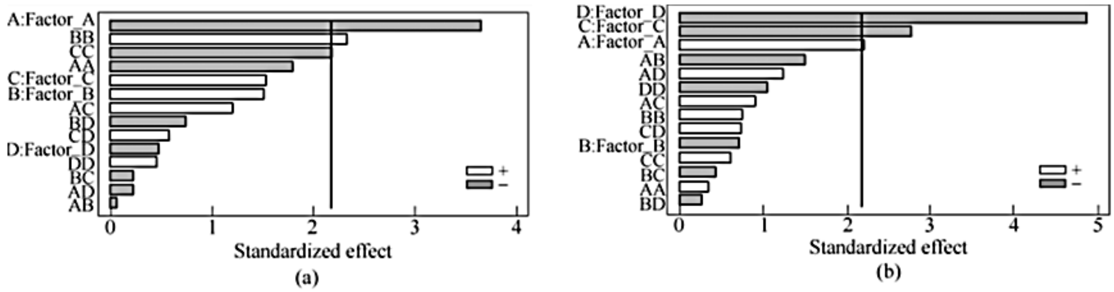
in which the free term gives the average value of *B*r in the anisotropic state in the chosen ranges of variation of the factors.

In the regression equation for coercive force H_{cB}, as can be seen from Pareto chart, the linear terms of *F*, *D* and *C* are statistically significant:

$$H_{cB} = 41 + 0.3A - 0.7D - 0.4C \quad (2)$$

The Pareto chart for maximum energy product $(BH)_{max}$ shows that statistically significant coefficients are linear D and square AA; the regression equation for $(BH)_{max}$ has the following form:

$$(BH)_{max} = 34{,}8 - 0{,}7D - 0{,}55AA \qquad (3)$$



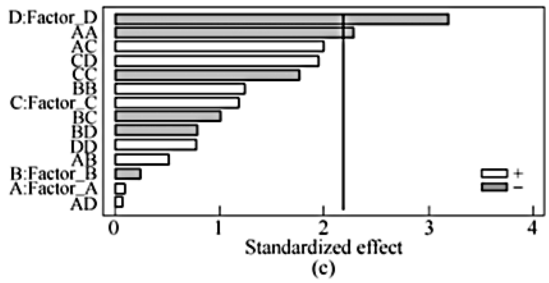


Figure 2. The standardized Pareto charts of alloy Fe-27Cr-10Co-2Mo for (*a*) residual induction B_r, (*b*) coercive force H_{cB} and (*c*) maximum energy product $(BH)_{max}$ in the anisotropic state.

The appearance of response surface in the phase space of the varied factors and especially their sections contains the useful and obvious information from the technological point of view. Figure 3 shows these response surfaces for B_r, H_{cB} and $(BH)_{max}$ with the corresponding sections for anisotropic state.

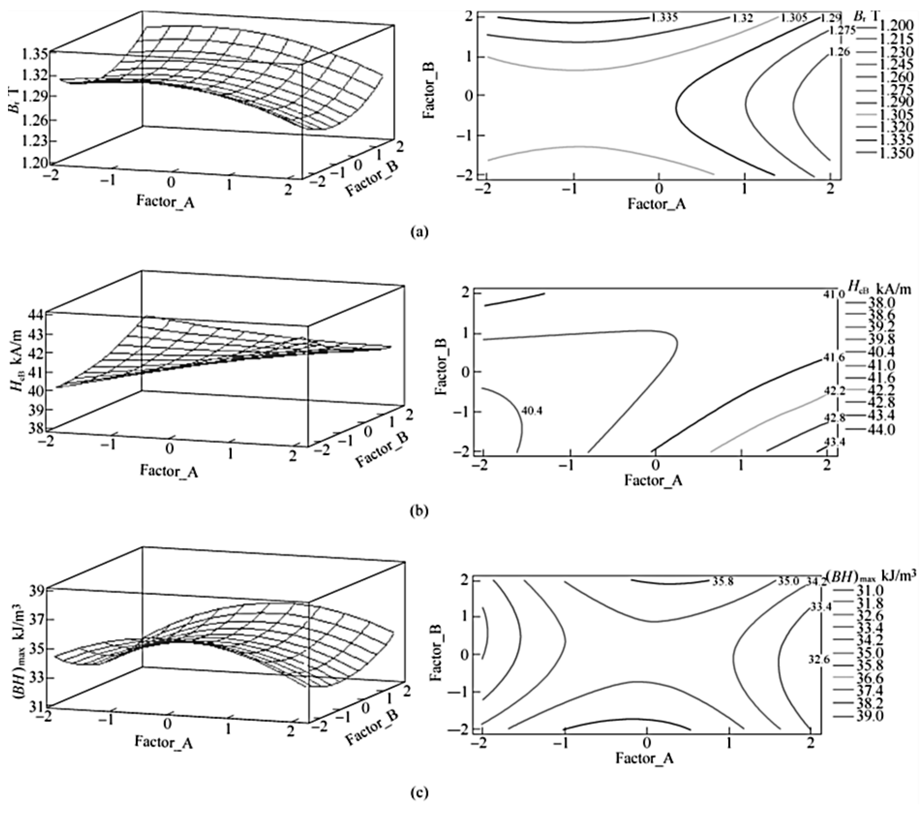


Figure 3. Estimated response surfaces and their sections for (*a*) residual induction B_r, (*b*) coercive force H_{cB} and (*c*) maximum energy product $(BH)_{max}$ (factor $C = 0$ and factor $D = 0$) for anisotropic state.

According to the data of table 2, for Fe–27Cr–10Co–2Mo alloy the maximum received value of coercive force H_{cB} = 43 kA/m (the average value of H_{cB} = 41 kA/m) that is confirmed by a type of the response surface for H_{cB} in figure 3.

Thus, the addition of 2 wt % molybdenum into the ternary Fe–27Cr–10Co alloy does not lead to an expected increase in the coercive force. However, we showed in [7] that the value of H_{cB} of a similar cast Fe–27Cr–10Co–0.4Si–0.7Ti–0.6Mo alloy reached 48–50 kA/m.

In this connection, it should be noted that if the optimum content of molybdenum in FeCrCo alloys containing more than 15–20 wt % cobalt is 2–3 wt %, in low-cobalt alloys (cobalt content of 10 wt % or less), it is apparently less than 1 wt %.

Lastly, note that molybdenum in hard magnetic FeCrCo alloys reduces the camber of the demagnetization curve in the second quadrant (see figure 4). The camber coefficient $\eta = (BH)_{max}/B_rH_{cB}$ in the ternary Fe–27Cr–10Co–0.5Mo alloy is 72% and only 68.6% in the Fe–27Cr–10Co–2Mo alloy.

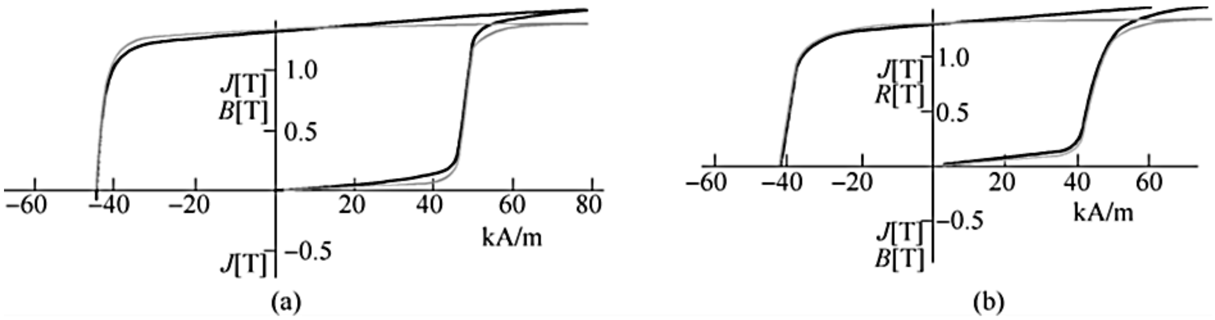


Figure 4. Curves of magnetization and demagnetization for (*a*) Fe–27Cr–10Co and (*b*) Fe–27Cr–10Co–2Mo alloys.

4. Conclusions

The addition of a small amount of molybdenum (0.5 wt. %) into the powder hard magnetic Fe–27Cr–10Co alloy leads to an increase in its magnetic hysteresis properties.

The additional alloying with molybdenum of up to 2 wt. % of the ternary alloy does not lead to an increase in the coercive force, there is a decrease in the residual induction B_r and maximum energy product $(BH)_{max}$.

The introduction of molybdenum into the low-cobalt hard magnetic FeCrCo alloys, just as in the alloys with moderate amount of cobalt and in the high-cobalt hard magnetic alloys, reduces the camber of the demagnetization curve in the second quadrant.

Acknowledgements

Authors would like to express their sincere gratitude to the leading researcher V. A. Zelenskii and research associate A. B. Ankudinov for the help in the receiving powder samples of the studied alloys.

Work performed on the state task No. 007-00129-18-00 with financial support of FTsNTP-2017 under the state contract of 26.09.2017 No. 14.579.21.0149.

References

[1] Jin S and Gayle N W 1980 *IEEE Trans. Magnetic.* **3** 526–529.
[2] Kaneko H and Inoue K 1974 Patent USA 3 806 336 Int. Cl. C22c 39/16 H01f 1/00. U.S. Cl. 75–122.

[3] Milyaev I M, Yusupov V S, Stelmashok S I and Milyaev A I 2016 *Innovatsionnye metallicheskie materialy* ed V M Kolokoltseva (Magnitogorsk, Nosov Magnitogorsk State Technical University) chapter 3 pp 59–75.
[4] Milyaev I M, Yusupov V S, Milyaev A I and Laysheva N V 2009 *Perspektivnye materialy* **6** 359–361.
[5] Milyaev I M, Milyaev A I and Yusupov V S 2008 *Perspektivnye materialy* 277–280.
[6] Milyaev I M, Milyaev A I and Yusupov V S 2009 *Russian Metallurgy (Metally)* **3** 250–252.
[7] Milyaev A I, Kovneristiy Yu K, Efimenko S P and Korznikova G F 2004 *Trudy Nizhegorodskogo gosudarstvennogo tekhnicheskogo universiteta Materialovedenie i metallurgiya* **42** 127–132.