Transmission electron microscope studies of the chromium cast iron modified at use of B₄C addition

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Abstract

Results of studies of the high alloy chromium cast iron with boron addition in form of the B₄C phase powder are presented in this paper. The main field of interest is the identification of phases based on the transmission electron microscope study, occurred in this alloy after solidification process. The structure mainly consists of the austenite matrix and M_7C_3 carbide identified as the Cr_7C_3 phase.

Keywords: Chromium cast iron, Crystallization, Modification, TEM

1. Introduction

Recently, boron carbide, B₄C (=B₁₂C₃) has attracted considerably attention as the alloy or modifying addition in cast iron which ifluences on useful properties, such as high hardness and strength.

Although there has been considerable long-term controversies about whether or not boron atoms dissolve in iron lattices in substitutional or interstitial sites, the boron solubility in ferrous alloys has been consistently accepted to be only 0.0005÷0.008 at.%. The minute solubility of boron in iron, compared with the relatively larger carbon solubility of 0.0218 wt.% in ferrite and 2.11 wt.% in austenite, was considered to be associated with the characteristic of the boron atom itself. It is known that the boron atomic diameter is 1.8 Å, too small to occupy a substitutional position in iron (d_{Fe} = 2.52 Å) and too large to put into the octahedral interstitial site in ferrite (d_{oct} = 0.38 Å) or the

octahedral interstitial site in austenite (d_{oct}= 1.085 Å). In contrast, in the case of carbon, the smaller size of the carbon atom (d_c=1.54 Å) allows carbon atoms to largely dissolve the interstitial site of iron lattices, which is consistent with reasonable interstitial solubility of austenite (~ 2 wt.%) and limited interstitial solubility (~ 0.02 wt.%) in ferrite. Hence, an increase of the interstitial site in iron lattices should lead to greater boron solubility in iron. Unfortunately, little is known about how to expand the interstitial size of iron lattices, except for increasing the temperature. However, the large increase of boron solubility to 120 ppm in a 20% Cr, 25% Ni, 0.6% Mn, 0.6% Nb and 0.6% Si (weight percent) austenitic steel suggested that some metallic elements may also have this effect. Knowledge of actual boron solubility in boron containing ferrous alloys is essential, because it is the basis for understanding the microstructures and mechanical properties of these alloys. The boron solubility in Fe–Cr–B alloys, containing approximately 1,35 wt.% of boron, 12 wt.% of chromium, as well as other alloying elements, such as Cr, Ni, Mo

and V, has been investigated and the results indicated that the solubility was much higher than the normal accepted figure [1].

The atomic structure responsible for these properties is rather unique: an arrangement of distorted $B_{11}C$ icosahedra located at the nodes of a rhombohedral Bravais lattice ($R\bar{3}m$ space group) [5].

The crystal structure of boron carbide has been known to the rhombohedral unit cell ($B_{12}C_3$) which is composed of the icosahedral subunit (B_{12}) and the three-atom chain of carbon atoms (C_3), as shown in Fig. 1. Boron atoms occupy two nonequivalent sites of $6H_1$ (bonded to carbon atom; closed small circle) and $6h_2$ (bonded to boron atom at the centre at the chain; closed large circle) [2].
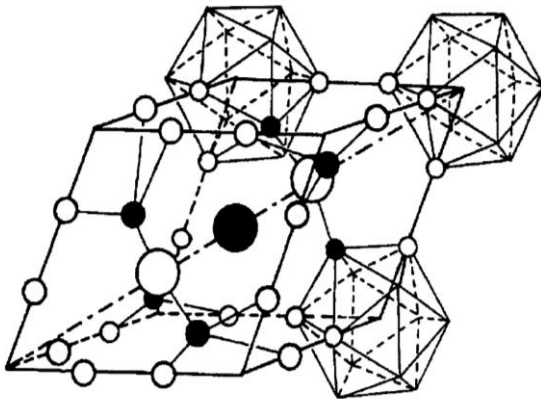
Fig. 1. Crystal structure of boron carbide. •: Boron 6H1, ○: Boron 6h2, ●: Carbon-1b, ○:Carbon-2c [2]

Boron carbide is an extremely hard ceramic material with a hardness value of 9.3 on the Mohs scale. Its other properties include a low density 2.52 g/cm^3, outstanding elastic modulus 540 GPa (slightly dependent on crystalline direction), chemical and temperature stability, and good neutron-absorption cross section. The high hardness and low density of boron carbide have resulted in the development of lightweight armour ceramic composites. Boron carbide also finds application in the aerospace industry as a rocket propellant. Bulk boron carbide has a low fracture toughness which makes it unsuitable for various applications where mechanical strength is important. To overcome this problem, there has been some work done in recent years to synthesize boron carbide nanostructures. Conventional techniques such as reduction of boron trioxide for the production of boron carbide are complex and expensive because of its high melting point. Hence, most research has been focused on chemical vapour deposition (CVD) to synthesize boron carbide at low processing temperatures. Boron carbides with a rhombohedral crystal structure are most stable. Common stoichiometries include $B_{13}C_2$, $B_{12}C_3$, and B_4C, and some that are close to $B_{12}C_3$. Other crystal structures such as tetragonal ($B_{50}C_2$, $B_{50}C$, $B_{48}C_3$, $B_{51}C$, $B_{49}C_3$ and orthorhombic (B_8C) have also been confirmed, but these structures are metastable. The latter phases are more difficult to synthesize than the stable rhombohedral phases, and their physical properties are also not well known [3].

It is well known that B_{12} icosahedra serve as structural elements in all boron carbides. The residual B and C-atoms occupy the large interstitial positions in the lattice and stabilize the structure [3].

The atomic structure of $B_{12}C_3$ (B_4C) boron carbide contains 15 atoms in four occupied crystallographic sites. Two sites form a distorted icosahedron, the polar and equatorial sites, with 6 atoms per site. The third and fourth sites are respectively the center of the triatomic chain (one atom) and the chain ends (two atoms) [4].

Experimentally, the three carbon atoms are difficult to distinguish from the twelve boron atoms [4].

TEM thin foils investigations performed by other authors revealed that the particles precipitated in the as cast material were the mixture of two kinds of bulk shaped boro-carbides [1]:
○ $Cr_7(C,B)_3$ orthorhombic crystallographic system structure and 62 - (P n m a) space group was found in the neighborhood of austenitic matrix areas,
○ $Cr_{23}(C,B)_6$ cubic crystallographic system structure and 225 - (F m -3 m) space group was found in border areas of austenitic matrix areas.

In higher magnification, above 100000 times there was discovered a kind of finer, as-yet unidentified M_7C_3 carbides. The large interdendritic hard phases contained a high level of Cr, low level of iron as was found in the performed microanalysis and have been identified also as Cr_7C_3 carbide with an orthorhombic structure. The solution treated microstructural morphologies are quite similar to those of the as-cast samples.

Hence, it can be concluded from the precipitation of secondary particles that the austenite matrix of Fe-Cr with B cast irons consisted of boron and carbon saturated solid solutions. Whether the B_4C particles used as B addition are present in the microstructure has not been established, but their compositions are different from the original B_4C borides.

The occurrence of phase about the similar structure to B_4C was affirmed however. Kopyciński [6] believes that boron carbide fulfilling the part of base-plates to nucleation the primary austenite the modifier of chromium cast iron, as a result of the crystal lattice similarity.

2. Experimental procedure

The material used for investigation was the chromium cast iron, it has been cast in a induction furnace. Of this material samples 40 x 2 mm were cut off for transmission electron investigation. The chemical composition of the investigated cast iron is presented in table 1.

To better be able to investigate the microstructural changes a study was carried out using the transmission electron microscope (TEM) as well the scanning electron microscope (SEM). The advantage of SEM is that it can be used on thicker samples, but compared with TEM the spatial resolution is much lower. TEM requires very thin foils taken from samples containing the shear band, and such specimens are both difficult and time consuming to produce.

The cast iron samples were investigated in a JEOL JEM 3010 transmission electron microscope (TEM) using a selected area (SAD) aperture of 1 μm for the diffraction pattern (with an illuminated diameter of approximately 10 μm).

Table 1.
Chemical composition of the investigated cast iron

	Mass concentration of the elements, wt. %				
Cast iron K16	**C**	**Mn**	Si	**P**	**S**
	3,06	0,17	0,58	0,053	0,029
	Cr	Cu	**Ni**	Mo	**B₄C** mod.
	20,9	0,04	0,67	0,07	0,5
Cast iron K3	**C**	**Mn**	**Si**	**P**	**S**
	2,88	0,12	0,33	0,036	0,018
	Cr	**Cu**	**Ni**	Mo	**B₄C** mod.
	18,06	0,03	0,62	0,08	0,2

To modyfication of chromium cast iron was used B_4C powder with the grain structure showed on Fig. 2. Diffraction pattern of B_4C are presented on Fig. 3 and 5 with the solutions showed on Fig. 4 and 6 with the zone axis [111] and [461]. These diffraction patterns are matrix for further possible B_4C phase determination in the investigated cast iron.
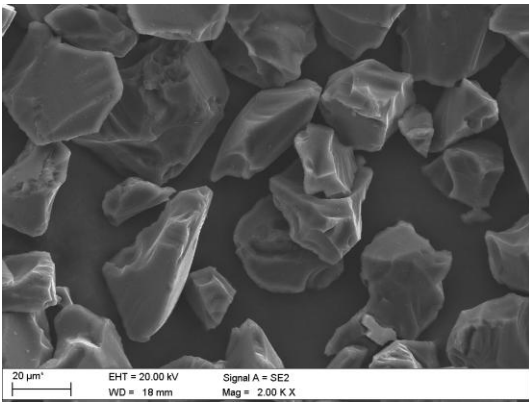
Fig. 2. B₄C powder used for modyfication
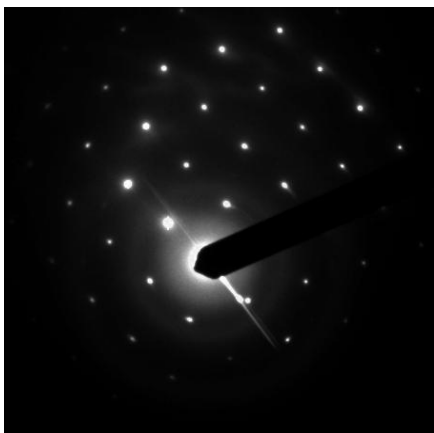
Fig. 3. B₄C powder diffraction pattern
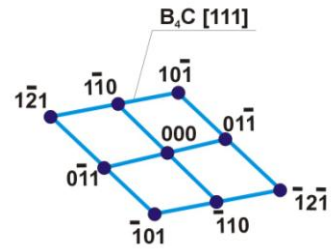
Fig. 4. Solution of the diffraction pattern from Fig. 3
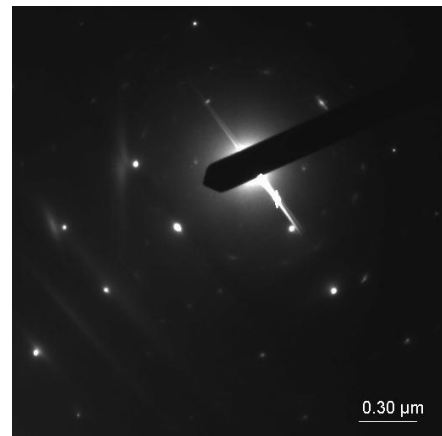
Fig. 5. B₄C powder diffraction pattern
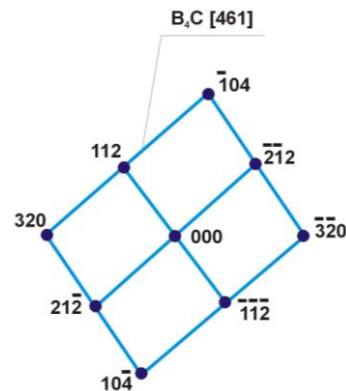
Fig. 6. Solution of the diffraction pattern from Fig. 5

Boron Carbide - one of the hardest materials known, ranking third behind diamond and cubic boron nitride. It is the hardest material produced in tonnage quantities. Originally discovered in mid 19th century as a by-product in the production of metal borides, boron carbide was only studied in detail since 1930.

Boron carbide powder (Fig. 2, Table 2) is mainly produced by reacting carbon with B_2O_3 in an electric arc furnace, through carbothermal reduction or by gas phase reactions. For commercial use B_4C powders usually need to be milled and purified to remove metallic impurities. The average granulation of the applied

powders was in the range of ca 20 μm. Some other physical parameters of the applied powders are presented in table 2.

Table 2.
Chosen physical parameters of B_4C powder

Property	Value
Melting Point (°C)	2445
Density (g.cm-3)	2.52
Hardness (Knoop 100g) (kg.mm-2)	2900÷3580
Fracture Toughness (MPa.m-½)	2.9 - 3.7
Young's Modulus (GPa)	450÷470
Electrical Conductivity (at 25°C) (S)	140
Thermal Conductivity (at 25°C) (W/m.K)	30÷42
Thermal Expansion Co-eff. x10-6 (°C)	5

TEM specimens were prepared by cutting thin plates from the material. The specimens were ground down to foils with a maximum thickness of 80 μm before 3 mm diameter discs were punched from the specimens. The disks were further thinned by ion milling method with the Precision Ion Polishing System (PIPS™), used the ion milling device model 691 supplied by Gatan until one or more holes appeared. The ion milling was done with argon ions, accelerated by a voltage of 15 kV, energy and angle are presented in Table 3.

Table 3.
Ion milling parameters using for polishing

Angle	Energy (KeV)	Time (min)
6°	3.8	180
3°	3.2	15

3. Results and discussion

The investigated cast iron has austenitic structure. TEM investigation results are showed on Figures from 7 to 26 and are performed using bright and dark field image technique and SAD method for phase identification.

The diffraction pattern calculation was performed using the "Eldyf" software supplied by the Z-Tech Firm.

Diffraction pattern analysis of the investigated areas has allows to identify the Feγ matrix in both of the cast iron materials - Fig. 7÷10 for the K16 cast iron and Fig. 11÷14 for the K3 cast iron. For both of the materials also the Cr_7C_3 phase occurrence was confirmed Fig. 15÷18 for the K3 cast iron. Also the $Cr_{23}C_6$ phase in the K3 cast iron matrix of the cubic 225 - Fm-3M space group with the [732] zone axis and a= 10,6595 Å lattice parameters was found (Fig. 19÷22). The $Cr_{23}C_6$ phase is relatively seldom present, so its impact on the mechanical properties an microstructure is not very high.

Occurrence of phase B_4C for cast iron K16 was also confirmed (Fig. 23÷26).

Microstructures presented on Figures from 27 and 28 have typical lamellar structure of pearlitic areas.
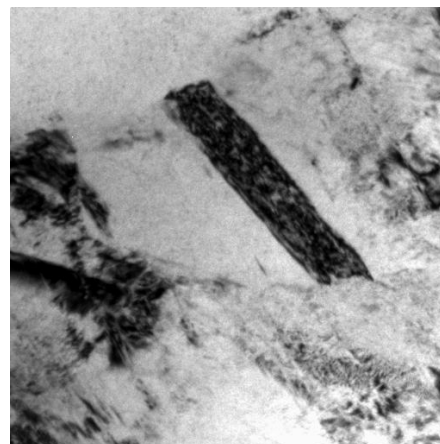

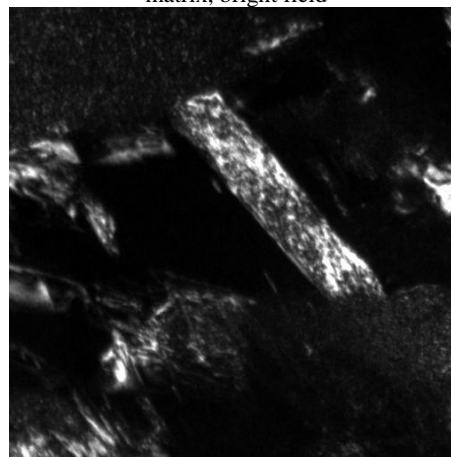Fig. 7. Microstructure of investigated cast iron K16, austenitic matrix, bright field

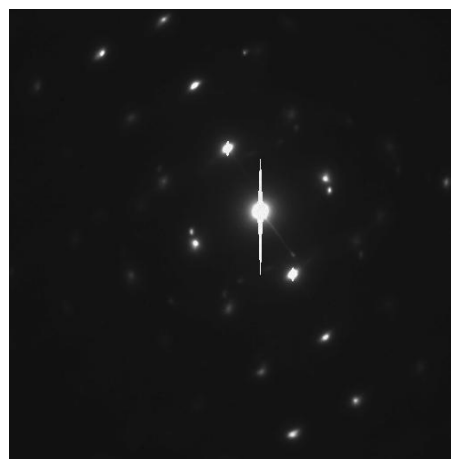Fig. 8. Microstructure of investigated cast iron K16, austenitic matrix, dark field

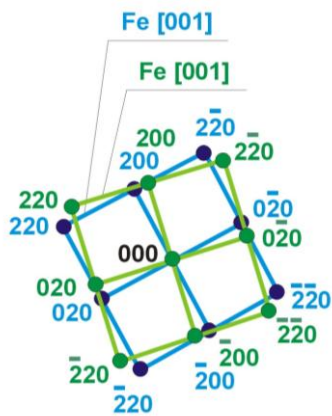Fig. 9. Diffraction pattern from the area as in Fig. 7

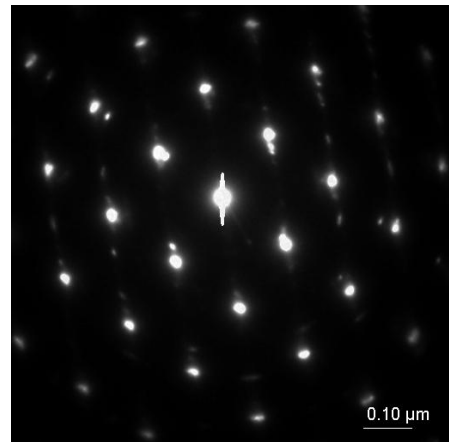Fig. 10. Solution of the diffraction pattern from Fig. 9

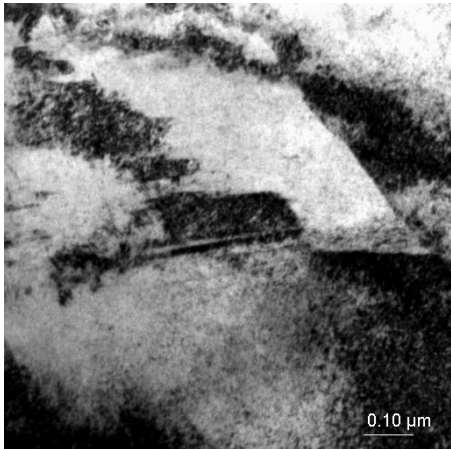Fig. 13. Diffraction pattern from the area as in Fig. 11

Fig. 11. Microstructure of investigated cast iron K3, austenitic matrix, bright field
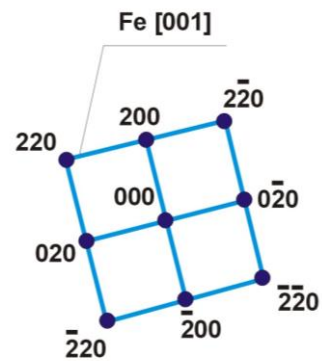

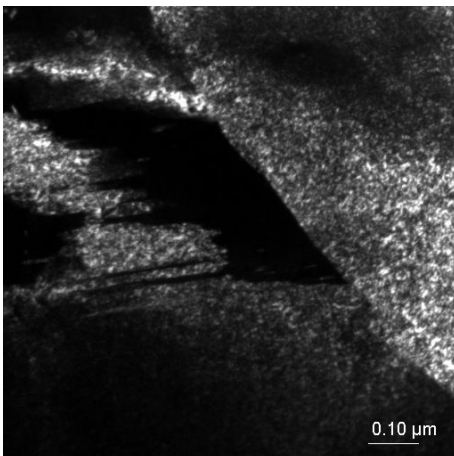Fig. 14. Solution of the diffraction pattern from Fig. 13

Fig. 12. Microstructure of investigated cast iron K3, austenitic matrix, dark field
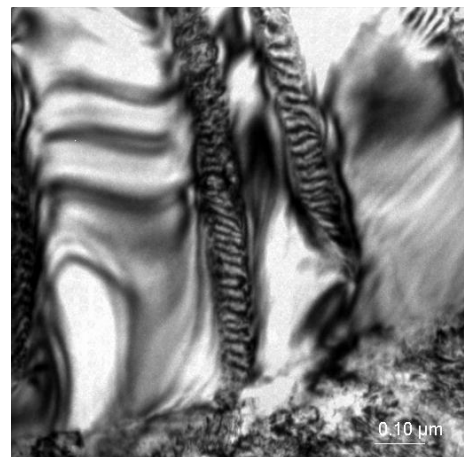

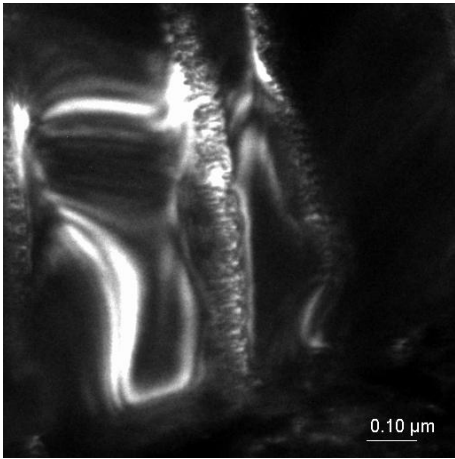Fig. 15. Particle of Cr_7C_3 carbide in microstructure of investigated cast iron K3, bright field

Fig. 16. Particle of Cr_7C_3 carbide in microstructure of investigated cast iron K3, dark field
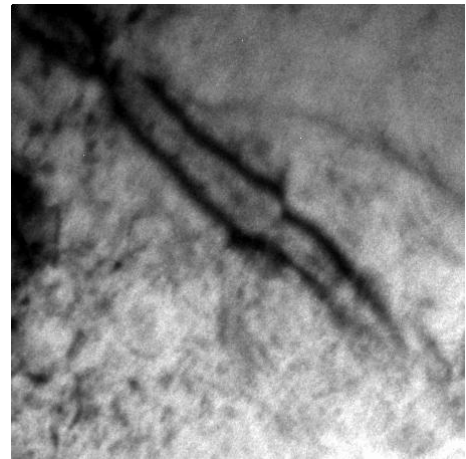
Fig. 19. Particle of $Cr_{23}C_6$ carbide in microstructure of investigated cast iron K3, bright field
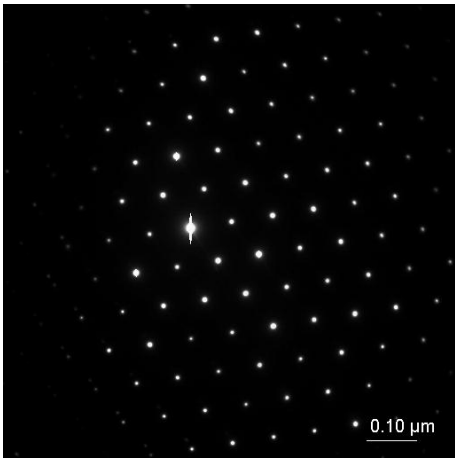
Fig. 17. Diffraction pattern from the area as in Fig. 15
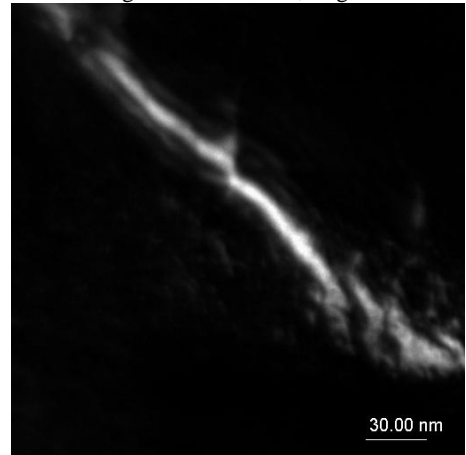
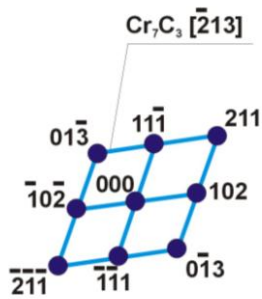Fig. 20. Particle of $Cr_{23}C_6$ carbide in microstructure of investigated cast iron K3, dark field

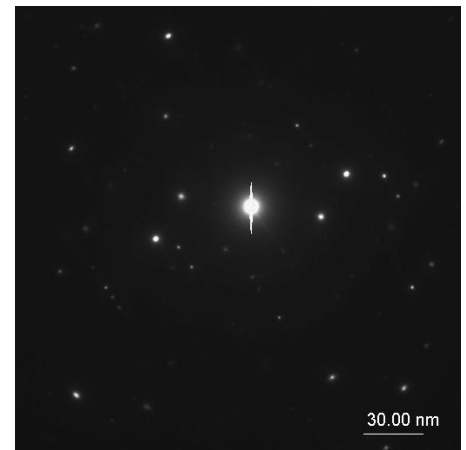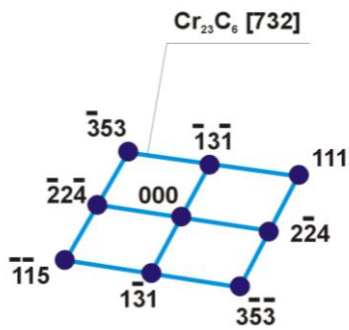Fig. 18. Solution of the diffraction pattern from Fig. 17

Fig. 21. Diffraction pattern from the area as in Fig. 19

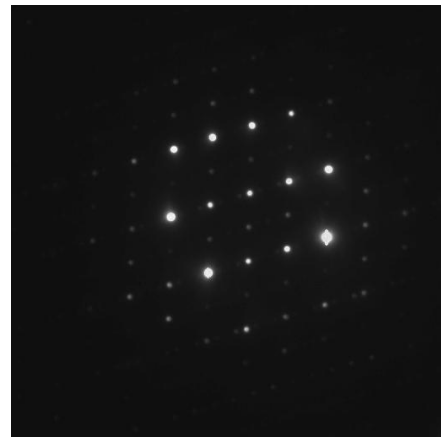Fig.22. Solution of the diffraction pattern from Fig. 21

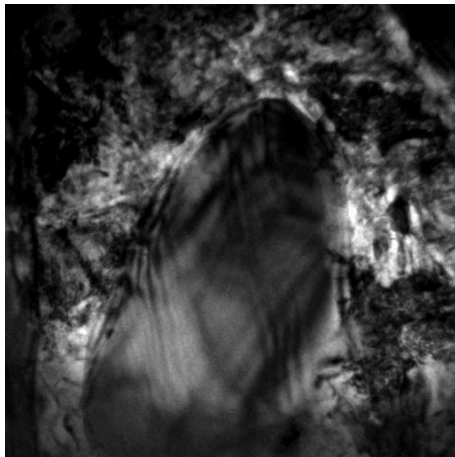Fig.25. Diffraction pattern from the area as in Fig. 23

Fig.23. Particle of B_4C carbide in microstructure of investigated cast iron K16, bright field
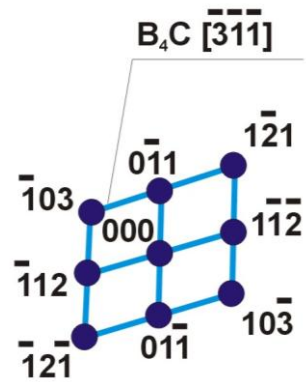

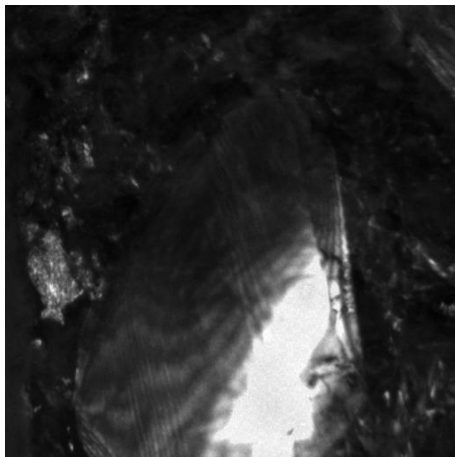Fig. 26. Solution of the diffraction pattern from Fig. 25

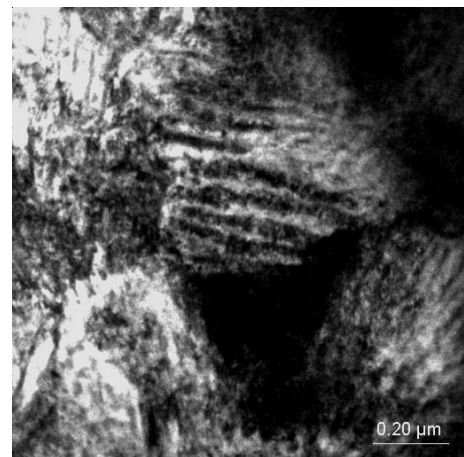Fig.24. Particle of B_4C carbide in microstructure of investigated cast iron K16, dark field

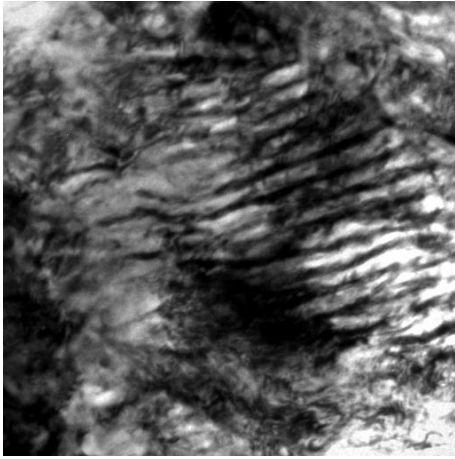Fig. 27. Area of lamellar microstructure in investigated cast iron K3

Fig. 28. Area of lamellar microstructure in investigated cast iron K16

4. Conclusions

o TEM investigations confirmed that i carbide phase of aalysed chromium cast iron are present mainly chromium carbides of type M_7C_3 and sporadically $M_{23}C_6$.

o Occurrence of the phase of the applied modifier B_4C in the matrix of studied cast iron using the diffractive investigations led utilization of the TEM was affirmed, but not very numerous.

o On the basis of the review of worked investigations, one can also in the different scientific centres was affirmed that the added powder B_4C gives dissolution partly and freed in this way boron is present in the affirmed phase of carbide Cr_7C_3.

Acknowledgements

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