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Homogenization annealing and magnetic properties of a sample of the Laves phase $GdNi_2$

© A.V. Mashirov[1], I.I. Musabirov[2], M.S. Anikin[3], M.A. Semkin[3], V.I. Mitsiuk[4], R.Y. Gaifullin[5], V.V. Koledov[1], V.G. Shavrov[1]

[1] Kotelnikov Institute of Radio Engineering and Electronics, Russian Academy of Sciences, Moscow, Russia
[2] Institute of Metal Superplasticity Problems, Russian Academy of Sciences, Ufa, Russia
[3] Ural Federal University after the first President of Russia B.N. Yeltsin, Yekaterinburg, Russia
[4] Scientific and Practical Materials Research Center, National Academy of Sciences of Belarus, Minsk, Belarus
[5] Bashkir State University, Ufa, Russia

E-mail: a.v.mashirov@mail.ru

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The paper shows the effect of homogenization annealing on the ferromagnet-paramagnet phase transition in the $GdNi_2$ alloy. In the cast sample, at the Curie point, a temperature hysteresis is observed, which in an external magnetic field of 13.5 T can be at least 3 degrees. The data of scanning electron microscopy of the electropolished samples showed a decrease in the impurity phase of GdNi and practically no temperature hysteresis of the phase transition in the annealed $GdNi_2$ sample. The value of the isothermal change entropy $\Delta S_m = -18.931\,\mathrm{J/(kg\cdot K)}$ for an annealed sample of the $GdNi_2$ alloy at the Curie point of 75 K in a magnetic field of 13.5 T.

Keywords: magnetocaloric effect, $GdNi_2$, Laves phases.

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1. Introduction

In alloys RM_2 (R — rare-earth metal, $M =$ Ni, Al) in the cryogenic temperature range, there is a ferromagnet and paramagnet phase transition and, as a consequence, high values of the magnetocaloric effect in the area of the ferromagnetic Curie point [1,2]. Therefore, when forming prototypes of cryogenic magnetic refrigerators, alloys of Laves phases are used as working fluids [3]. As will be shown below, homogenization annealing during the synthesis of these compounds can reach one month and complicate the manufacturing technology, which determines the purpose of this work to study the opportunity of reducing the heat treatment time.

Let us review the heat treatment modes of $GdNi_2$ sample of the Laves phase and related alloys. For the $DyNi_2$ compound, the congruent reaction temperature is approximately 950 K according to the data of the Dy-Ni phase diagram [4]. In the work [5] the $DyNi_2$ alloy was placed in tantalum foil to avoid oxidation during heat treatment, after which it was annealed in vacuum at 1173 K for 48 hours. The work [6] mentions various methods of heat treatment of annealing from several days to a month at temperatures of 723 − 1073 K. Stoichiometric alloys $TbNi_2$ are also subjected to various heat treatments. For example, in the work [7], two types of heat treatment were applied, annealing at 923 K for 720 hours or at 1473 K for 15 hours, which gave comparable results. The sample is also heat-treated in tantalum foil and in an evacuated quartz vessel for a month at a temperature of 1123 K [2]. Up to the use of the tape melt spinning technique, without subsequent annealing [8]. There are works where heat treatment after melting is not described [9] or melting by induction heating is used [10]. A number of works describing the synthesis of $GdNi_2$ alloys does not contain information on heat treatment by homogenization annealing [11]. In this work [12] the $GdNi_2$ alloy is annealed after several meltdowns for the purpose of homogenization for 360 hours at a temperature of 1073 K. In works [13–15] for 72 hours at 900, 1170 and 1200 K, respectively, and for 96 hours at 1073 K [16]. The $DyAl_2$ alloy is heat-treated in a vacuum furnace for 100 hours at a temperature of approximately 1073 K [17]. Indicating congruent melting for the $DyAl_2$ sample, only short-term strain annealing (approximately 24 hours) at a temperature of approximately 1273 K was carried out [18]. There is also a work in which homogenization annealing was not carried out [19].

2. Samples and experimental methods

A cast sample of $GdNi_2$ was synthesized by argon-arc melting on a water-cooled copper pallet from high-purity weights of Gd and Ni metals with three flips and four meltdowns. For the purpose of homogenization, the sample sealed in an evacuated quartz vessel was annealed for 100 hours at a temperature of 1073 K, followed by natural cooling in a switched off furnace.

A D8 Advance (Bruker) powder diffractometer with a Cu-$K\alpha$, $\lambda = 1.5406$ Å radiation source was used to perform X-ray diffraction (XRD) measurements for phase analysis and accurate determination of the compound crystal structure parameters. XRD patterns were processed using the full-profile Rietveld method in FullProf Suite [20].

The study of the microstructure and identification of the elemental composition of the alloy was carried out on a Vega 3 SBH (Tescan) scanning electron microscope using X-Act back-scattered electron and energy-dispersive analysis detectors (Oxford Instruments). The measurements were made at an accelerating voltage of 20 kV. The section for study was prepared by polishing on abrasive paper of various grain sizes and finishing polishing on a diamond suspension.

Magnetization measurements in magnetic fields up to 13.5 T were carried out on a universal physical properties gauging device from Cryogenic Ltd. The mass of the samples was 151 for cast and 48 mg for annealed ones. The rate of heating and cooling at magnetization measurement is 1−1.5 K/min.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of the sample after casting (*a*) and annealed for 100 hours at 1073 K (*b*) of $GdNi_2$, it should be noted that the experimental points are well described by the pitch lines. All X-ray diffraction pattern reflections of $GdNi_2$ are well described by the cubic Fd-$3m$ space group. The common divergence factor of X-ray diffraction patterns of the samples is $\chi^2 = 1.3$ and 1.2%, respectively. In the $GdNi_2$ crystal structure, the Gd ions occupy the 8*b* position with coordinates (3/8, 3/8, 3/8), the Ni^+ ions occupy position 16*c* with coordinates (0, 0, 0). The revised values of the crystal lattice parameters are: $a = 7.2106(5)$ Å for cast and $a = 7.2131(3)$ Å for annealed samples, which is well compliant with the literature data $a = 7.206$ Å [11]. It can be seen that after annealing, the lattice cell volume of $GdNi_2$ increased insignificantly, approximately by 0.1%.

Microstructural studies of the $GdNi_2$ alloy in the states after casting and homogenization annealing were carried out. Figure 2, *a* shows the results of studying the microstructure of the alloy in the mode of registration of back-scattered electrons (BSE) in the state after casting. There are three phases in the microstructure, which differ in structure. Analysis of the elemental composition by the energy-dispersive analysis method shows that the main matrix corresponds to the $GdNi_2$ intermetallic phase. A common analysis of the pattern allows to reveal the grain contrast of the main matrix of the alloy. The equiaxed grains have a size of 100 μm. There are two more phases in the microstructure, which have a light shade. One phase in the form of elongated light stripes is approximately 2 μm thick and up to 50 μm long. It corresponds to the GdO (35−65%) oxide phase. The presence of oxygen is apparently due to the quality of the sample material. To remove it, additional heat treatment is required before adding the alloy to the sample. According to the volume fraction, the content of this phase is relatively small and should not affect the integral functional properties of the alloy under study. The third phase, which has a lattice pattern, corresponds to the GdNi intermetallic phase. The study of the microstructure of the $GdNi_2$ alloy after homogenization annealing for 100 hours at 1073 K is shown in Fig. 2, *b*. A series of measurements is made similar to the cast alloy. A common analysis of the microstructure in the BSE mode shows that there are also three different phases in the structure. However, compared with the initial state after homogenization annealing, the proportion of the matrix phase increased significantly. This is noticeable by the decrease in phases that have light shades. The proportion of the phase corresponding to the GdNi intermetallic phase has decreased significantly.

Thus, the study of the microstructure of the $GdNi_2$ alloy in the cast state and after homogenization annealing shows that there is a significant proportion of the GdNi intermetallic phase in the initial state. As a result of annealing, this phase is partially dissolved and the proportion of the desired $GdNi_2$ intermetallic phase increases. The presence of oxygen in the alloy may be due to the quality of the gadolinium used for the sample. To reduce the proportion of the oxide phase, preliminary meltdown of Gd is required for the alloy sample.

The results of magnetization measurement of samples as a function of temperature at a constant external magnetic field of 0.01, 1, 10, 13.5 T are shown in Figs 3 and 4. The magnetization at 5 K in a magnetic field of 100 Oe for the cast and annealed sample is 3.1 and 3.5 emu/g, respectively, and in a magnetic field of 135 kOe it is approximately 139 emu/g for both samples. It can be seen from these figures that with an external magnetic field at the Curie point equal to 75 K, there is a wider temperature hysteresis for the sample after casting than for the homogenized one, according to the table. The presence of a temperature hysteresis of approximately 1 degree for a homogenized sample can be explained by the experimental

Temperature hysteresis values at the Curie point

Magnetic field, T	0.01	0.5	1	9	13.5
Temperature hysteresis of the sample after casting, K	2.06	2.44	2.44	4.07	3.66
Temperature hysteresis of the annealed sample, K	1.34	1.03	1.03	0.23	0.23

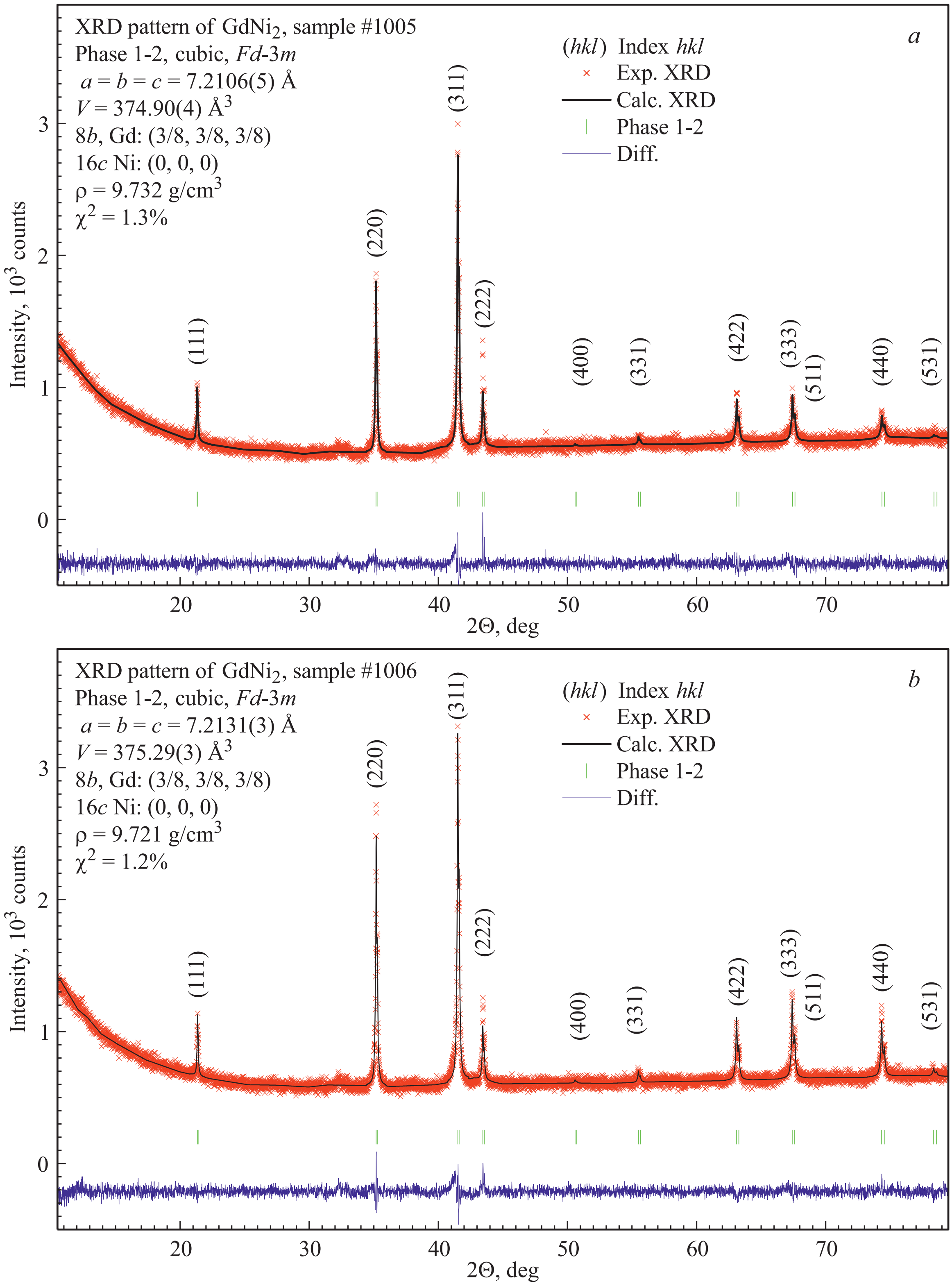

Figure 1. Experimental (points) and pitch (line) X-ray diffraction patterns of $GdNi_2$ samples after casting (*a*) and annealed for 100 hours at 1073 K (*b*); lines at the bottom — difference between X-ray diffraction patterns; a series of dashes — angular positions of the Bragg reflections of the main phase, the corresponding Miller indices are given in parentheses.

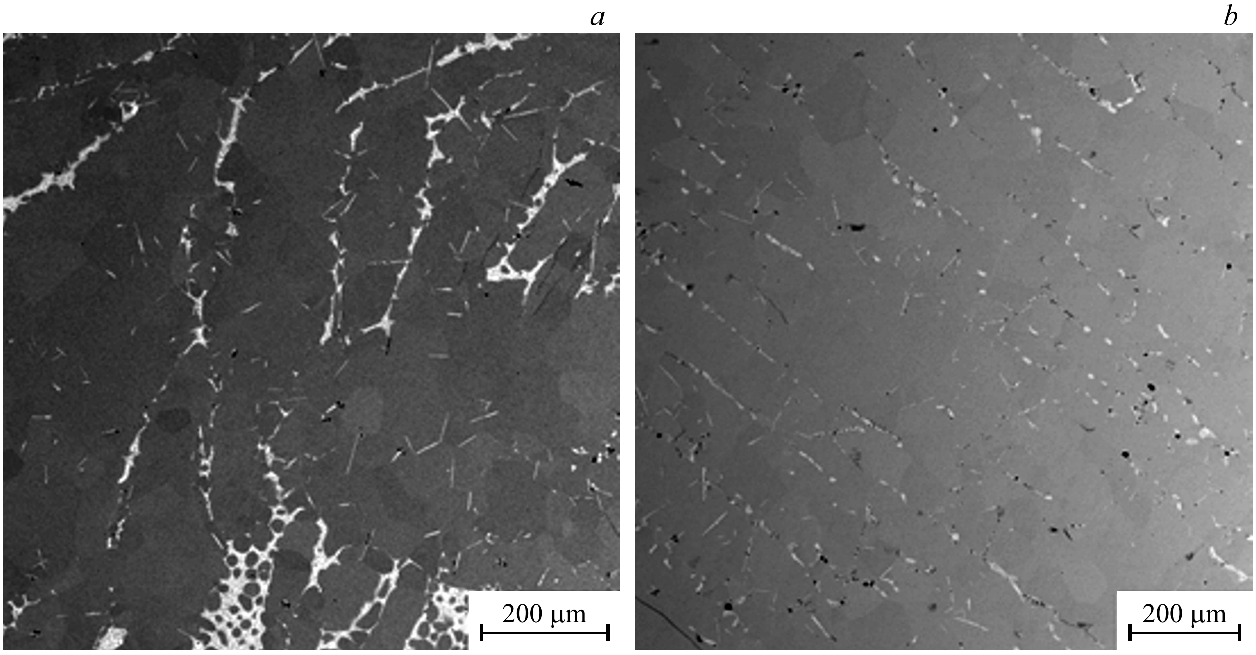

Figure 2. The microstructure of the $GdNi_2$ alloy in condition after casting (*a*) and after homogenization annealing for 100 hours at 1073 K (*b*).

conditions. The cast sample shows an increase in temperature hysteresis to values of approximately 4 degrees. Apparently, this can be explained by the presence of a significant proportion of the GdNi intermetallic phase, which dissolves during annealing with an increase in the proportion of the $GdNi_2$ parent phase. It is known that the Curie temperature for the GdNi intermetallic compound is approximately 80 K [21].

Isothermal curves of technical magnetization in a magnetic field up to 13.5 T at temperatures from 5 to 120 K are shown in Fig. 5. There is saturation of the curve of technical magnetization at 1.25 T with the value for the sample after

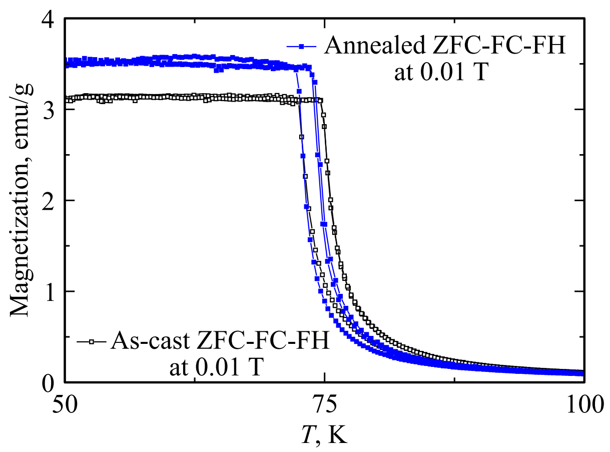

Figure 3. Dependence of the magnetization of the sample after casting (black) and annealed (blue) on temperature in a magnetic field 0.01 T.

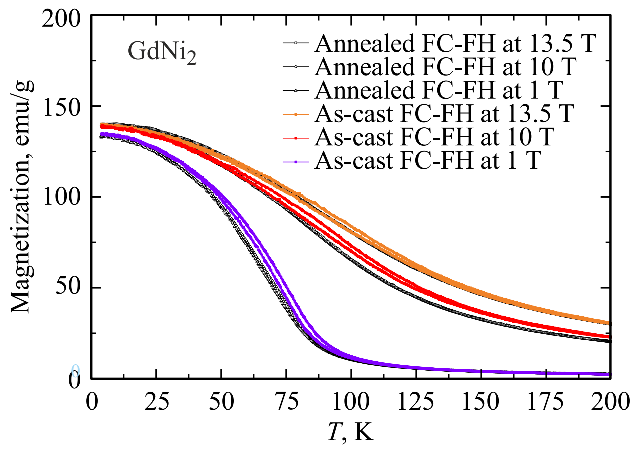

Figure 4. Dependence of the magnetization of the sample after casting and annealed on temperature in a magnetic fields 1, 10, 13.5 T.

casting and annealed 134.9 and 134.6 emu/g, respectively. These values change slightly with increasing magnetic field up to 13.5 T and are equal to 138.5 and 137.5 emu/g, respectively. Using the isothermal curves of technical magnetization, one can calculate the magnetocaloric effect in the form of an isothermal change in the entropy of the magnetic subsystem ΔS_m [22]. Figure 6 shows the results of this calculation, which amounted to the maximum value at the Curie point in a magnetic field of 13.5 T for cast and annealed samples -18.616 and -18.931 J/(kg · K) respectively. This value is almost half the value of ΔS_m

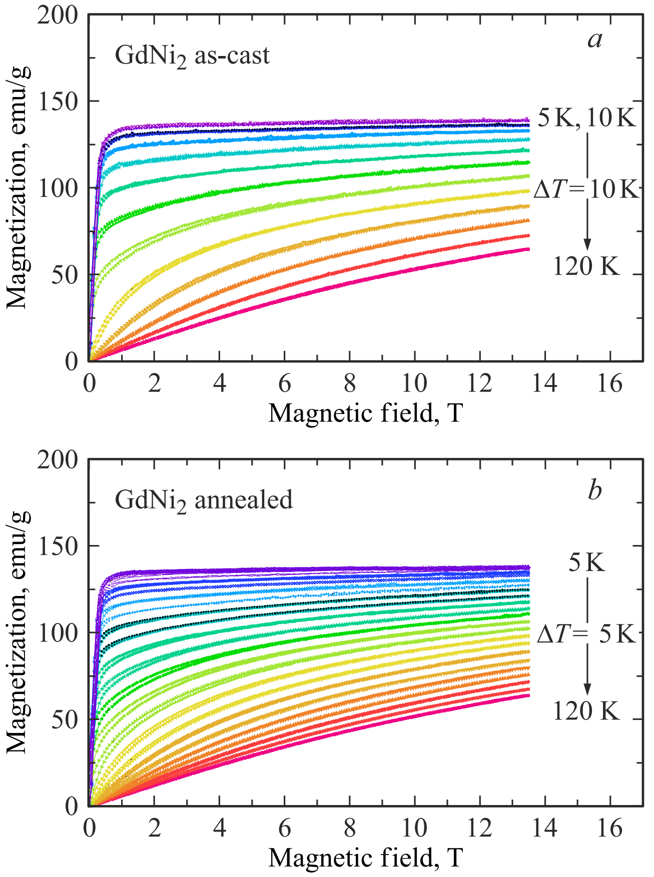

Figure 5. Curves of isothermal technical magnetization up to 13.5 T after casting (a) and annealed (b) sample of the $GdNi_2$ alloy.

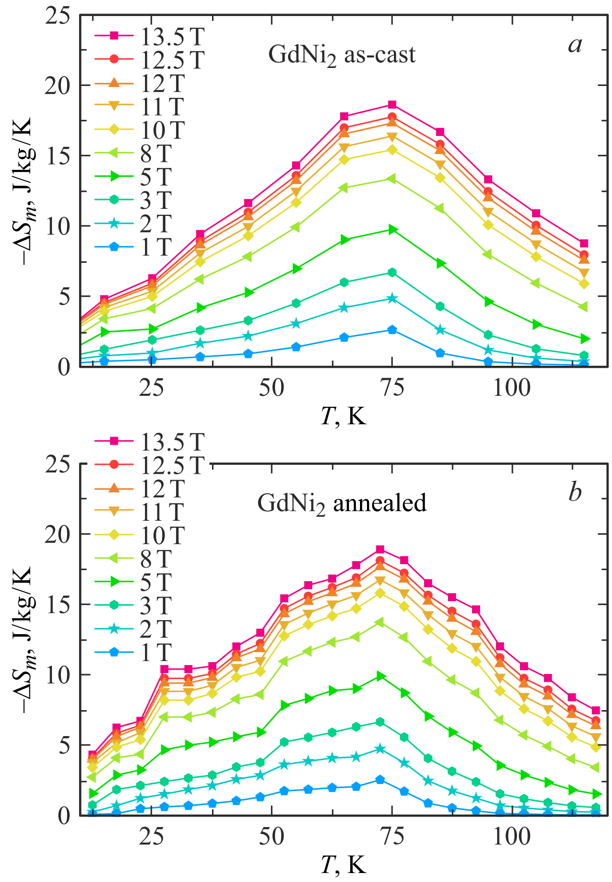

Figure 6. Temperature dependence of the isothermal change in the entropy of the magnetic subsystem after casting (a) and annealed (b) sample of the $GdNi_2$ alloy.

for GdNi equal to $-31.2\,J/(kg \cdot K)$ in the field 14 T at the Curie temperature 80 K [21]. In the work [11] the value ΔS_m of the magnetocaloric effect at the Curie point 70 K for $GdNi_2$ in a magnetic field 10 T was $-17\,J/(kg \cdot K)$, versus $-15.8\,J/(kg \cdot K)$ at 75 K for the annealed sample in this work. In the work [23] the value ΔS_m of the magnetocaloric effect at the Curie point 75 K for $GdNi_2$ spheres with a diameter of $500-850\,\mu m$ in a magnetic field 5 T was $-3.9\,J/(kg \cdot K)$, versus $-9.9\,J/(kg \cdot K)$ massive samples in this work.

Thus, heat treatment in the form of annealing for 100 hours at 1073 K of the $GdNi_2$ alloy does not affect the value of the isothermal magnetocaloric effect, it reduces the width of the temperature hysteresis due to the heterogeneity of the sample, which is important for direct measurement magnetocaloric effect in heating or cooling mode.

4. Conclusion

Homogenizing annealing reduces the amount of the impurity phase in the Laves phase alloy $GdNi_2$. The temperature hysteresis at the Curie point of this alloy in the unannealed state can reach values of 3 degrees. Heat treatment in the form of annealing for 100 hours at 1073 K reduces the value of the temperature hysteresis to values in the order of the instrumental error of magnetization measurements. The value ΔS_m of the magnetocaloric effect obtained in this work for an annealed $GdNi_2$ sample at the Curie point 75 K in a magnetic field 13.5 T is equal to $-18.931\,J/(kg \cdot K)$, which is much less than the value ΔS_m for GdNi equal to $-31.2\,J/(kg \cdot K)$ in the field 14 T at the Curie temperature 80 K.

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Conflict of interest

The authors declare that they have no conflict of interest.

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