



Changes in the Microstructure and Abrasion Resistance of Tool Cast Steel after the Formation of Titanium Carbides in the Alloy Matrix

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Abstract

Cast martensitic alloy steel is used for the production of parts and components of machines operating under conditions of abrasive wear. One of the most popular grades is cast steel GX70CrMnSiNiMo2 steel, which is used in many industries, but primarily in the mining and material processing sectors for rings and balls operating in the grinding sets of coal mills.

To improve the abrasion resistance of cast alloy tool steel, primary titanium carbides were produced in the metallurgical process by increasing the carbon content to 1.78 wt.% and adding 5.00 wt.% of titanium to test castings. After alloy solidification, the result was the formation of a microstructure consisting of a martensitic matrix with areas of residual austenite and primary titanium carbides evenly distributed in this matrix.

The measured as-cast hardness of the samples was 660HV and it increased to as much as 800HV after heat treatment.

The abrasion resistance of the sample hardened in a 15% polymer solution increased at least three times compared to the reference sample after quenching and tempering.

Keywords: Cast tool steel, Microstructure, Titanium carbides, Heat treatment, Hardness, Resistance to abrasive wear

1. Introduction

One of the most popular grades of cast martensitic steel resistant to abrasive wear is cast GX70CrMnSiNiMo2 steel and its numerous varieties. It belongs to the group of cast tool steels and is used for castings (mainly of ball mills), which require high abrasion resistance and may experience dynamic loads. After normalizing, it has a pearlitic structure with a hardness of 300-450 HV, while after hardening its hardness can reach 700-800 HV

[1-4]. Table 1 shows the basic chemical composition of this cast steel and its common varieties.

The addition of Mn, Si, Cr and Mo is introduced to obtain, after normalizing, an appropriately hard pearlitic structure and a significant improvement in hardenability, while nickel addition improves the steel plasticity. Owing to the addition of Mo, usually not exceeding 0.8 wt.%, the risk of brittle fracture in thick-walled castings can be reduced to a minimum.



Table 1.

Chemical composition of cast martensitic abrasion-resistant steel [1,2,4,5]

GX70CrMnSiNiMo2	Chemical composition [wt. %]							
	C	Mn	Si	P	S	Cr	Ni	Mo
Other varieties	0.6-0.75	0.9-1.05	<0.55	<0.040	<0.040	1.8-1.95	0.6-0.8	0.4-0.50
	0.9	0.7	0.5	<0.040	<0.040	2.2	–	0.4
	0.8	0.8	0.5	<0.040	<0.040	1.7	0.8	0.3
	0.7-1.10	0.6-0.90	0.3-0.80	<0.040	<0.040	1.5-3.0	<1.50	0.3-0.50
	0.7-1.2	0.3-1.0	0.4-0.8	<0.040	<0.040	1.3-7.0	<1.5	0.4-1.2
	0.5-0.70	0.6-0.90	0.3-0.80	<0.040	<0.040	1.0-2.5	<1.50	0.3-0.50
	0.6	0.7	0.5	<0.040	<0.040	2.2	–	0.4
	0.4-0.7	0.6-1.5	0.6-1.5	<0.040	<0.040	0.9-2.2	<1.5	0.2-0.7

Grades with high carbon content are used for castings that should offer both excellent hardness and abrasion resistance - e.g., castings operating in ore crushing mills, while low-carbon grades are intended for castings operating in ball mills, which may experience the effect of dynamic loads. Due to the fact that these cast steels are used for thick-walled castings that cannot be hardened in water, the additions of alloying elements combined with high carbon content ensure the hardenability sufficiently high to reduce the heat treatment of these cast steels to heating up to 920-980°C and cooling in air. After this treatment, the highest values of the hardness are obtained. Figure 1 shows the TTT chart for cast GX70CrMnSiNiMo2 steel [4].

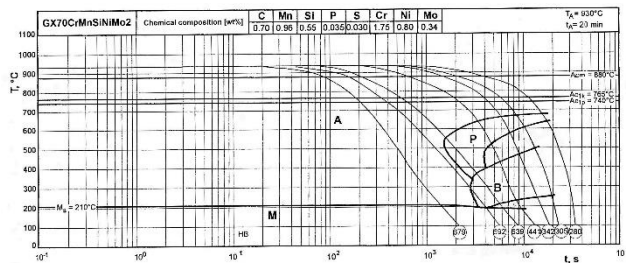


Fig. 1. The TTT chart for cast GX70CrMnSiNiMo2 steel [4]

The second stage of heat treatment is always tempering of the hardened components from temperature depending on the required hardness. When the components are annealed at a temperature of 200-280°C, the decrease in hardness is small and so is the change in plasticity. By increasing the tempering temperature to 420-650°C, the hardness of the castings decreases and their plasticity increases [4]. However, it should be remembered that with such a change in microstructure, the abrasion resistance will also decrease. Figure 2 compares the abrasive wear resistance of cast GX70CrMnSiNiMo2 steel used for balls and rings operating in ball mills. The cast steel has a typical composition but undergoes different types of heat treatment. After hardening and stress relief annealing, its wear rate is small and amounts to approximately 0.24g/16h. High tempering makes the wear rate of castings increase more than twice.

The microstructure of such cast steel in the as-cast or normalized state consists of pearlite and, after hardening of alloys with a lower carbon content, of martensite. Sometimes, in alloys with a higher carbon content, the presence of residual austenite is observed after hardening, but most often it is partially transformed

into martensite after tempering. Figure 3 shows the characteristic microstructures of this cast steel.

The presence of residual austenite is undesirable as it causes uneven hardness and uneven wear during operation. Figure 4a shows a section of the ball surface after operation with visible areas of uneven wear. Additionally, this constituent may cause cracks in castings during operation and catastrophic destruction of the device.

Figure 4b shows the surface of cast martensitic steel samples used for ball mills. The samples were subjected to various heat treatments and tested for abrasion resistance in the Miller test. One sample was hardened and stress relief annealed to a hardness of approximately 700HV, the other was quenched and tempered and had a hardness slightly above 400HV. In alloys of this type, the uneven surface wear is in most cases partially due to the surface abrasion and partially to the formation of small scratches (Fig. 4b-1) and grooves (Fig. 4b-2) on the surface. It increases with a decrease in the hardness of the samples and is closely related to the microstructure and the presence of residual austenite.

To improve functional properties and make wear more uniform, and also because of the grain growth tendency observed in thick-walled castings, before casting, the steel melt is modified in a ladle to refine the grains. This is achieved by the addition of strongly carbide-forming elements such as Ti or V, and the addition is at the level of tenths of a percent. Recently, research has been carried out to explore other variants of the modification process.

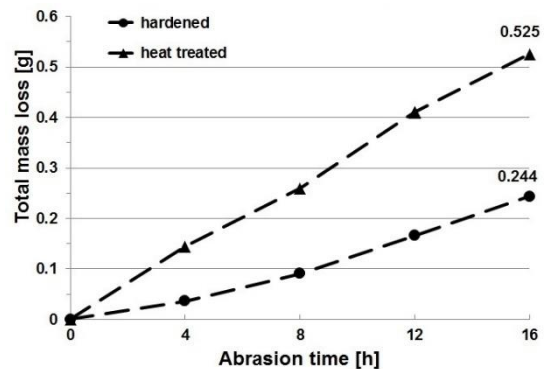


Fig. 2. The effect of heat treatment on the total weight loss of cast GX70CrMnSiNiMo2 steel samples plotted as a function of abrasion time in the Miller test [own research]

For example, in [6], the effect of Ti and Nb on the microstructure of cast K100 tool steel was investigated, where Ti was added in amounts of 0.3, 0.7 and 1 wt. % and Nb in amounts of 0.2 and 1 wt. %. The addition of 0.7 and 1 wt. % Ti had a strong modifying effect and a uniform grain size was obtained in different places of the ingot. In [7], the authors examined the effect of modification with niobium, tantalum and titanium on the grain size in hot work tool steel. Three types of steel modified with 0.06 wt. % Nb, 0.03 wt. % Ta, and 0.006 wt. % Ti were used. In the samples of modified steel, a positive effect on mechanical properties and a reduced grain growth rate were observed.

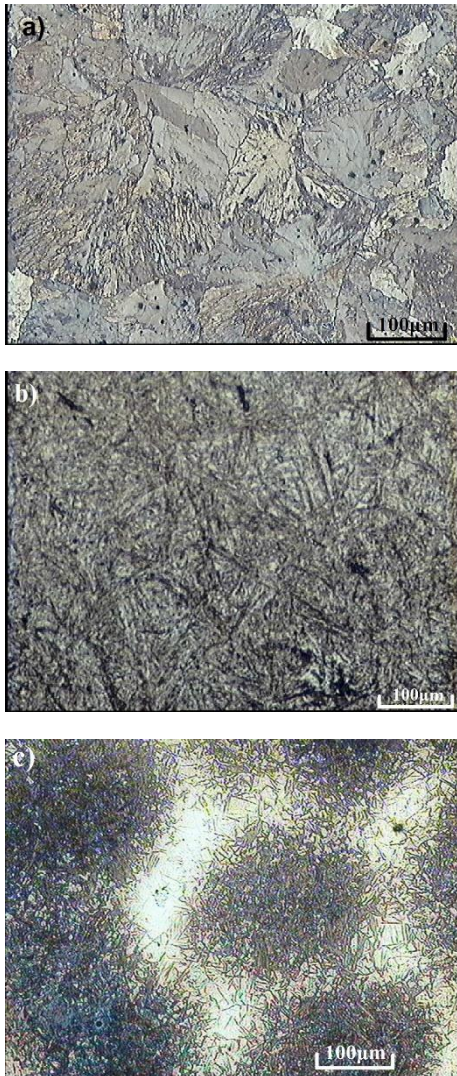


Fig. 3. Microstructures of cast GX70CrMnSiNiMo2 steel: a) as-cast, pearlite; b) after hardening, martensite; c) after hardening, dark martensite, bright residual austenite; etched with nital

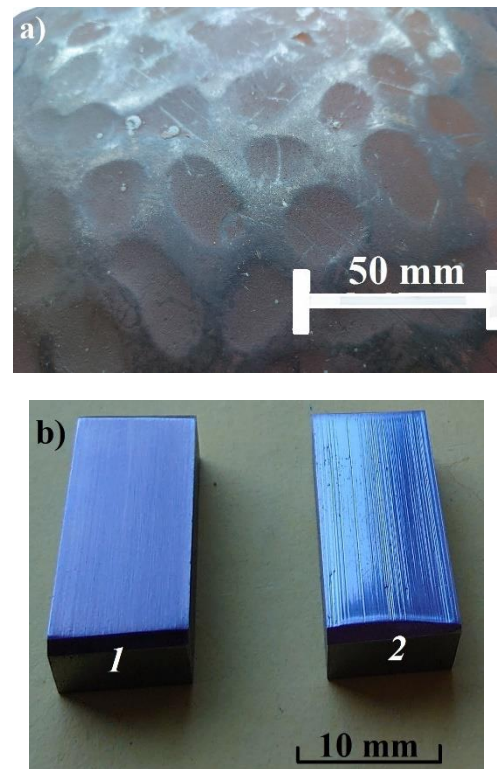


Fig. 4. a) surface of the coal mill ball after operation, b) surface topography of samples taken from the ball after abrasion in the Miller test; 1-after hardening and stress-relief annealing, 2-after quenching and tempering

A review of the literature on the wear behaviour of materials indicates that scientific research has mainly been devoted to studies of multi-phase alloys, including cast tool steel, in which the matrix is reinforced with carbides, nitrides and other ceramic particles [8,9]. Other studies are focused on the possibility of making castings with abrasion-resistant composite zones produced by the use of SHS powder synthesis (Self-propagating High-temperature Synthesis). Using the SHS process, areas resistant to abrasive wear are obtained in specific casting zones as a result of the reaction generating high temperature in the alloy and synthesis of carbides from a mixture of powders [10-12]. A very popular development trend is still the enrichment of the surface layer of tools with alloying elements or ceramic particles introduced after remelting of this layer [13,14].

Attempts have also been made to produce composite surface layers on castings by pouring castings into the mould cavity with the applied coatings that contain TiC formation substrates. Under the effect of high temperature, the reaction of the TiC synthesis occurs and a composite layer is formed in situ on the casting surface [15,16].

The development of new techniques and technologies for tool production is currently mainly focused on precision casting, which is a faster and cheaper method of making tools and where castings do not require expensive finishing. Additionally, compared to wrought steels which have limited forgeability, castings have a great advantage - they can be enriched with more alloying additions and can have more phases in the matrix, including primary

carbides, which makes them very attractive as abrasion-resistant materials. Unfortunately, however, numerous carbides and their large sizes significantly deteriorate the cast steel plasticity [17]. Even when a plastic austenitic matrix is produced, the formation of a large number of primary carbides may cause a double drop in the impact strength [18].

In his research, the author uses a simple solution, which ensures the formation of primary carbide particles in the entire volume of liquid steel during the metallurgical process, and later also in the casting. Yet, he believes that it is necessary to develop a technology for liquid metal processing that will generate the primary carbides small, oval and free from the tendency to form clusters. Then it will be possible to obtain sufficient plasticity of tool components.

In previous studies [19,20] on the properties of cast austenitic steel with titanium carbides, the author and his associates presented changes in the microstructure and abrasive wear resistance (determined in the Miller test) of high-manganese alloys containing 0.4-2.5 wt. % Ti and Cr-Ni alloys containing 1.3-6.9 wt. % Ti. Compared to reference cast steels, the tested alloys always showed an increase in matrix hardness and at least a several dozen percent higher abrasion resistance determined in the abrasion resistance test.

2. Test materials and methods

The author's previous research on changes in the microstructure and wear behaviour of cast steels with an austenitic structure prompted him to conduct similar experiments on cast martensitic steel.

The reference material was cast GX70CrMnSiNiMo2 alloy tool steel used for coal grinding sets in coal-fired power plants. The

cast steel composition (in % by weight) included 0.7% C, 1.0% Mn, 0.5% Si, 1.8% Cr, 0.6% Ni and 0.4% Mo. The reference material was subjected to quenching and tempering, obtaining an average hardness of 400 HV.

The carbon content in the tested alloy was increased so that, after adding titanium and producing primary carbides, the chemical composition of the matrix of the test castings corresponded to the reference cast steel. Primary titanium carbides produced during steel melting and distributed throughout the entire volume of the casting reduced the abrasive wear and made it more uniform in samples tested in the Miller test.

The samples were cut out from the "Y" type test castings with a wall thickness of 25 mm and a weight of approximately 0.9 kg, cast from the steel melted in a Balzers VSG-02 induction laboratory vacuum furnace. The charge material was cast GX70CrMnSiNiMo2 steel scrap and, to increase the carbon content, high-purity pig iron with known chemical composition. To supplement the alloying additives, metallic chromium, low-carbon Fe-Mn85, electrolytic nickel and Fe-Ti70 were added. After melting the charge and heating to a temperature of about 1600°C, the liquid steel was deoxidized in two stages using Fe-Ca-Si+Al in an amount of about 0.7+0.8g/kg, and ferrotitanium was added in portions to avoid a drop in steel temperature. As a result of the reaction, primary titanium carbides, evenly distributed in the alloy matrix after casting solidification, were produced in liquid steel. The steel after melting was cast into ceramic moulds, which were heated to a temperature of 200÷250°C. A Foundry Master spectrometer was used to analyze the chemical composition. Titanium content was determined with a Spectro Midex energy dispersive X-ray fluorescence spectrometer. Table 2 shows the chemical composition of the tested samples.

Table 2.
Chemical composition of the tested cast martensitic steel

Alloy designation	Chemical composition [wt. %]										
	C	Mn	Si	P	S	Cr	Ni	Mo	V	Al	Ti
k-ti	1.78	0.96	1.75	0.02	0.04	1.1	0.9	0.3	0.2	0.02	5.0

Table 3.
Heat treatment of tested samples and their hardness

Sample designation	Heat treatment	Average hardness [HV]
k-ti	As-cast	662
k-ti1	920°C/0.7h/air	777
k-ti1*	920°C/0.7h/ HI 15% polymer	799
k-ti1**	920°C/0.7h/oil	740

Chemical analysis shows that with the carbon and titanium content of 1.78 wt. % and 5.0 wt. %, respectively, the chemical composition of the cast steel matrix (Mn, Cr, Ni and Mo) approximately corresponds to the chemical composition of the reference cast steel. Only the silicon content is higher as a result of double deoxidation of steel in the furnace.

Samples were cut out from the test ingot and subjected to heat treatment. As a next step, their hardness was measured by the Vickers method under a load of 30 kg. The heat treatment parameters and the average hardness values calculated from at least

four measurements are presented in Table 3. After hardening, all samples were tempered at temperature of 200°C for 2 hours.

A Neophot 32 light microscope with a digital image recording system was used for the microstructural examinations.

Chemical analysis of the test alloy matrix and of carbides present in this matrix was performed using a JEOL, JSM-5500LV scanning electron microscope equipped with an EDS microanalyzer.

The phase composition of the tested samples was determined with a Siemens Kristalloflex 4H X-ray diffractometer, using

characteristic Cu radiation ($K\alpha = 0.154 \text{ nm}$) at a step of 0.05 $2\theta/\text{s}$.

The abrasive wear resistance was determined in a Miller machine that complies with ASTM G75 and allows comparison of wear on samples made of different construction materials. Additionally, the choice of this test method allowed the author to compare previously obtained results with the results obtained by his associates [21-23], provided, however, that all test parameters were constant and repeatable. The most important parameters included sample dimensions of $25.4 \times 12.7 \times 9 \text{ mm}$, constant load of 22.2 N and an abrasive medium in the form of a mixture of water and silicon carbide in a 50/50g ratio. Silicon carbide with a grain size of 220 according to the FEPA standard, which corresponds to $53 \div 73 \mu\text{m}$, was used in the abrasion tests. Four four-hour abrasion cycles were performed on each sample and after each of these cycles the sample was weighed with an accuracy of 0.001 g . Based on the obtained changes in the mass of the samples, wear curves were plotted and compared with the wear of the reference sample. A detailed description of the test procedure can be found in the author's previous studies, e.g. in [18-20].

The surfaces of the tested cast steel samples after abrasion test were compared with the surface of the sample cut out from the mill ball, subjected to a heat treatment and examined in the Miller test. Based on the macroscopic appearance of the surfaces, the wear mechanism can be approximately determined. However, it should be remembered that for a thorough analysis of the surface of worn out materials, additional tests should be carried out using a profilometer, which is a standard device for assessing and comparing the condition of the surface after use. This research will be made as a next step in the conducted experiments.

3. Test results and discussion

Based on the appearance of microstructures examined by the light microscopy (Figs. 5 and 6) and scanning microscopy (Fig. 7), chemical analysis of visible precipitates (Fig. 8 and Table 4) and X-ray phase analysis (Fig. 9), it was found that the as-cast microstructure of the tested alloys consisted of a martensitic matrix with a small amount of residual austenite in the interdendritic spaces (Fig. 5b) and evenly distributed faceted titanium carbides (TiC), (Figs. 5a and 7b, pt 1, Fig. 8a and Table 4, Pt 1), which had a slight tendency to form clusters. A few areas with complex lamellar carbides ($(\text{Ti,Fe,Mo})_3\text{C}$, the chemical composition of which is presented in Table 4, Pt 3, were also observed (Fig. 7a and c, pt 3). Compared to the as-cast state, the change in the microstructure of the tested samples after hardening in air, oil or in an aqueous polymer solution consisted in a decrease in the content of residual austenite (Figs. 5b and 6a). Complex lamellar carbides rich in molybdenum were not dissolved during hardening. Another change resulted from the hardening operation and involved the change in hardness, which increased to 800 HV for samples hardened from a temperature of 920°C and cooled in a 15% aqueous solution of the HI polymer (Table 3). The use of oil or air reduced the obtained hardness only by several dozen units. The small amount of residual austenite after hardening and the possibility of hardening at a low cooling rate indicate a very good hardenability of the alloy. In fact, the hardenability was so high that

test castings with a wall thickness of 25 mm were hardened during cooling in the mould.

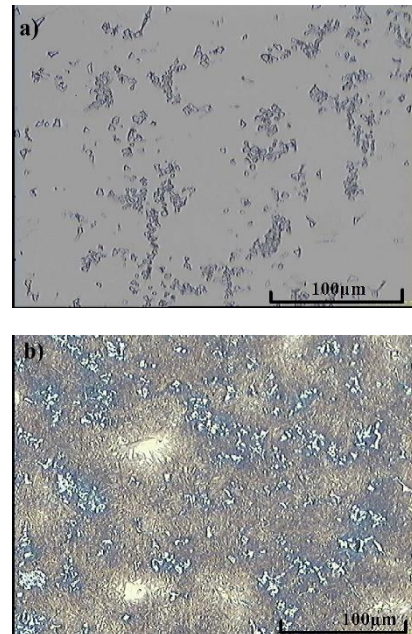


Fig. 5. As-cast microstructure of the tested alloy; a) - unetched specimen, titanium carbides evenly distributed in the alloy matrix; b) - nital-etched specimen section, dark martensite, bright residual austenite and titanium carbides

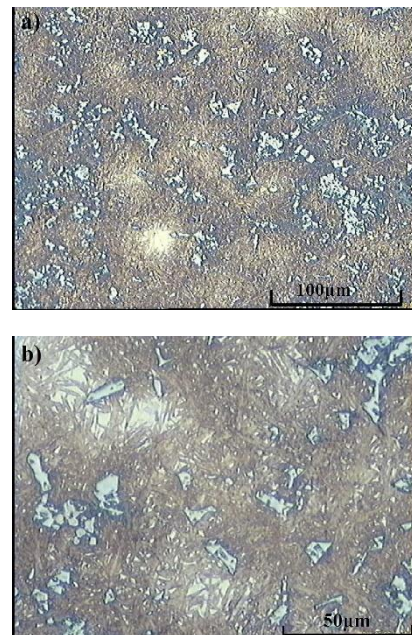


Fig. 6. Microstructure of the tested alloy after hardening; dark martensite, bright residual austenite and titanium carbides; nital etching; a) - $400 \times$, b) - $800 \times$

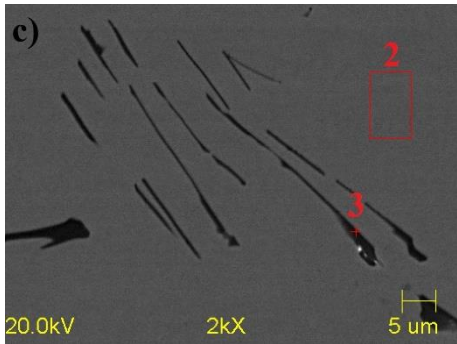
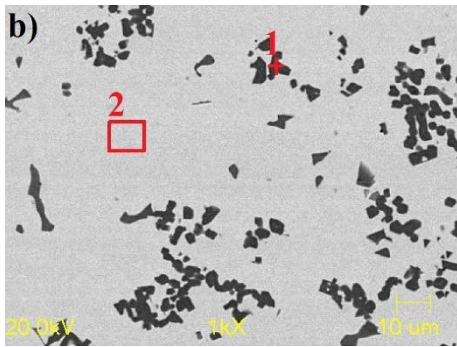
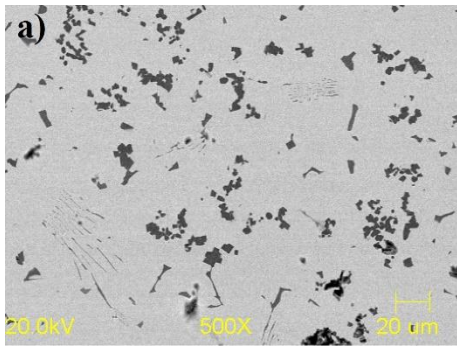


Fig. 7. Scanning images of the sample after hardening with marked analysis locations; a) - carbides evenly distributed in the alloy matrix, b) - faceted carbides, c) - lamellar carbides

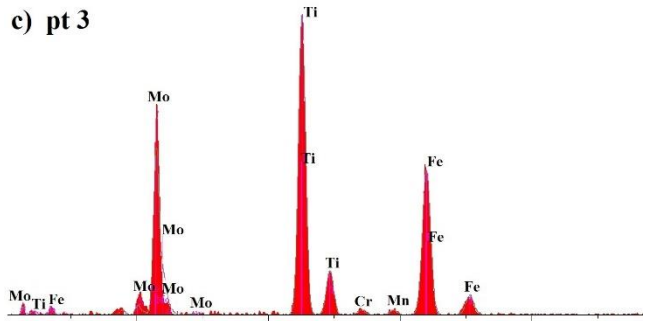
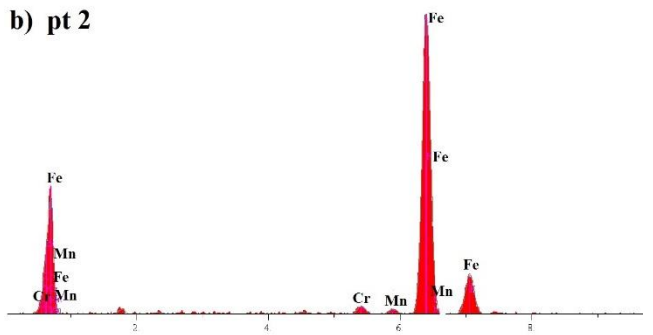
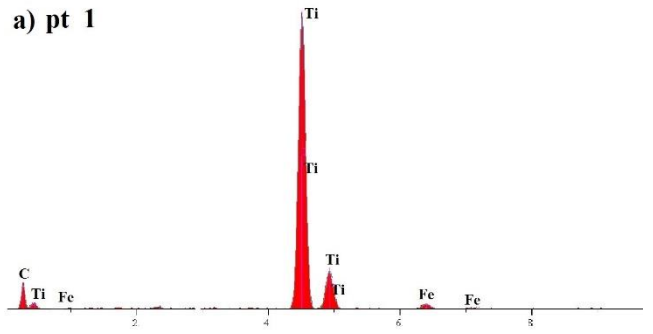


Fig. 8. Example of the energy spectrum from EDS a) - for carbides visible at pt 1, b) - for the matrix at pt 2, c) - for carbides visible at pt 3

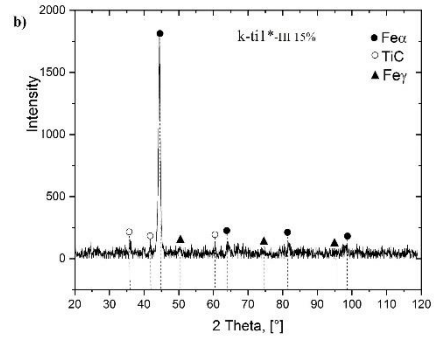
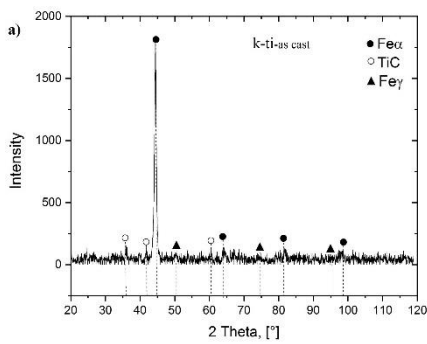


Fig. 9. X-ray diffractograms of the tested samples; a) - as-cast, b) - after hardening in a 15% aqueous solution of HI polymer

Table 4.

Chemical composition of areas at points 1, 2 and 3 in Figure 7

Analysis location	[at. %]							Total
	C	Ti	V	Cr	Mn	Fe	Mo	
Pt 1; faceted carbides	53.8	44.4	–	0.1	0.1	1.5	0.1	100.0
Pt 2; matrix	1.9	0.2	0.2	1.1	0.7	95.7	0.2	100.0
Pt 3; faceted carbides	29.8	32.5	0.4	0.7	0.7	26.7	9.2	100.0

To compare the abrasion resistance of samples after different heat treatments and with different hardness values, the following samples were tested: one sample as-cast, one sample hardened in air, and one sample hardened in a 15% polymer solution. Based on the obtained changes in the mass of the tested samples in individual runs, the total mass loss of the samples during the entire test was calculated and a graph of the total mass loss of the samples was plotted as a function of abrasion time (Fig. 10).

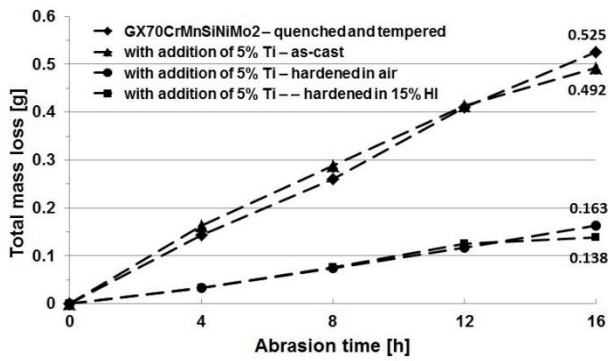


Fig. 10. Comparison of total mass losses of the tested samples during abrasion

Based on the obtained mass losses, it was found that the abrasive wear resistance of the tested as-cast martensitic steel was comparable to the wear behaviour of the reference cast GX70CrMnSiNiMo2 steel after heat treatment. The wear rate was 0.525 g/16h for the reference cast steel and 0.492 g/16h for the tested alloy. Hardening of cast steel with the addition of 5.0 wt. % Ti made the wear rate decreased at least three times, i.e. to 0.138 g/16h for the sample hardened in a 15% polymer solution. A similar value of the wear rate, i.e. 0.163 g/16h, was obtained for the sample hardened in air.

Figure 11 shows macroscopic images of the sample surface after abrasion compared with a reference sample made of cast GX70CrMnSiNiMo2 steel, the surface of which bears traces of uneven wear (Fig. 11a) with scratches and grooves visible in some areas. The addition of 5 wt. % Ti made the sample wear even. The grooves and scratches are no longer observed on the sample surface, which is now even, slightly rough, and with particles protruding from the alloy matrix. This type of the surface image indicates the wear mechanism, which involves the wear of the martensitic alloy matrix first, and gradual exposure of carbides as a result of this wear next. Further analysis of the wear mechanism and comparison of surfaces require additional profilometric tests.

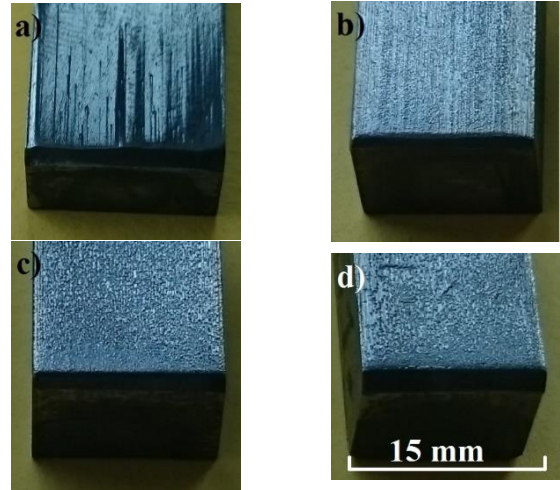


Fig. 11. Surface of samples after abrasion; a) - reference sample made of cast GX70CrMnSiNiMo2 steel after heat treatment, b) - as-cast martensitic steel with the addition of 5 wt. % Ti, c) - cast martensitic steel with the addition of 5 wt. % Ti after hardening in air, d) - cast martensitic steel with the addition of 5 wt. % Ti after hardening in a 15% polymer solution

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4. Conclusions

The addition of a strong carbide-forming element like titanium promotes the formation of primary carbides in the alloy matrix and increases the abrasion resistance of the alloy. The following conclusions can be drawn from the collected data:

1. The tested alloys are characterized by very high hardenability.
2. The as-cast microstructure of the tested alloys consists of a martensitic matrix with small amounts of residual austenite.
3. Primary faceted titanium carbides are evenly distributed in the matrix, but they show a slight tendency to form clusters.
4. There are areas that contain complex lamellar carbides rich in molybdenum which are not dissolved during heat treatment.
5. After hardening, a martensitic structure with a small amount of residual austenite was obtained.
6. The highest hardness of approximately 800HV was obtained for samples hardened in a 15% aqueous polymer solution.

7. The formation of primary Ti carbides in the matrix increases the abrasive wear resistance at least three times.
8. Titanium carbides distributed in the matrix change the nature of the wear in the tested samples and make it more uniform.

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