Effect of nanosized particles on the bainitic transformation in austempered ductile irons

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Abstract: The austempered ductile iron was austenitized at 900 °C for 1 h and quenched in an isothermal quenching furnace at 380 °C, 0.5 h, 1 h, 2 h, 4 h, 6 h. This paper aims to investigate the effects of nanosized particles (50nm) of titanium carbide+titanium nitride (TiCN+TiN), titanium nitride (TiN) and cubic boron nitride (cBN) on the bainitic transformation in austempered ductile irons (ADI). The samples upper bainitic microstructure is studied by metallographic microscope (OM), X-ray diffractometer (XRD) and scanning electron microscope (SEM). 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 and hardness measurements are carried out. It is established that the presence of nanoadditives in the bainitic cast irons leads to the changes in their microstructure which increases their abrasive wear resistance. The studied nanocomposite materials expand the potential for new ADI applications in the industry.

1. Introduction

Bainitic cast iron is a structural material characterized by high strength, toughness and wear resistance. It is obtained by heat treatment involving isothermal quenching in the bainitic area [1]. Depending on the isothermal quenching mode, cast iron with a structure of lower bainite (220–280°C) or upper bainite (350–450°C), which have high strength and increased toughness, are produced. Graphite present in the cast iron provides resistance to mechanical wear and improves workability. Changes in the composition of the cast iron, changes in the heat treatment regime, or a combination of these two processes can influence the morphology of the graphite and the structure of the metal base in order to obtain castings with optimal properties [2].

Isothermal quenching in the bainitic area is widely used in the heat treatment of structural steels and ductile cast iron [1,3]. Incomplete isothermal quenching is also applied to the heat treatment of some hypereutectoid and ledeburite steels. The possibility of wider practical application of this type of heat treatment requires additional data on the bainitic conversion of iron-carbon alloys of different composition, including alloys with nanosized particles.

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

The aim of this study is to investigate the kinetics of the bainitic transformation, the bainitic structure morphology in the upper temperature range of the bainitic area, the hardness and the wear resistance of the austempered ductile cast irons (ADI) containing additives of nanosized particles - titanium carbonitride + titanium nitride (TiCN + TiN), titanium nitride (TiN) and cubic boron nitride (cBN).

2. Materials and investigation methods

The samples tested are made of unalloyed ductile cast iron with the following composition: Fe-3.55C-2.67Si-0.31Mn-0.009S-0.027P-0.025Cr-0.08Ni-0.06Mg wt.%. During the casting in the cast iron melt nanosized particles of TiCN+TiN, TiN and cBN (table 1) are added. The nanosized particles are coated by electroless nickel coating EFTTOM-NICKEL prior to the edition to the melt [9]. The nickel coating improves the particles wetting into the melt and their uniformity distribution into the casting volume.

| № 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 |
| 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 |

Bainitic cast iron are obtained by isothermal quenching in the upper temperature range of the bainitic area, 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 austempered ductile irons (ADI) 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 2θ = 22°-104° (20), on a Philips PW 1050 diffractometer, equipped with Cu–Kα tube and scintillation detector. Quantitative analysis is carried out by BRASS - Bremen Rietveld Analysis and Structure Suite [10].

For the samples with an upper bainitic structure obtained for 2 hours isothermal retention at 380°C (samples 1.3; 2.3; 3.3; 4.3;) an abrasion test is performed.

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 cast iron samples. The test data are: nominal contact pressure, \( P_a=0.4.10^6 \) (Pa); average sliding speed, \( V=24.5 \) (cm/s); nominal contact surface, \( A_a=50.24 \) (mm²); density, \( \rho=7.80.10^3 \) (kg/m³).

3. Experimental results and discussion

In the cast condition, the unalloyed ductile cast iron has a structure consists of ferrite, perlite and graphite. The quantitative metallographic analysis carried out show that nano-sized particles influence the amount and size of the graphite phase without altering the shape of the graphite.
They decrease the average diameter of the graphite sphere \( D_{mid} \) from 11.00 to 10.34 \( \mu m \) and increase the quantity of the graphite phase with 35\%-94\% [5].

SEM analysis of the fracture of the impact destructed cast iron sample with nanoparticles additives, show the nanoparticles presence in the graphite [6]. The results from SEM analysis and quantitative metallographic analysis prove the modifying effect of the nanosized particles on the graphite phase in the cast iron [5, 6].

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 austempered ductile iron is austenitized at 900\(^\circ\)C for 1 h and quenched in an isothermal quenching furnace at 380\(^\circ\)C, 0.5 h, 1 h, 2 h, 4 h and 6 h. As a result of this heat treatment, the cast iron obtains an upper bainitic structure ‘figure 1’.

![Figure 1. 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 4 hs at 380\(^\circ\)C.](image)

The bainite is an oriented structure consisting of \( \alpha \)-phase needles (bainitic ferrite), carbides and non-converted austenite. The \( \alpha \)-phase is formed by a martensitic mechanism from the austenitic regions of low carbon content [1,3]. During cooling from the temperature of the isotherm to a room temperature, part of the non-converted 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 \( \alpha \)-phase needles (bainitic ferrite) and develops with the formation of new oriented needles placed close to each other and forming a package of alternating \( \alpha \)-phase plates and non-converted austenite enriched with carbon \( A \) (c) [1,3].

In an optical metallographic analysis, this package appears as a separate needle in the lower bainitic structure. In the upper bainitic structure \( \alpha \)-phase and \( A(c) \) in the package are perceived as separate phases. The carbide phase is formed as a result of self-tempering of the \( \alpha \)-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 non-converted austenite A(c). This structure is characterized by high mechanical properties. At austempering modes over 4 ÷ 6 hours, 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 [1,3].

Nanosized particles accelerate the transformation of the 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 nanoadditives, the amount of the retained austenite decreases to 30.2÷27.1% for 2 hours of isothermal retention at 380°C ‘figure 2’.

With the development of the bainitic conversion from 2 to 6 hours, the amount of the retained austenite in all samples tested decrease, (table 1, figure 2). The hardness of the tested ADI samples is in the range from 294 to 322 HV10 (table 1).

\[ \text{Figure 2. Dependence of the retained austenite quantity } A \text{ on the time of austempering } h \text{ at 380°C for austempered ductile irons (ADI) without and with nanoadditives of (TiCN+TiN), TiN and cBN.} \]

After completion of the isothermal quenching and final cooling to ~20°C, a complex structure is formed consisting of bainitic ferrite (α-phase), carbides, retained austenite and martensite formed by the unreacted carbon-enriched austenite A (c), with cooling from 380°C to room temperature (~20°C). The properties of austempered ductile irons (ADI) depend on the type of phases and their quantity in the structure of ADI.

‘Figure 3’ shows a microstructure observation by SEM analysis of the fracture of the impact destructed sample 2.3 with nanoparticles (TiCN + TiN) and with upper bainitic structure obtained by isothermal quenching at 900°C, 1h + 380°C, 2h.

For the samples after an isothermal retention for 2 hours at 380 °C, an abrasion resistance test is conducted (table 2). An increase in the wear resistance for ADI specimens with nanoadditives is found compared to those without nanoadditives ‘figure 4’. The amount of the retained austenite in the cast iron samples is determined before and after the tribological test ‘figure 4’.

The austempered ductile iron samples hardness with an upper bainitic structure varies from 308 to 322 HV10 for 2 hours of isothermal retention at 380°C (table 2).

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 characterised with a high hardness and ability for intensive strengthening by wear [7,11].

**Figure 3.** SEM analysis of the fracture of the impact destructed sample 2.3 from ADI with nanoadditives of (TiCN+TiN) at different magnification (a,b,c,d).

**Table 2.** Hardness HV10, wear resistance I and retained austenite quantity A of austempered ductile irons (ADI).

| № of sample | Austempering mode | Hardness HV10 | Wear resistance I | Retained austenite A (%) before wear test | Retained austenite A (%) after wear test |
|-------------|-------------------|---------------|-------------------|------------------------------------------|----------------------------------------|
| 1.3         | 900°C, 1 h        | 320           | 7.67.10⁶          | 40.4                                     | 31.3                                   |
| 2.3         | +                 | 322           | 9.42.10⁶          | 27.1                                     | 11.6                                   |
| 3.3         | 380°C, 2 h        | 312           | 7.72.10⁶          | 31.8                                     | 31.2                                   |
| 4.3         |                   | 308           | 8.03.10⁶          | 30.2                                     | 25.3                                   |

The amount of the retained austenite decreases in all ADI samples tested after the tribological test. Mostly, the amount of the retained austenite decreases in the sample with (TiCN + TiN) nanoparticles - from 27.1% to 11.6% (table 2, figure 4). This specimen also has the highest abrasion resistance \( I=9.42.10^6 \).

The formation of strain-induced martensite from the metastable retained austenite in the frictional area (microrip-effect), probably is one of the reasons for the wear resistance increase of these materials.
Figure 4. Wear resistance $I$ and retained austenite $A$ 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.

4. Conclusions

Nanosized additives in the spheroidal graphite cast irons 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 the undercooled austenite into bainite.

Austempered ductile irons (ADI) with nanosized additives possess higher wear resistance (until 23%) in comparison to the samples without nanoadditives. The influence of the nanoadditives on the graphite phase characteristics and on the extent of the transformation of the austenite to bainite explains 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 also affects their wear resistance.

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