The effect of annealing temperatures on magnetic and electric properties of electrodeposited $Ni_{85,3}Fe_{10,6}W_{1,4}Cu_{2,2}$ alloy

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$Ni_{85,8}$ $Fe_{10,6}$ $W_{1,4}$ $Cu_{2,2}$ alloy powder consisting of an amorphous matrix and nanocrystals of an FCC solid solution of Fe, W and Cu in nickel was produced by electrodeposition. Heating the pressed powder sample over the temperature range of 20 to 600°C permitted structural changes to take place in the alloy, causing changes in its electrical resistivity and magnetic permeability. The alloy exhibits structural stability up to 150°C. In the temperature interval 150-360°C, the alloy undergoes intensive structural relaxation resulting in an increase in electrical conductivity and magnetic permeability. Less intensive structural relaxation occurs at temperatures between 360°C and 460°C. In this interval, under heat treatment, magnetic domain arrangement decreases and, hence, the interaction between magnons and conduction electrons is reduced, leading to a decrease in the temperature coefficient of electrical resistivity (TCER). Amorphous matrix crystallization and FCC crystal growth take place in the temperature interval 460-520°C, causing a decline in electrical resistivity and magnetic permeability.

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1. Introduction

Nanostructured materials have been extensively used in novel technologies due to their specific physical and chemical properties [1-4]. Nanostructured nickel-iron-tungsten alloys exhibit good mechanical, electrical and magnetic properties, high thermal stability and high corrosion resistance [5-18]. The metallurgic production of these alloys is an expensive process. Therefore, more recently, cheaper procedures for their production have been developed [5-18]. Nanostructured nickel-iron-tungsten alloys can be obtained by electrochemical methods from environmentally friendly citrate ammonia solutions without any environmental and health risks.

Electrodeposition can result in the production of alloys with specific mechanical, chemical and physical properties dependent on operating and kinetic parameters of electrolysis [19-29]. More recently, a significant number of works explaining the mechanism of codeposition of tungsten and molybdenum with iron-group metals have been conducted [25-37]. The effects of current density, solution composition, solution pH and temperature on the chemical composition, microstructure, mechanical, electrical and magnetic properties, corrosion and thermal stability of electrodeposited Ni-Fe-W alloys have been reported in several studies [11-18, 37]. Nanostructured alloys exhibit a metastable structure. Annealing changes their microstructure, affecting their mechanical, magnetic, electrical, chemical and other properties [38-42].

Ni-Fe-W alloy powders cannot be electrodeposited from a citrate ammonia bath at high current efficiencies. The codeposition of small amounts of copper, Ni, Fe and W can result in the production of Ni-Fe-W-Cu alloy powder at high current efficiencies and with the desired particle size obtained [43]. The objective of this study was to investigate the magnetic and electrical properties of electrochemically produced Ni-Fe-W-Cu alloys containing a small amount of copper, and determine the effect of heat treatment on these properties.

2. Experimental

Nickel-iron-tungsten-copper alloy powder containing 85,8 wt.% Ni, 10,6 wt.% Fe, 1,4 wt.% W and 2,2 wt.% Cu ($Ni_{85,8}$ $Fe_{10,6}$ $W_{1,4}$ $Cu_{2,2}$) was electrodeposited at a current density of 450 $mAcm^{-2}$ from a citrate ammonia bath onto a titanium cathode. The electrolytic solution contained 0.2 mol dm^{-3} $NiSO_4$, 0.02 mol dm^{-3} $FeSO_4$, 0.004 mol dm^{-3} Na_2WO_4, 0,005 mol dm^{-3} $CuSO_4$, 0.24 mol dm^{-3} $Na_3C_6H_5O_7$, 0.8 mol dm^{-3} NH_4Cl, 0.3 mol dm^{-3} Na_2SO_4. The solution temperature during the electrolysis was 60±0.5°C, and pH was 9.2±0.05. The pH of the solution

was adjusted by the addition of 0.6 mol dm^{-3} NH_4OH. The chemical composition of the powder was determined by atomic absorption (PEKTAR-AA 200-VARIAN).

The magnetic properties of $Ni_{85,8}$ $Fe_{10,6}$ $W_{1,4}$ $Cu_{2,2}$ alloy were investigated by measurement of its magnetic permeability in the temperature interval 20-600°C using disc-shaped alloy samples of 8.0 mm diameter and 1.0 mm thickness obtained by powder pressing at 500mPa. The Faraday method based on the effect of an inhomogeneous field on the magnetic specimen was used. The measurements were made under an argon atmosphere on a balance with 10^{-6}N sensitivity.

The electrical resistivity of the pressed parallelepiped-shaped samples sized 4mm x 1.2mm x 0.5 mm was measured by the four-point method. During the measurement, 100 mA of constant current was passed through the sample. A change in voltage signal as a function of the temperature of the samples heated under argon was recorded. The sensitivity of the voltmeter equipped with a recorder was $5 \cdot 10^{-6}$V.

3. Results and discussion

Black nickel-iron-tungsten-copper alloy powder was electrodeposited from a citrate ammonia bath onto a titanium cathode. The chemical composition of the powder was determined by atomic absorption. Five different samples obtained under identical conditions were analyzed. The difference in the results was less than 0.5 wt.%. The measurements revealed the following average composition of the alloy: 85,8 wt.% Ni, 10,6 wt.% Fe, 1,4 wt.% W and 2,2 wt.% Cu ($Ni_{85,8}$ $Fe_{10,6}$ $W_{1,4}$ $Cu_{2,2}$).

As shown in our earlier studies [18, 43], the powder comprises an amorphous matrix with embedded nanocrystals of the FCC solid solution of Fe, W and Cu in Ni, with an average crystal grain size of 6 nm. X-ray diffraction showed that amorphous phase crystallization and FCC crystal grain growth take place during annealing at temperatures above 460°C [18, 43].

Magnetic and electrical properties of the alloy were investigated by measurement of the electrical resistivity and magnetic permeability of the pressed alloy powder.

Figs. 1 and 2 show the experimentally obtained temperature dependencies of relative magnetic permeability. During heating at a rate of 20°C min^{-1} to a pre-defined temperature, a change in magnetic permeability was recorded. Thereafter, the sample was cooled to room temperature, and then re-heated at the same rate to a higher temperature. The heating treatment was conducted in seven replications. The first four temperature dependencies are shown in Fig. 1, and the succeeding three are illustrated in Fig. 2 for better clarity.

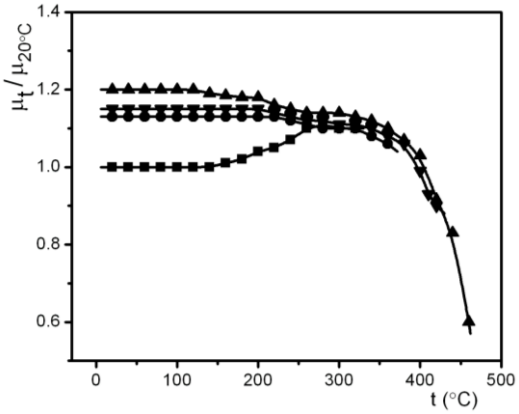

Fig. 1. A relative change in magnetic permeability, $\mu_t/\mu_{20°C}$ as a function of temperature t. Heating rate 20°C min^{-1}. ■ - first heating up to 310°C; ● - second heating up to 360°C; ▼ - third heating up to 420°C, and ▲ – fourth heating up to 470°C.

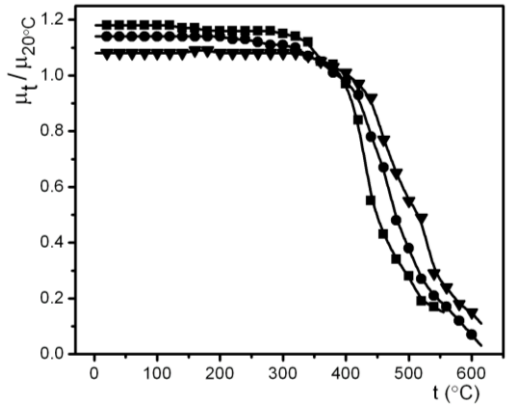

Fig. 2. A relative change in magnetic permeability, $\mu_t/\mu_{20°C}$ as a function of temperature. Heating rate: 20°C min^{-1}. ■ - fifth heating up to 540°C; ● - sixth heating up to 600°C, and ▼ - seventh heating up to 600°C.

The results presented in Figs. 1 and 2 indicate that the relative change in the magnetic permeability of the samples cooled at room temperature is dependent on the previous annealing temperature. The dependence is shown in Fig. 3.

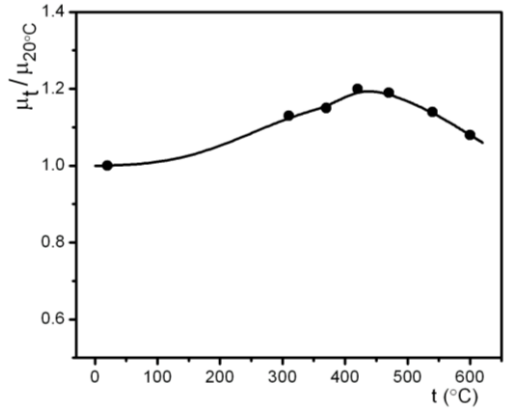

Fig. 3. A relative change in the magnetic permeability of the samples cooled at room temperature (20°C) as a function of previous annealing temperature.

The diagram presented in Fig. 3 shows that the structural changes occurring in the temperature interval 150-420°C cause an increase in the magnetic permeability of the sample cooled at t=20°C. Structural changes taking place at temperatures exceeding 420°C lead to a decrease in the magnetic permeability of the cooled sample.

The structural changes occurring during the annealing process were experimentally found to cause changes in electrical resistivity. Fig. 4 shows the temperature dependence of electrical resistivity.

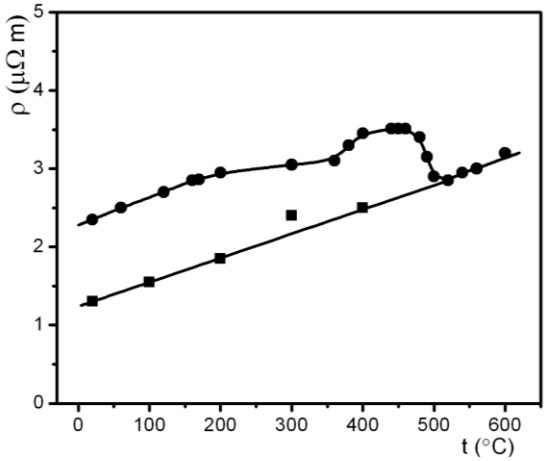

Fig. 4. Temperature dependence of electrical resistivity: ● - first heating; ■ - second heating.

The analysis of the experimental results presented in Figs. 1, 2. and 4. reveals five temperature subintervals in the temperature range 20-600°C, with different structural changes observed. In the first temperature subinterval 20-150°C, relative magnetic permeability does not change during heating, whereas electrical resistivity increases linearly with increasing temperature. The temperature coefficient of electrical resistivity (TCER) in this interval was $\alpha_1 = 0.36 \cdot 10^{-8}$ μΩm°C^{-1}. The magnetic permeability and electrical resistivity of the sample cooled to room temperature upon annealing at temperatures up to 150°C were identical to those of the as-deposited sample. The results indicate no significant structural changes in the as-deposited sample during heating up to 150°C.

The second temperature subinterval was between 150°C and 360°C. In this range, magnetic permeability abruptly increases with increasing temperature, whereas electrical resistivity increases linearly, as in the first interval, but shows a lower TCER ($\alpha_2 = 1.6 \times 10^{-8}$μ Ω m °$C^{-1}$). These results suggest that the alloy undergoes structural relaxation in this subinterval. During the structural relaxation, short-term structural arrangement takes place in the alloy, along with a simultaneous decrease in internal microstrain and density of chaotically distributed dislocations. Owing to the heat employed, certain atoms that have a high potential energy cross the energy barrier and reach somewhat lower energy levels. At these lower levels, their 3d and 4s orbitals overlap to a higher extent with identical orbitals of neighboring atoms, thus contributing to an increase in electron density of states in the conduction band near the Fermi level [4, 22, 44]. The ensuing structural changes, during the short-term structural arrangement, also result in an increase in the electronic mean free path [4, 22, 44].

As the free electron density of states and the electronic mean free path increase, the electrical conductivity of the alloy increases and TCER decreases. The decrease in both internal microstrain and the density of chaotically distributed dislocations increases the mobility of magnetic domain walls and enables the atoms translocated into lower energy levels and positioned between the magnetic domain walls to attach to energetically more favorable neighboring domains. The said decrease also facilitates domain orientation in the external magnetic field. These structural changes lead to an approximately 14% increase in magnetic permeability of the cooled sample, compared to the as-deposited sample.

In the third temperature subinterval 360-460°C, TCER was higher than the value measured in the second subinterval (Fig. 4). It was shown [43] that nanostructured $Ni_{85,8}$ $Fe_{10,6}$ $W_{1,4}$ $Cu_{2,2}$ alloy does not undergo crystallization in this interval. The diagrams presented in Figs. 1, 2. and 3. show that magnetic permeability is somewhat higher in the sample cooled upon annealing at 360°C and 420°C than in the cooled sample pre-annealed at 310°C. This indicates that structural relaxation, although to a lower extent, also takes place over the temperature range 360-460°C. In this interval, TCER and relative magnetic permeability gradually decrease with increasing temperature up to 400°C, declining thereafter more rapidly at temperatures between 400°C and 460°C. The diagrams showing the temperature dependence of relative magnetic permeability (Fig. 1) indicate a gradual decline in relative magnetic permeability as the temperature increases from 360°C to 400°C. However, at temperatures higher than 400°C, relative magnetic permeability abruptly decreases with increasing temperature. Over the temperature range 360-460°C, magnetic domain arrangement is reduced due to heat - gradually, at first, up to 400°C, and then abrupt up to 460°C. The reduction in magnetic domain arrangement leads to reduced interaction between conduction electrons and magnons, causing a decrease in TCER.

Upon the fourth heating to 470°C, the relative magnetic permeability of the cooled sample was only 2% lower than that of the cooled sample pre-heated to 420°C. This suggests that complete structural relaxation takes place in the alloy during annealing up to 460°C.

In the fourth temperature subinterval 460-520°C, the electrical resistivity of the alloy suddenly decreases, with TCER having a negative value. The abrupt decrease in electrical resistivity in this interval was due to amorphous phase crystallization and FCC crystal growth. Crystallization in this interval was confirmed by X-ray diffraction [18, 43]. The crystallization and crystal grain growth cause an increase in electronic mean free path in the conduction band as well as an increase in electron density of states near the Fermi level. The two effects lead to an abrupt decrease in the electrical resistivity of the alloy [4, 18, 43].

Crystallization was found to reduce the magnetic permeability of $Ni_{85,8}$ $Fe_{10,6}$ $W_{1,4}$ $Cu_{2,2}$ alloy. The orientation of magnetic domains becomes reduced by increasing stability of the crystal structure. The relative magnetic permeability of the cooled alloy decreased by 7% and about 13% after the fifth heating up to 540°C and sixth heating up to 600°C, respectively, in relation to the maximum value for the cooled sample after the third annealing up to 420°C. The increase in annealing temperature up to 600°C induces an increase in Curie temperature (Fig. 2). Annealing at increased temperatures results in greater stability of the structure which exhibits larger crystal grains and provides higher thermal stability of the oriented magnetic domains in the external magnetic field.

At temperatures above 520°C, electrical resistivity increases linearly with increasing temperature. After annealing at temperatures higher than 520°C, the sample was gradually cooled to room temperature, and then reheated to 600°C. During the reheating procedure, electrical resistivity was measured. A linear temperature dependence of electrical resistivity was obtained in the temperature interval 20-600°C.

The experiment suggests that the low copper content of $Ni_{85,8}$ $Fe_{10,6}$ $W_{1,4}$ $Cu_{2,2}$ alloy enables the nanostructured powder electrodeposited from a citrate ammonia bath onto a titanium cathode at high current densities and high current efficiencies to exhibit good magnetic properties and a higher Curie temperature compared to the nanostructured powder of alloys without copper [18, 43].

4. Conclusion

Nanostructured $Ni_{85,8}$ $Fe_{10,6}$ $W_{1,4}$ $Cu_{2,2}$ alloy powder was electrodeposited from a citrate ammonia bath. The alloy comprises an amorphous phase with embedded nanocrystals (6 nm average size) of FCC solid solution of Fe, W and Cu in Ni. Heating the pressed powder sample over the temperature range of 20 to 650°C permitted structural changes to take place in the alloy, causing changes in its electrical resistivity and magnetic permeability. During annealing up to 150°C, no structural changes take place in the as-deposited sample. In the temperature interval 150 -360°C, the alloy undergoes intensive structural relaxation involving short-term structural arrangement and decreases in internal microstrain and density of chaotically distributed dislocations, leading to an increase in the mean free path of electrons in the conduction band as well as to an increase in the electron density of states near the Fermi level. These structural changes cause an increase in the electrical conductivity and magnetic permeability of the nanostructured alloy. Less intensive structural relaxation occurs at temperatures between 360°C and 460°C. In this interval, under heat treatment, magnetic domain arrangement and, hence, the interaction between magnons and electrons in the conduction band decrease, leading to a decrease in TCER. Amorphous matrix crystallization and FCC crystal growth take place in the temperature interval 460-520°C, causing an abrupt decrease in electrical resistivity and a decline in magnetic permeability.

The codeposition of a small amount of copper, Ni, Fe and W enables the nanostructured $Ni_{85,8}$ $Fe_{10,6}$ $W_{1,4}$ $Cu_{2,2}$ alloy powder obtained on the titanium cathode to exhibit good magnetic properties and a higher Curie temperature compared to the nanostructured alloys without copper.

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References

[1] P. Haasen, R. I. Joffe, Amorphous Metals and Semiconductors, Pergamon, London, 1986.
[2] H. Steerb, H. Warlimont, Rapidly Quenched Metals, Elsevier, Amsterdam, 1985.
[3] A. Maričić, M. Spasojević, L. Rafailović, V. Milovanović, L. Ribić-Zelenović, Mater. Sci. Forum **453**, 411 (2004).
[4] L. Ribić-Zelenović, L. Rafailović, M. Spasojević, A. Maričić, Phys. B **403**, 2148 (2008).
[5] S. H. Hong, H. J. Rya, Mater. Sci. Eng. A **344**, 253 (2003).
[6] J. L. Fan, B.Y. Huang, X. I. Qu, Trans Nonferrous Met. Soc. China **10**(1), 57 (2000).
[7] Z. He, T. H. Courtney, Mater. Sci. Eng. A. **346**, 141 (2003).
[8] Z. W. Zhang, J. I. E. Zhou, S. Q. Xi, et al., J. Alloys Compd. **370**, 186 (2004).
[9] Z. W. Zhang, J. N. Zhou, S. Q. Xi, Mater. Sci. Eng A **379**, 148 (2004).
[10] K. R. Sriraman, S. G. Raman, S. K. Seshadri, Mater. Sci. Eng. A **418**, 303 (2006).
[11] K. R. Sriraman, S. Ganesh Sundara Raman, S. K. Seshadri, Mater. Sci. Technol. **22**, 14 (2006).
[12] M. Donten, H. Cesiulis, Z. Stojek, Electrochim. Acta **39**, 3389 (2000).
[13] F. He, J. Yang, T. Lei, C. Gu, Appl. Surf. Sci. **253**, 7591 (2007).
[14] P. Esther, C. Joseph Kennady, P. Saravanan, T. Venkatachalam, J. Non-Oxide Glasses, **1**, 301 (2009).
[15] M. Banerjee, A. Singh, A. K. Majumdar, A. K. Nigam, J. Phys.: Condens. Matter **23**, 3060004 (2011).
[16] L. Ribić-Zelenović, N. Ćirović, M. Spasojević, N. Mitrović, A. Maričić, V. Pavlović, Mater. Chem. Phys. **135**, 212 (2012).
[17] A. Mondal, A. Upadhyaya, D. Agrawal, J. Alloys Compd. **509**, 301 (2011).
[18] M. Spasojević, L. Ribić-Zelenović, N. Ćirović, P. Spasojević, A. Maričić, Sci. Sinter. **44**, 197 (2012).
[19] A. R. Despić, K. I. Popov, Modern Aspects of Electrochemistry, **7**, Plenum Press, New York, 1972.
[20] M. Spasojević, L. Ribić-Zelenović, A. Maričić, Sci.

Sinter. **43**, 313 (2011).
[21] M. G. Pavlović, Lj. J. Pavlović, E. R. Ivanović, V. Radmilović, K. I. Popov, J. Serb. Chem. Soc. **66**, 923 (2001).
[22] L. Ribić-Zelenović, M. Spasojević, A. Maričić, M. M. Ristić, Sci. Sinter. **41**(2), 175 (2009).
[23] L. Ribić-Zelenović, M. Spasojević, A. Maričić, Materials Chemistry and Physics, **115**, 347 (2009).
[24] M. A. Meyers, A. Mishra, D. J. Benson, Progress in Materials Science, **51**, 427 (2006).
[25] K. I. Popov, M. G. Pavlović, in. B. E. Conway, J. O'M. Bockris, R. E. White (Eds.), **24**, Plenum, New York, 299 (1973).
[26] L. M. Chang, Z. T. Wang, S. Y. Shi, W. Liu, J. Alloys Compd. **509**, 1501 (2011).
[27] M. A. Oliver-Tlentino, E. M. Arce-Estrada, C. A. Córtes-Escobedo, A. M. Bolarin-Miro, F. Sánches-De Jesús, R. de G. Gonzáles-Huerta, A. Manzo-Robledo, J. Alloys. Compd. **536** S, S245 (2012).
[28] L. X. Phua, N. N. Phuoc, C. K. Ong, J.Alloys Compd. **520**, 132 (2012).
[29] L. D. Rafailović, C. Gammer, C. Rentenberger, P. Angerer, H. P. Karnthaler, J. Alloys Compd. **543**, 167 (2012).
[30] O. Younes, E. Gileadi, Electrochem. Solid State Lett. **3**, 543 (2000).
[31] O. Younes, L. Zhu, Y. Rosenberg, Y. Shacham-Diamond, E. Gileadi, Langmuir **17**, 8270 (2001).
[32] E. Chassaing, K.Vu Quang, R. Wiart, J. Appl. Electrochem. **19**, 839 (1989).
[33] D. Landolt, E. J. Podlaha, N. Zech, Zh. Phys. Chem. **208**, 167 (1999).
[34] E. J. Podlaha, D. Landolt, J. Electrochem. Soc. **143**, 893 (1996).
[35] E. J. Podlaha, D. Landolt, J. Electrochem. Soc. **144**, 1672 (1997).
[36] M. D. Obradović, R. M. Stevanović, A. R. Despić, J. Electroanal. Chem. **552**, 185 (2003).
[37] Seong-Joe Mun, Minsoo, Toe-Hong Yim, Joe-ho Lee, Tak Kang, J. Electrochem. Soc. **157**, D177 (2010).
[38] G. Herzer, IEEE Trans. Magn. **25**, 3327 (1989).
[39] S. Roth, H. Grahl, J. Degmova, N. Schlorke-de Boer, M. Stoica, J. M. Borrego, A. Conde, N. Mitrović, J. Eckert, J. Optoelectron. Adv. Mater. **4**, 199 (2002).
[40] N. Mitrović, J. Magn. Magn. Mater. **262**, 302 (2003).
[41] J. D. Bernal, Nature **185**, 68 (1960).
[42] A. Kalezić-Glišović, V. A. Maričić, D. A. Kosanović, S. Đukić, R. Simeunović, Sci. Sinter. **41**, 283 (2009).
[43] M. Spasojević, L. Ribić-Zelenović, A. Maričić. Sci. Sinter. in press.
[44] L. Ribić-Zelenović, L. Rafailović, A. Maričić, M. Spasojević, J. Optoelectron. Adv. Mater. **9**, 2681 (2007).

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