

Synthesis of Transition Metal Coatings Using Arabinogalactan

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Abstract—Carbon-containing transition metal (Fe, Co, Ni) coatings are synthesized via chemical deposition with arabinogalactan. The crystal structure and chemical composition of the coatings are determined. Data from magnetometry and X-ray diffraction show that carbon is not included in the crystal lattice of a metal. Instead, it exists in the form of graphite inclusions. Degradation of arabinogalactan in an alkaline medium on the surface of a galvanic pair is investigated.

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INTRODUCTION

The chemical deposition of metallic coatings from aqueous solutions using a reducing agent is easy and cost-efficient. This technique is based on the interaction between metal ions and a dissolved reducing agent, which forms a metal (e.g., Fe, Co, Ni, Cu, Pd) layer on a catalytically active surface. With no autocatalysis, reduction can proceed over the volume of the solution and form a metal powder. The reducing agents used in the synthesis of 3d magnetic metal coatings are formaldehyde, hydrazine, sodium hypophosphite, sodium borane, and hydrazineborane. The reducing agent most widely used in the synthesis of Co and Ni coatings is sodium hypophosphite NaH_2PO_2 . Metal–metalloid substitutional solid solutions are in this case obtained and phosphides are isolated. Having phosphorus in a metallic coating reduces the magnetic and mechanical properties of the latter. Despite the drawbacks mentioned above, the industrial production and use of coatings based on nickel and cobalt alloys obtained with NaH_2PO_2 are growing steadily [1]. Iron-based alloys synthesized via chemical deposition have high microhardness and corrosion resistance. A problem in depositing iron coatings is that Fe^{2+} (0.44 V) has a higher reduction potential than Ni^{2+} (0.24 V) and Co^{2+} (0.27 V), so reduction/precipitation cannot occur using only NaH_2PO_2 reducing agent (iron coatings can be obtained using sodium borohydride). A chemical iron coating on a copper

substrate was first obtained in [2] using hypophosphite to create a galvanic bond between a copper substrate and an aluminum plate in an alkaline medium. When dissolving in an alkaline environment, aluminum imparts a negative charge to the copper substrate and reduces its potential, thereby ensuring the chemical reduction of metal ions. The structure, properties, and features of the formation of magnetic coatings via chemical deposition were studied in [3–6].

New approaches to metal reduction (referred to as green synthesis) are now being developed. They are based on using, e.g., microorganisms [7, 8] and extracts of natural plant products [9]. They are promising environmentally friendly means that will allow us to overcome the existing barriers to chemical synthesis. The extracts that are used are generally not toxic and serve as dispersing and coating agents which minimize oxidation. A promising field is the production of nanostructured materials using polysaccharides, especially arabinogalactan [10–12]. Arabinogalactan is a branched polysaccharide with the chemical formula $[(\text{C}_5\text{H}_8\text{O}_4)(\text{C}_6\text{H}_{10}\text{O}_5)_6]_n$, in which six galactose links correspond to one arabinose link. Arabinogalactan belongs to a family of water-soluble plant polysaccharides and is contained in coniferous trees. Its content is especially high in larch. This all-natural water-soluble fiber forms solutions with low viscosity and exhibits high surface activity and stability at different concentrations, acidities, and temperatures.

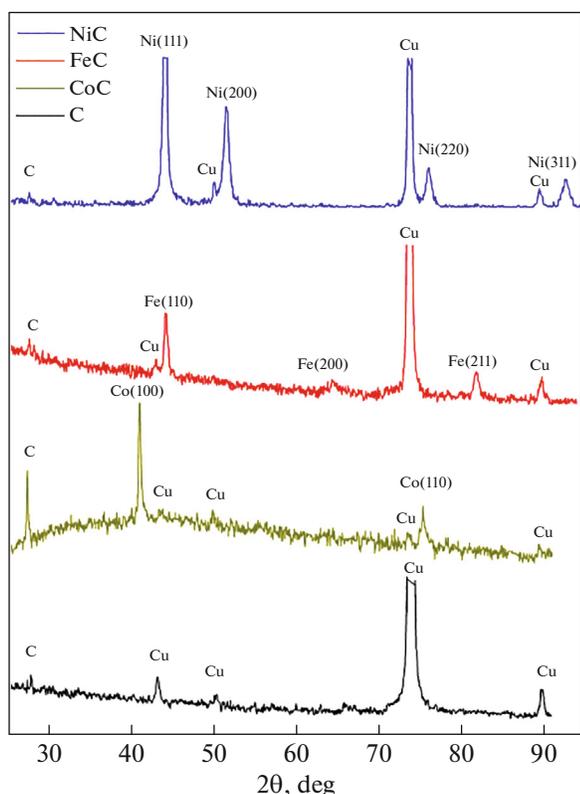


Fig. 1. X-ray diffraction patterns of Fe–C, Co–C, and Ni–C coatings on a copper substrate, and of copper foil after treatment in an alkaline solution of arabinogalactan.

The need to develop more cost-efficient absorbers of electromagnetic waves with broader absorption bands and better absorbing properties is always growing. It is known that loss to absorption depends on a material's permeability and permittivity. It is expected that absorbers consisting of magnetic and carbon materials will display high efficiency over a wider range of frequencies. Carbon/magnetic metal composites are therefore of great interest as absorbers of microwave radiation [13].

The aim of this work was to synthesize 3d metal/carbon magnetic coatings by means of green chemistry and investigate their properties.

EXPERIMENTAL

Carbon-containing transition metal coatings were synthesized via chemical deposition using arabinogalactan (AO Ametis, Russia) isolated from larch. Solutions containing metal sulfate and polysaccharide were added with sodium citrate as a complexing agent. Alkali NaOH (ammonium hydroxide NH_4OH) was added to the obtained solution until pH 11. The coatings were deposited onto copper foil in direct contact with aluminum foil. A TZh-TS-01 water thermostat

was used to maintain a temperature of 80°C during deposition.

The synthesized samples were studied on a Hitachi HT7700 transmission electron microscope (accelerating voltage, 100 kV) and the CarlZeiss EVO 60 scanning electron microscope at the shared resource center of the Krasnoyarsk Scientific Center (Siberian Branch, Russian Academy of Sciences). The structure of the coatings was studied on a DRON-4 X-ray diffractometer. Their magnetic properties were investigated using a Quantum Design MPMS XL7 SQUID magnetometer.

The degradation of arabinogalactan was studied via gel permeation chromatography on an Agilent 1260 Infinity II Multi-Detector GPC/SEC System chromatograph with triple detection. The system contained a refractometer (RI), a viscometer (VS), and a light scatter (LS) meter. Separation was done on two combined PL Aquagel-OH Mixed-M columns using a mixture of 0.2 M NaNO_3 + 0.01 M NaHPO_4 as the mobile phase for aqueous solutions. The columns were calibrated according to Agilent polyethylene glycol polydisperse standards (United States). The eluent flow rate was 1 mL/min, and the volume of the injected sample was 100 μL . The solutions were filtered through a Millipore 0.45- μm PTFE membrane. Data were collected and processed using the Agilent GPC/SEC MDS software.

RESULTS AND DISCUSSION

Chemical deposition with arabinogalactan was used to synthesize 3d metal coatings on a copper substrate consisting of copper foil 100 μm thick in contact with aluminum foil. The ferromagnetic coatings were several micrometers thick. Transmission electron microscope elemental analysis of the coatings showed that carbon was present in concentrations of 15–20 at %. Scanning electron microscopy energy dispersive X-ray analysis revealed a uniform distribution of carbon over the synthesized coatings. Figure 1 shows X-ray diffraction patterns of the resulting Ni–C, Fe–C, Co–C samples and their interpretation. The X-ray patterns contain reflections corresponding to both the ferromagnetic metals (fcc-Ni, hcp-Co, and bcc-Fe) and the copper substrate. The X-ray diffraction data allowed us to determine the lattice constant of the investigated alloys. The values that were obtained corresponded to the reference data for pure Ni, Fe, and Co, meaning there was no carbon in the crystal lattice of the metal. No reflections characteristic of 3d-metal carbides were observed [14]. Low-intensity reflections corresponding to the graphite phase were recorded in the X-ray diffraction patterns at $2\Theta = 27^\circ$, along with reflections of the metal planes (see Fig. 1). This suggests that carbon was deposited in the form of graphite. Figure 1 also shows the X-ray diffraction pattern of the copper foil in contact with the aluminum foil in the arabinogalactan solution in an alkaline medium. This

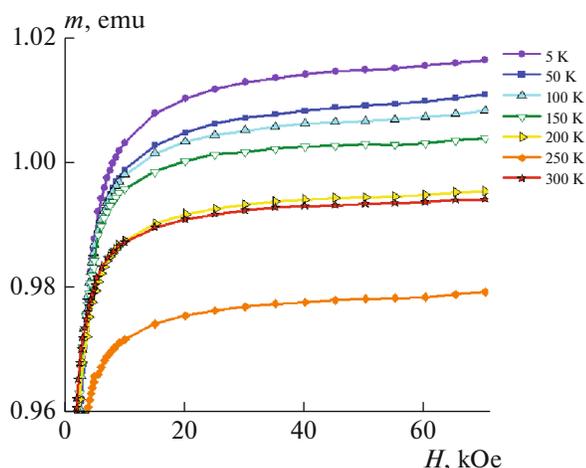


Fig. 2. Magnetization curves at different temperatures.

X-ray diffraction pattern contains the reflection from the graphite phase as well.

Figure 2 presents the magnetization curves measured for the Co–C coating in the 5–300 K range of temperatures. The temperature dependence of magnetization m in the maximum field (70 kOe) is close to the magnetization of saturation. The gradient of the spontaneous (saturation) magnetization of a ferromagnet at low temperatures is determined by Bloch's constant $T^{3/2}$, which is uniquely specified by the constant of exchange [15]. The latter is sensitive to the immediate environment of the exchange-coupled magnetic moments of atoms. A small fraction of impurities can greatly reduce the constant of exchange and raise Bloch's constant [16, 17]. Figure 3 presents data on the low-temperature behavior of magnetization alongside literature data for pure hcp cobalt [18, 19]. Note that pure cobalt is characterized by the least steep gradient of magnetization for pure $3d$ metals. The similarity observed in Fig. 3 between the temperature gradient of the cobalt coatings' magnetization and the literature data shows how close the short-range chemical order is to the order of pure hcp cobalt. This confirms there were no impurity atoms (of carbon in particular) in the cobalt lattice (which is consistent with the data given in Fig. 1) and the conclusion that carbon was in the form of a graphite phase in the cobalt coating.

The degradation of arabinogalactan in an alkaline medium on the surface of a galvanic pair was studied experimentally. Copper and aluminum plates in contact with each other were immersed in a solution containing 200 mL of water, 2 g of arabinogalactan, and 20 mL of NH_4OH (25 vol %). The solution was heated to 80°C , and samples of it were taken every 20 min. The samples were numbered AG0, AG20, AG40, and AG60. Gel permeation chromatography was used to determine weight average molecular weight M_w , number average molecular weight M_n , and the polydisper-

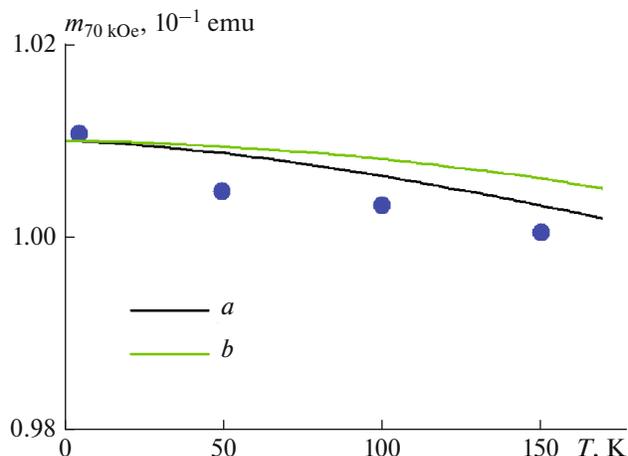


Fig. 3. (symbols) Temperature dependence of the magnetization of cobalt coatings in comparison with (solid curves) the literature data for pure cobalt phases: [18] (a) hcp Co, [19] (b) fcc Co.

sity (PD) of the initial samples of the arabinogalactan (AG) and solution. The distribution of the molecular weight of the initial arabinogalactan and samples AG0, AG20, AG40, and AG60 of the solution are given in Table 1.

Our data showed that the molecular weight distribution in the samples changed somewhat as the length of the process grew. Weight average molecular weight M_w fell from 19088 (at 0 min) to 18482 (at 60 min). The molecular weight distribution curves shifted slightly to the region of low molecular weight, while the degree of polydispersity remained virtually unchanged (Fig. 4). The peak region, which illustrates the shift in the molecular weight distribution, is shown separately. Considering the structural characteristics of AG molecules and the medium of the solution, we may assume the alkaline hydrolysis of AG molecules proceeds during the process. Changes in the molecular weights show that an average of one particle of monosaccharide (arabinose or galactose) residue with a molecular weight of ~ 150 Da detaches from each molecule every 20 min. These particles can exhibit reducing properties and carbonize on a metal surface under conditions of local overheating.

Table 1. Molecular weight distributions of the initial arabinogalactan and samples AG0, AG20, AG40, and AG60 of the solution

Sample	M_n , Da	M_w , Da	PD
AG0	16783	19088	1.14
AG20	16121	18779	1.17
AG40	16033	18606	1.16
AG60	15914	18482	1.16

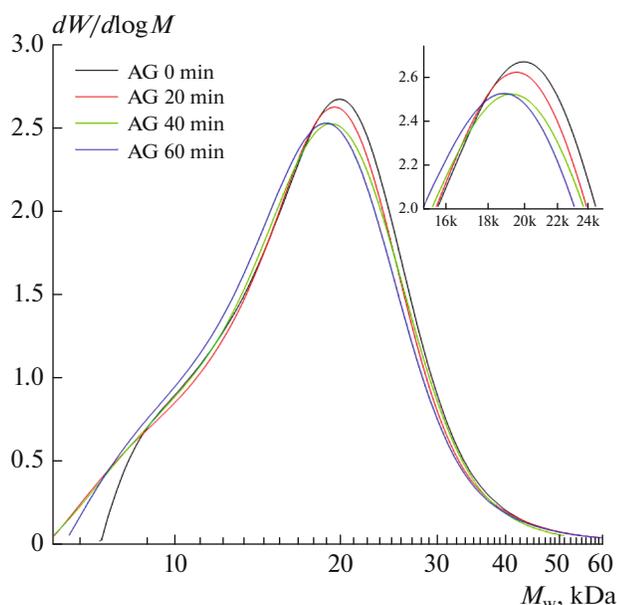


Fig. 4. Molecular weight distribution curves for the arabinogalactan-containing samples.

We used a combination of several processes to synthesize metallic coatings with carbon inclusions: electrochemical, using Cu/Al galvanic pairs and the dissolution of Al, and chemical, with the reduction of Fe, Co, and Ni cations using a polysaccharide. Arabinogalactan is a branched polysaccharide with the chemical formula $[(C_5H_8O_4)(C_6H_{10}O_5)_6]_n$, in which six galactose links correspond to one arabinose link. Both monosaccharides exhibit reducing properties. As it dissolves in an alkaline medium, aluminum imparts a negative charge to a copper substrate and reduces its potential, thereby ensuring the chemical reduction of 3d metal ions. A metallic coating can form via catalytic decomposition of the polysaccharide onto metal substrates. The glycosidic bonds of a polysaccharide molecule are stable in an alkaline medium at low temperatures. It is known, however, that degradation proceeds at the ends of polysaccharide molecules under such conditions. The open aldehyde groups at the ends of the molecules exhibit reducing properties, so the monosaccharide link is detached and oxidized to carboxylic acid. The catalytic decomposition of the polysaccharide on the substrate is apparently not limited to this reaction, since the final product of polysaccharide decomposition is graphite, which can be detected via X-ray diffractometry. Carbon, a product of the reactions that occur on a metal surface, transforms exclusively into graphite and does not penetrate the crystal lattice of the resulting ferromagnetic coating, as was confirmed by magnetic measurements.

CONCLUSIONS

The synthesized coatings can be considered metal/carbon composites in which carbon takes the

form of bulk graphite inclusions. Since magnetic materials with carbon inclusions absorb electromagnetic waves well because of their magnetic and dielectric components, our composite coatings can be used as absorbers of electromagnetic radiation.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Agarwala, R.C. and Agarwala, V., *Sadhana*, 2003, vol. 28, nos. 3–4, p. 475.
2. Ruscior, C. and Croial, E., *J. Electrochem. Soc.*, 1971, vol. 118, p. 696.
3. Zhou, H. and Guo, J., *J. Electrochem. Soc.*, 2013, vol. 160, no. 6, D233.
4. Ge, Y., Bangwei, Z., Lingling, W., et al., *J. Electrochem. Soc.*, 2013, vol. 160, no. 9, D403.
5. Zhang, X., Han, W., Fan, D., et al., *Mater. Lett.*, 2014, vol. 130, p. 154.
6. Vazhenina, I.G., Chekanova, L.A., and Iskhakov, R.S., *Bull. Russ. Acad. Sci.: Phys.*, 2019, vol. 83, no. 6, p. 713.
7. Gallo, G., Baldi, F., Renzone, G., et al., *Microb. Cell Fact.*, 2012, vol. 11, no. 1, p. 152.
8. Stolyar, S.V., Bayukov, O.A., and Gurevich, Yu.L., *Inorg. Mater.*, 2006, vol. 42, no. 7, p. 763.
9. Machado, S., Pinto, S.L., Grosso, J.P., et al., *Sci. Total Environ.*, 2013, vols. 445–446, p. 1.
10. Trofimov, B.A., Sukhov, V.G., Aleksandrova, G.P., et al., *Dokl. Chem.*, 2003, vol. 393, nos. 4–6, p. 287.
11. Gasilova, E.R., Matveeva, G.N., Aleksandrova, G.P., et al., *J. Phys. Chem. B*, 2013, vol. 117, no. 7, p. 2134.
12. Stolyar, S.V., Chekanova, L.A., Yaroslavtsev, R.N., et al., *J. Phys.: Conf. Ser.*, 2019, vol. 1399.
13. Wang, B., Wu, Q., Fu, Yo., et al., *J. Mater. Sci. Technol.*, 2021, vol. 86, p. 91.
14. Iskhakov, R.S., Stolyar, S.V., and Zhigalov, V.S., *Bull. Russ. Acad. Sci.: Phys.*, 2005, vol. 69, no. 4, p. 676.
15. Iskhakov, R.S., Shepeta, N.A., Komogortsev, S.V., et al., *Fiz. Met. Metalloved.*, 2003, vol. 95, no. 3, p. 37.
16. Varnakov, S.N., Komogortsev, S.V., Bartolome, J., et al., *Phys. Met. Metallogr.*, 2008, vol. 106, no. 1, p. 51.
17. Chekanova, L.A., Denisova, E.A., Goncharova, J.A., et al., *Phys. Met. Metallogr.*, 2013, vol. 114, no. 2, p. 122.
18. Andreev, A.S., d'Espinose de Lacaillerie, J.-B., Lapina, O.V., and Gerachenko, A., *Phys. Chem. Chem. Phys.*, 2015, vol. 17, no. 22.
19. Komogortsev, S.V., Iskhakov, R.S., Barnakov, Ch.N., et al., *Phys. Met. Metallogr.*, 2010, vol. 109, no. 2, p. 130.

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