

## Magnetic Properties of Fe, Co and Ni Based Nanopowders Produced by Chemical-Metallurgy Method

Tien Hiep Nguyen<sup>1,2</sup>, Y.V. Konyukhov<sup>1\*</sup>, Nguyen Van Minh<sup>3</sup>, D.Y. Karpenkov<sup>1</sup>, V.V. Levina<sup>1</sup>, G. Karunakaran<sup>4</sup>, A.G. Buchirina<sup>1</sup>

<sup>1</sup>National University of Science and Technology MISiS, Leninskiy prospekt 4, Moscow, Russia

<sup>2</sup>Le Quy Don Technical University, Hoang Quoc Viet Str. 236, Bac Tu Liem, Ha Noi, Viet Nam

<sup>3</sup>Institute of Technology, Cau Vong Str. 3, Bac Tu Liem, Hanoi, Vietnam

<sup>4</sup>Seoul National University of Science and Technology, Gongneung-ro 232, Nowon-gu, Seoul, Republic of Korea

### Article info

*Received:*

21 May 2020

*Received in revised form:*

13 August 2020

*Accepted:*

6 November 2020

### Keywords:

Nanopowder  
Nanocomposite  
Chemical metallurgy method,  
Magnetic properties

### Abstract

This research study describes the magnetic properties of Fe, Co and Ni metallic nanopowders (NPs) and their ternary nanocomposites (NCs), which can be used as fillers in radio-wave absorbing composite materials and coatings, as well as for magnetic protection of banknotes and security paper. The nanopowders were prepared by the chemical metallurgy method. The desired properties of Fe, Co and Ni NPs and NCs were achieved by co-precipitation, the addition of surfactants and changes in reduction temperature and time parameters. Magnetic measurements showed that all samples of pure metal NPs are semi-hard magnetic materials. The added surfactants have distinct effects on the dimensional and magnetic characteristics of Fe, Co and Ni NPs. Ni–Co–Fe NCs are also mainly semi-hard magnetic materials. Fine-tuning of their composition and chemical reduction temperatures allows controlling the values of  $M_s$  and  $H_c$  in large ranges from 49 to 197 A·m<sup>2</sup>/kg and from 4.7 to 60.6 kA/m, respectively.

## 1. Introduction

Today, due to unique properties, Fe, Co and Ni nanopowders (NPs) are widely used in various industries as catalysts, gas sensors, capacitors, metamaterials, additives to improve the quality of sintered products, etc. [1–6]. A special place is occupied by the sphere of application of Fe, Co and Ni nanoparticles as magnetic materials [7]. This is due to the fact that the magnetization and magnetic anisotropy of NPs are much higher than those of bulk samples, and the differences in Curie ( $T_C$ ) or Néel ( $T_N$ ) temperatures (temperatures of the spontaneous establishment of parallel or antiparallel spin orientation) of nano and macroscopic materials reach hundreds of degrees. In addition, several unusual properties were discovered in magnetic nanomaterials – high values of the exchange interaction, an anomalously large magneto-caloric

effect, etc. [8]. In this regard, Fe, Co and Ni metallic NPs, as well as NCs based on them are used in biomedicine for targeted delivery of drugs to a diseased organ at the lesion site. They can also be used as materials for magnetic resonance imaging. The materials based on Fe, Co and Ni NPs can be used in magneto-electronic devices, as fillers in radar absorbing materials and coatings, as well as for magnetic protection of banknotes and securities.

The greatest influence on the magnetic properties of materials is exerted by their chemical composition, dispersion and particle morphology [9–12]. There are many methods to obtain metal NPs and NCs, but not all of them allow to control of the properties of intermediate and final products during synthesis. It should be noted that mechanical and physical methods of obtaining metal-based NPs tend to consume a large amount of energy, require expensive equipment, while biological methods have low productivity [13–17]. The most promising method for producing metal NPs and

\*Corresponding author. E-mail: ykonukhov@misis.ru

their composites is a chemical-metallurgy method, the stages of which include the deposition of metal hydroxides, followed by washing, drying, and metallization in a stream of hydrogen [18]. With a relatively simple hardware design, this method satisfies requirements such as high purity of the product, low oxygen content, narrow particle size distribution and reproducibility of properties. In addition, this method allows using surface-active substances (surfactants) that adsorbing on the surface of the particles, can stabilize sols, limit particle growth, and thereby affect the morphology and dispersion of final products [19].

In connection with the foregoing, this work aimed to study the magnetic properties of pure Fe, Co and Ni metallic NPs and their ternary composites with different dispersion, to form scientific and technical approaches of synthesizing nano-dispersed materials with desired magnetic properties.

## 2. Experimental procedure

NPs were obtained by the chemical-metallurgical method, which allows synthesizing NPs with desired properties by precipitation, the addition of surfactants and changes in the temperature-time parameters of the reduction process. As precursors to produce Fe, Co and Ni hydroxides, the chemically pure nitrate salts  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  ( $\geq 99.95\%$ ),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $\geq 98\%$ ), and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $\geq 99\%$ ) (AO Vekton, Russian standard) were used for the synthesis of 5 wt.% iron, cobalt and nickel nitrate solutions, accordingly. Precipitation of hydroxides compounds was carried out using a 10 wt.% alkali solution in the presence of surfactants added to control the dispersion of the synthesized products. Sodium dodecyl sulfate  $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$  (SDS) 0.1 wt.% and disodium salt of ethylenediaminetetraacetic acid  $\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2\text{Na}_2$  (EDTA) 0.3 wt.% were chosen as surfactants. The obtained hydroxides precipitates  $\text{FeOOH}$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$  were washed in a centrifuge, dried and reduced in a hydrogen atmosphere for 3 h at temperatures of 400, 285 and 280 °C, respectively.

Magnetic nanocomposites (NCs) were synthesized by the chemical-metallurgical method by co-precipitation using precursor materials as hydrated salts of iron, cobalt, nickel nitrates with different concentrations of  $\text{Fe}^{3+}$  and alkali NaOH 10 wt.% at the conditions of pH = 11, room temperature and continuous mixing. Three mixtures of 5 wt.% iron, cobalt and nickel nitrate water solu-

tions were prepared with the following Ni–Co–Fe mole ratio of (1:1:1); (1:1:3), and (1:1:5) to produce the desired Ni–Co–Fe (NCF), Ni–Co–3Fe (NCF3) and Ni–Co–5Fe (NCF5) NCs, respectively. The obtained hydroxides NCs were washed in a centrifuge, dried and reduced in a hydrogen atmosphere for 3 h at temperatures ( $T_r$ ) of 300, 400 and 500 °C.

The facility for synthesizing Fe, Co and Ni NPs and NCs based on them consist of a reactor made of glass with a 5-liter volume, a pH-meter (Mettler Toledo, USA), two peristaltic pumps, an electric mixer, and a PC controller.

The study of structural, dimensional and morphological properties of the obtained NPs and NCs samples was carried out by methods of low-temperature nitrogen adsorption “Brunauer-Emmett-Teller” (BET), X-ray diffraction (XRD) phase analysis and transmission/scanning electron microscopy (TEM, SEM). The magnetic properties of the samples were studied using a vibrating sample magnetometer “7410 VSM” (Lake Shore, USA).

## 3. Results and discussion

The XRD of synthesized Fe, Co and Ni NPs and NCs were analyzed and discussed in detail in reported works [20]. The obtained result shows that all synthesized Fe, Co and Ni NPs samples contain pure metal phases. On the other hands, it was found that NCs samples reduced at  $T_r = 300$  °C contained oxide phases of  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3 \cdot \text{CoO}$  and  $\text{Fe}_2\text{O}_3 \cdot \text{NiO}$ . The samples obtained by reduction at  $T_r = 400$  °C contained intermetallic and oxide phases. After reduction at  $T_r = 500$  °C, all the XRD showed the formation of metallic and intermetallic phases in the obtained NCs samples.

The result of TEM and SEM analysis of investigated Fe, Co and Ni NPs samples (Fig. 1) agrees well with measurement data of the average nanoparticles size obtained *via* BET method.

It has been shown that the addition of surfactants to initial mediums for the synthesis of hydroxide compounds significantly affects the dispersion of the obtained Fe, Co and Ni NPs.

It is clear that, regardless of the production conditions, the particles of all Fe NPs samples (Fig. 1. a-1, a-2, a-3) have a rounded and spherical shape. According to the results of the BET method measurement, the particles of Fe NPs sample obtained without the use of surfactants (Fig. 1. a-1) have an average size of ~ 110 nm. The average particle size of Fe NPs sample obtained in case of using 0.1 wt.% SDS (Fig. 1. a-2) is ~ 95 nm. The average particle

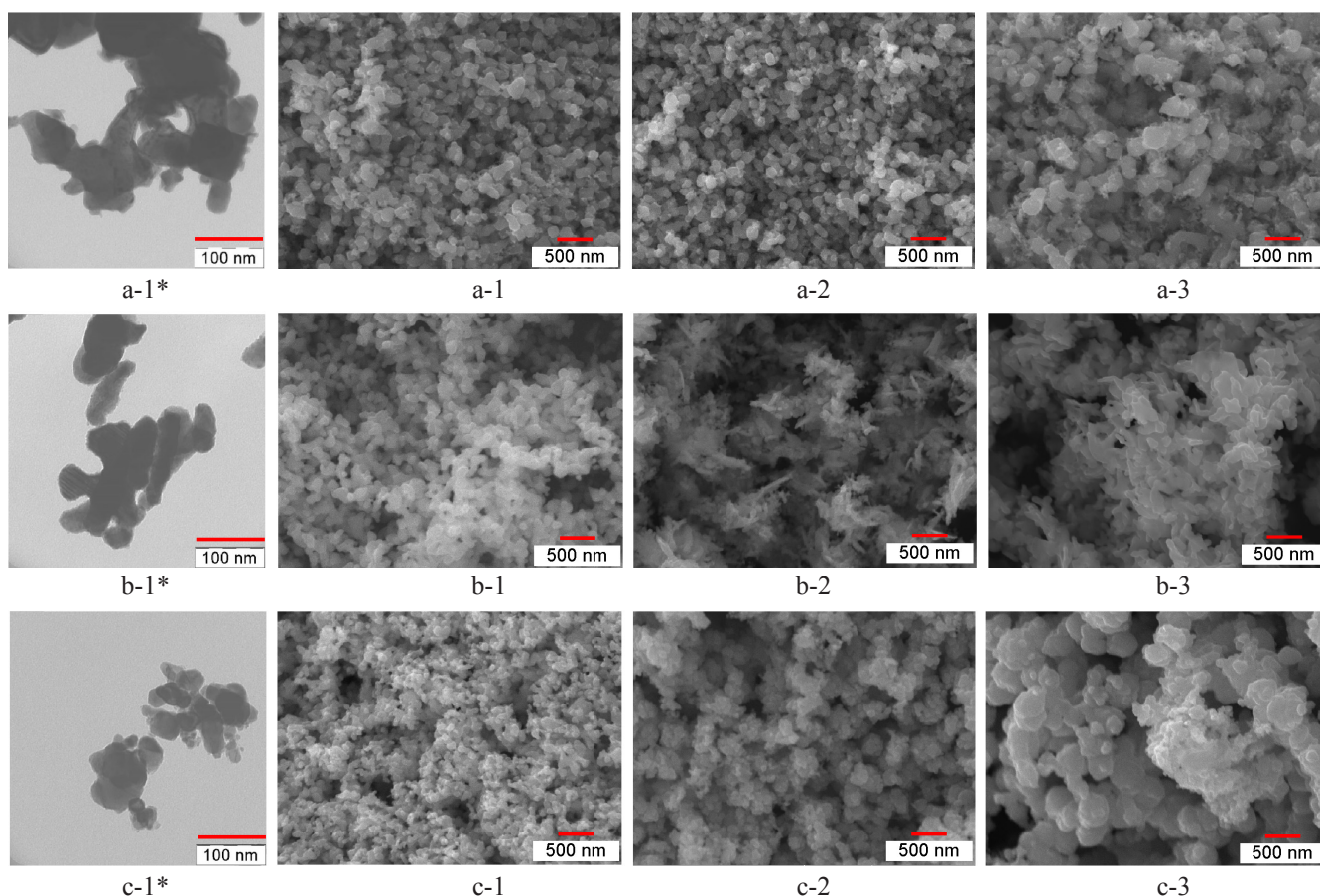


Fig. 1. TEM (\*) and SEM images of Fe (a), Co (b) and Ni (c) NPs obtained under various conditions: without surfactant (1); with 0.1 wt.% SDS (2); with 0.3 wt.% EDTA (3).

size of Fe NPs sample obtained using 0.3 wt.% EDTA (Fig. 1. a-3) was found to be 187 nm, this is the largest value in comparison with cases without the use of surfactants and with the addition of 0.1 wt.% SDS.

The particles of all obtained Co NPs samples (Fig. 1. b-1, b-2, b-3) tend to aggregate and form flakes. The average particle size was found to be  $\sim 92$ , 86 and 122 nm, for the case without the use of a surfactant (Fig. 1. b-1), with 0.1 wt.% SDS (Fig. 1. b-2) and 0.3 wt.% EDTA (Fig. 1. b-3), respectively.

In the case of Ni NPs samples (Fig. 1. c-1, c-2, c-3), the Ni NPs obtained without using a surfactant (Fig. 1. c-1) and with 0.1 wt.% SDS (Fig. 1. c-2) have the average sizes of  $\sim 79$  and 66 nm, respectively, whereas they are in a highly sintered state (each of particle is connected with several adjacent particles by isthmuses). The particles of Ni NPs sample obtained with using 0.3 wt.% EDTA (Fig. 1. c-3) have the average size of  $\sim 265$  nm.

Thus, in all cases, the use of 0.1 wt.% SDS allows obtaining smaller nanoparticles, whereas the use of 0.3 wt.% EDTA leads to an increase in the average particle size.

A study of the obtained magnetic hysteresis loop (Fig. 2) shows that all samples of pure metal Fe, Co and Ni NPs have semi-hard magnetic properties. Compared to samples without a surfactant, the addition of 0.1 wt.% SDS leads to a decrease in the size of synthesized NPs, consequently, to a decrease in the saturation magnetization ( $M_s$ ), and an increase in the coercive force ( $H_c$ ). The addition of 0.3 wt.% EDTA has an inverse effect on the magnetic properties of the obtained metal Fe, Co and Ni NPs, it leads to an increase in the particle size, an increase in the value of  $M_s$ , and a decrease in the value of  $H_c$ . The  $M_s$  values of obtained metal Fe, Co and Ni NPs range of 49–197  $A \cdot m^2/kg$ , and  $H_c$  of 7.6–34.2 kA/m.

The obtained results of the dimensional characteristics and magnetic properties of all Fe, Co and Ni NPs and NCs samples are presented in Table.

It is shown that among the synthesized metal NPs, Fe NPs have the largest value of  $M_s$  (197  $A \cdot m^2/kg$ ) and Ni NPs have the smallest value (49  $A \cdot m^2/kg$ ). In the case of NCs samples an increase in the reduction temperature from 300 to 500  $^{\circ}C$  leads to significant increases in the  $M_s$  value which is close to the  $M_s$  value of pure metal Fe NPs.



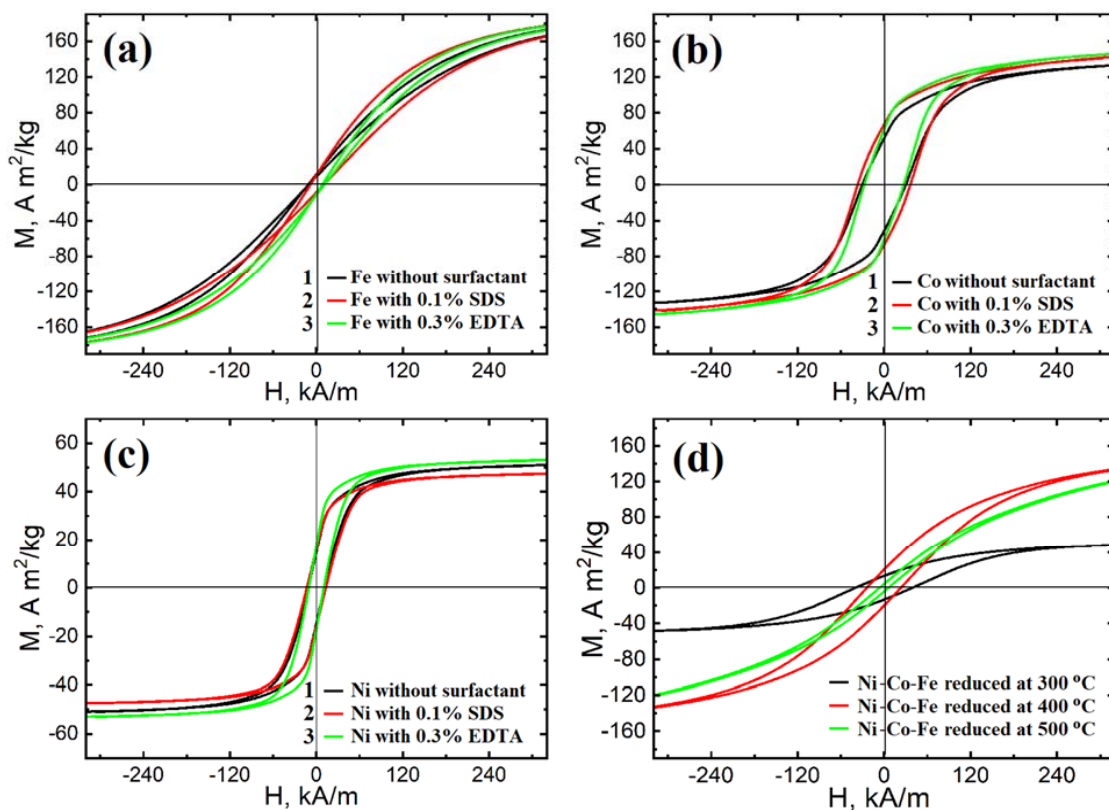


Fig. 2. Magnetic hysteresis loops of Fe (a), Co (b) and Ni (c) NPs obtained under various conditions: without surfactant (1); with 0.1 wt.% SDS (2); with 0.3 wt.% EDTA (3) and magnetic hysteresis loops of Ni–Co–Fe NCs samples, reduced at various temperatures (d).

**Table**

Dimensional characteristics and magnetic properties of Fe, Co and Ni NPs and NCs

#	Sample	Condition for obtaining	$S_a$ , m <sup>2</sup> /g	$D_{BET}$ , nm	$D_{SEM}$ , nm	$M_{ss}$ , A·m <sup>2</sup> /kg	$H_c$ , kA/m	$M_r$ , A·m <sup>2</sup> /kg	$M_r/M_s$
1	Fe	Without surfactant	7.3	105	110	196	10.1	12	0.06
2		With 0.1% SDS	7.7	99	95	193	11.2	9	0.05
3		With 0.3% EDTA	5.8	131	187	197	7.6	11	0.05
4	Co	Without surfactant	6.0	112	92	154	27.9	53	0.37
5		With 0.1% SDS	7.5	90	86	143	34.2	69	0.45
6		With 0.3% EDTA	4.7	143	122	156	25.1	64	0.41
7	Ni	Without surfactant	7.0	96	79	52	10.8	15	0.28
8		With 0.1% SDS	8.4	80	66	49	12.8	16	0.33
9		With 0.3% EDTA	2.3	293	265	54	10.2	18	0.33
10	NCF	$T_r = 300\text{ °C}$	20.3	54	82	52.3	41.6	14.8	0.28
11	NCF3		24.2	49	66	130.9	60.2	39.7	0.30
12	NCF5		53.3	36	46	84.1	60.6	27	0.32
13	NCF	$T_r = 400\text{ °C}$	5.9	77	84	155.8	24.3	25.1	0.16
14	NCF3		7.0	75	80	176.6	26.3	21.5	0.12
15	NCF5		8.5	72	69	176.6	21.8	17.6	0.10
16	NCF	$T_r = 500\text{ °C}$	0.5	151	247	156.3	4.7	4.8	0.03
17	NCF3		1.2	135	255	192.5	5.0	6.2	0.03
18	NCF5		1.9	115	181	185.2	5.9	3.7	0.02

The average  $H_c$  value of pure metal Fe, Co and Ni NPs is in the range of 7.6–34.2 kA/m, whereas the combination of Fe, Co and Ni in the NCs samples allows getting a wide range of  $H_c$  value from 4.7 to 60.6 kA/m. From the obtained  $H_c$  values of pure metal Fe, Co and Ni NPs and the NCF, NCF3, NCF5 NCs, we can conclude that the synthesized Fe, Co and Ni NPs and NCs samples are mainly semi-hard magnetic materials.

It should be noted that for all NCs samples, an increase in the content of  $Fe^{3+}$  initially leads to an increase in  $M_s$  value of the material, and after reaching the maximum, the fall in the saturation magnetization happened. The NCF3 sample has the highest  $M_s$  value within the obtained NCs. The reduction process of NCs samples at low temperatures allows achieving high remanence magnetization  $M_r$  and coercivity  $H_c$ .

The combination of three metals Fe, Co and Ni in the NCs and changes in the reduction temperature allows controlling their remanent magnetization ( $M_r$ ) in a wide range from 3.7–39.7 A·m<sup>2</sup>/kg.

Thus, the combination of metal Fe, Co and Ni in the NCs and variation in the reduction temperature makes it possible to control magnetic properties of Fe, Co and Ni-based nanomaterials over a wide range of values.

#### 4. Conclusions

In this research work, we synthesized Fe, Co and Ni NPs and NCF, NCF3, NCF5 NCs samples using the chemical precipitation method followed by the reduction process. The obtained NPs and NCs are mainly semi-hard magnetic materials.

Unlike the samples produced without the surfactant, the addition of 0.1 wt.% SDS leads to decreased particle size; consequently, it allows to reduce the saturation magnetization  $M_s$  and increase the coercive force  $H_c$  of metal Fe, Co and Ni NPs. The EDTA surfactant has the opposite effect on the magnetic properties of the produced metal Fe, Co and Ni NPs, the addition of 0.3 wt.% EDTA leads to an increase in the particles size, an increase in  $M_s$  value and a decrease in  $H_c$  value. The  $M_s$  values were found to be in ranges of 193–197, 143–156, 49–54 A·m<sup>2</sup>/kg, and  $H_c$  values: 7.6–11.2, 25.1–34.2, 10.2–12.8 kA/m for Fe, Co and Ni NPs, respectively.

The combination of Fe, Co and Ni in the NCs and changes in the reduction temperature allow to control magnetic properties of the NCs over a fairly wide range of values:  $M_s$  values in the range

of 52.3–192.5 A·m<sup>2</sup>/kg and  $H_c$  values from 4.7 to 60.6 kA/m, respectively. For all the NCs samples, an increase in the content of  $Fe^{3+}$  initially leads to an increase in  $M_s$  value of the material, and after reaching the maximum, the fall in the saturation magnetization happened. The reduction process of NCs samples at low temperatures allows achieving high remanence magnetization  $M_r$  and coercivity  $H_c$ .

#### References

- [1]. V.V. Mody, R. Siwale, A. Singh, H.R. Mody, *J. Pharm. Bioall. Sci.* 2 (2010) 282–289. DOI: [10.4103/0975-7406.72127](https://doi.org/10.4103/0975-7406.72127)
- [2]. H. Hahn, K.A. Padmanabhan, *Nanostruct. Mater.* 6 (1995) 191–200. DOI: [10.1016/0965-9773\(95\)00042-9](https://doi.org/10.1016/0965-9773(95)00042-9).
- [3]. V.M. Nguyen, G. Karunakaran, T.H. Nguyen, E.A. Kolesnikov, M.I. Alymov, V.V. Levina, Y.V. Konyukhov, *Lett. Mater.* 10 (2020) 174–178. DOI: [10.22226/2410-3535-2020-2-174-178](https://doi.org/10.22226/2410-3535-2020-2-174-178)
- [4]. H.E. Schaefer, R. Würschum, R. Birringer, H. Gleiter, *Phys. Rev. B* 38 (1988) 9545–9554. DOI: [10.1103/PhysRevB.38.9545](https://doi.org/10.1103/PhysRevB.38.9545)
- [5]. F.E. Kruis, H. Fissan, A. Peled, *J. Aerosol Sci.* 29 (1998) 511–535. DOI: [10.1016/S0021-8502\(97\)10032-5](https://doi.org/10.1016/S0021-8502(97)10032-5)
- [6]. V.V. Rybin, A.A. Zisman, N.Y. Zolotarevsky, *Acta Metall. Mater.* 41 (1993) 2211–2217. DOI: [10.1016/0956-7151\(93\)90390-E](https://doi.org/10.1016/0956-7151(93)90390-E)
- [7]. D. Sellmyer, R. Skomski, *Advanced Magnetic Nanostructures*, Springer, New York, 2006. DOI: [10.1007/b101199](https://doi.org/10.1007/b101199)
- [8]. Z. Tang, P. Sheng, *Nano Science and Technology: Novel Structures and Phenomena*, CRC Press, 2003, p. 272. ISBN-10: 0415308321
- [9]. A.S. Lileev, O.A. Arinicheva, M. Reissner, F. Kubel, A.A. Sein, *Met. Sci. Heat Treat.* 56 (2015) 591–594. DOI: [10.1007/s11041-015-9804-7](https://doi.org/10.1007/s11041-015-9804-7)
- [10]. A.S. Lileev, V.A. Sein, E.S. Khotulev, *J. Phys.: Conf. Ser.* 1134 (2018) 012035. DOI: [10.1088/1742-6596/1134/1/012035](https://doi.org/10.1088/1742-6596/1134/1/012035)
- [11]. A.S. Lileev, V.V. Pinkas, K.V. Voronchikhina, A.V. Gunbin, *Met. Sci. Heat Treat.* 60 (2018) 489–493. DOI: [10.1007/s11041-018-0306-2](https://doi.org/10.1007/s11041-018-0306-2)
- [12]. A.S. Lileev, A.V. Gunbin, A.S. Perminov, *Met. Sci. Heat Treat.* 61 (2019) 171–172. DOI: [10.1007/s11041-019-00395-1](https://doi.org/10.1007/s11041-019-00395-1)
- [13]. L. Lin, S.A. Starostin, V. Hessel, Q. Wang, *Chem. Eng. Sci.* 168 (2017) 360–371. DOI: [10.1016/j.ces.2017.05.008](https://doi.org/10.1016/j.ces.2017.05.008)
- [14]. A. Zolriasatein, A. Shokuhfar, *Physica E* 74 (2015) 101–107. DOI: [10.1016/j.physe.2015.06.015](https://doi.org/10.1016/j.physe.2015.06.015)

- [15]. J. Xie, J. Jiang, P. Davoodi, M.P. Srinivasan, C.-H. Wang, *Chem. Eng. Sci.* 125 (2015) 32–57. DOI: [10.1016/j.ces.2014.08.061](https://doi.org/10.1016/j.ces.2014.08.061)
- [16]. N.S. Kanhe, A.K. Tak, A.B. Nawale, S.A. Raut, S.V. Bhoraskar, A.K. Das, V.L. Mathea, *Mater. Des.* 112 (2016) 495–504. DOI: [10.1016/j.matdes.2016.09.078](https://doi.org/10.1016/j.matdes.2016.09.078)
- [17]. F. Yilmaz, D.-J. Lee, J.-W. Song, H.-S. Hong, H.-T. Son, Jae-Sik Yoon, S.-J. Hong, *Powder Technol.* 235 (2013) 1047–1052. DOI: [10.1016/j.powtec.2012.10.024](https://doi.org/10.1016/j.powtec.2012.10.024)
- [18]. S.A. Tikhomirov, M.I. Alymov, I.V. Tregubova, V.S. Shustov, *Nanotechnol. Russia* 6 (2011) 268–271. DOI: [10.1134/S1995078011020170](https://doi.org/10.1134/S1995078011020170)
- [19]. Y.V. Konyukhov, V.V. Levina, D.I. Ryzhonkov, I.I. Puzik, *Nanotechnol. Russia* 3 (2008) 352–357. DOI: [10.1134/S1995078008050108](https://doi.org/10.1134/S1995078008050108)
- [20]. T.H. Nguyen, G. Karunakaran, Y.V. Konyukhov, N.V. Minh, D.Y. Karpenkov, I.N. Burmistrov, *Nanomaterials* 11 (2021) 341. DOI: [10.3390/nano11020341](https://doi.org/10.3390/nano11020341)