

Morphology of Excess Carbides Damascus Steel

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Abstract

Considered the nature of changes in the morphology of carbides of the unalloyed high-carbon alloys type Damascus steel depending on the degree of supercooling of the melt, heat treatment and plastic deformation. It is shown that iron-carbon alloy with carbon content as in white cast iron at high degrees of supercooling can crystallize as a high-carbon steel. Considered three hypotheses for the formation of the eutectic carbides in pure iron-carbon alloys. The first hypothesis is based on the thermal process of dividing plates of secondary cementite or of ledeburite on isolated single grain. The second hypothesis is based on the deformation process of crushing of secondary cementite or of ledeburite into separate fragments (the traditional view on the formation of eutectic carbides). The third hypothesis is based on the transformation of metastable ledeburite in a stable phase of eutectic carbide prismatic morphology. Found that some types of wootz, which carbon content as in of white cast irons not is contain its structure of ledeburite. It is shown that the structure of consists entirely of the eutectic carbides prismatic morphology.

Keywords: Bulat, Damascus steel, wootz, Indian steel

1. Introduction

Modern tool steels are produced by complications of chemical composition and heat treatment. The highest achievement in the field of cutting tools include are high-speed steels and die steels as ledeburitic steels. Heat treatment of these steels is a complex technological process, including multi-stage heating and cooling and cold treatment. High-speed steels and die steels because of their physico-chemical peculiarities of the structure have low plasticity, which constrains their application as a cutting tool subject to dynamic loads. The aim of this work is to develop an alternative steels ledeburite without expensive alloying elements and the creation of resource-saving technologies of producing cutting tools of high elasticity under dynamic loads. Such conditions are responsible unalloyed high-carbon alloys on the carbon content, in the field of white cast irons. After thermomechanical processing of these alloys acquire the structure of the ledeburitic steels, which are called Damascus steel (Bulat, Wootz). Cutting properties and elasticity of these steels will depend on morphological features of excess carbide phase and ability of the matrix pearlite to take the load.

Today, it is increasingly common belief that Damascus steel lost its practical value. From our point of view, this is because there is no single agreed upon theory about the chemical composition and the microstructure the Damascus steel, which would define its technological properties and expand the field of application in modern industry. Therefore, in order to understand why high cutting capacity the Damascus steel of the blade of combined with high elasticity, it is necessary to reveal its true structure and to establish the main signs of alloys.

The morphology of the excess carbide phase in the Damascus steel has always been of interest to researchers. After analyzing the works that have studied samples of ancient Damascus steels blades (Anosov, 1841; Gaev, 1965; Tavadze, Amaglobeli, Inanishvili, & Eterashvili, 1984; Basov, 1991; Gurevich, 2007; Schastlivtsev, Gerasimov, & Rodionov, 2008; Schastlivtsev, Urtsev, Shmakov, 2013; Arkhangelsky, 2007; Sherby & Wadsworth, 1985; Wadsworth & Sherby, 2001; Wadsworth, 2015; Verhoeven, Pendray, & Gibson, 1996; Barnett, Sullivan, & Balasubramaniam, 2009), we can make a preliminary conclusion that the excess carbides is a special morphological type of cementite, is fundamentally different from the excess phases of secondary cementite, the ledeburite and primary cementite in iron-carbon alloys. Virtually all authors have noted that the morphological

feature of the cementite is in the size abnormality of the carbides having the shape of an irregular octahedral and prisms, which from our point of view, more similar in morphology to the carbides of the ledeburite steels (Sukhanov, 2014; Sukhanov & Arkhangelski, 2016). The size of carbides in the Damascus steel in different parts of the deformation are in the range of 0.005 - 0.1 mm. It is also noted that the heterogeneity of the distribution and morphology of abnormally large carbides remain after annealing at temperatures above 900 °C. The nature of these abnormally large carbide formations the authors to identify and failed. There were attempts, but none successful.

In the periodical literature, there is no consensus about how to call an abnormally large carbide formation. In the field of ledeburite steel, for all values of large carbides having the shape of an irregular octahedral and prisms, are such names as "angular carbides", "prismatic carbides", "faceted carbides" and "eutectic carbides" (Geller, 1968; Kremnev & Zabolotsky, 1969; Golikov, 1958; Taran, Nizhnekovskaya, & Mironova, 1981). Most often used, the term "eutectic carbide". It is formed from the eutectic the transformation of metastable complexes type M_6C and M_3C in stable carbide formation type MC , M_2C and M_7C_3 with hexagonal structure.

The mechanism of formation of faceted carbides in pure iron-carbon alloys type Damascus steel is still not clear. Question about the transformation of the cementite in the carbide prismatic of the morphology is one of the most interesting and important in the analyzed problem. It has not only scientific, but also practical value, because knowing the answer to this question and affecting the process of conversion of cementite, it is possible to control the whole complex of mechanical and physical properties of high carbon alloys of the Damascus steels (wootz).

2. Materials and Methods

The object of the study was chosen high-carbon alloy type BU22A (2.25 %C; 0.065 %Si; 0.024 %Mn; 0.002 %P; 0.004%S, all the rest elements in hundredths and thousandths fractions). On the initiative of L.B Arkhangelsky, experiments have been carried out for melting in a crucible high-carbon alloys a vacuum furnace without deoxidation in the Federal State Unitary Enterprise (FSUE) I.P. Bardin Central Research Institute for Ferrous Metallurgy. In the marking of alloy letters and numbers signify the following: BU is carbon Bulat (Damascus steel, wootz) containing not more than 0.1% of manganese and silicon (each individually); 22 is the average carbon weight fraction (2.25 wt.%); A is a high-quality alloy containing not more than 0.03% sulfur and phosphorus (each individually); all the rest elements in hundredths and thousandths fractions. Deformation of the alloy was carried out with the help of forging under an oblique angle of 45 degrees in the temperature range from 850 °C to 650 °C. The essence of forging under an oblique angle lies in the broach of the metal initially at a right angle, and then at an acute angle of 45 degrees to the front of the dies. Structural investigations were carried out using an optical microscope of a series METAM RV-21-2 in the zoom range from 50 to 1100 fold. Deeper structural investigations were carried out on scanning electron microscope CarlZeiss EV050 XVP using microanalyzer EDS X-Act. The chemical composition of the alloy controlled with the help of optical emission spectrometer ARL 3460 type on the Novosibirsk State Technical University (NSTU). The sizes of the analyzed samples was 15x15x30 mm. Phase analysis was performed by x-ray diffractometer ARL X'tra. The diffraction patterns of samples were recorded using copper x-ray tube as an x-ray source at a voltage of 40 kV and current of 40 mA. Analysis of samples was performed in the reflection geometry without monochromatization of the incident and reflected radiation. Average recorded energy dispersive Si(Li) detector wave length of the beam was $\lambda = 0,15406$ nm. Diffraction patterns were recorded repeatedly in the time mode ($t = 4...9$ seconds.) with step $\Delta 2\theta = 0.02$ and 0.05 degrees.

3. Results and Discussion

It is known that the elastic properties and the cutting ability of the tool depend on the morphology and volume fraction of excess carbide phase. The main technological parameters determining the morphology of excess cementite are heating temperature, cooling rate and degree of deformation. In this article we are interested in the question of how the degree of supercooling of the melt, temperature regimes of heat treatment and the degree of plastic deformation of the ingot affect the morphology of the excess carbides in pure iron-carbon alloys containing 2,25% carbon.

During melting in a vacuum, the degree of melt supercooling is quite high, since a crucible is cooled at room temperature (+20 °C). Due to the high degree of undercooling of the melt, there is a matrix of lamellar pearlite with of the excess phase of Widmanstätten cementite with a volume fraction of about 20%. The volume fraction of Widmanstätten cementite was determined by a random set of points marked on the microstructure of the sample. The number of points per area of Widmanstätten cementite divided by the total number of points was their relative volume fraction. The shape of crystals of the excess of cementite was determined by constructing the dependence of the area of their cross section from the degree of elongation. The character of distribution of values allows you to define elongated crystals of cementite, like the plates, because with increasing elongation of the observed cross sections for their area decreases.

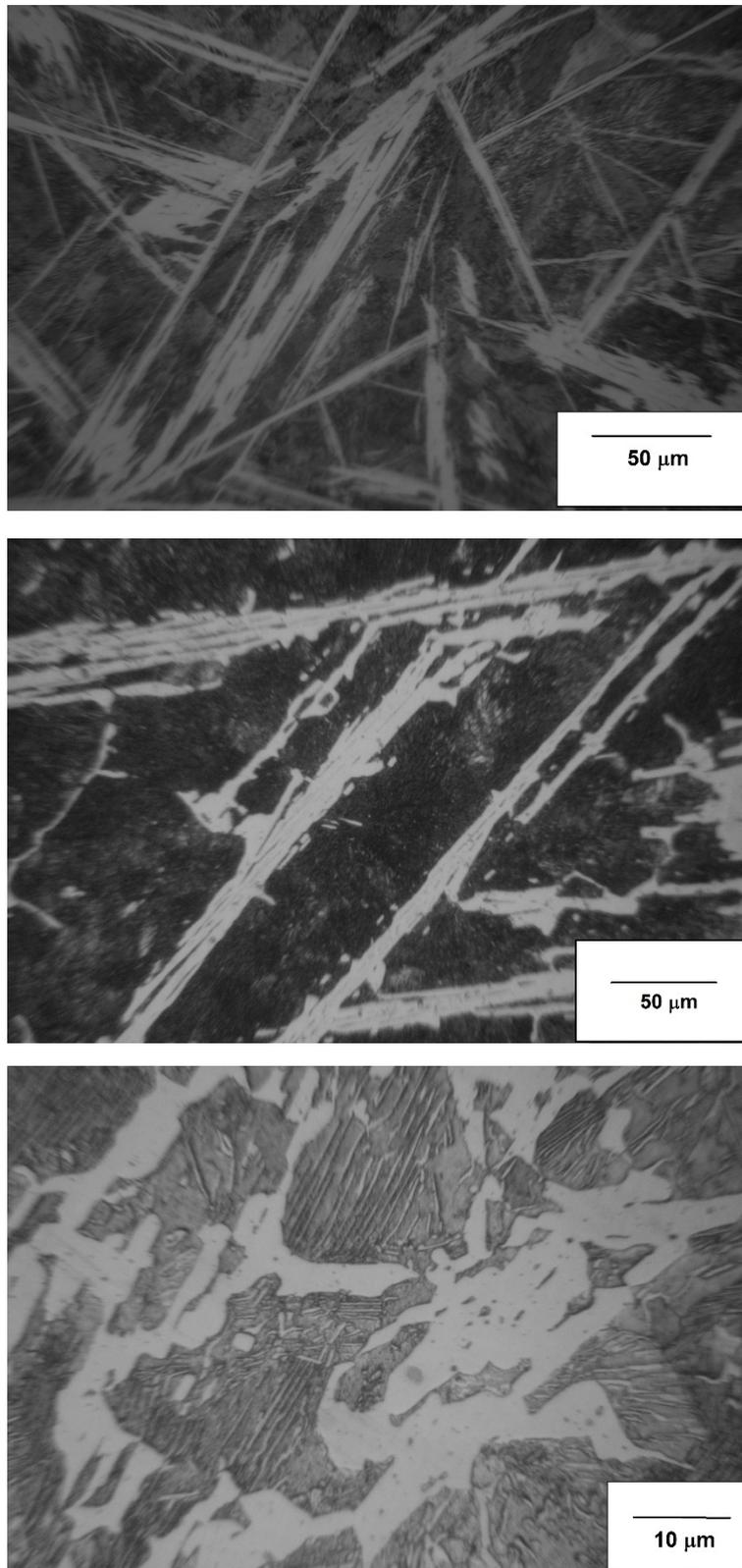


Figure 1. Morphology of excess cementite in the alloy BU22A
a – vacuum melting, is cooled at room temperature (+20 °C) (Widmanstätten cementite);
b – annealing at 700 °C, for 2 hours (Widmanstätten cementite);
c – annealing at 1150 °C, for 2 hours (metastable ledeburite)

In alloy BU22A, excess phase of Widmanstätten cementite of thickness is about 7-10 μm (Figure 1, a). Explicit plots with ledeburite eutectic in not observed. Which gives the basis of take of the maximum saturation of the primary crystals of austenite carbon during the crystallization of the melt. At the time of rapid cooling of the melt, the diffusion processes cannot develop fully. There is a situation in which critical size nuclei is extremely small, which leads to the formation of a huge number of crystallization centers. As a result, the alloy with carbon as white cast iron is crystallized as high carbon steel. Upon further cooling of the alloy, all the excess carbide supersaturated austenite is allocated mostly public in the form of secondary cementite Widmanstätten type as shown in Figure 1, a.

As there is a change in the morphology of the excess cementite Widmanstätten type at annealing? In particular, we were interested in changing the shape of the cementite at temperature at which not occurs the dissolution of excess phases (below 727 $^{\circ}\text{C}$) and at which occurs the dissolution the excess phase (above 1147 $^{\circ}\text{C}$). To answer this question, we have conducted studies of samples of alloy BU22A, which were subjected to isothermal annealing at 700 $^{\circ}\text{C}$ for 2 hours and at 1150 $^{\circ}\text{C}$ for 2 hours.

During annealing at 700 $^{\circ}\text{C}$ for 2 hours, the structure of the alloy does not undergo polymorphic transformations. In the pearlite matrix residual stresses are removed which appear during crystallization of the melt. In excessive carbide phase smoothed the sharp peaks Widmanstätten cementite. Microstructural studies showed that on the surface of the plates of Widmanstätten cementite appear protrusions in the form of spikes (Figure 1, b). In the working (Baranov, Bunin, Evsukov, & Pritomanova, 1969) it was noted that the opening angle of spines-protrusions is about 60 degrees and their presence is associated with the separation of the plates of Widmanstätten cementite to pieces, starting the process of spheroidization carbides. In these annealing conditions, morphology of the excess phases Widmanstätten cementite does not change drastically.

In the process of annealing at 1150 $^{\circ}\text{C}$ for 2 hours, the structure of the alloy experiences phase transformation. After slow cooling with the furnace, the matrix alloy BU22A becomes coarse structure of pearlite with interlamellar spacing of about 0.6-1.0 μm (Figure 1, c). Noticeable changes occur in the morphology of the excess carbide phase. In the plane of the thin section observed coarse conglomerates excess carbide formations (Figure 1, c). Which is identify as metastable ledeburite. Characteristic morphological feature of this metastable ledeburite is that it, compared to lamellar and unmodified (cell) ledeburite white cast iron (Sukhanov & Arkhangelski, 2016) contains in its structure a reduced number of micropores and not has a pronounced layering (Golikov, 1958), i.e. it is already not of ledeburite white cast iron, but still not quite eutectic carbide.

Widmanstätten cementite has low thermal stability and contributes to a drastic embrittlement of the steel. In order to preserve the elasticity and the cutting edge of the tool for a longer time, needed another morphology of the carbide contributing to the increase in thermal stability. Such a morphological feature of the carbides have a faceted prismatic shape, which are formed in the structure of the unalloyed high-carbon alloys during deformation by forging.

During the deformation of alloy BU22A with excess phase in the form of metastable ledeburite (Figure 1, c), which was performed using with the help of forging under an oblique angle of 45 degrees in the temperature range from 850 $^{\circ}\text{C}$ to 650 $^{\circ}\text{C}$, with the beginning of the deformed austenitic matrix. Metastable ledeburite is under the influence of the normal compressive stress of austenite and the shear stress of deformation. As noted in article (Nizhnikovskaya, 1982), in the process the deformation around carbide accumulated defects such as dislocations. When the dislocation density reaches a critical value in metastable ledeburite changes occur, because of which, less stable carbides of ledeburite turning in the sustainable eutectic carbides prismatic shape (Figure 2).

Analysis of the diffraction lines showed that the major phase in the alloy BU22A are ferrite ($\alpha\text{-Fe}$) and cementite (Fe_3C). X-ray phase analysis did not specifically identify this excess carbide phase due to interference of - overlapping lines of secondary cementite. At this stage of research it is possible to speak only about what we are faced with the particular morphology of cementite.

From our point of view, we can distinguish three fundamental hypotheses that explain why, under certain thermomechanical conditions, the cementite is stabilized and acquires a trigonal-prismatic morphology in Damascus steel (wootz).

The first hypothesis is based on the thermal process of dividing plates of secondary cementite or of lamellar ledeburite on isolated single grain. The mechanism of the process heat division is described in detail in (Baranov, Bunin, Evsukov, & Pritomanova, 1969). The authors of this article it is shown that in the process of annealing on the surface of the cementite at the junction of the boundaries of austenite appear protrusions in the form of spikes. In the process of isothermal of annealing of high-carbon alloys, between the spikes (protrusions) in thin places of plates of cementite are divided into parts. As a result, between the individual particles formed of grains boundaries of austenite. Angular carbides have is faceted of the close to equilibrium and, as a rule, are located along the former cementite plates.

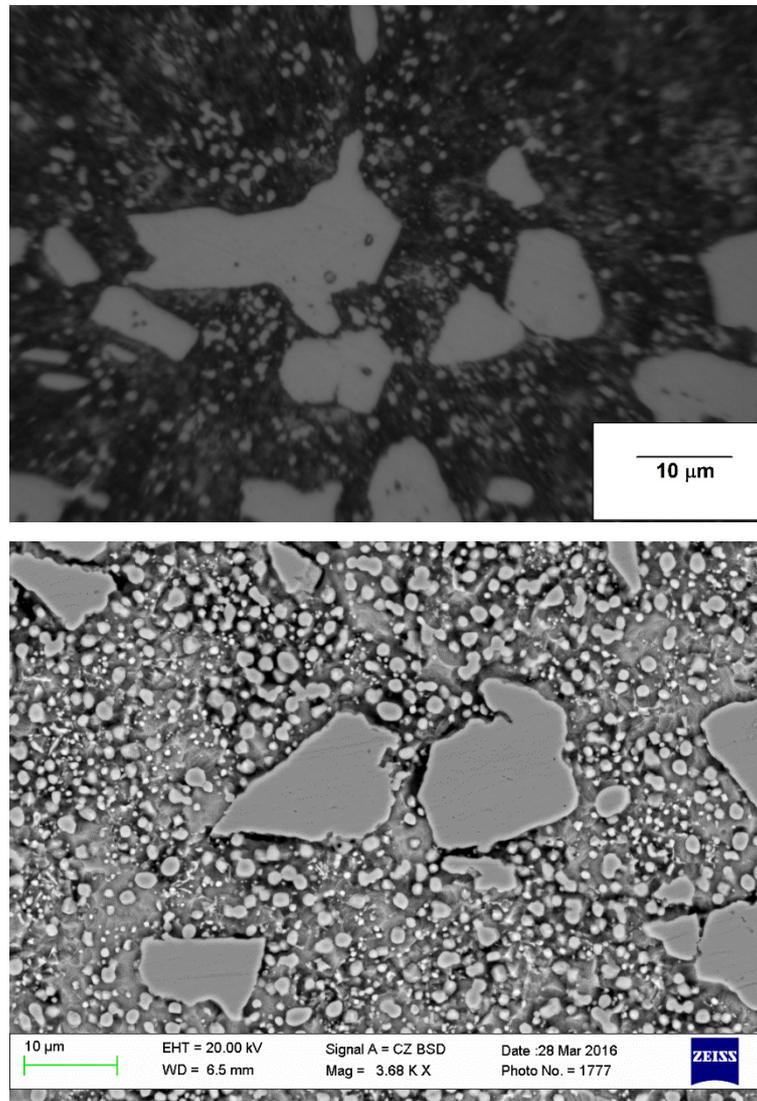


Figure 2. Morphology of excess carbides in the alloy BU22A (forging was performed on samples with metastable ledeburite):
a – optical microscope (eutectic carbides); b - electron microscope (eutectic carbides).

The second hypothesis is based on the deformation process of crushing of secondary cementite or of lamellar ledeburite into separate fragments. This traditional view on the formation of angular carbides are described in detail in article (Geller, 1968). It is assumed that the anomalously large angular carbides are formed as a result of fragmentation of cementite of lamellar ledeburite in the process of plastic deformation into separate parts (fragments). The greater the degree of deformation during forging, the more are of crushing of the carbides on parts. Crushing carbide conglomerates occur in places of a congestion of dislocations. It can be assumed that the data of the angular carbide formation are of splinters of the ledeburite eutectic.

The basis of the third hypothesis are laid of the conclusion about what the plasticity of white cast irons, possible as a result to the carbide transformation (Nizhnikovskaya, 1982). The essence of the hypothesis about the formation of angular carbides consists in transformation of metastable ledeburite in the process of plastic deformation in a stable phase of eutectic carbide prismatic morphology. According to author of articles (Nizhnikovskaya, 1984), decrease resistance inside the lattice of cementite in the process of transformation happen due to the weakening of the barriers of Peierls-Nabarro and the formation depleted of carbon areas of cementite.

All three mechanisms of transformation of metastable ledeburite in eutectic carbides prismatic shape, in varying degrees, encountered in practice. The above explanations would have been enough had we not met some of the circumstances that are contrary to these explanations. We are talking about the fact that some grains of the eutectic

carbides prismatic morphology exceed or commensurate with ledeburite colonies. This may indicate that the formation of eutectic carbides prismatic morphology happen is not crushing of metastable ledeburite at the deformation but is a transformation of metastable ledeburite in the of stable eutectic carbide. Otherwise, one should assume that there are additional energy factors associated with the growth mechanisms of cementite to abnormal size during plastic deformation. Deformation accelerates the process of complete of transformation of metastable ledeburite in the eutectic carbides prismatic shape.

Carbide phase at the number, at size and at morphology is distributed in volume of pearlite matrix is uneven (Figure 3). Professor N.I. Golikov in their work (Golikov, 1958) shows that almost all tool steel industrial production is chemically heterogeneous. In this work, we demonstrated that some types of Damascus steel, which carbon content as in of white cast irons not is contain its structure of ledeburite. The structure Damascus steel of consists entirely of the eutectic carbides prismatic morphology.

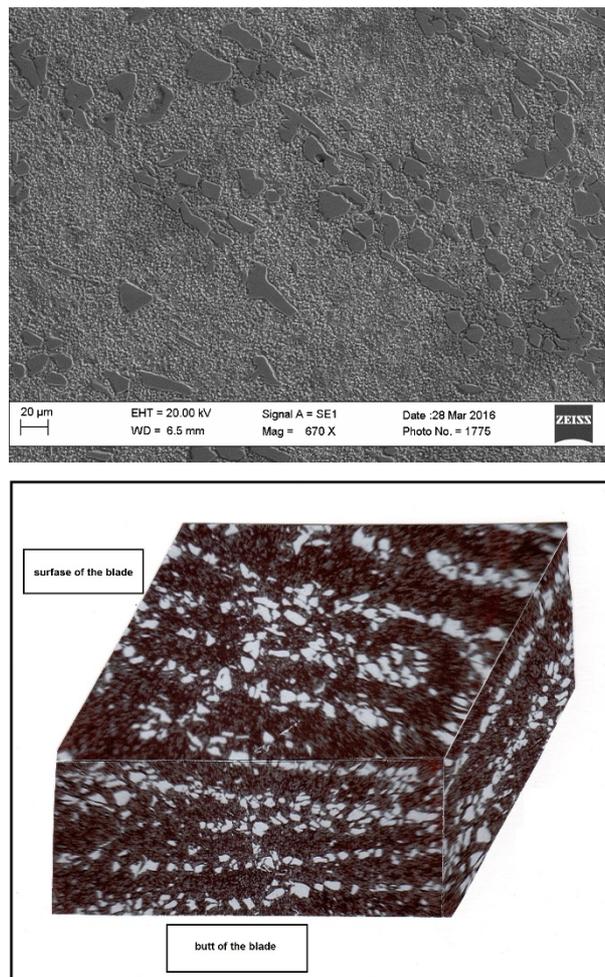


Figure 3. Carbide inhomogeneity of the alloy BU22A:
a - electron microscope (eutectic carbides); b - diagram of the structure of blade Damascus steel.

4. Conclusions

4.1 In some types of Damascus steel excess carbides are a special morphological type of cementite, is fundamentally different from the excess phases of secondary cementite, phases of ledeburite and primary cementite in iron-carbon alloys. The morphological features of excess cementite in these samples Damascus steel consists of anomalous particle size of the carbides having the shape of an irregular octahedra and prisms, which is similar to eutectic ledeburite carbides alloyed steels.

4.2 The major phases in the alloy structure BU22A in which excess carbides are in the form of faceted crystals of trigonal-prismatic morphology are ferrite (α -Fe) and cementite (Fe_3C).

4.3 There are two types of process of formation of excess carbides in the form of separate particles: first, the spheroidization of carbides - carbides have the correct round or oval, without distinct angles; secondly, the faceted of carbides – carbides have an irregular trigonal-prismatic morphology.

4.4 It is revealed that the main mechanism of formation of the faceted crystals of cementite trigonal-prismatic morphology is the recrystallization of metastable ledeburite complexes in the process of plastic deformation in a stable phase of the eutectic carbide.

4.5 It is shown that some types of Damascus steel, which carbon content as in of white cast irons not is contain its structure of ledeburite. Structure Damascus steel (wootz) of consists entirely of the eutectic carbides prismatic morphology.

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