

Effect of Nanoadditives on the Wear Behavior of Spheroidal Graphite Cast Irons

J. Kaleicheva^a, V. Mishev^a, Z. Karaguiozova^b, G. Nikolcheva^a, A. Miteva^b

^aTechnical University of Sofia, 1000 Sofia, blvd. Kl. Ohridski 8, Bulgaria,

^bBulgarian Academy of Sciences, Space Research and Technology Institute, 1113 Sofia, Acad. Georgy Bonchev Str., bl.1, Bulgaria.

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ABSTRACT

The tribological characteristics of spheroidal graphite cast irons with and without nanosized additives are investigated. The tests are performed as in cast iron condition as well after austempering. The spheroidal graphite irons are undergone to austempering in the bainite field, including heating at 900 °C for an hour, after that isothermal retention at 280 °C, 2 h and at 380 °C, 2 h. The lower bainitic and upper bainitic structures are formed during the process. Nanosized additives of titanium carbonitride and titanium nitride TiCN+TiN influence on the graphite phase characteristics and on the microstructure of the cast and austempered spheroidal graphite irons. The changes in the micro structure the irons with nanoadditives lead to an abrasive wear resistance increase. The formation of the strain induced martensite from the retained austenite in the friction contact area during wear is determined in the austempered irons. This is the reason for the wear resistance increase of the irons. The experimental testing of the wear is carried out by cinematic scheme tapper-disc under friction on the fixed abrasive. The microstructure of the patterns is observed by optical and quantitative metallography, X-Ray analysis, SEM and EDX analysis. The hardness testing is performed by Brinell and Vickers methods.

Corresponding author:

Julieta Kaleicheva
Technical University of Sofia, 1000
Sofia, blvd. Kl. Ohridski 8, Bulgaria.
E-mail: jkaleich@tu-sofia.bg

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1. INTRODUCTION

The austempering of iron – carbon alloys in the bainitic area forms a structure with improved physical and mechanical properties. Austempering is a reason of formation of upper or lower bainitic structure characterized with a high strength and increased toughness. Austempering has a wide practical application in processing of the structural steel and spheroidal graphite cast irons [1,2]. Austempered ductile irons (ADI) are

characterized with a high strength, toughness and wear resistance.

Graphite in the iron ensures resistance to a mechanical wear and improves its processing. Alloying or by heat treatment or using both of this processes the graphite morphology and substrate structure could be changed with an aim to obtain irons with optimal properties.

The investigation of new composition metallic alloys in cast condition or after heat treatment is

an opportunity to extent the application area of these materials. The heat treatment change the micro structure and has a significant impact on the mechanical and tribological properties of the alloys [3,4].

Perspective to achieve this aim is the use of nanosized additives. The role of added nanoparticles in the melt is in the changing of the graphite morphology for lamellar to vermicularis one [5], in the quantity graphite increase [6] and in the changing the substrate structure, which reflect in the increase irons' wear resistance [5-9].

The aim of the present work is to investigate the microstructure and tribological properties of austempered ductile irons (ADI) with nanosized additives of titanium carbonitride and titanium nitride TiCN+TiN.

2. MATERIALS AND INVESTIGATION METHODS

The composition of the spheroidal graphite cast iron samples is: Fe-3,55C-2,67Si-0,31Mn-0,009S-0,027P-0,04Cu-0,025Cr-0,08Ni-0,06Mg wt.%. The samples with and without nano-additives of titanium carbonitride and titanium nitride TiCN+TiN (Table 1) are studied. The TiCN and TiN nanosized particles are coated by electroless nickel coating EFTTOM-NICKEL [10] prior to the edition to the melt. The nickel coating improves the particles wetting into the melt and their uniformity distribution into the casting volume.

The microstructure of the cast iron samples before austempering is tested by quantity metallography, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Scanning microscopy EVO® MA10 „Carl Zeiss” Energy Dispersive X-ray Microanalyser - "Bruker" is used. The quantity metallographic analysis is performed by „Olympus MicroImage” Software and the data for an average diameter D_{mid} of the graphite grains,

their roundness as well the volume parts of graphite, pearlite and ferrite are received.

The spheroidal graphite cast iron samples are undergone an austempering, including heating at 900 °C for an hour, after that isothermal retention at 280 °C, 2h and at 380 °C, 2h. The austempered ductile iron samples' microstructure is observed by means of an optical metallographic microscope GX41 OLIMPUS. The samples surface is treated with 2 vol.% nital solution. The austempered ductile iron samples are tested by X-Ray diffraction analysis the retained austenite quantity in the structure to be defined. The retained austenite quantity is determined before and after abrasion wear. For a phase identification X-ray powder diffraction patterns are recorded in the angle interval $20 \div 103^\circ(2\theta)$, on a Philips PW 1050 diffracto-meter, equipped with Cu $K\alpha$ tube and scintillation detector. The data for cell refinements and quantitative analysis are collected in $\theta \div 2\theta$, step-scan mode in the angle interval from 20 to $103^\circ(2\theta)$, at steps of $0.03^\circ(2\theta)$ and counting time of 3 s/step. A quantitative analysis is carried out by BRASS - Bremen Rietveld Analysis and Structure Suite [11].

The hardness test is carried out by Brinell method (for cast samples) and by Vickers method (for austempered samples).

The experimental study of the wear is carried out using method and device for accelerated testing in kinematic scheme "thumb-disc" under friction over a fixed abrasive [6,8]. The impregnated material Smirdex 330 Duraflex P80 117SV is used for the spheroidal graphite cast iron samples. The test data are: nominal contact pressure $P_a=0,21 \cdot 10^6$ [Pa]; average sliding speed, $V=26,38$ [cm/s]; nominal contact surface, $A_a=50,24$ [mm²]; density, $\rho=7,80 \cdot 10^3$ [kg/m³] [6]. The impregnated material Corundum 220 is used for the austempered ductile iron samples. The test data are: nominal contact pressure, $P_a=0,4 \cdot 10^6$ [Pa]; average sliding speed, $V=24,5$ [cm/s]; nominal contact surface, $A_a=50,24$ [mm²]; density, $\rho=7,80 \cdot 10^3$ [kg/m³] [8].

Table 1. Nanoadditives, graphite characteristics, graphite, pearlite and ferrite quantity, hardness and tribological properties of spheroidal graphite cast irons.

№ of sample	Nanosized additive	D_{mid} μ m	Roundness	Volume part of: [%]			Hardness <i>HB</i>	Intensity of wear <i>i</i>	Wear resistance <i>I</i>
				Graphite	Pearlite	Ferrite			
1	-	11,00	1,59	8,44	32,12	59,44	185	$0,124 \cdot 10^{-6}$	$8,06 \cdot 10^6$
2	TiCN+TiN	10,52	1,28	16,36	25,36	58,28	180	$0,08 \cdot 10^{-6}$	$12,5 \cdot 10^6$

3. RESULTS AND ANALYSIS

The tested spheroidal graphite cast iron substrate consists of ferrite and pearlite [6]. The quantity metallographic analysis is performed the influence of the nanosized additives on the graphite quantity, size and morphology as well as on the quantity ratio between ferrite and pearlite to be determined (Table 1). The analyses are carried out on three randomly chosen field of the ground joint and the average data are presented. Nanosized additives of TiCN+TiN in the spheroidal graphite cast irons don't change the graphite shape, but they decrease the average diameter of the graphite spheres D_{mid} from 11,00 to 10,50 μm (Fig. 1a).

Nanosized additives increase the graphite phase quantity to 94 % compared to this one of the irons without nanoparticles (Fig. 1b).

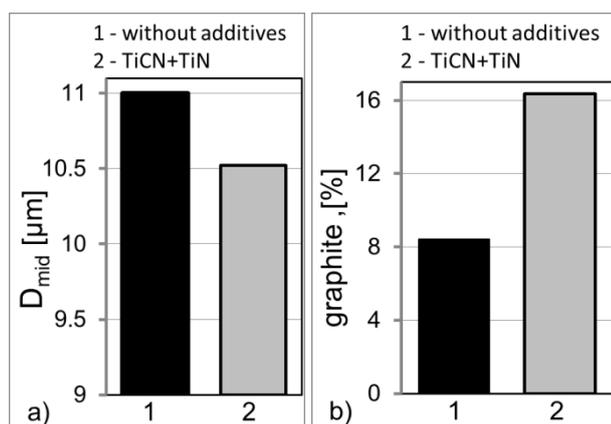


Fig. 1. Average diameter of the graphite spheres D_{mid} (a) and graphite quantity (b) in spheroidal graphite cast irons: samples number - 1 and 2.

They change the quantity of the pearlite and ferrite in the structure of the cast iron samples (Table 1). The hardness of the tested irons is 185 HB for the sample 1 and 180 HB for the sample 2 (Table 1).

SEM analysis of the fracture of the impact destructed spheroidal graphite cast iron sample with TiCN+TiN nanoparticles additives (Fig. 2) and EDX analysis of the graphite phase (Fig. 3) are performed and the nanoparticles presence in the graphite is observed. These results and that achieved from the quantity metallographic analysis prove the modifying influence of the nanoparticles on the size and shape of the graphite phase in the iron samples.

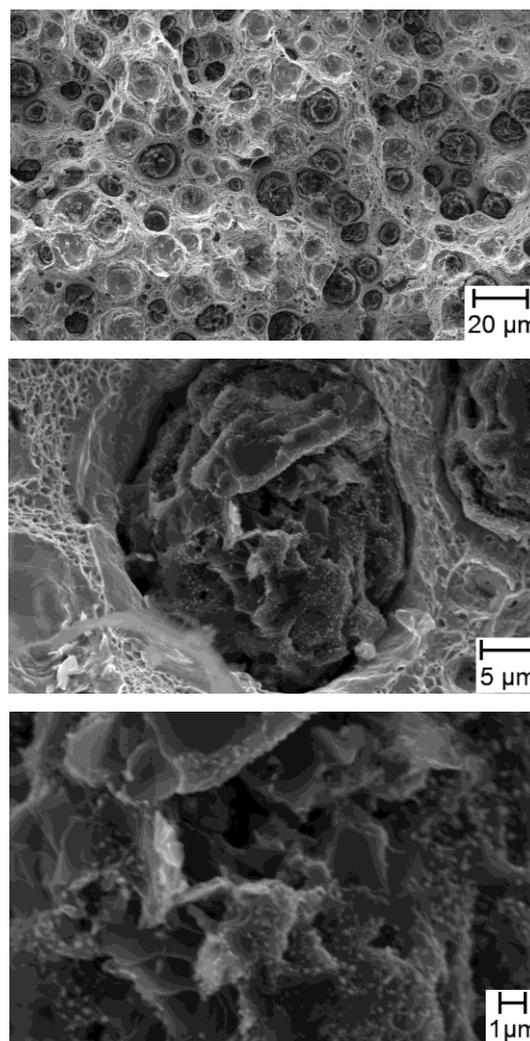


Fig. 2. SEM analysis of the fracture of the impact destructive sample from spheroidal graphite cast irons with nanoadditives of TiCN+TiN (sample 2).

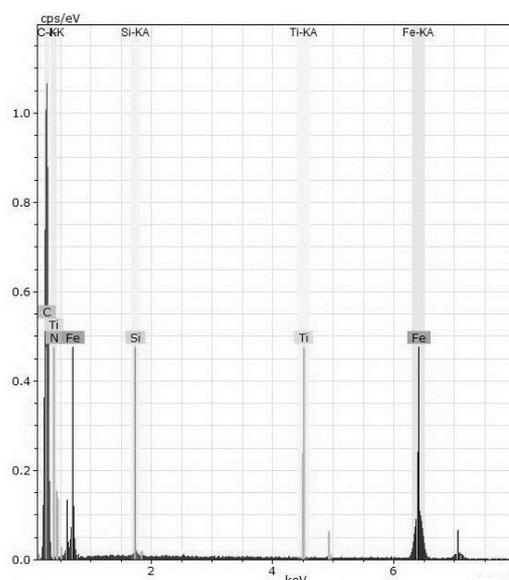


Fig. 3. EDX analysis of the graphite phase in spheroidal graphite cast irons with nanoadditives of TiCN+TiN (sample 2).

In assessing the wear resistance of the iron base structure is necessary to take into account its ability to be changed as a result of a complex set of processes in operation. In the materials with a stable structure obtained after casting, improvement or normalization changes in the microgeometry, appearance of a sizable retained tension and strengthening of the surface layers by a formation of strips of sliding is observed.

Graphite in the gray cast iron structure has an essential role in their behavior in wear. In the dry friction in individual sections of the contact surface is not observed practically wear caused by adhesion. This is related to the presence of graphite in the structure, which has a lubricating ability and acts as a lubricant material.

The wear resistance of the cast irons with a pearlite base at specified conditions of wear (contact pressure and sliding speed) is inversely proportional to the average distance between the graphite grains. By reducing the distance between the graphite grains the protective properties of the surface carbon layer improve and the wear resistance of the cast iron increases. The studied spheroidal graphite cast irons with or without nanosized particles have an equilibrium ferrite-pearlite structure of the substrate and inclusions of graphite spheres. The results of the quantitative metallographic analysis, SEM and EDX analysis show that the nano-sized additives possess modifying influence on the graphite and without changing its shape, increase its quantity leading to a reduction of the average distance between the graphite grains. The intensity of wear of the cast iron with nanoadditives of TiCN+TiN decreases and the wear resistance increases by 55 % compared to this one of the cast iron without nanoparticles (Table 1, Fig. 4).

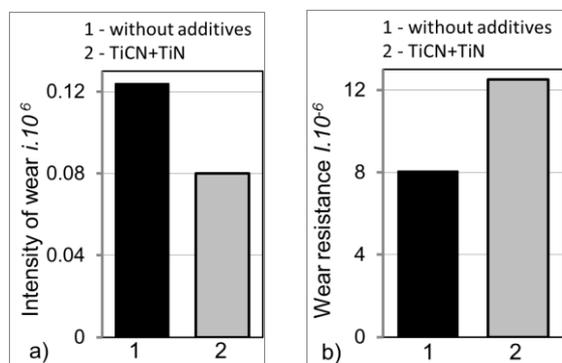


Fig. 4. Intensity of wear i (a) and wear resistance I (b) of spheroidal graphite cast irons: samples number – 1 and 2.

The wear resistance increase observed in the tested samples probably is connected not only with the defined changes in the quantity and size of the graphite phase, but also with the nanoadditives influence on the surface strengthening in friction.

The ductile cast irons are undergone to austempering in the bainitic area. The austempering mode includes austenitization at 900 °C, 1 h followed by isothermal retention at 280 °C, 2 h with formation of a lower bainitic structure (Fig. 5) and isothermal retention at 380 °C, 2 h with formation of an upper bainitic structure (Fig. 6).

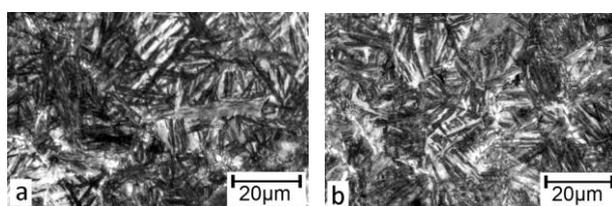


Fig. 5. Lower bainite in austempered ductile irons: a-sample 3; b-sample 4.

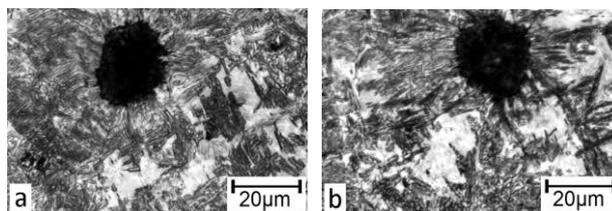


Fig. 6. Upper bainite in austempered ductile irons: a-sample 5; b-sample 6.

Bainite is an oriented structure consisting of needles α - phase (bainitic ferrite), carbides and unconverted austenite. α -phase is formed by martensitic mechanism in austenitic areas with low carbon content [1,2,8]. Upon cooling on the temperature of isotherm to ambient temperature, the part of the unconverted austenite undergoes martensitic transformation, and another part thereof remains in the structure as a retained austenite A.

The austenite bainitic transformation begins with the formation of individual needles α -phase (bainitic ferrite) and is developed with the formation of new oriented needles located close to each other and forming a package of alternating plates α -phase and the unconverted austenite enriched with carbon A (c). Optical metallographic analysis shows this package as an individual needle in the low bainitic structure.

Carbide phase is formed as a result of self-tempering of the α -phase or directly from A(c).

The microstructure and crystallographic characteristics of the lower and upper bainite are similar. The main difference is that the bainitic ferrite (α phase) in a lower bainite is supersaturated with a larger amount of carbon compared to this one of the upper bainite.

This means that the carbide particles in the lower bainite are separated mainly in the inner part of the ferrite plates, as in the upper bainite the carbide phase mainly is separated directly from the enriched with carbon austenite A (c).

Silicon in the spheroidal graphite cast irons (2-3 %) hinders process of the carbide formation. A transformation to a bainitic ferrite and enriched with carbon unconverted austenite A(c) structure with high mechanical characteristics is realized at austempering for 2÷4 hours. An austempering mode over 6 hours could lead to a decomposition of the enriched with carbon austenite to a composite of ferrite and carbide (α +carbide), which decreases the iron mechanical properties and practically not carried out [1,2].

The hardness HV10 of the tested austempered samples with a lower bainitic structure is in the range of 388 HV10 (sample 3) and 422 HV10 (sample 4), whereas this one of the upper bainitic structure is – 314 HV10 (sample 5) and 319 HV10 (sample 6) (Table 2, Fig. 7). The higher lower bainitic hardness is correlated to the higher carbon saturation of the α -phase and to the higher degree of the austenite transformation in the lower temperature range of the bainitic area.

The quantity of the retained austenite in the samples with upper bainitic structure is higher than this one in the samples with the lower bainitic structure after 2 hours austempering at

380 °C and 280 °C (Table 2). This correlates with the characteristics of the bainitic transformation mechanism in the upper and lower temperature range of the bainitic area [1,2]. Nanosized additives of TiCN+TiN in the austempered ductile irons change the bainitic transformation kinetics and accelerate the austenite transformation to bainite. The retained austenite quantity decreases from 30,6 % for the samples without nanoadditives to 24,9 % for the samples with nanoadditives after 2 hours austempering at 280 °C. For 2 hours austempering at 380 °C the retained austenite quantity decreases from 40,4 % to 27,1 % for the samples with the same composition (Table 2).

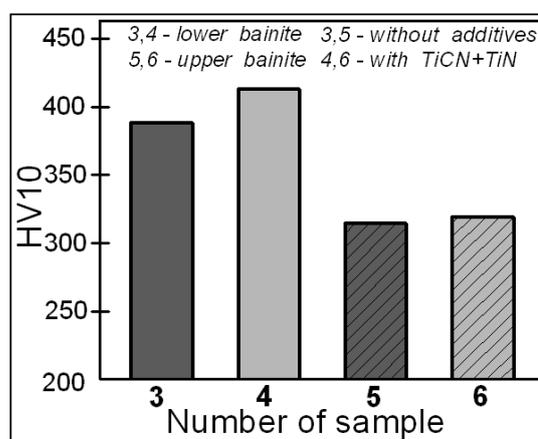


Fig. 7. Hardness HV10 of austempered ductile irons with a lower bainitic structure (samples 3 and 4) and upper bainitic structure (samples 5 and 6).

The results achieved for the intensity of the wear i and for the wear resistance I of the tested samples of austempered ductile iron are shown in the Table 2 and Figs. 8 and 9. The 4 and 6 samples with nanoadditives of TiCN+TiN possess higher wear resistance of 73 % (for a lower bainitic structure) and of 23 % (for a upper bainitic structure) compared to the wear resistance of the samples 3 and 5 without nanoadditives.

Table 2. Tribological properties, hardness and retained austenite quantity of austempered ductile irons.

No of sample	Structure after austempering	Nanosized additive	Hardness HV10	Intensity of wear i	Wear resistance I	Retained austenite A, %	
						before wear test	after wear test
3	lower bainite	-	388	$0,14 \cdot 10^{-6}$	$7,13 \cdot 10^6$	30,6	25,0
4		TiCN+TiN	413	$0,08 \cdot 10^{-6}$	$12,3 \cdot 10^6$	24,9	12,2
5	upper bainite	-	314	$0,13 \cdot 10^{-6}$	$7,67 \cdot 10^6$	40,4	31,3
6		TiCN+TiN	319	$0,10 \cdot 10^{-6}$	$9,42 \cdot 10^6$	27,1	11,6

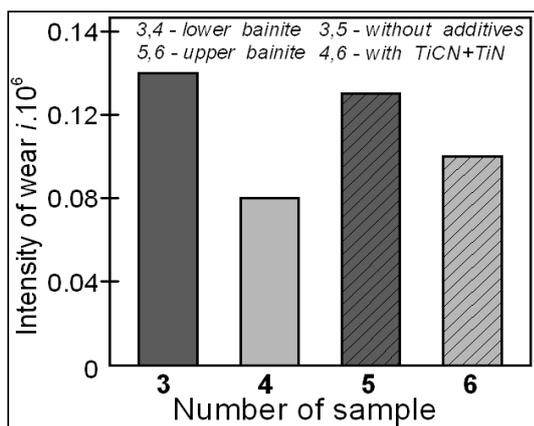


Fig. 8. Intensity of wear i of austempered ductile irons with a lower bainitic structure (samples 3 and 4) and upper bainitic structure (samples 5 and 6).

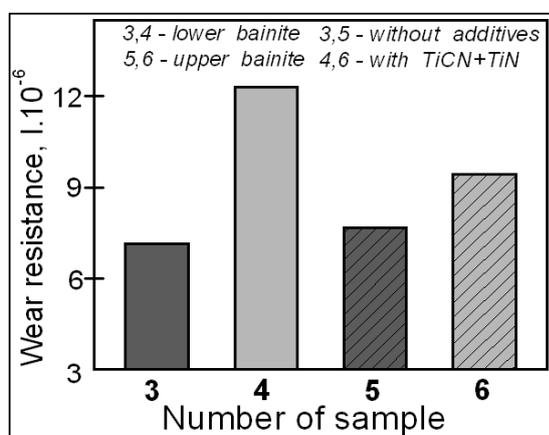


Fig. 9. Wear resistance I of austempered ductile irons with a lower bainitic structure (samples 3 and 4) and upper bainitic structure (samples 5 and 6).

The tribological properties of the metal materials depend in a great extent on the structural condition, formed on the contact surface in friction. In the conditions of intensive plastic deformation of the metal in the area of the friction contact in the metastable structures (retained austenite, martensite, bainite) occur structural transformations that have a strong influence on the effective strength of the surface and, accordingly, on the tribological properties of the materials.

To the structural transformations of the α -martensite, initiated by plastic deformation, strain dynamic ageing or “strain tempering” of the martensite is connected. The processes of a strain dynamic ageing are characterized with a formation of segregates (atmospheres) of carbon atoms on the emerging in friction dislocations. The strong fixing of the dislocations with dopands determines intensive strain

strengthening of high carbon martensite in friction as well an increase in its resistance to various types of wear.

To the metastable structures refers also retained austenite, which undergoes strain induced $\gamma \rightarrow \alpha$ martensite transformation in friction. In friction the retained austenite partially transforms to a strain induced martensite with the same quantity carbon as well a high carbon austenite and It appears untempered martensite with high hardness and capacity for intensive strengthening in a wear processing [8,12].

X-Ray analysis is carried out for defining the possibility of martensite formation as a result of a strain induced $\gamma \rightarrow \alpha$ martensite transformation in the area of the friction contact in the wear test. The quantity of the retained austenite is determined in the tested samples before and after the tribological testing (Table 2). It is found that the quantity of the retained austenite decreases in the all of the tested samples (Fig. 10).

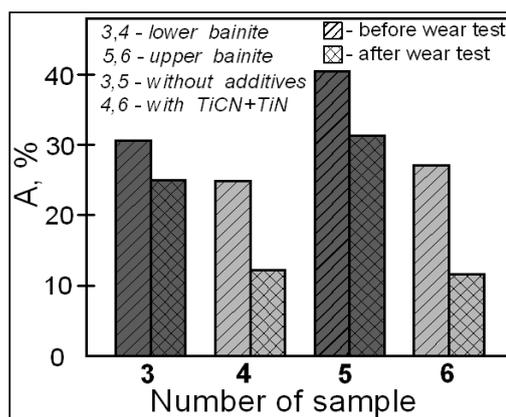


Fig. 10. Quantity of the retained austenite A_i of austempered ductile irons with a lower bainitic structure (samples 3 and 4) and upper bainitic structure (samples 5 and 6) before and after tribological testing.

For the samples without nanoadditives (sample 3) the decrease is from 30,6 % to 25,0 % and from 40,4 % to 31,3 % (sample 5) and for the samples with nanoadditives of TiCN + TiN - from 24,9 % to 12,2 % (sample 4) and from 27,1 % to 11,6 % (sample 6) (Table 2; Figs. 11 and 12).

In the area of the friction contact from the metastable retained austenite the strain induced martensite is formed, which probably additionally increases the wear resistance of the austempered ductile irons. The tests performed show that in the irons with nanoadditives of

TiCN + TiN the transformation of the retained austenite to strain induced martensite takes place in a greater extent in the wear and they have higher wear resistance compared to the irons without nanosized additives.

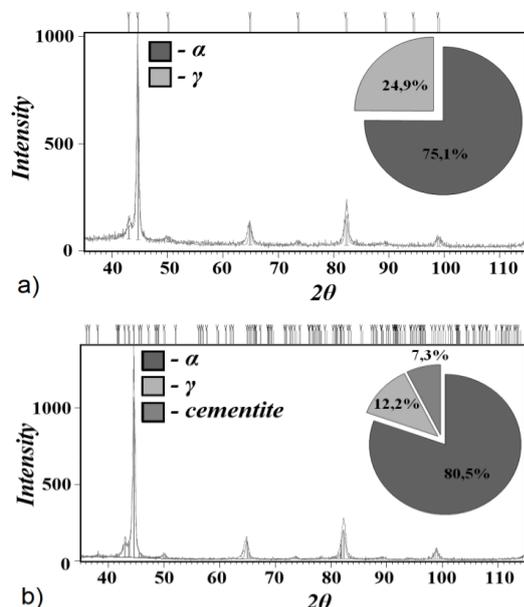


Fig. 11. X-ray diffraction pattern of austempered ductile iron sample 4 before (a) and after (b) wear test.

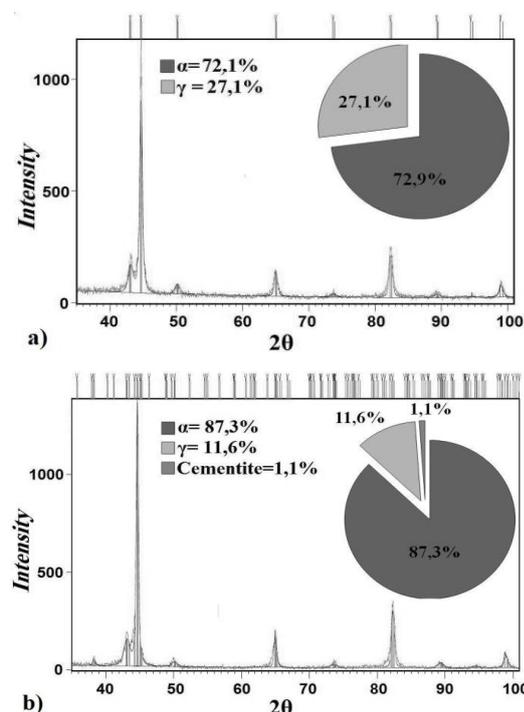


Fig. 12. X-ray diffraction pattern of austempered ductile iron sample 6 before (a) and after (b) wear test.

The observed effect of the nanoadditives on the graphite phase characteristics and on the extent of the transformation of the austenite to bainite, also the greater extent of the metastable retained

austenite transformation to a strain induced martensite in the area of the friction contact in friction explain higher abrasion wear resistance of the tested austempered ductile irons with nanoadditives compared to the same without nanoadditives.

4. CONCLUSION

Nanosized additives of TiCN + TiN in the spheroidal graphite cast irons have a modifying effect on the graphite phase. Without changing the graphite shape, they decrease the graphite spheres size and increase the graphite quantity in the irons' structure. The spheroidal graphite cast irons with nanosized particles have a higher abrasion wear resistance compared to this one of the irons without nanoparticles.

It is specified that retained austenite in the structure of austempered ductile irons is partially transformed to a strain induced martensite in the wear testing as in a greatest extent, this conversion takes place in the cast irons with nano-sized additives of TiCN + TiN. These irons possess higher abrasion wear resistance compared to this one of the irons without nanoadditives. The increase of the wear resistance of the irons with nanoadditives is a result of the complex influence of the nanosized particles on the graphite phase characteristics, on the kinetics of the bainitic transformation under austempering and on the range of the metastable retained austenite conversion to a strain induced martensite in an wear testing.

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