Effect of Nanoadditives on the Characteristics of Bainitic Transformation in Spheroidal Graphite Cast Irons

Die Wirkung der Nanoadditiven auf die Eigenschaften der bainitischen Umwandlung in kugelgraphitischen Gußeisen

Julieta Kaleicheva*, Valentin Mishev*, Zdravka Karaguiozova†

*Faculty of Industrial Technology, Technical University of Sofia,
Sofia, Bulgaria, e-mail: jkaleich@tu-sofia.bg, v_mishev@tu-sofia.bg
†Space Researche and Technology Institute, Bulgarian Academy of Sciences
Sofia, Bulgaria, e-mail: karazuzi@yahoo.com

Abstract — In the present study austempered ductile cast irons (ADI) with upper bainitic structure are investigated. Nanosized particles (50nm) of titanium carbite+titanium nitride (TiCN+TiN), titanium nitride TiN and cubic boron nitride cBN are added to the casting volume. The samples microstructure is studied by means of optical metallography, scanning electron microscopy and X-Ray analysis. The influence of the nanosized additives on the kinetic of the bainitic transformation and on the morphology of the bainitic structure is investigated. The abrasive wear testing, hardness measurements and impact strength are carried out. It is established that the presence of nanoadditives in the bainitic irons leads to the changes in their microstructure which increases their mechanical characteristics and abrasive wear resistance. The studied nanocomposite materials expand the potential for new ADI applications in the industry.

Zusammenfassung —In dem vorliegenden Artikel werden isotherm gehärtete kugelgraphitische Gusseisen (ADI) mit oberbainitischer Struktur untersucht, die Naniaditiven (50nm) – Titancarbonitrid + Titannitrid (TiCN+TiN), Titannitrid TiN und kubisches Bornitrid cBN enthalten. Die Mikrostruktur der Proben wird durch optische Metallographie, Rasterelektronenmikroskopie und Röntgenstrukturanalyse erforscht. Der Einfluß der Nanoadditiven auf die Kinetik der bainitische*n* Umwandlung und auf die Morphologie der bainitischen Struktur der Gußeisen ist studiert. Es wird eine Untersuchung des abrasiven Verschleißes, der Härteprüfung und der Schlagzähigkeit durchgeführt. Es ist festgestellt, dass die Änderungen der Mikrostruktur der bainitischen Gußeisen unter der Wirkung der Nanoadditiven eine Erhöhung der mechanischen Kennzahlen und der abrasiven Verschleißfestigkeit der ADI verursachen. Die erforschten Nanokomposite erweitern die Möglichkeiten für neue industrielle Anwendungen der ADI.

I. Introduction

Bainitic irons are spheroidal graphite ductile cast irons with a bainitic structure of the metal matrix, obtained after austempering in the bainitic area. Austempering of the iron-carbon alloys in the bainitic area is a heat treatment with a wide practical application in the processing of the structural steels and ductile cast iron [1,2]. Austempered spheroidal graphite ductile irons with a bainitic structure combine high strength with increased toughness and plasticity. Alloyed spheroidal graphite irons have a high wear resistance due to a graphite phase and a bainitic metal matrix. Depending on the austempering mode, a lower bainitic structure (220÷280°C) or upper bainitic structure (350÷450°C) of cast irons are obtained.

Austempered spheroidal graphite irons (ADI) find application in the production of responsible details in the transport equipment and other industries.

The possibility for a wider application of these materials in the industry includes investigation of ADI with additions of a small quantity of nanosized particles during the casting process, which could improve their structure and properties.

Nanosized particles added to the casting of cast iron in small quantities can alter the graphite morphology from laminated to vermicular [3], also increase the amount of graphite and reduce the size of the graphite sphere [4], alter the structure of the metal matrix of cast irons and austempered ductile irons (ADI), which increases the mechanical and tribological properties of the cast irons [3-7].

The aim of this study is to investigate the peculiarities of the structure formation in the bainitic area, mechanical and tribological properties of spheroidal graphite cast irons containing additives of nanosized particles - titanium carbonitride + titanium nitride *(TiCN + TiN)*, titanium nitride *TiN* and cubic boron nitride *cBN.*

II. 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-0,040Cu-0,025Cr-0,08Ni-0,06Mg wt.%. The samples without and with nanoadditives of (*TiCN+TiN), TiN* and *cBN* are tested (Table 1). The *TiCN, TiN* and *cBN* nanosized particles are coated by electroless nickel coating EFTTOM-NICKEL prior to the edition to the melt [8]. The nickel coating improves the particles wetting into the melt and their uniformity distribution into the casting volume.

The spheroidal graphite iron samples are undergone to austempering, including heating at 900°C for an hour, after that isothermal retention at 380°C, 0,5 h, 1 h, 2 h, 4 h, 6 h. 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.% solution of HNO3 in ethanol. The microstructure of the cast samples before austempering is tested by scanning electron microscopy (SEM). The scanning microscope EVO MA10 „Carl Zeiss" is used. The hardness testing is performed by Vickers method. The austempered ductile iron samples are tested by X-Ray diffraction analysis the retained austenite quantity in the structure to be defined. X-ray powder diffraction patterns for phase identification are recorded in the angle interval 22÷104° (2θ), on a Philips PW 1050 diffractometer, equipped with Cu Kα tube and scintillation detector. Data for cell refinements and quantitative analysis are collected in θ-2θ, step-scan mode in the angle interval from 22 to 104° (2θ), at steps of 0.03° (2θ) and counting time of 3 s/step. Quantitative analysis is carried out by BRASS - Bremen Rietveld Analysis and Structure Suite [9].

For the samples with an upper bainitic structure, obtained for 2 hours of austempering at 380 °C the impact toughness and abrasive wear tests are performed.

The impact strength test is carried out with Charpy hammer. 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]. The impregnated material Corundum 220 is used for the austempered ductile iron samples. The test data are: nominal contact pressure, $Pa=0,4.10^6$ (Pa); average sliding speed, V=24.5(cm/s); nominal contact surface, Aa=50.24 (mm^2); density, $\rho=7.80.10^3$ (kg/m^3) [7].

III. Experimental results and discussion

The examined cast iron structure consists of ferrite, pearlite and graphite after casting. The nanosized additives change the quantity and size of the graphite phase, as the pearlite and ferrite quantity in the cast iron structure. Nanosized additives in the spheroidal graphite cast iron don't change the graphite shape. They decrease the average diameter of the graphite sphere D_{mid} from 11, 00 to 10, 34 µm. The increase of the quantity of the graphite phase with 35÷94% and the change of the pearlite and ferrite quantity in the cast iron structure are observed in the presence of the nanosized particles [4].

SEM analysis of the fracture of the impact destructed cast iron sample with nanoparticles additives (Fig.1), show the nanoparticles presence in the graphite. These results and that achieved from the quantitative metallographic analysis [4] prove the modified influence of the nanoparticles on the graphite phase in the cast iron samples.

The spheroidal graphite cast irons with and without nanosized additives are subjected to austempering in order to obtain a bainitic structure of the metal base. The austempering regimens include austenitization at 900°C, 1 h and subsequent isothermal retention at 380°C, 0.5 h, 1 h, 2 h, 4 h and 6 h. As a result of this heat treatment, the cast iron is given an upper bainitic structure (Fig. 2).

The binite is an oriented structure consisting of α-phase needles (bainitic ferrite), carbides and unconverted austenite. The α-phase is formed by a martensitic mechanism from the austenitic regions of low carbon content [1, 2]. During cooling from the temperature of the isotherm to room temperature, part of the unconverted austenite undergoes martensitic transformation, and another part remains in the structure as retained austenite A.

The bainitic transformation of the austenite begins with the formation of separate α-phase needles (bainitic ferrite) and develops with the formation of new oriented needles placed close to each other and forming a package of alternating α-phase plates and unconverted carbon enriched austenite $A_{(c)}$ [1,2].

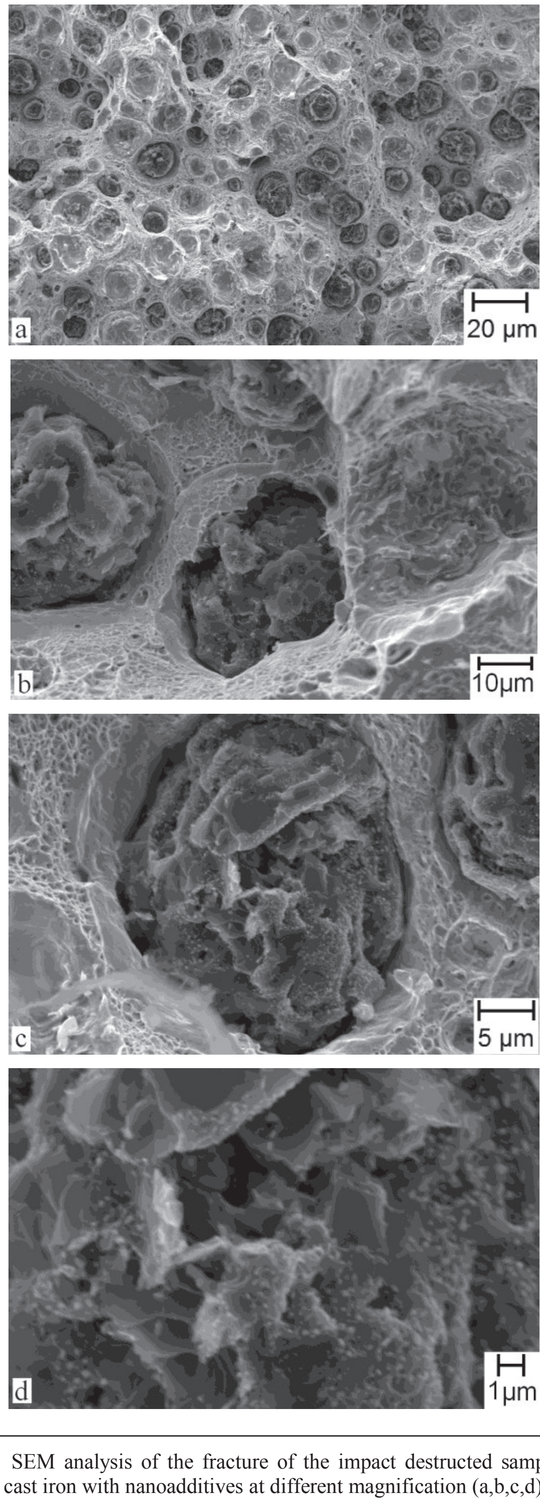

Fig. 1. SEM analysis of the fracture of the impact destructed sample from ductile cast iron with nanoadditives at different magnification (a,b,c,d).

By an optical metallographic analysis, this package appears as a separate needle in the lower bainitic structure. In the upper bainitic structure α-phase and $A_{(c)}$ in the package are perceived as separate phases. The carbide phase is formed as a result of self-release of the α-phase or directly from $A_{(c)}$. Silicon in ductile cast iron (2÷3%) hinders the process of a carbide formation. Isothermal retention up to 2÷4 hours produces a formation of a bainitic ferrite structure and carbon-enriched unconverted austenite $A_{(c)}$. This structure is characterized by high mechanical properties. At austempering modes over 4÷6hours, it is possible to observe carbides separation directly from $A_{(c)}$ or decomposition of the carbon-enriched austenite $A_{(c)}$ to the ferrite-carbide mixture (α+carbide), which reduces the mechanical properties of the cast iron and it is not actually carried out in practice [1,2].

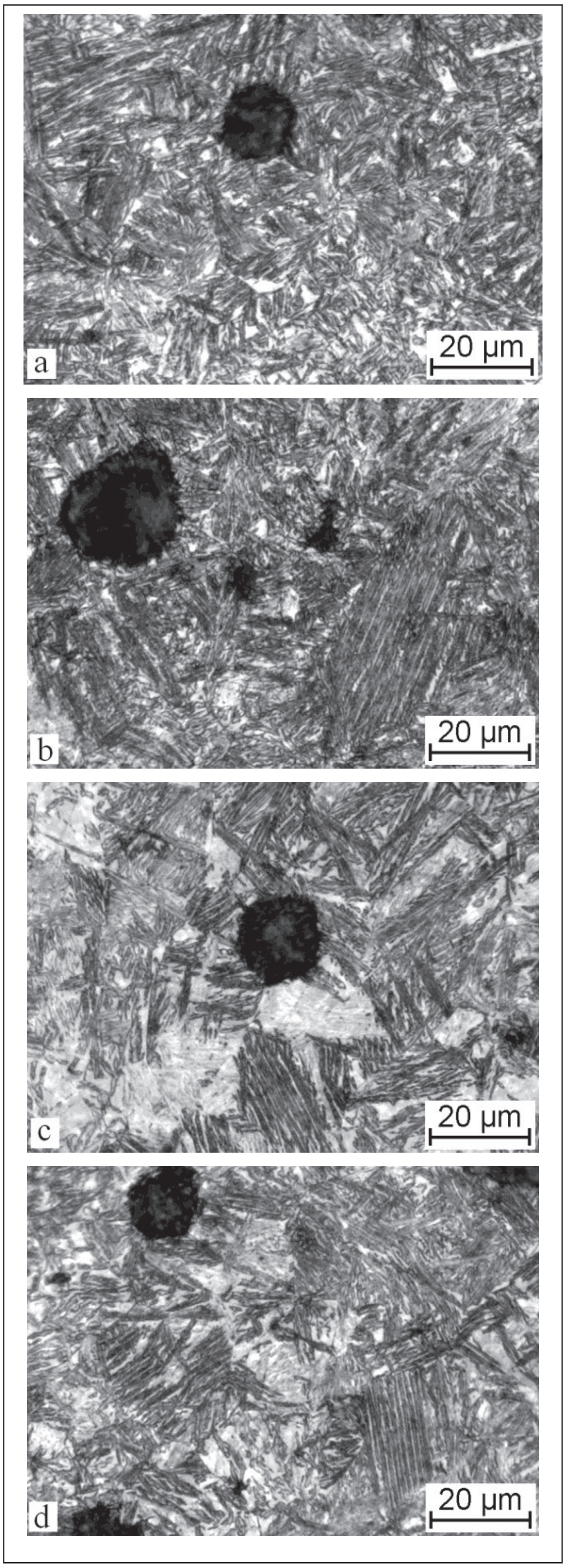

Fig. 2. Upper bainitic structure in ADI samples without nanoadditives (a) and with nanoadditives of (*TiCN+TiN)* (b), *TiN* (c) and *cBN* (b) after isothermal retention for 30 min at 380 ° C.

Nanosized particles accelerate the transformation of austenite to bainite. The amount of the retained austenite in the samples without nanoparticles additives for 2 hours isothermal retention at 380°C is 40.4%. In the samples with nanoaditives, the amount of the retained austenite decreases to 30.2÷27.1% for 2 hours of isothermal retention at 380°C.

With the development of bainitic transformation from 2 to 6 hours the amount of retained austenite in all analyzed samples decreases, which can be explained or with the separation of carbide phase directly from the carbon enriched austenite $A_{(c)}$ or with its decomposition to the ferrite-carbide mixture (α+carbide) (Table 1, Fig. 3). The hardness of the tested ADI is in the range 294÷322 HV10 (Table 1).

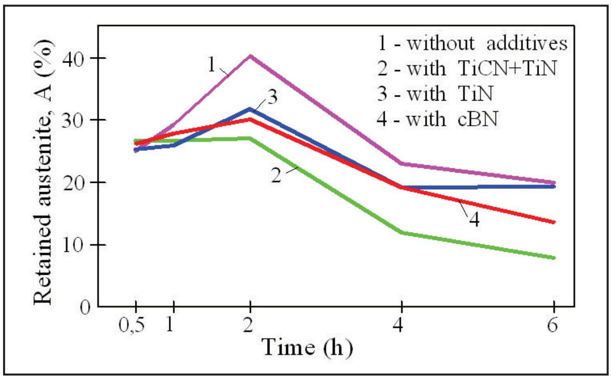

Fig. 3. Dependance of the retained austenite quantity on the time of austempering τ at 380ºC (upper bainitic structure) for spheroidal graphite ductile irons without and with nanoadditives of (*TiCN+TiN*), *TiN* и *cBN*

After final austempering, a complex structure is formed in the tested samples consisting of bainitic ferrite (α-phase), carbides, retained austenite and martensite formed by the unconverted carbon enriched austenite $A_{(c)}$ during cooling from 380°C to an ambient temperature. The properties of the austempered ductile cast irons depend on the type of the phases and the quantitative ratio between them.

The samples after austemepring for 2 hours at 380° C are put to test for impact toughness and abrasive wear (Table 2). The increase of the impact toughness and wear resistance of ADI samples with nanoadditives in comparison to these one without nanoadditives is established (Fig. 4 and 5). The quantity of the retained austenite in the irons samples before and after tribological testing is defined (Table 2).

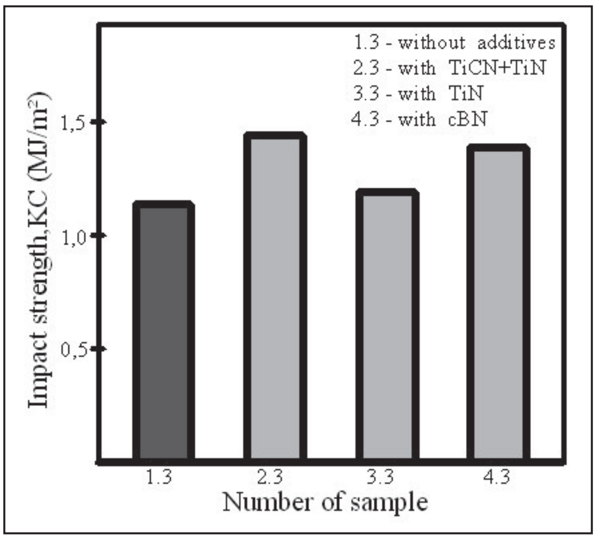

Fig. 4. Impact strength KC of austempered ductile iron samples without nanoadditives (1.3) and with nanoadditives of (*TiCN+TiN)* (2.3), *TiN* (3.3) and *cBN* (4.3) after isothermal retention for 2 h at 380 °C.

TABLE I. RETAINED AUSTENITE QUANTITY *A* AND HARDNESS *HV10* OF AUSTEMPERED DUCTILE IRONS ADI.

№ of sample	Nanosized additives	Time of austempering									
		0,5 h		*1 h*		*2 h*		*4 h*		*6 h*	
		A (%)	*HV10*	*A (%)*	*HV10*	*A (%)*	*HV10*	*A (%)*	*HV10*	*A (%)*	*HV10*
1.1÷1.5	-	25.1	297	29.3	306	40.4	320	23.1	313	20.0	321
2.1÷2.5	*TiCN+TiN*	26.7	314	26.8	304	27.1	322	12.0	309	7.9	318
3.1÷3.5	*TiN*	25.3	294	26.0	292	31.8	312	19.3	317	19.4	311
4.1÷4.5	*cBN*	26.2	298	27.9	305	30.2	308	19.3	314	13.6	301

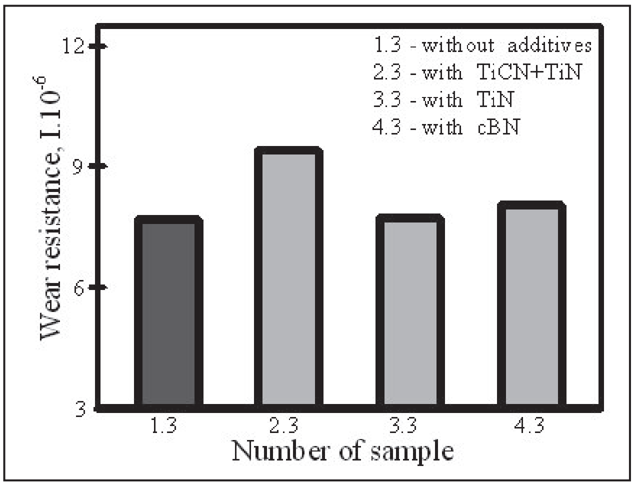

Fig. 5. Wear resistance I of austempered ductile iron samples without nanoadditives (1.3) and with nanoadditives of (*TiCN+TiN)* (2.3), *TiN* (3.3) and *cBN* (4.3) after isothermal retention for 2 h at 380 °C.

TABLE II. NANOADDITIVES, HARDNESS HV10, IMPACT STRENGHT KC, WEAR RESISTANCE I AND RETAINED AUSTENITE QUANTITY A OF AUSTEMPERED DUCTILE IRONS ADI.

№ of sample	Austem-pering mode	Impact strength *KC* (MJ/m^2)	Wear resistance *I*	Retained austenite *A* (%)	
				before wear test	*after wear test*
1.3	900°C, 1 h + 380°C, 2 h	1.137	$7.67.10^6$	40.4	31.3
2.3		1.442	$9.42.10^6$	27.1	11.6
3.3		1.190	$7.72.10^6$	31.8	31.2
4.3		1.387	$8.03.10^6$	30.2	25.3

The austempered ductile iron samples hardness with upper bainitic structure varies from 308 to 322 HV10 (Table1).

The standard measured properties (hardness, etc.) not always are reliable criteria for the steel and cast iron wear resistance. The tribological properties of the metallic materials significantly depend on the structural condition, forming on the contact surface during the friction. When the material is exposed to an intensive plastic deformation the structural transformation goes off in the frictional contact area in the metastable structures (retained austenite, martensite, bainite). They greatly influence on the effective surface strength and respectively on the material tribological properties. During friction the retained austenite transforms partly into strain-induced martensite with the same amount of carbon as in high carbon austenite. This strain-induced martensite is untempered martensite characterized by high hardness and ability for intensive strengthening by wear [7]. The quantity of the retained austenite decreases in all of the tested ADI samples after tribological test. The highest decrease in the quantity of the retained austenite is observed in the sample with nanoparticles of *(TiCN+TiN)* - from 27.1% to 11.6% (Table 2). This sample has highest wear resistance ($I = 9.42.10^6$). The formation of strain-induced martensite from the metastable retained austenite in the frictional area (microtrip-effect) probably is one of the reasons for the wear resistance increase of these materials.

IV. CONCLUSIONS

Nanosized particles in the spheroidal graphite cast irons have a modifying effect on the graphite phase. In the case of austempering of spheroidal graphite cast iron, nanosized additives influence on the structure formation in the temperature range of the bainitic area. They alter the kinetics of the bainitic transformation and accelerate the transformation of austenite into bainite.

Austempered ductile irons (ADI) with nanosized additives possess higher wear resistance (to 23%) and higher impact strength (to 27%) in comparison to the samples without nanoadditives. The observed effect of the nanoadditives on the graphite phase characteristics and on the extent of the transformation of the austenite to bainite explain higher abrasion wear resistance of the tested austempered ductile irons with nanoadditives compared to the same without nanoadditives. Partially transformation of the metastable retained austenite to strain-induced martensite during friction, which is observed in the austempered ductile irons, affects their wear resistance.

REFERENCES

[1] E. Dorasil, *High-strenght Bainitic Nodular Cast Iron*. Academia, Prague,1985.

[2] H.K.D.H. Bhadeshia, *Bainite in Steels*, 2st ed., Inst. of Materials, Cambridge, London, 2001.

[3] Y.Wang, Z. Pan, Z. Wang, X. Sun, and L. Wang, "Sliding wear behavior of Cr–Mo–Cu alloy cast irons with and without nanoadditives", in *Wear*, vol. 271, 2011, pp. 2953– 2962.

[4] J. Kaleicheva, V. Mishev, R. Lasarova, and Z. Karaguiozova, "Study of Spheroidal Graphite Cast Irons with Nanosized Additives", in *Nanoscience & Nanotechnology'15*, eds. E. Balabanova, E. Mileva, Sofia, vol. 15 (1), 2015, pp. 40-43.

[5] J. Li, M. Chen, H. Gao, and Y. Zhao, "Structures and Properties of Cast Irons Reinforced by Trace Addition of Modified SiC Nanopowders", in *Chinese Journal of Chemical Physics*, vol.20 (6), 2007, pp. 625- 631.

[6] J. Kaleicheva, M. Kandeva, V. Mishev, and Z. Karaguiozova, "Wear Behavior of Ductile Cast Irons with Nanoparticle Additives", in *J. Chem. Chem. Eng.*,vol.7 (11), 2013, pp. 1044–1049.

[7] J. Kaleicheva, V. Mishev, G. Avdeev, Z. Karaguiozova, and B. Dineva, (2014). "Influence of Nanoadditives on the Structure and Properties of Austempered Ductile Irons", in *Conference Proceedings: European Conference on Heat Treatment and 21st IFHTSE Congress,* Munich, May 2014, pp. 537-543.

[8] G. Gavrilov, and C. Nicolov, *Electroless Nickel and Composite Coatings.* Tehnika, Sofia, 1985.

[9] J. Birkenstock, R. X. Fischer, and T. Messner, BRASS 2003: The Bremen Rietveld Analysis and Structure Suite. Ber. DMG, Beih. z. Eur. J. Mineral. 15(1), 21, 2003.