

Effect of severe plastic deformation on the saturation magnetization of ferromagnetic DO₃-type ordered Fe₃Al alloy

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Abstract. The effect of severe plastic deformation in Bridgman anvils at room temperature on the specific saturation magnetization (SSM) of the ferromagnetic DO₃ ordered Fe–24 at.% Al alloy was studied by X-Ray diffraction analysis and magnetic measurements. High pressure torsion at certain deformation parameters was shown to fully suppress the long-range ordering in the alloy and simultaneously increase its SSM by 11% relative to that in the equilibrium state. A theoretical model which qualitatively explains this phenomenon is proposed.

1. Introduction

At present, methods of a substantial increase in physical and mechanical properties of metallic materials based on severe plastic deformation (SPD) attract a great attention of researchers [1]. One of the most commonly used SPD methods is high pressure torsion (HPT) in Bridgman anvils [2]. In the literature, much attention is paid to the effect of SPD on the mechanical properties of many metals and alloys [3]. Unfortunately, only a few papers are devoted to the effect of SPD on the magnetic properties of ferromagnetic alloys. One can mention only some publications, in which the structure-dependent magnetic properties (coercivity, permeability, frequency characteristics) of crystalline Nd(Pr)-Fe-B [4], Fe-C [5], α -Fe, FeCo, Ni₃Fe [6], Fe-Ni [7,8], Fe-Si [8], Fe-Co [9], Ni₃Al [10] and amorphous Fe-Ni-B, Fe-Cr-B, Fe-Si-B, Fe-Si-B-Nb-Cu, Ni-Fe-Co-Si-B [11,12] ferromagnetic metals and alloys are considered as functions of SPD. However, in some studies, SPD by HPT in Bridgman anvils has been found to noticeably affect the saturation magnetization of crystalline [6,7] and amorphous [11-13] alloys. As is known [14], this characteristic is not a structure-dependent parameter of ferromagnetic materials and is normally determined only by chemical and phase compositions of a ferromagnetic material regardless of its structural state. No reasonable explanation for this phenomenon has been found yet. Only assumptions related to the densification of the crystal lattice [6] or a change in the degree of short-range order [7] upon SPD have been put forward.

The aim of this paper is to analyze in detail the nature of the possible effect of SPD (by the HPT method) on the fundamental characteristic of ferromagnetic materials (specific saturation magnetization σ) in relation to the DO₃-type Fe–24 at. % Al alloy of the composition close to the stoichiometric A₃B one. In addition to the specific saturation magnetization σ , the lattice parameter (a)



of the BCC Fe-24 at % Al solid solution and the degree of the DO₃ long-range order (η) in the first coordination sphere have been analyzed as functions of HPT.

2. Experimental

The Fe-24 at.% Al alloy was melted in a vacuum furnace in the form of rods with a diameter of 10 mm. Then discs with a thickness of 0.3 mm were cut from the rods and annealed in an argon atmosphere at a temperature of 500 °C for 50 hours to attain an equilibrium state corresponding to the DO₃ atomic order [15]. Then the disc samples were subjected to plastic deformation in Bridgman anvils at room temperature to a certain fraction / number of full revolutions N ($\frac{1}{4}$, $\frac{1}{2}$, 1, 2, 3, 4, and 6) of the movable anvil under quasi-hydrostatic pressure $P = 4$ GPa at a movable anvil rotation velocity of 1 rev/min.

The specific saturation magnetization σ was measured with a VSM-250 vibrating magnetometer after room-temperature HPT to $N = 0.25$ -6. X-ray structure analysis of the samples before and after SPD was carried out with a RigakuUltima IV diffractometer using Co K_α radiation and graphite monochromator.

3. Results and discussion

Figure 1 shows the measured magnetic hysteresis curves for the Fe-24 at.% Al alloy samples in the initial state and after room-temperature HPT to $N = 1$. One can see a noticeable increase in σ from 160 emu/g (without HPT processing) to 177 emu/g after HPT, i.e. by approximately 11%.

Figure 2 shows the measured specific saturation magnetization σ (a), the lattice parameter a (b), and the long-range order parameter η (c) of the alloy as functions of the degree of deformation (number of revolutions N) at room temperature.

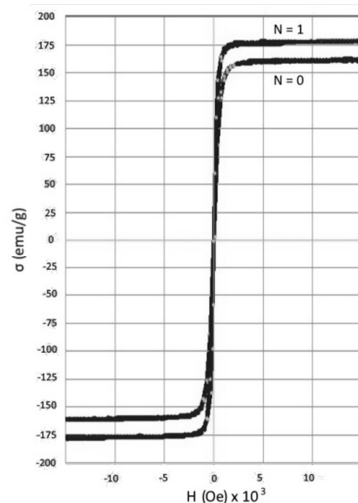


Figure 1. Magnetic hysteresis curves for the Fe-24 at.% Al alloy in the initial state ($N=0$) and after HPT ($N=1$).

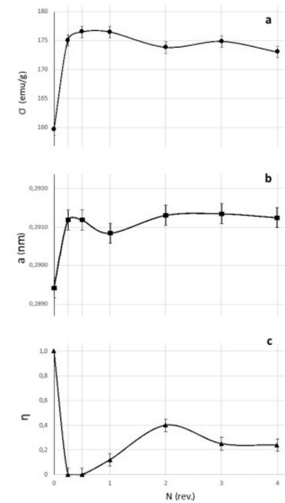


Figure 2. Effect of the degree of deformation (N) on the specific saturation magnetization σ (a), lattice parameter a (b), and long-range order parameter η (c).

At $N \leq 1$, there is a noticeable increase in both σ and a , while η is substantially reduced to almost zero, and the alloy undergoes deformation-induced disordering. Then, at $N > 1$, the long-range order is partially restored (the η parameter increases). There is also a stabilization of a and a weak decrease in σ , which, however, remains substantially higher than that in the initial state prior to the HPT processing.

The nature of the unusual change in the long-range order parameter η (figure 2 c) was analyzed in detail in our work [16]. The earlier unknown phenomenon of a partial recovery of a completely

destroyed $D0_3$ long-range order has been found to occur upon room-temperature HPT deformation in the Fe_3Al (Fe - 24 at.% Al) super lattice. The established effect was attributed [16] to low-temperature dynamic recrystallization, at which a high-temperature two-phase A2+B2 state is formed in the grains dynamically recrystallized upon SPD. At high degrees of deformation by HPT ($N \geq 2$), a stationary state which includes a "two-phase mixture" of deformation fragments and dynamically recrystallized grains is formed in the alloy in accordance with the laws of nonequilibrium thermodynamics. In addition, note that we apparently for the first time succeeded to get the Fe-24 at. % Al alloy with a composition close to the one of stoichiometric Fe_3Al alloy in an unordered state using HPT method at $N < 1$. It is known [17] that even melt quenching at a rate of about $10^6 K/s$ cannot suppress the long-range ordering, which occurs in the stoichiometric Fe_3Al alloy at relatively high temperatures as a second-order phase transition (the T_C temperature is $730^\circ C$ [15]).

We assume that a significant increase in the magnetic parameter σ in figure 2 a is partially related only to the suppression of the long-range ordering in the ferromagnetic BCC Fe-Al solid solution. To check this assumption, we constructed the $\sigma - \eta$ parametric dependence (figure 3), at which each point corresponds to σ and η for all considered HPT processing regimes including the initial (undeformed) state. Extrapolating the experimental data from figure 3 as a linear correlation function, we obtain a very high correlation coefficient $K = -0.85$. This, of course, means that the degree of long-range order in the first coordination sphere actually strongly affects the specific saturation magnetization of the alloy, although the character of such dependence can be nonlinear.

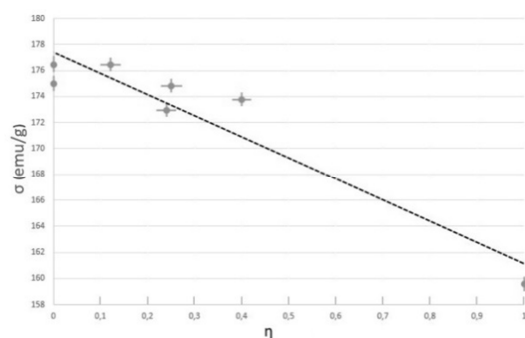


Figure 3. Linear correlation between the specific saturation magnetization σ and the degree of long-range order η corresponding to a constant degree of HPT deformation N ($K = -0.85$).

The experimental results presented above allow one to conclude that a decrease in the degree of atomic order η leads to an increase in the specific saturation magnetization σ and, therefore, to an increase in the degree of magnetic ordering of the Fe-24 at.% Al ferromagnetic alloy. In addition, the change in lattice parameter upon HPT (figure 2 b) is mainly due to the order-disorder transformations in the Fe-Al system [17]. It was shown experimentally [18] that a change in the lattice parameter in ordered iron-based alloys can affect the saturation magnetization. Therefore, the structure changes occurring under HPT can be conventionally considered as a sequence of order-disorder phase transitions accompanied by the appearance of transformation-induced deformation $\varepsilon = \Delta a/a$ at increased N . To establish an analytical relationship between the long-range order parameters in the

magnetic and atomic subsystems, we use, according to [19], the following equation for the thermodynamic potential of the spatially inhomogeneous system (G), in which the phase transition characterized by the φ parameter is accompanied by the appearance of the transformation-induced deformation $\hat{\varepsilon}$:

$$G = \int_V \{g(\varphi, \hat{\varepsilon}) + \nabla \varphi \hat{\alpha} \nabla \varphi\} dV \approx \int_V \left\{ g(\varphi, \hat{\varepsilon}_0) + \nabla \varphi \hat{\alpha} \nabla \varphi + \frac{1}{2} (\hat{\varepsilon} - \hat{\varepsilon}_0) \hat{E} (\hat{\varepsilon} - \hat{\varepsilon}_0) \right\} dV. \quad (1)$$

Here $g(\varphi, \hat{\varepsilon})$ is the specific thermodynamic potential; $\hat{\varepsilon}$ is the total deformation characterizing the lattice distortion at a certain point; $\hat{\varepsilon}_0(\varphi)$ is the transformation-induced deformation corresponding to the parameter φ ; \hat{E} is the tensor of elastic moduli; $\hat{\alpha}$ is the parameter, which characterizes the interaction attempting to keep the system in a uniform state; and V is the volume.

We consider a spatially uniform system, in which the processes of changes in long-range order simultaneously occur in the magnetic and atomic subsystems and the interaction between such

processes occurs through an elastic field caused by the transformation-induced deformation in the crystal. In this case, the formula for the thermodynamic potential takes the following form:

$$G = g(\eta; \xi; \widehat{\epsilon}_0)V = -\frac{N}{2}W(\widehat{\epsilon}_0)\eta^2 - \frac{N}{2}A(\widehat{\epsilon}_0)\xi^2 + \frac{1}{2}\widehat{\epsilon}_0\widehat{E}\widehat{\epsilon}_0V - TS(\eta; \xi), \quad (2)$$

where $g(\eta, \xi, \widehat{\epsilon}_0)$ is the specific thermodynamic potential of a spatially homogeneous system; $\xi = \sigma/\sigma_0$, $\eta, \widehat{\epsilon}_0$ are the parameters of magnetic and atomic order and the transformation-induced deformation, respectively; σ_0 is the specific saturation magnetization at absolute zero. N_0 is the number of atoms in the alloy; $W(\widehat{\epsilon}_0)$ is the mixing energy; $A(\widehat{\epsilon}_0)$ is the exchange interaction energy; $S(\eta, \xi)$ is the entropy; and T is the absolute temperature.

The dependences of the mixing energies and exchange interaction can be represented in the form of expansions in powers of the transformation-induced deformation. Due to the small degree of the transformation-induced deformation $\varepsilon = \Delta a/a \ll 1$, we restrict ourselves by the linear terms of the formula and have:

$$\begin{aligned} W(\widehat{\epsilon}_0) &= W_0(1 + \widehat{\beta}_1\widehat{\epsilon}_0), \\ A(\widehat{\epsilon}_0) &= A_0(1 + \widehat{\beta}_2\widehat{\epsilon}_0), \end{aligned} \quad (3)$$

where $\widehat{\beta}_{1,2}$ are the coefficients of the expansion at the linear members of the transformation-induced deformation.

Taking into account the cubic symmetry of the crystal lattice of the alloy and the dilatational character of the transformation-induced deformation, we have:

$$\widehat{\epsilon}_0 = (\varepsilon_0, \varepsilon_0, \varepsilon_0); \quad \widehat{\beta}_{1,2} = (1/3\beta_{1,2}, 1/3\beta_{1,2}, 1/3\beta_{1,2}).$$

From the conditions of the minimum of thermodynamic potential

$$\frac{\partial G}{\partial \varepsilon_0} = \frac{\partial G}{\partial \eta} = \frac{\partial G}{\partial \xi} = 0, \quad (4)$$

we obtain the following equations for determining the equilibrium degrees of the transformation-induced deformation (5) and the parameters of the atomic (6) and magnetic (7) order:

$$\varepsilon_0 = \frac{N}{2VE} (W_0\beta_1\eta^2 + A_0\beta_2\xi^2), \quad (5)$$

$$\frac{1}{4}kT \ln \frac{(1+3\eta)(3+\eta)}{(1-\eta)^2} = W_0 \left(1 + \frac{N}{2V} \frac{A_0}{E} \beta_1\beta_2\xi^2\right) \eta + \frac{N}{2V} \frac{W_0^2}{E} \beta_1^2\eta^3, \quad (6)$$

$$\frac{1}{2}kT \ln \frac{1+\xi}{1-\xi} = A_0 \left(1 + \frac{N}{2V} \frac{W_0}{E} \beta_1\beta_2\eta^2\right) \xi + \frac{N}{2V} \frac{A_0^2}{E} \beta_2^2\xi^3, \quad (7)$$

where $E = 3(C_{11} + 2C_{12})$; C_{11} , C_{12} are the components of the elastic modulus tensor of the cubic lattice in the Voigt notation.

A qualitative analysis of Eqs. (6) and (7) leads to the conclusion that the character of the interaction of the order parameters in the magnetic and atomic subsystems within the proposed model is determined by the sign of the product of coefficients β_1 and β_2 . Upon atomic ordering, the magnetic order parameter and, consequently, the saturation magnetization increase at $\beta_1\beta_2 > 0$ and decrease at $\beta_1\beta_2 < 0$.

The proposed theoretical model explains the experimentally observed (figure 2) effect of the DO₃ atomic order on the long-range ordering in the magnetic subsystem. Since a decrease in the order in the atomic subsystem leads to an increase in magnetization (figure 2), then, in accordance with the proposed theoretical model, we find that, in the Fe-24 at.% Al alloy, the product $\beta_1\beta_2 < 0$. To determine the sign of each coefficient, we use Eq. (5) and obtain:

$$\beta_1 = \frac{EV}{W_0 N \eta} \frac{\partial \varepsilon_0}{\partial \eta} \sim \frac{EV}{W_0 N \eta} \frac{\partial}{\partial \eta} \left(\frac{\Delta a}{a} \right) < 0$$

$$\beta_2 = \frac{EV}{A_0 N \xi} \frac{\partial \varepsilon_0}{\partial \xi} \sim \frac{EV}{A_0 N \xi} \frac{\partial}{\partial \xi} \left(\frac{\Delta a}{a} \right) > 0, \quad (8)$$

Since, in accordance with figure 2, the lattice parameter in the alloy is increased by magnetic ordering and decreased by atomic ordering, it follows from Eqs. (8) that $\beta_1 < 0$ and $\beta_2 > 0$. Experiments in [15] show that exactly this situation occurs in binary Fe-Al alloys.

Our experiments in the Bridgman anvils allowed us to obtain a wide range of atomic order parameters η (figure 2c). In particular, for the first time it was possible to obtain the alloy of near-stoichiometric composition Fe₃Al in a fully disordered state ($\eta \cong 0$). Accordingly, this allowed us to obtain an extremely high magnetic order parameter ξ of the Fe-24 at.% Al alloy under the action of HPT and, therefore, the maximum possible specific saturation magnetization σ , which is noticeably (by about 11%) higher than the initial σ of the alloy in the equilibrium state.

4. Conclusions

The effect of severe plastic deformation in the Bridgman anvils at room temperature on the specific saturation magnetization of the ferromagnetic DO₃ ordered Fe-24 at.% Al alloy was discovered. Torsion under high pressure at certain deformation parameters was shown to fully suppress the long-range ordering in the alloy and simultaneously increase the specific saturation magnetization by 11% relative to that of the equilibrium state. It was shown that a strong correlation occurred between the specific saturation magnetization and the degree of DO₃-type long-range order in the ordered states. It was shown that a theoretical model, including consideration of transformation-induced lattice deformation, can qualitatively explain this phenomenon.

It was shown that a theoretical model, including consideration of lattice deformation caused by the transformation, can qualitatively explain this phenomenon.

Acknowledgments

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References

- [1] Vinogradov A and Estrin Yu 2018 *Progr. Mater. Sci.* **95** 172
- [2] Edalati K and Horita Z 2016 *Mater. Sci. Eng. A* **652** 325
- [3] Glezer A M, Kozlov E V, Koneva N A, Popova N A and Kurzina I A 2017 *Plastic Deformation of Nanostructured Materials* (Taylor & Francis Group, N-Y)
- [4] Stolyarov V V, Gunderov D V, Popov A G, Gaviko V S and Ermolenko A S 1998 *J. Alloys Compd.* **281** 69
- [5] Straumal B B, Mazilkin A A, Protasova S G, Dobatkin S V, Rodin A O, Baretzky B, Goll D and Schütz G 2009 *Mater. Sci. Eng. A* **503** 185
- [6] Hosokawa A, Ohtsuka H, Li T, Li S and Tsuchiya K 2014 *Mater. Trans.* **55** 1286
- [7] Glezer A M, Tomchuk A A, Savchenko A G, Korovushkin V V and Shchetinin I V 2016 *Bull. Russ. Acad. Sci.: Phys.* **80** 1021
- [8] Scheriau S, Rumpf K, Kieber S and Pippan R 2008 *Mater. Sci. Forum* **584-586** 923
- [9] Grossinger R, Mehboob N and Zehetbauer M 2014 *IOP Conf. Series: Mater. Sci. Eng.* **60** 012019
- [10] Kazantseva N V, Pilugin V P, Zavalishin V A, Rigmant M B, Davidov D I and Stepanova N N 2013 *Lett. Mater.* **3** 16
- [11] Glezer A M, Plotnikova M R, Shalimova A V and Dobatkin S V 2009 *Bull. Russ. Acad. Sci.:*

Phys. **73** 1233

- [12] Abrosimova G, Aronin A, Matveev D and Pershina E 2013 *Mater. Lett.* **97** 15
- [13] Zhilyaev A P and Langdon T G 2008 *Prog. Mater. Sci.* **53** 893
- [14] Kakehashi Y 2012 *Modern Theory of Magnetism in Metals and Alloys* (Springer, Heidelberg)
- [15] Swann P R, Duff W R and Fisher R M 1972 *Metal. Trans.* **3** 413
- [16] Glezer A M, Timshin I A, Shchetinin I V, Gorshenkov M V, Sundeev R V and Ezhova A G 2018 *J. Alloys Compd.* **744** 791
- [17] Glezer A M and Permyakova I E 2013 *Melt-Quenched Nanocrystals* (N-Y, Taylor & Francis Group)
- [18] Shiga M 1974 *AIP Conf. Proc.* **18** 463
- [19] Khachaturyan A G 2008 *Theory of Structural Transformations in Solids* (N-Y, Dover)