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High-Temperature Evolution of the Magnetization of Aluminum Reduction Cell Steel

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Abstract. The magnetic properties of steel of a structural element of an aluminum reduction cell have been investigated in the temperature range of 300–900 K. The analysis of the temperature dependence of the saturation magnetization $M_S(T)$ showed (i) the applicability of the Bloch's 3/2 law and a reasonable value of the Bloch's constant for steel and (ii) the quadratic dependence $M_S(T){\sim}(1 - T^2)$ in the temperature range of 380–700 K.

Keywords: steel, aluminum reduction cells, saturation magnetization, Bloch's constant.

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Introduction

The problem on the behavior of magnetization of metals at high (above 300 K) temperatures has been discussed for a long time [1–6]. On the one hand, in metals, the Bloch's law is experimentally observed, which follows from the consideration of spin wave damping [1–6] and can be written in the form

$$M_S(T) = M_{S0}\left(1 - BT^{3/2} - CT^{5/2}\right). \tag{1}$$

In Eq. (1), M_S is the saturation magnetization, M_{S0} is its value at $T = 0$ K, and B and C are the coefficients. On the other hand, in conducting ferromagnets, one can expect also the quadratic dependence of the saturation magnetization [3–5, 7–9]:

$$M_S(T) \approx M_{S0}\left(1 - DT^2\right) \sim \left(1 - T^2\right). \tag{2}$$

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Equation (2) follows from the consideration of the Fermi excitations in metals [10]; in addition, the dependence of type (2) has been recently obtained in the framework of the dynamic spin-fluctuation theory [9]. In the low-temperature region, the applicability of Bloch's law (1) for metals is undoubted, since coefficient B in Eq. (2) unambiguously determines the spin wave stiffness parameter, which is a reference value for a specific metal [7,8]. Nevertheless, the behavior of the magnetization of metals at sufficiently high temperatures is still argued [4, 5, 9, 11].

Study of the high–temperature behavior of the magnetization is important for application of a material (steel) used in aluminum production to fabricate reduction cells. The operation of a reduction cell depends on many parameters [12–15] and its resulting magnetohydrodynamic (MHD) characteristics are determined, in particular, by the magnetization of structural elements of a cell [13, 15]. To optimize the MHD characteristics, it is necessary to know the magnetization of a ferromagnetic material of an electrolytic vessel at sufficiently high working temperatures of a cell.

The aim of this study was to investigate the behavior of the saturation magnetization of a cell material (steel) in the temperature range of 300–900 K and analyze the results obtained using the available approaches to describing ferromagnetic materials.

1. Experimental

We investigated the steel of the bottom of a reduction cell that has been operating at the Krasnoyarsk aluminum smelter (RUSAL) for twenty-five years. To measure the magnetization, a needle-shaped sample ($m = 1.65 \pm 0.02$ mg) was prepared from a steel slug. We examined two samples and obtained the identical results. The data for one of them are presented below.

The magnetic measurements were performed with a Quantum Design PPMS-9 vibrating sample magnetometer.

2. Results and discussion

Fig. 1 shows isotherms of the $M(H)$ curves obtained for the sample under study in the temperature range of 300–900 K with a step of 30 K. The $M(H)$ dependences are almost saturated in fields of stronger than 1 kOe. The magnetization approaches saturation, according to the law [16]

$$M(H)/M_S = 1 - A_1H^{-1} - A_2H^{-2}, \tag{3}$$

where A_1 and A_2 are the constants, whose ratio determines the strong-field magnetization plot. In the inset to Fig. 1, some of the $M(H)$ dependences are given in coordinates M and $1/H$. The linear shape of the $M(H)$ dependences in these coordinates in fields stronger than 10^3 Oe ($1/H < 10^{-3}$ Oe^{-1}) is indicative of the dominance of the term $-A_1H^{-1}$ in Eq. (3); consequently, for the field range of $H > 10^3$ Oe, we can write

$$M(H)/M_S \approx 1 - A_1H^{-1}. \tag{4}$$

Dependence (4) allows us to find the saturation magnetizations M_S at each temperature by extrapolating the data to $1/H = 0$. Below, we operate with the $M_S(T)$ dependence obtained using the above-described approach, as well as the data obtained in a fairly strong field ($H = 2$ kOe), i.e., the $M_{H=2\mathrm{kOe}}(T)$ dependence.

The $M_S(T)$ and $M_{H=2\mathrm{kOe}}(T)$ dependences are presented in Fig. 2. First, we touch upon the problem of absolute values of the magnetization. At $T = 300$ K, the M_S value is 187.5±2.5 emu/g, which is lower than the saturation magnetization of pure iron by 10–12%. Such a decrease relative to the perfect Fe sample is caused by impurities contained in the nominal steel composition and other possible uncontrolled impurities, as well as partial oxidation of iron. Our data showed that the M_S(300 K) absolute values for steel in different structural parts of the cell lied within 170–190 emu/g.

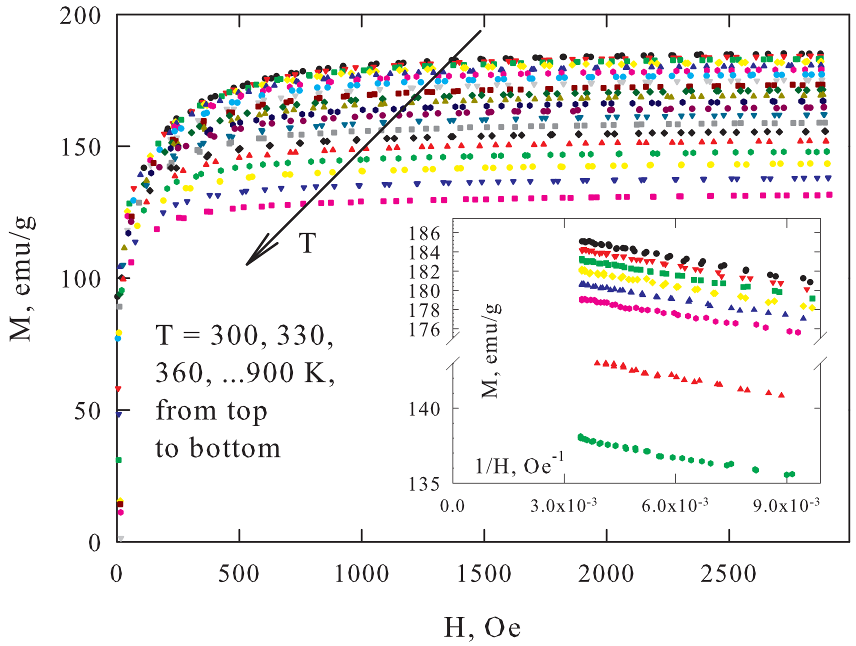

Fig. 1. Magnetization curves $M(H)$ obtained for the investigated sample at temperatures from 300 to 900 K with a step of 30 K. Inset: representative $M(H)$ data in coordinates M and $1/H$ demonstrating the linear dependence consistent with Eq. (4)

Fig. 2 and the inset therein illustrate also the results of fitting of the experimental data to dependences (1) (solid lines) and (2) (dashed lines). The coefficients of the fitting curves are given in the figure caption. It can be seen that both approaches yield satisfactory agreement with the experiment in a wide temperature range. It should be noted that the fitting data for the $M_S(T)$ and $M_{H=2\mathrm{kOe}}(T)$ dependences are only different in the M_{S0} value and this difference is no more than 2%.

Let us consider the obtained fitting parameters. The coefficient $B = 3.5(\pm 0.2) \times 10^{-6}$ K$^{-3/2}$ for Eq. (1) is similar to the Bloch's constant for bcc iron (3.4×10^{-6} K$^{-3/2}$ [6–8]). Importantly, the Bloch's constant B obtained from the 3/2 law is related to the main magnetic constant of a material, i.e., to the exchange coupling constant [6, 7]; consequently, the 3/2 law is reasonably met. The exchange coupling constant A obtained using the equation [7]

$$A = \frac{k_B}{8\pi}\left(\frac{M_{S0}}{g\mu_B}\right)^{\frac{1}{3}}\left(\frac{2.612}{B}\right)^{\frac{2}{3}}, \tag{5}$$

where k_B is the Boltzmann constant, μ_B is the Bohr magneton, and the g factor is 2, was

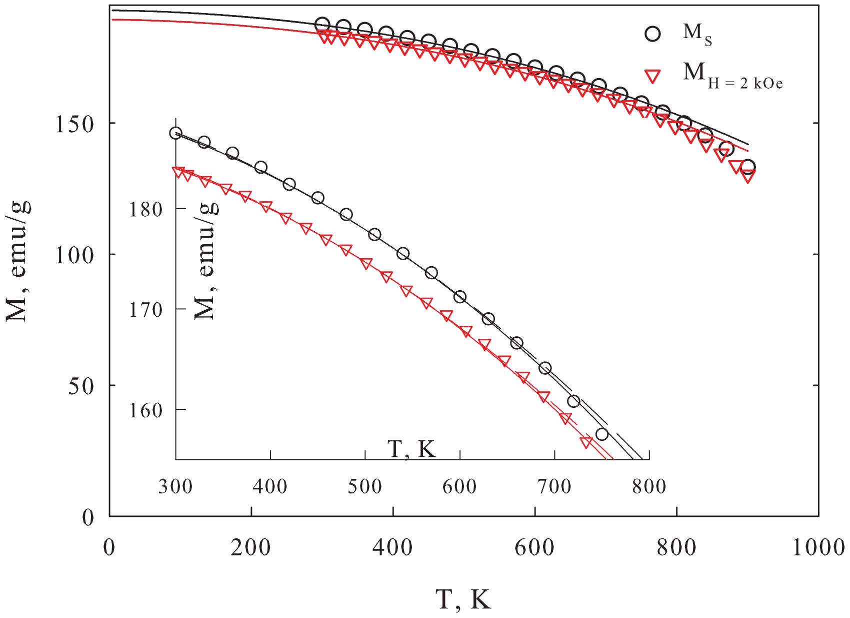

Fig. 2. Temperature dependences of magnetization $M_{H=2\mathrm{kOe}}(T)$ in a field of $H = 2$ kOe and saturation magnetization $M_S(T)$ obtained using the data from Fig. 1 and Eq. 4 (symbols). Inset: the same on an enlarged scale. Solid and dashed curves correspond to the fitting using Eqs. (1) and (2) for the $M_S(T)$ and $M_{H=2\mathrm{kOe}}(T)$ dependences, respectively. At $B = 3.5 \times 10^{-6}$ $\mathrm{K}^{-3/2}$ and $C = 0.7(\pm 0.03) \times 10^{-8}$ $\mathrm{K}^{-5/2}$, the curves are plotted using Eq. (1); at $D = 3.13 \times 10^{-7}$ K^{-2}, using Eq. (2); the M_{S0} values for the $M_S(T)$ and $M_{H=2\mathrm{kOe}}(T)$ dependences are 193 and 189 emu/g, respectively. The inset illustrates good agreement in a fairly wide temperature range

found to be $2.044(\pm 0.02) \times 10^{-6}$ erg/cm, which is similar to the A value for pure bcc iron (2.1×10^{-6} erg/cm [7]).

As was shown in some studies, the 3/2 term for metal ferromagnets usually manifests itself only at sufficiently low temperatures $T < 0.05T_C$ (T_C is the Curie temperature) [3], although in other works, this range was increased to about $(0.2 - 0.4)T_C$ [6–8, 17]. In our case, it might seem surprising that the 3/2 law works fairly well around room temperature, in fact, at $0.3T/T_C$ ($T_C \sim 1040$ K) and higher. At the same time, the constant $C = 0.7(\pm 0.03) \times 10^{-8}$ at the 5/2 term in Eq. (1) exceeds by far the corresponding value for bcc iron ($C = 0.1 \times 10^{-8}$ $\mathrm{K}^{-5/2}$ [8]). This fact is indicative also of only partial applicability of Eq. (1) for describing the experimental data.

On the other hand, as can be seen in Fig. 2, quadratic dependence (2) describes well the experiment, similar to dependence (1). This is shown in Fig. 3, which presents the relative change in the saturation magnetization $1 - M(T)/M_{S0}$ as a function of the normalized temperature T/T_C on the logarithmic scale. It can be seen in Fig. 3 that the straight with a slope coefficient of 2 yields the best agreement with the experiment in a wide temperature range.

The aforesaid allows us to make the following conclusions:

(i) The Bloch's constant similar to the nominal value for iron is an echo of the low-temperature behavior of the saturation magnetization and satisfaction of the 3/2 law.

(ii) The larger (as compared with the nominal) coefficient C at fitting using Eq. (1) is indicative

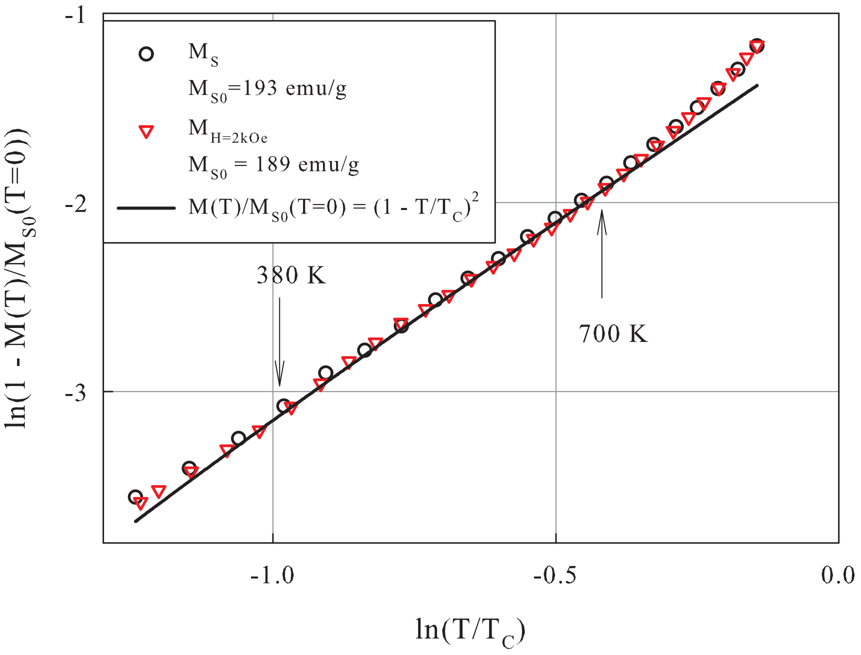

Fig. 3. Dependence of the relative change in the saturation magnetization $1 - M(T)/M_{S0}$ and $1 - M_{H=2\text{kOe}}(T)/M_{S0}$ (the M_{S0} values are indicated in the figure) on the normalized temperature T/T_C on the logarithmic scale (symbols)

of the transition of the saturation magnetization to the other functional temperature dependence. In fact, the C value fitted for the best agreement with the experiment leads to the identity of Eq. (1) and quadratic law (2) in the temperature range of 300–700 K (see Fig. 2).

It should be emphasized that, as was shown in recent work [9], not only the consideration of magnons, but also the calculation using the dynamic spin-fluctuation theory yield the 3/2 law for iron at low temperatures, as well as a quadratic decrease in the magnetization around room temperatures. In our experiment, the quadratic temperature dependence of the magnetization is observed in the range of 380–700 K (Fig. 3).

Conclusions

The saturation magnetization M_S of the investigated samples of aluminum reduction cell steel is ~ 190 emu/g and lower at room temperature; such a low (as compared with perfect bcc iron) value is caused by impurities and partial oxidation of iron. The $M(H)$ curves approach the saturation in a field of about 1 kOe; in the range of $H > 1$ kOe, the $M(H)$ dependences obey the law $M(H)/M_S \sim (1 - H^{-1})$. The temperature dependences of the magnetization measured in a dc field of $H = 2$ kOe behave similarly to the $M_S(T)$ dependence, which allows one to choose a characteristic most convenient for the measurements ($M(T)$ at $H > 1$ kOe or $M_S(T)$) for further analysis of these data.

In the temperature range above room temperature, the $M_S(T)$ dependence can be described by the Bloch's law taking into account the powers of 3/2 and 5/2. The exchange coupling constant A obtained from the Bloch's constant is similar to pure bcc iron. At the same time, the quadratic law of the magnetization drop $M_S(T) \sim (1 - T^2)$ is observed in a fairly wide temperature range (380–700 K).

The magnetization of steel significantly changes in the temperature range of 300–900 K. This temperature range approximately corresponds to the window of working temperatures of some structural elements of the aluminum reduction cell. To correctly take into account the magnetization of the cell material in the calculation and optimization of the MHD characteristics, it is reasonable to use the temperature dependence of the magnetization of steel.

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Высокотемпературная эволюция намагниченности стали алюминиевого электролизера

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Аннотация. В работе исследованы магнитные свойства стали конструктивного элемента алюминиевого электролизера в области температур 300–900 K. Проведенный анализ температурной зависимости намагниченности насыщения $M_S(T)$ показал: (i) применимость "закона 3/2" Блоха, а также разумное значение константы Блоха и константы обменного взаимодействия для стали; (ii) квадратичную зависимость $M_S(T) \sim (1 - T^2)$ в температурном диапазоне 380–700 K.

Ключевые слова: сталь, алюминиевые ячейки восстановления, намагниченность насыщения, постоянная Блоха.