Journal of Engineering and Technology Management 78 (2025)

The effect of boron addition on the change in microstructure and abrasion resistance of martensitic tool alloy with the addition of vanadium, tungsten and molybdenum

Grzegorz Tęcza [a]

[a] AGH University of Krakow, Faculty of Foundry Engineering, 30-059 Krakow, 30 Mickiewicza Ave, Poland; ORCID: 0000-0001-8075-6526

Keywords: abrasive wear, martensitic alloy, heat treatment, hardness, microstructure, vanadium carbides, complex carbides

Abstract

The abrasion resistance of martensitic iron alloys used for cast machine components operating under abrasive wear conditions can be improved by producing carbides of elements such as V, W, and Mo in the alloy matrix. The aim of the conducted research was to evaluate the effect of the addition of carbide-forming elements such as V, W, and Mo on the microstructure and abrasion resistance determined in the Miller test. During the metallurgical process, carbide-forming elements such as vanadium and tungsten were introduced into the tested alloys at approximately 13 and 11 wt.%, and at 3.3 and 2.6 wt.%, respectively, with a total carbon content of approximately 4 wt.%. To improve hardenability and modify the alloy microstructural morphology, the second melt additionally contained 0.006 wt.% addition of boron. The measured hardness of the tested samples was approximately 450-500 HV in the as-cast condition. This value increased to approximately 890 HV after hardening, and the highest hardness of about 940 HV was obtained for the alloy modified with boron. The microstructure of the tested samples was composed of a martensitic matrix with traces of retained austenite and rod-shaped carbides with a spherical cross-section, which were identified as complex (V,W)xCy carbides. The highest abrasive wear resistance was obtained for the martensitic alloy with 17.9 wt.% V + 0.1 wt.% W, quenched from 880°C and cooled in 15% HI polymer. Its hardness was approximately 940 HV, and the mass loss was two times lower than that of the reference cast GX70CrMnSiNiMo2 steel.

Introduction

The mining, extraction, energy, and aggregate processing industries are the main consumers of large-sized, thick-walled castings made from alloyed tool steel. The need to harden large cross-sections means that the alloys used for these castings should be characterized by the highest possible hardenability. The castings most often operate under metal-nonmetal abrasive conditions, and the generally accepted principle that the higher is the alloy hardness, the higher is the wear resistance is only partially true, since the second factor determining the degree of wear is the presence of hard carbide particles, both primary and secondary, in the alloy matrix and their volume fraction.

The analysis of the literature indicates that research is currently being conducted to improve the abrasion resistance by applying special heat treatments not only to cast Hadfield tool steel but also to alloys with a martensitic structure, which require not only quenching and tempering but often also precipitation hardening [1-3]. Another method to increase the abrasion resistance of selected casting surfaces is to produce surface layers on the castings in a casting mould [4-6]. The next solution described in the literature is the manufacture of castings with abrasion-resistant composite zones, which involves the formation of carbides in specific casting zones as a result of the reaction and synthesis of carbides from a powder mixture, which occurs by the self-propagating high-temperature synthesis [7-9]. There is also a method for producing primary carbides throughout the casting volume thanks to in situ reactions in the gating system of a closed casting mould [10-11]. However, the most interesting approach due to its simplicity and low cost seems to be the manufacture of castings with a composite structure produced within the whole casting volume in a metallurgical process. This is achieved by introducing carbide-forming elements into the liquid steel, where said elements form hard, abrasion-resistant carbides already in the steel melt. This procedure ensures that the carbides which provide high abrasion resistance are evenly distributed in the alloy matrix, and castings produced in this way can be subjected to further dedicated heat treatment. In previous publications, the author has presented the microstructure and the abrasive wear resistance compared in the Miller test of austenitic alloys with V, Ti, and Nb carbides, as well as cast martensitic steel with Ti carbides. In the conducted studies, at least twice as high abrasive wear resistance was achieved compared to reference cast steels [12-14].

Test materials and methods

The latter technology ensures that primary carbides formed in the liquid steel and secondary carbides precipitated in the solid state are uniformly distributed throughout the alloy matrix, providing exceptionally high abrasion resistance. In his research, applying the 16-hour Miller test according to ASTM G75-07, the author examined changes in the microstructure and abrasive wear resistance of test castings made from Fe-C alloys with V, W, and Mo additions, including the effect of boron on these properties. The results were compared with the results obtained for cast alloyed martensitic GX70CrMnSiNiMo2 tool steel. The examined material consisted of "Y" type test castings with a wall thickness of 25 mm and a weight of approximately 900 g, melted and cast in a Balzers VSG-02 laboratory induction furnace. Chemical analysis of the tested alloys was carried out under industrial conditions using a Spectro Maxx LMF04 spectrometer. Additionally, the content of carbide-forming elements was confirmed by analysis using an energy dispersive X-ray fluorescence spectrometer (Spectro Midex). The test samples were subjected to various heat treatments, which were performed in a Czylok FCF75HM laboratory chamber furnace. After hardening, all samples were annealed at 200°C for one hour. Table 1 shows the chemical composition of the tested alloys, the conducted heat treatment and hardness values obtained for the tested alloys.

In the tested castings, the carbon content was 4.0 wt.% in the first casting and 4.3 wt.% in the second casting, The Mn content was from 0.6 to 0.7 wt.% and the Si content was 0.8 wt.%, both of which were expected to ensure the required hardenability. Additionally, to further improve hardenability, molybdenum (0.21 wt.%) and boron (0.006 wt.%) were added to the second alloy. Chromium and nickel added in the amount of 0.1 wt.% were acting as micro-additions, and as such had no significant impact on the hardenability of the tested alloys or their hardness after quenching. The Al content of 0.02 wt.% indicates proper deoxidation of the alloys. The content of vanadium in the tested alloys was 12.7 wt.% and 10.6 wt.%, respectively, while that of tungsten was 3.3 wt.% and 2.6 wt.%, respectively. The hardness of the tested samples in the as-cast condition and after heat treatment was measured with a Vickers hardness tester under a standard load of 30 kg.

The microstructure of the tested alloys was examined under a Neophot 32 light microscope equipped with a camera for digital image recording.

Phases present in the tested samples were identified with a Kristalloflex 4H X-ray diffractometer from Siemens using the characteristic Cu radiation (Kα = 0.154 nm) with a step size of 0.052 theta/1 s.

Microstructural analysis was also performed with a JEOL JSM-5500LV scanning electron microscope equipped with an EDS detector from Oxford.

Table 1. Chemical composition of the tested alloys, their heat treatment and hardness obtained

Alloy designation	**Chemical composition [wt.%]**											
	C	**Mn**	**Si**	**P**	**S**	**Cr**	**Ni**	**Mo**	**W**	**V**	**B**	**Al**
M1 (12.7 wt.% V+3.3 wt.% W)	4.0	0.6	0.8	0.04	0.02	0.1	0.1	0.02	**3.3**	**12.7**	_	0,02
M2 (10.6 wt.% V+2.6 wt.% W+0.006 wt.% B)	4.3	0.7	0.8	0.04	0.03	0.1	0.1	0.21	**2.6**	**10.6**	**0.006**	0.02

	Heat treatment	**Hardness [HV]**
M1 (12.7 wt.% V+3.3 wt.% W)	As-cast	564, 568, 522
	880°C/0.7h/ HI 15% polymer	894, 862, 869
	880°C/0.7h/ HI polymer 15%+O:580°C/2h	550, 543, 530
M2 (10.6 wt.% V+2.6 wt.% W+0.006 wt.% B)	As-cast	466, 449, 457
	880°C/0.7h/HI 15% polymer	912, 919, 938
	1250°C/0.7h/oil	736, 730, 685
	1250°C/0.7h/oil+O:600°C/2h	705, 690, 662
M1(12.7 wt.% V+3.3 wt.% W) M2 (10.6 wt.% V+2.6 wt.% W+0.006 wt.% B)	No stress relief treatment	1020, 1030

Test results and discussion

From the test results presented in Figures 1 and 2 and Table 1 and 2, it follows that the microstructure of the tested alloys consists of a martensitic matrix containing large, evenly distributed, complex lamellar (V,W)xCy carbides, identified as MC and M_2C carbides. No retained austenite was observed in the metallographic specimens, although X-ray studies indicated its presence. The addition of boron had no effect on the microstructure and, in particular, on the carbide morphology. In both tested alloys, carbides appear as characteristic, well-developed plates. The hardness values obtained after quenching from 880°C in an aqueous polymer solution are as high as 890HV for the M1 alloy and nearly 940HV for the M2 alloy (Table 1). The high hardness values obtained after heat treatment of both alloys indicate their good hardenability, and the addition of boron is not necessary, as also confirmed by the absence of retained austenite in microstructural examinations. In samples designated M2 (with Mo and B), which were quenched from 1250°C in oil and tempered at 600°C for 2 hours, precipitates of dispersive complex (Fe, W, V)xCy carbide particles were observed on the martensite laths, though no increase in alloy hardness followed the effect of dispersion hardening. An example of such precipitates with their chemical composition is shown in

Figure 2. The hardness of the tested alloys quenched from 880°C followed by cooling in an aqueous polymer solution and not stress-relieved immediately after quenching was the highest and amounted to 1020 and 1030HV, respectively. However, after a few hours, the samples fractured spontaneously, demonstrating the high tendency of the tested alloys to develop post-quench cracks and indicating the need for stress relieving, preferably immediately after quenching. Figure 3 shows such cracks on the surface of metallographic specimens.

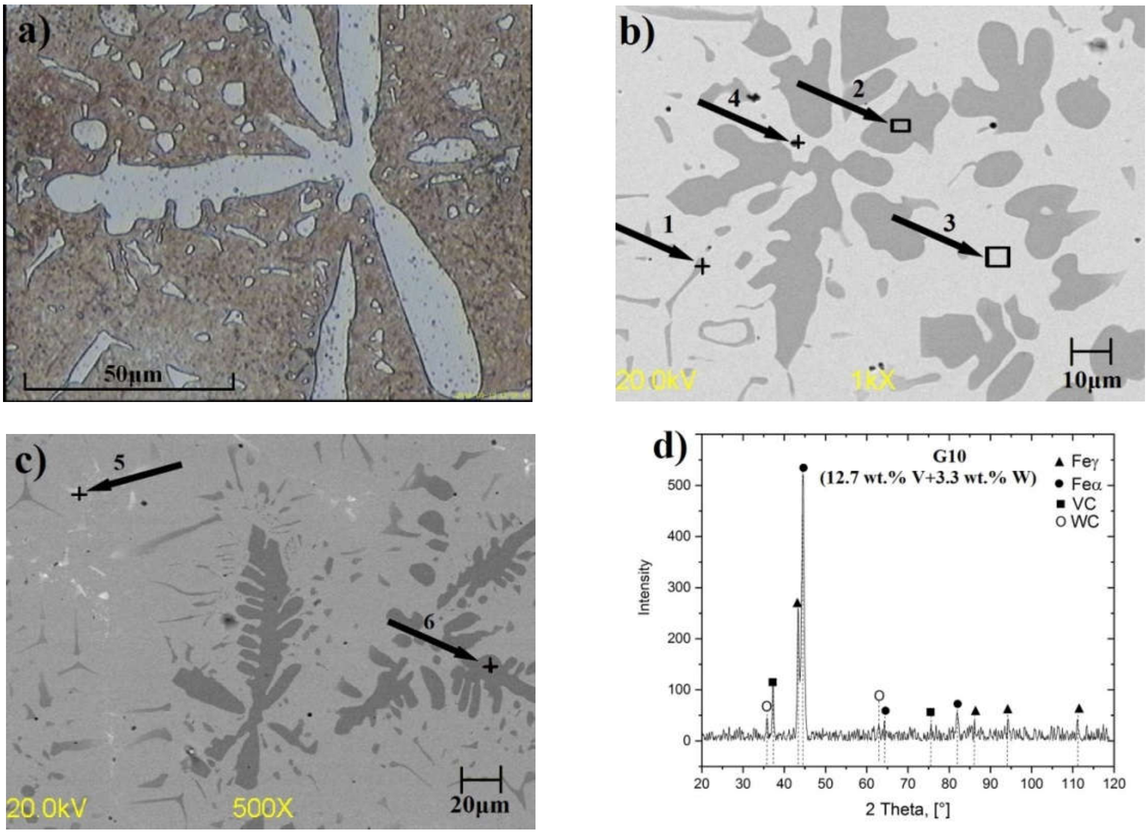

Figure 1. Microstructure of the M1 sample (12.7 wt.% V + 3.3 wt.% W); a-c) - lamellar carbides evenly distributed in the alloy matrix; a) - martensitic matrix; b, c) - scanning image with marked locations of analysis; d) - X-ray diffraction pattern; etched with nital

Table 2. Chemical composition of carbides at points 1-6

Location of analysis	[at.%]										
	C	Si	V	Mn	Ni	Mo	W	Al	S	Ca	Fe
Point 1	52.1	-	43.4	0.1	0.1	-	1.9	-	-	-	Balance
Point 2	47.7	-	49.7	0.1	0.1	-	1.5	-	-	-	Balance
Point 3	7.2	1.6	2.2	0.3	0.1	-	0.6	-	-	-	Balance
Point 4	28.2	0.3	2.5	0.2	0.1	-	0.2	31.9	2.4	2.8	Balance
Point 5	43.8	39.8	-	0.4	0.1	0.2	8.0	-	-	-	Balance
Point 6	54.3	43.5	-	0.1	0.1	0.1	1.3	-	-	-	Balance

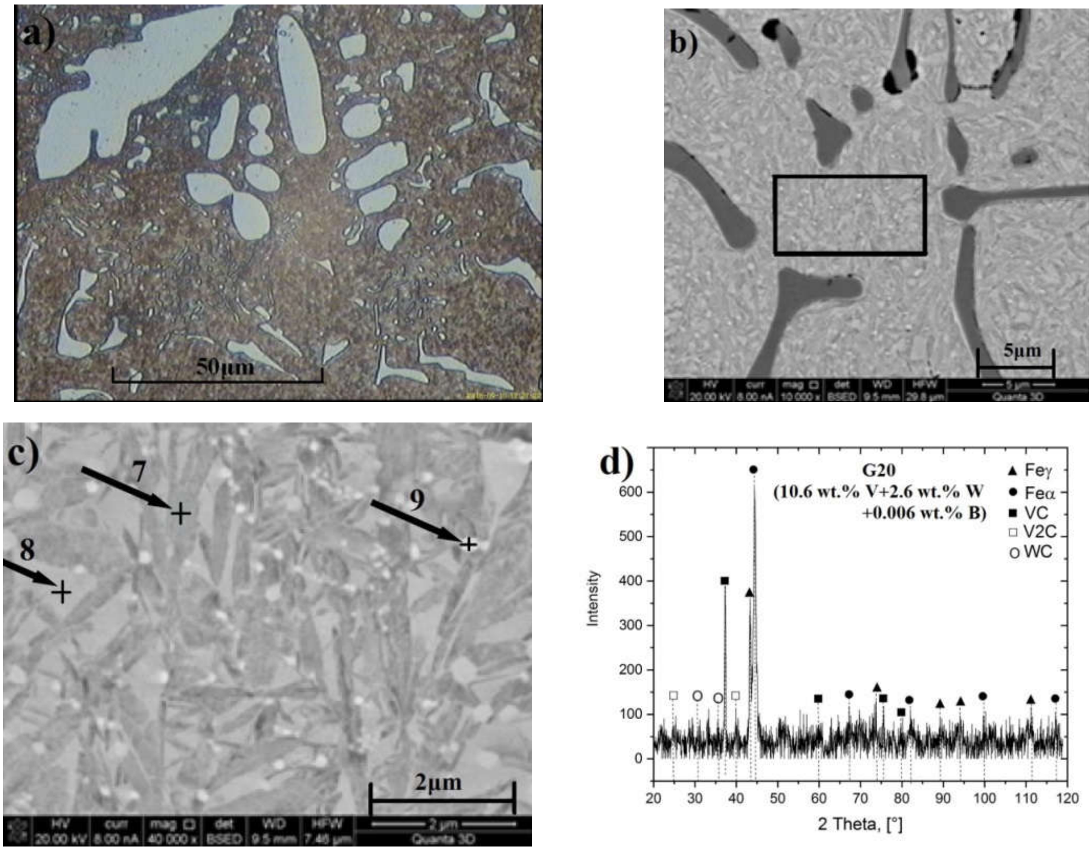

Figure 2. Microstructure of the M2 sample (10.6 wt.% V + 2.6 wt.% W + 0.006 wt.% B); a, b - lamellar carbides evenly distributed in the alloy matrix; b, c - scanning image of the martensitic matrix with marked locations of analysis; c - dispersive (Fe, V, W)xCy carbides precipitated on the martensite laths in the sample after quenching from 1250°C in oil and tempering at 600°C for 2 hours; d) - X-ray diffraction pattern; etched with nital.

Table 2. Chemical composition of carbides at points 7-9

Location of analysis	[at.%]						
	C	Si	Cr	Mo	V	W	Fe
Point 7	9.8	1.5	0.1	0.2	2.3	0.5	Balance
Point 8	7.3	1.6	0.1	0.2	2.1	0.7	Balance
Point 9	44.1	0.1	0.1	0.1	7,6	5.8	Balance

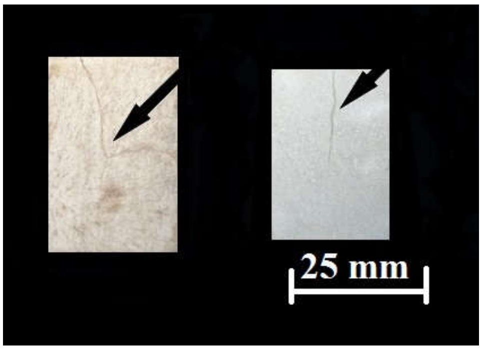

Figure 3. Post-quench cracks in the test samples.

Abrasion resistance tests were performed on samples of both alloys which obtained the highest hardness values, compared in Table 1. Both alloys were quenched from 880°C in a 15% aqueous polymer solution and had a hardness of approximately 890 HV (alloy M1) and 940 HV (alloy M2). Tests were also carried out on a reference sample of cast

GX70CrMnSiNiMo2 tool steel. According to the standard, two abrasion tests were performed for each tested alloy, from which average wear values were calculated for each cycle. Figure 3 compares the total mass losses of the tested samples as a function of abrasion time.

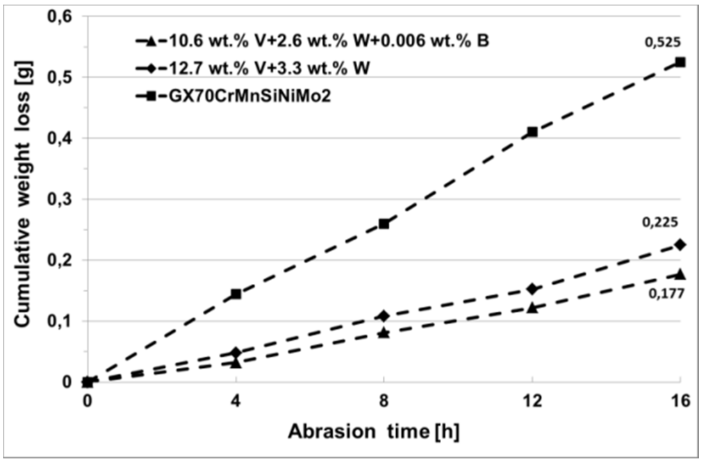

Figure 4. Total mass losses of the tested alloys as a function of abrasion time.

Based on the obtained total mass losses of the tested samples, it was found that the highest abrasive wear resistance (the wear rate of 0.177 g/16 h) was achieved for the martensitic M2 alloy with the addition of 10.6% V and 2.6% W, hardened in a polymer solution. The hardness of this alloy after quenching was approximately 940 HV, and the abrasive wear rate was almost three times lower than that of the reference cast tool steel. The wear of the tested alloys increases slightly with the increasing content of V, W and Mo in the alloy, which is due to the lower matrix hardness of these alloys compared to the M2 alloy. A higher content of carbide-forming elements in the alloy means a lower carbon content in the matrix, and this in turn indicates that the matrix has been depleted of carbon by the formed carbides.

Figure 5 shows a macroscopic image of the alloy sample surface after abrasion test, while Figure 6 compares the sample wear profiles. The analysis and comparison of the surfaces after abrasion test show significant differences in their wear mechanism. It was found that the wear mechanism dominant in the reference martensitic sample is uneven wear, the formation and deepening of scratches or even grooves, and the embedding of SiC abrasive particles into the surface.

Samples with the addition of V and W tested in a 16-hour abrasion test were characterized by the surfaces even and homogeneous, with well-visible carbides protruding from the alloy matrix. No scratches or grooves were formed on the abraded surfaces and there was no sign of carbide chipping from these surfaces. Due to the high hardness of the matrix and protruding carbide particles, the wear was uniform, and SiC particles were not penetrating into the abraded surfaces.

The differences in the height of the wear profiles visible in Figure 6, where the protruding particles form local peaks and the worn out matrix forms depressions, confirm this mechanism.

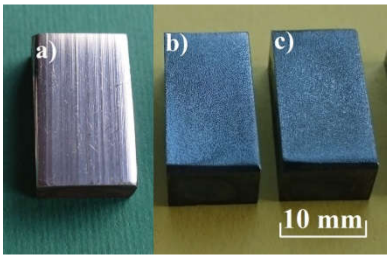

Figure 5. The surface of specimens after abrasion test: a)-reference cast GX70CrMnSiNiMo2 steel, b)-martensitic alloy M1 with the addition of (12.7 wt.% V+3.3 wt.% W), c)-martensitic alloy M2 with the addition of (10.6 wt.% V+2.6 wt.% W+0.006 wt.% B).

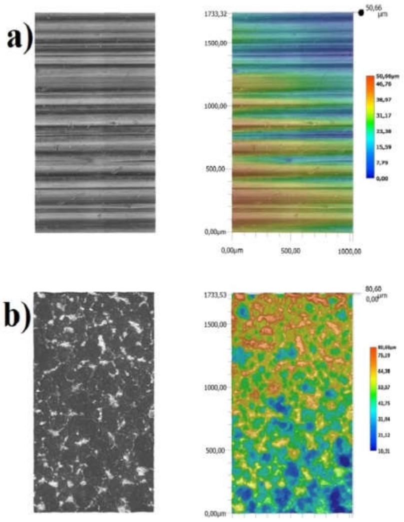

Figure 6. Comparison of wear surface profiles obtained in the Miller test: reference cast GX70CrMnSiNiMo2 steel-(a) and martensitic alloy M1 (12.7 wt.% V + 3.3 wt.% W)-(b).

Conclusions

The high carbon content in Fe-C alloys and the large number of carbide-forming additives introduced into the alloys allow for the formation of carbides in castings, the presence of which determines the abrasive wear resistance of tool alloys. From the conducted research, the following conclusions can be drawn:

1. The microstructure of the tested alloys after heat treatment consists of a martensitic matrix in which carbides are evenly distributed.
2. The observed carbides were identified as MC and M_2C carbides.
3. They are predominantly complex lamellar $(V,W)_xC_y$ carbides.
4. No retained austenite was observed in the metallographic microsections.
5. The highest hardness of approximately 940 HV was obtained for the boron-containing 10.6 wt.% V + 2.6 wt.% W + 0.006 wt.% B alloy.
6. The addition of boron was observed to have no effect on the alloy microstructure.
7. In the alloy with the additions of Mo and V, the precipitates of dispersive carbides were present, but no secondary hardening effect occurred.
8. The formation of vanadium and tungsten carbides in the martensitic matrix brings an even two-fold increase in the abrasive wear resistance.
9. Compound vanadium and tungsten carbides in a martensitic matrix cause uniform wear and the addition of boron does not affect the nature of this wear.

Acknowledgments: The article was prepared under the contract 16.16.170.654/B02.

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflict of interest.

Data availability: The data are available on request from the corresponding author.

References

1. Dziubek, M,; Rutkowska-Gorczyca, M.; Grygier, D. The effect of the austenitisation temperaturefor the two-stage heat treatment of high-manganesesteels on its wear resistance under abrasiveconditions. Tribologia. 2023, 305, 9426.
2. Dziubek, M.; Rutkowska-Gorczyca, M.; Dudzinski, W.; Grygier, D. Investigation into Changes of Microstructure and Abrasive Wear Resistance Occurring in High Manganese Steel X120Mn12 during Isothermal Annealing and Re-Austenitisation. Process. Materials. 2022, 15, 2622.
3. Maher, M.; Iraola-Arregui, I.; Ben Youcef, H.; Rhouta, B.; Trabadelo, V. Microstructural evolution of heat-treated Cr-W-V-Mo steels: Effect of core-shell carbides and secondary precipitation on their abrasion resistance. Journal of Materials Research and Technology. 2023, 24, 27-38.
4. Szymański, Ł.; Olejnik, E.; Tokarski, T.; Kurtyka, P.; Drożyński, D.; Żymankowska-Kumon S. Reactive casting coatings for obtaining in situ composite layers based on Fe alloys. Surface and Coatings Technology. 2018, 350, 346-358.
5. Szymański, Ł.; Olejnik, E.; Sobczak, J. J.; Szala, M.; Kurtyka, P,; Tokarski, T.; Janas A. Dry sliding, slurry abrasion and cavitation erosion of composite layers reinforced by TiC fabricated in situ in cast steel and gray cast iron. Journal of Materials Processing Technology. 2022, 308.
6. Szymański, Ł.; Olejnik, E.; Sobczak, J. J.; Tokarski, T. Improvement of TiC/Fe in situ composite layer formation on surface of Fe-based castings. Materials Letters. 2022, 309.
7. Olejnik, E.; Tokarski, T.; Sikora, G.; Sobula, S.; Maziarz, W.; Szymański, Ł.; Grabowska, B. The Effect of Fe Addition on Fragmentation Phenomena, Macrostructure, Microstructure, and Hardness of TiC-Fe Local Reinforcements Fabricated In Situ in Steel Casting. Metall. Mater. Trans. A, 2019, 50, 975–986.
8. Sobula, S., Olejnik, E., Tokarski, T. Wear Resistance of TiC Reinforced Cast Steel Matrix Composite. Arch. Foundry Eng. 2017, 17, 143-146.
9. Olejnik, Ewa. (2025). Local composite reinforcements of WC/Fe-C type obtained in-situ via SHS synthesis in gray cast iron castings. Journal of Alloys and Compounds. 1034. 181260. 10.1016/j.jallcom.2025.181260.
10. Marosz, J., Sobula, S. Analysis of fragmentation phenomenon of composite layers of Fe-TiC type obtained ”in situ” in steel casting. Arch. Foundry Eng. 2024, 2, 131-136.
11. Marosz, J., Kawalec, M., Górny, M. Structure of ADI cast iron as a cast “in situ” composite reinforced with TiC ceramic particles. Arch. Foundry Eng. 2024, 4, 95-102.
12. Tęcza, G. Changes in abrasive wear resistance during miller test of Cr-Ni cast steel with Ti carbides formed in the alloy matrix. Arch. Foundry Eng. 2021, 21, 110-115.
13. Tęcza, G. Changes in Microstructure and Abrasion Resistance during Miller Test of Hadfield High-Manganese Cast Steel after the Formation of Vanadium Carbides in Alloy Matrix. Materials 2022, 15, 1021.
14. Tęcza, G. Changes in the Microstructure and Abrasion Resistance of Tool Cast Steel after the Formation of Titanium Carbides in the Alloy Matrix. Arch. Foundry Eng. 2023, 23, 173-180.