Letters on Materials 10 (2), 2020 pp. 174-178 www.lettersonmaterials.com

https://doi.org/10.22226/2410-3535-2020-2-174-178 PACS: 61.46.+w, 62.20.-x, 62.20.M-

Enhancement of structural and mechanical properties of Fe + 0.5% C steel powder alloy via incorporation of Ni and Co nanoparticles

V. M. Nguyen[1], G. Karunakaran[†,2], T. H. Nguyen[3], E. A. Kolesnikov[3],

M. I. Alymov[4], V. V. Levina[3], Yu. V. Konyukhov[3]

[†]karunakarang5@gmail.com

[1]Institute of Research and Development, Duy Tan University, Danang 550000, Vietnam
[2]Biosensor Research Institute, Department of Fine Chemistry, Seoul National University of Science and Technology (Seoul Tech), Gongneung-ro 232, Seoul, 01811, Republic of Korea
[3]Department of Functional Nanosystems and High-Temperature Materials, National University of Science and Technology "MISiS", 4 Leninskiy Av., Moscow, 119049, Russia
[4]A. G. Merzhanov Institute of Structural Macrokinetics and Materials Science RAS (ISMAN), 8 Academician Osipyan St., Chernogolovka, 142432, Russia

The effect of Ni and Co metal microparticles (MPs) and nanoparticles (NPs) on the structural and mechanical properties of Fe + 0.5% C steel powder alloy was analyzed. The results revealed that the modification of the alloy by (Ni, Co) NPs can lead to the formation of a fine-grained compact and less porous structure, hence, significantly improve the mechanical properties of the sintered material. MPs modified samples were found to be highly porous when compared to the control. The introduction of 0.5 wt.% Co NPs increased the hardness value of the alloy to 58 HRB, whereas 0.5 wt.% Co MPs reduced the hardness to 47 HRB. The most beneficial effect is observed with 0.5 wt.% Ni NPs addition, wherein the hardness value increased to 63 HRB when compared to 52 HRB of the control sample. The highest flexural strength of 313 MPa was observed for Ni NPs incorporated alloy, whereas the least flexural strength of 156 MPa was noticed for the alloy containing 0.5 wt.% Co MPs. The fracture study confirmed that (Ni, Co) NPs increased the degree of densification, whereas Co MPs additives lead to the formation of large pits and cracks, consequently, to the destruction of material by a brittle inter-granular mechanism. Thus, this study introduces the use of Ni and Co NPs as modifiers in Fe + 0.5% C alloy via powder metallurgy.

Keywords: steel alloy, nanoparticles, microstructure analysis, mechanical properties.

УДК: 621.762.3К

Улучшение структурных и механических свойств стального порошкового сплава Fe + 0.5% C за счет включения наночастиц Ni и Co

Нгуен В. М.[1], Карунакаран Г.[†,2], Нгуен Т. Х.[3], Колесников Е. А.[3],

Алымов М. И.[4], Левина В. В.[3], Конюхов Ю. В.[3]

[1]Университет Дуя Тана, Институт исследований и разработок, Дананг, 550000, Вьетнам
[2]Сеульский Национальный исследовательский технологический университет (Сеултех), Институт исследований биосенсоров, факультет Тонкой химии, Каннын 232, Сеул, 01811, Республика Корея
[3]Национальный исследовательский технологический университет «МИСиС», кафедра Функциональных наносистем и высокотемпературных материалов, Ленинский пр., 4, Москва, 119049, Россия
[4]Институт структурной макрокинетики и проблем материаловедения им. А.Г. Мержанова РАН, ул. Академика Осипьяна, 8, Черноголовка, 142432, Россия

Было проанализировано влияние микрочастиц и наночастиц металлов Ni и Co на структурные и механические свойства сплава из порошковой стали Fe + 0.5% C. Результаты показали, что модификация сплава наночастицами

(Ni, Co) может привести к образованию мелкозернистой компактной и менее пористой структуры, следовательно, значительно улучшить механические свойства спеченного материала. Обнаружено, что образцы, модифицированные микрочастицами, являются высокопористыми по сравнению с контрольным образцом. Введение наночастиц 0.5 мас.% Co увеличивало твердость сплава до 58 HRB, тогда как введение микрочастиц 0.5 мас.% Co снижало твердость до 47 HRB. Наиболее благоприятный эффект наблюдается при добавлении наночастиц 0.5 мас.% Ni, причем значение твердости увеличилось до 63 HRB по сравнению с 52 HRB контрольного образца. Самая высокая прочность на изгиб 313 МПа наблюдалась для сплава с наночастицами Ni, тогда как наименьшая прочность на изгиб 156 МПа была отмечена для сплава, содержащего микрочастицы 0.5 мас.% Co. Исследование на разрушения подтвердило, что наночастицы (Ni, Co) увеличивали степень уплотнения, в то время как добавки микрочастиц Co приводили к образованию крупных ям и трещин, а, следовательно, к разрушению материала по хрупкому межзерновому механизму. Таким образом, это исследование представляет эффективное использование наночастиц Ni и Co в качестве модификаторов в сплаве Fe + 0.5% C с помощью порошковой металлургии.

Ключевые слова: стальной сплав, наночастицы, микроструктурный анализ, механические свойства.

1. Introduction

Currently, there is a great interest in the area of manufacturing iron-based alloys via powder metallurgy [1, 2]. Iron-based alloys are widely used in automobile industries, power engineering, nuclear research, and medicine [3]. Powder metallurgy is one of the best methods to produce alloys of various structure, composition, and properties because of its ease-of-use and cost-effectiveness [4, 5].

Nickel and cobalt are efficiently used materials in the manufacturing of alloys. They can enhance the mechanical properties of different alloys [6 – 8].

Nowadays, most of the researches are focusing on improvement of the structural and mechanical properties of steel alloys using different metal additives which activate the sintering process, form the less porous material and inhibit of grain growth [9 –11]. The use of NPs as additives will provide a promising platform towards the development of modern material science. In a recent study, Si and B NPs are used as modifiers to improve the mechanical and structural properties of Fe + 0.5% C steel powder alloy [12]. With this connection, the present work aimed at studying the influence of (Ni, Co) MPs and NPs as modifiers on the structural and mechanical properties of Fe + 0.5% C alloy.

2. Materials and experimental procedures

Micropowders Fe (PJR-3.100.30), Ni (PNE-1), and Co (PK-1u) were procured from Brovary Powder Metallurgy Factory, Ukraine. Nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$, cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$, sodium hydroxide NaOH, and graphite (Technical graphite) were purchased from Reachem, Russia. 10% nickel nitrate, cobalt nitrate, and sodium hydroxide solutions were prepared, dropped in the reactor, and homogenously mixed. pH 10.0 was maintained till the end of the reaction. The obtained precipitin was washed using centrifuge (at 4000 rpm for 30 min) until the pH reached 7.0, further dried at 40°C for 48 h. The obtained powder was reduced under hydrogen atmosphere (Ni: 280°C, 90 min; Co: 265°C, 120 min) followed by passivation under nitrogen atmosphere for 8 h. The characterization of obtained powders was performed using scanning (SEM) (Vega3-Tescan, Czech Republic) and transmission electron microscope (TEM) (JEOL, Japan).

To prepare alloy powder samples, iron micropowder was annealed at 600°C for 1 h under hydrogen flow to reduce the moisture content, crystal defects and homogenize structure. Thereafter, the annealed iron micropowder underwent two-stage mixing. At the first stage, the mixture of graphite with nano and micro modifiers (Ni, Co) at the ratio of 1:1 was sonicated at 10 kHz for 10 min, using ethanol as a dispersing agent. The obtained homogeneous mixtures were dried at 60°C for 5 h to remove ethanol. Then, the annealed iron powder was mixed with the prepared graphite modified mixture using mechanical mixer C2.0 TURBULA (Garnet, Russia) for 40 min to obtain a uniform mixture. The fluidity and apparent density of the obtained mixtures were analyzed according to the GOST 20899-75 and GOST 19440-94 protocols, respectively [13,14].

The powder samples were subjected to static cold pressing (SCP) procedure in a hydraulic press (2PG-125, Russia) under a pressure of 450 MPa. The obtained prismatic workpieces had the base dimensions of 42.4 × 6.1 × ~4 mm (length × width × height) and were further sintered using a vacuum furnace (VMS-22-10.5, Russia) at 1000°C for 1 h. The microstructure of the sintered alloys was analyzed using an Axio Observer D1m optical microscope (Carl Zeiss, Germany), wherein the average grain size was evaluated by the method of counting grain intersections (GOST 21073.3-75). The hardness of the samples was determined on a scale of Rockwell hardness (HRB) using a TR 5006M hardness tester (Tochpribor, Russia).

The shrinkage/swelling of the prepared alloys after sintering was analyzed using an electronic micrometer.

The flexural strength of the sintered samples was analyzed using Testing Machines (LF 100 kN, Switzerland). The absolute density ρ of the material was determined by hydrostatic weighing in accordance with the GOST 18898-89 protocol [15]. Relative density Θ of the samples was calculated by the formula:

$$\Theta = \frac{\rho}{\rho_o}, \qquad (1)$$

where, ρ_0 — theory density of compact material (alloy), g/cm^3.

The fracture study of samples after flexural strength analysis was carried out using the SEM method (Vega3-Tescan, Czech Republic).

3. Results and discussion

3.1. Characterization of nano- and micropowders

The SEM and TEM micrographs of MPs and synthesized NPs are shown in Fig. 1. Co and Ni MPs were approximately less than 50 μm in size (Fig. 1a, c). The micrographs show that the obtained metal NPs is mainly round. The average size of Co and Ni NPs was 67 nm (Fig. 1b) and 82 nm (Fig. 1d), respectively.

3.2. Measurement of fluidity and apparent density of Fe + 0.5% C mixture with modifiers

The results of the fluidity and apparent density analyses of the prepared powders are shown in Table S1 (Supplementary Material). The fluidity as well as the apparent density of the powder mixtures decreased on the addition of nano and micro modifiers. The observed order of flow time was nano Co > micro Co > nano Ni > micro Ni > control (powder without modifiers). The order of the apparent density was found to be as follows: control > micro Ni and Co > nano Co > nano Ni. In a study of the flow and apparent density of the iron-copper-graphite powder (FC-0208), it was shown that the addition of different NPs led to a decrease in the fluidity and apparent density of the FC-0208 premix [16]. The cited report is well in agreement with our results.

3.3. Microstructural and mechanical properties of Fe+0.5% C alloy with modifiers

The microstructure of Fe + 0.5% C alloy sintered samples is shown in Fig. 2.

It was shown that the addition of Co and Ni NPs led to the formation of a fine-grained compact structure of the material (Fig. 2b, d) with the average grain size of 23 and 21 μm, accordingly, as compared with the value of 24 μm for the control sample. The reduction in grain size may be due to inhibition of grain growth by reinforcing NPs at grain boundaries, thereby preventing their motion. A study of the effect of Ni on the microstructure of an aluminum alloy (Al-1Si-1Fe) reported that the addition of 0.5% Ni changed the morphology of the alloy, which coincides with our results [17]. It is also observed in the study of the Fe_3Al alloy that the incorporation of Ni leads to the formation of intermetallic compounds, as a result of which changes in the final grain size of material occurred [18]. Whereas, it is more difficult for cobalt to form intermetallic compounds with iron.

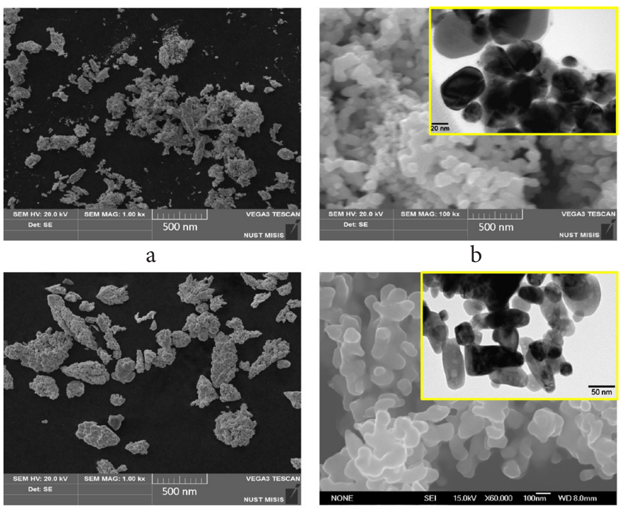

Fig. 1. SEM and TEM images of MPs and NPs additives: micro cobalt (a), nano cobalt (b), micro nickel (c) and nano nickel (d).

The incorporation of Ni and Co NPs also led to the formation of a less porous alloy. This could be due to the filling up of pores and intergranular spaces in Fe + 0.5% C alloy by the NPs. In addition, NPs had increased the contact area between the iron micron grains due to their high surface area, thus facilitating the sliding up of iron particles due to capillary forces acting on them. This, in turn, intensified the mass transfer process during the sintering of nano-modified samples, resulting in a high density with less porous structures [19].

Co MPs had increased the grain size (Fig. 2c), whereas, Ni MPs led to grain refinement (Fig. 2e), the average grain size was found to be 27 and 20 μm for Co MPs- and Ni MPs modified sample, respectively. Still, MPs incorporated samples were found to be highly porous and micro Co incorporated sample was the most porous. It is well known that the mechanical properties of a material remarkably depend on its porosity [20]. Thus, it is advisable not to use Co MPs in the formation of the Fe + 0.5% C alloy as it may reduce the strength of the material. Srinivas et al. found that the addition of 0.5 wt.% Co MPs led to changes in the structure and lowered the yield strength of Armco iron by about 70 MPa [21].

The results of volume shrinkage of the studied samples are shown in Fig. S1, a (Supplementary Material). The least volume shrinkage (−0.03%) was observed for 0.5% Co MPs incorporated alloy and the highest volume shrinkage (2.01%) was observed for the alloy containing 0.5% Ni NPs. The order of volume shrinkage percentage was as follows: nano Ni > micro Ni > nano Co > control alloy > micro Co. It is well known that the higher volume shrinkage value the greater the compactness of the material and hence, the better its mechanical properties [22].

The relative density of sintered alloy samples is shown in Fig. S1b (Supplementary Material). Additive modifiers greatly influenced the relative density of the alloy. The results revealed that the highest relative density (95%) was obtained for the alloy incorporated with 0.5% Ni NPs and the least relative density (85%) was noticed in alloy with 0.5% Co MPs.

Hardness and flexural strength were analyzed for sintered samples (Fig. 3). Fig. 3a revealed that both Co and Ni NPs increased the hardness of the Fe + 0.5% C alloy. Introduction of 0.5 wt.% Co NPs in the Fe + 0.5% C alloy increased the hardness value to 58 HRB, whereas 0.5 wt.% Co MPs reduced the hardness value to 47 HRB. The most beneficial effect is observed with 0.5 wt.% Ni NPs addition, wherein the hardness value increased to 63 HRB as compared to 52 HRB of the control sample.

The flexural strength of Fe + 0.5% C alloy samples is shown in Fig. 3b. The highest flexural strength of 313 MPa was observed for 0.5 wt.% Ni NPs incorporated alloy, whereas

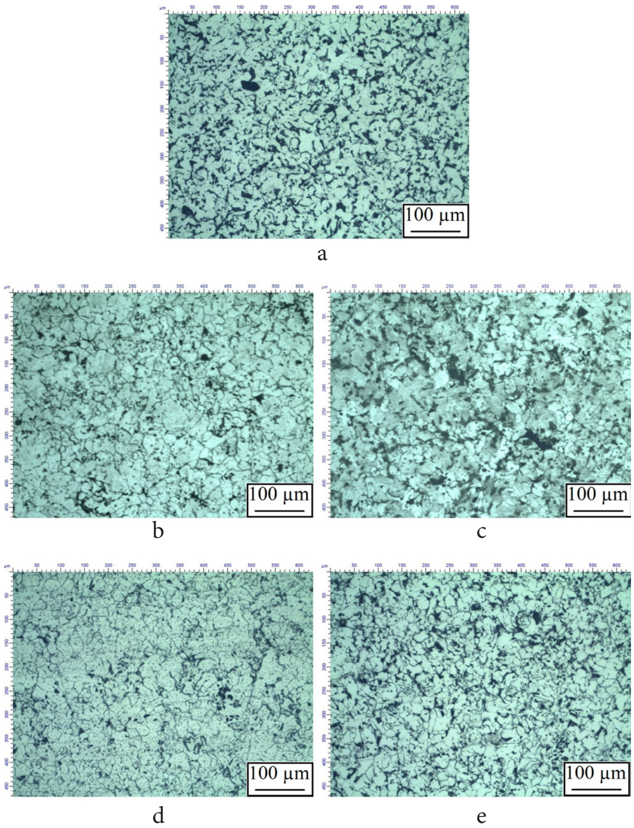

Fig. 2. (Color online) Microstructures of Fe + 0.5% C alloy without modifier (control) (a), nano cobalt modified (b), micro cobalt modified (c), nano nickel modified (d) and micro nickel modified (e).

the least flexural strength of 156 MPa was noticed for alloy containing 0.5 wt.% Co MPs. The flexural strength was found to be 214 and 254 MPa for alloys incorporated with Ni MPs and Co NPs. The increase in the flexural strength is due to the compact structure of the alloy with less porosity. The improvement in the strength due to addition of Ni also may be due to the diffusion of Ni with the Fe to form the corresponding dense intermetallic compounds of Ni-Fe [23].

Fig. 3c represents the force-displacement curves of Fe + 0.5% C alloys. The maximum force (P_{max}) for control was 776 N with a displacement of 0.82 mm. On addition of 0.5 wt.% Ni and Co NPs, P_{max} values increased up to 1248 and 1018 N with the displacement values of 1.20 and 1.04 mm, respectively. The addition of 0.5 wt.% Ni MPs increased P_{max} to 882 N with displacement of 0.80 mm. But, 0.5 wt.% Co MPs reduced P_{max} to 645 N with the displacement value of 0.58 mm.

Thus, the addition of Co and Ni NPs improved the mechanical properties of Fe + 0.5% C alloy. NPs inhibited the grain growth and maybe served as barriers to the motion of dislocations in the crystal lattice, thereby increasing the force required for plastic deformation [24]. Hence, the alloy acquired a low-porous fine grained structure with enhanced strength characteristics. In a recent research, addition of Ni NPs greatly improved the mechanical properties of Sn-Ag-Cu alloy [25].

The microstructure analysis of the fractured samples is shown in Fig. S2 (Supplementary Material). It shows that the addition of Ni and Co NPs plays an important role in compactness of material, by increasing the degree of densification. This, in turn, improves the structural and mechanical properties of the alloy.

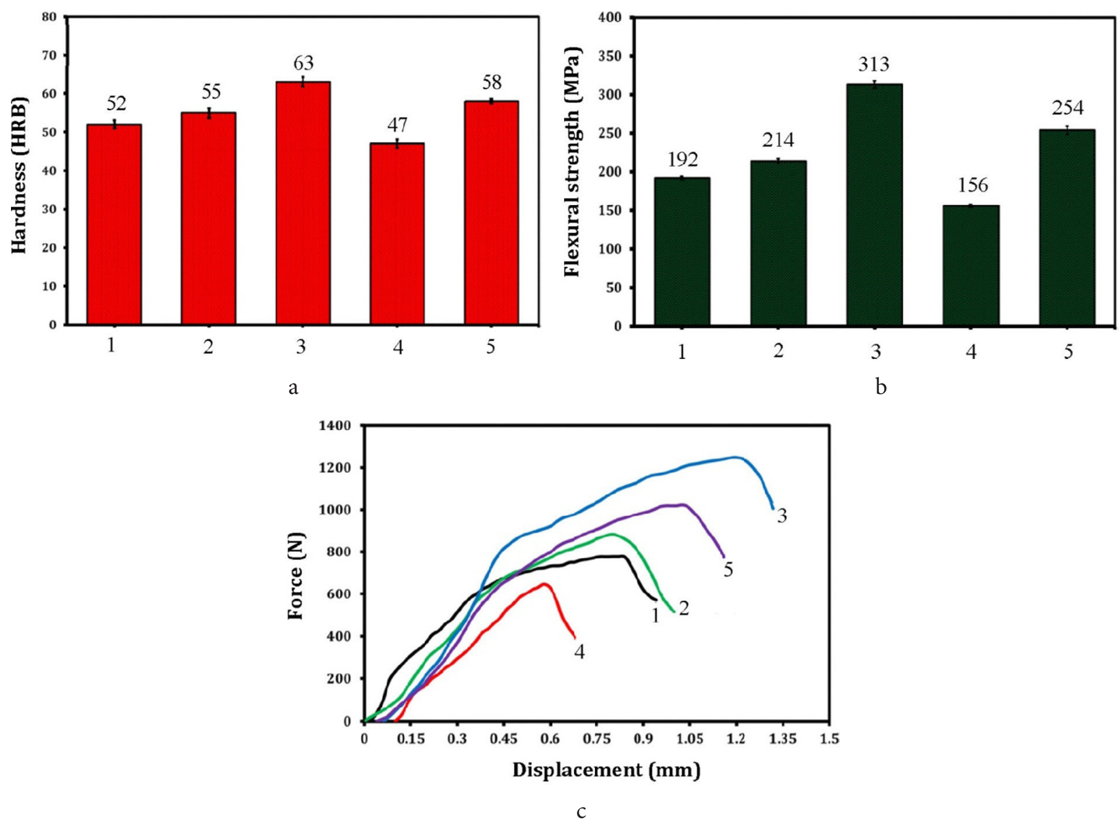

Fig. 3. (Color online) Hardness analysis (a), flexural strength analysis (b) and force-displacement curves of Fe+0.5% C alloy (1) without modifier (control) (c), micro nickel modified (2), nano nickel modified (3), micro cobalt modified (4) and nano cobalt modified (5).

It is confirmed that for all the samples except the Co MPs added alloy, the fracture mechanism is based on brittle-ductile, which take place according to the inter-granular and dimple fracture [26,27]. The force-displacement curves distinctly show that the curve passes through two stages. The first stage is with a high fold increase in the force load, and the second stage is with a reduced fold, accompanied by a large displacement value. The degree of plastic deformation for the samples will be higher, if the fracture occurs mainly by the ductile mechanism.

The Co MPs modified sample was fractured by a brittle inter-granular mechanism, as revealed by the observation of a clear border between the grains. In this case, the force-displacement curve monotonically grows to the point of destruction with a high fold increase in force load, accompanied by a small deformation degree, thus the material is brittle. In contrast, the addition of NPs intensifies the mass transfer process of micron iron grains during the sintering, leading to ductile destruction.

4. Conclusion

Ni and Co metal MPs and NPs were incorporated in the Fe + 0.5% C alloy via powder metallurgy. Co and Ni NPs formed a fine-grained compact structure and a less porous alloy. The alloy incorporated with 0.5 wt.% Ni NPs exhibited the highest relative density suggesting that Ni NPs could improve the compact nature of the alloy and enhance the mechanical properties. Ni and Co NPs decreased the porosity of the alloy. Ni and Co NPs and Ni MPs increased the hardness of the alloy, whereas Co MPs reduced the hardness. The highest P_{max} value of the alloy containing 0.5 wt.% Ni and Co NPs demonstrated its excellent flexural strength. The addition of Co MPs increased the formation of large pits and cracks, therefore, led to the destruction of material by a brittle inter-granular mechanism. Hence, the application of Ni and Co NPs could improve the structural and mechanical properties of the Fe + 0.5% C alloy.

Supplementary Material. *The online version of this paper contains supplementary material available free of charge at the journal's Web site (lettersonmaterials.com).*

Acknowledgement. The work was carried out with financial support from the Ministry of Education and Science of the Russian Federation in the framework of increase Competitiveness Program of NUST "MISIS", implemented by a governmental decree dated 16th of March 2013, N 211 (Grant No. K3-2017-055). Authors also acknowledge supports under the Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education (NRF-2019R1I1A1A01062458).

References

1. I.M. Milyaev, M.I. Alymov, D.M. Abashev et al. Letters on Materials. 9 (3), 349 (2019). (in Russian) [И.М. Миляев, М.И. Алымов, Д.М. Абашев и др. Письма о материалах. 9 (3), 349 (2019). Crossref
2. A.S. Ustyuhin, A.B. Ankudinov, V.A. Zelenskii, I.M. Milyaev, M.I. Alymov. Letters on Materials. 7 (3), 249 (2017). (in Russian) [А.С. Устюхин, А.Б. Анкудинов, В.А. Зеленский, И.М. Миляев, М.И. Алымов. Письма о материалах. 7 (3), 249 (2017).] Crossref
3. M.L. Marucci, F.G. Hanejko. Advances in Powder Metallurgy and Particulate Materials. MPIF. 7, 11 (2010).
4. D. Sharma, K. Chandra, P.S. Misra. Mater. Des. 32 (6), 3198 (2011). Crossref
5. H. Arik, M. Turker. Mater. Des. 28 (1), 140 (2007). Crossref
6. V.S. Warke, R.D. Sisson Jr, R.D. Makhlouf. Mater. Sci. Eng. A. 528 (11-12), 3533 (2011). Crossref
7. M. Sha, S. Wu, X. Wang et al. Mater. Sci. Eng. A. 535, 258 (2012). Crossref
8. A. de P. Barbosa, G.S. Bobrovnitchii, A.L.D. Skury et al. Mater. Des. 31 (1), 522 (2010). Crossref
9. M. Li, S. Lu, F. Long. JOM. 67 (5), 922 (2015). Crossref
10. S.S. Rathore, M.M. Salve, V.V. Dabhade. J. Alloy Compd. 649, 988 (2015). Crossref
11. S. Li, Y. Wang, X. Wang. Mater. Sci. Eng. A. 639, 640 (2015). Crossref
12. G. Karunakaran, V.M. Nguyen, Y. Konyukhov et al. Archives of Civil and Mechanical Engineering. 17 (3), 669 (2017). Crossref
13. GOST 20899-75. 01.02.2017, Moscow. (in Russian). [ГОСТ 20899-75. 01.02.2017, Москва]
14. GOST 19440-94. 01.02.2017, Minsk. (in Russian). [ГОСТ 19440-94. 01.02.2017, Минск]
15. GOST 18898-89. 01.02.2017, Moscow. (in Russian). [ГОСТ 18898-89. 01.02.2017, Москва]
16. L.-P. Lapierre-Boire, C. Blais, S. Pelletier. Powder Technol. 299, 156 (2016). Crossref
17. Y.H. Cho, H.W. Kim, W. Kim et al. Materials Today: Proceedings. 2 (10), 4924 (2015). Crossref
18. X. Wang, J.V. Wood. Powder Metall. 38 (1), 59 (1995). Crossref
19. V.M. Nguyen, G. Karunakaran, Yu. Konyukhov et al. J Clust Sci. 28 (4), 2157 (2017). Crossref
20. J. Park, S. Lee, S. Kang et al. Powder Technol. 284, 459 (2015). Crossref
21. M. Srinivas, G. Malakondaiah, P. Rama Rao. Proc. R. Soc. Lond. A. 447, 223 (1994). Crossref
22. M. Aloe, F. Anton. Tabira/IV Forum TecnicoInternacional de fundicion. Spain (2007).
23. G.F. Hancock, G.M. Leak. Metal Science Journal. 1, 33 (1967). Crossref
24. K. Saeidi, L. Kvetkova, F. Lofaj et al. RSC Advances. 5, 20747 (2015). Crossref
25. A.K. Gain, L. Zhang. J Mater Sci: Mater Electron. 27, 3982 (2016). Crossref
26. O.Yu. Elagina. Tekhnologicheskiye metody povysheniya iznosostoykosti detaley mashin. Uchebnoye posobiye. University Book, Logos, Moscow (2009) 485 p. (in Russian) [О.Ю. Елагина. Технологические методы повышения износостойкости деталей машин. Учебное пособие. Университетская книга, Логос, Москва (2009) 485 с.]
27. H. Zhang, L. Zhang, G. Dong et al. Powder Technol. 288, 435 (2016). Crossref