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NATURE OF ANGULAR CARBIDES IN DAMASCUS STEEL

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It is detected that in some specimens of Damascus steel part of the excess cementite is of unusual origin, in contrast to excess phases of secondary cementite, ledeburite cementite, and primary cementite in iron-carbon alloys. It is revealed that a morphological feature of separate particles of cementite in Damascus steel includes anomalously large excess carbides in the form of irregular octahedral and prisms. It is shown that angular carbides form within the original metastable ledeburite colonies, and therefore they are called "eutectic." It is established that unalloyed materials of the carbide class acquire Damascus properties steel properties during isothermal exposure on annealing, which leads to thermal separation of colonies of metastable ledeburite, to limitation of newly formed eutectic carbides, and to their subsequent coalescence. It is revealed that some sorts of Damascus steel, being within the field of white cast iron with respect to carbon content, do not contain broken ledeburite within their structure. It is shown that the pattern of carbide inhomogeneity entirely consists of eutectic of angular carbides of non-etching triangular-prismatic morphology.

Keywords: *bulat, Damascus steel, tool steel, ledeburite class steel.*

High-purity iron-carbon alloys, being with respect to carbon content in the boundary region between cast iron and steel (about 2% C), are not used in contemporary industrial practice. Some researchers of metal cold armament [1, 2] have suggested that in fact these alloys, clean with respect to impurities (hundredths of a percent) and with developed carbide inhomogeneity (coarse pattern), are one of the best sorts of Damascus steel (Wootz). The level of industrial and technological culture of contemporary metallurgical production up until now has not made it possible on a wide scale to prepare large objects of high-carbon alloys with a minimum amount of impurities (hundredths of a percent). However, smiths of ancient India and Persia effectively used low-productivity crucible melting in order to prepare steels blades of the talwar and shamshir types, acquiring considerable popularity up to the 19th century [3, 4]. Damascus steel blades exhibited high hardness (45–60 HRC) and wear resistance, and also withstood dynamic loads quite well. Creation of resource saving technology for preparing cutting tools from alloys with a carbon content in the region of white cast iron, hitherto is an important task.

The operating properties of Damascus steel objects depend directly on the shape and nature of excess carbide phase distribution within a pearlitic matrix. The nature and morphological feature of this carbide phase in Damascus steel has always given rise to the interest of researchers. Contemporary ideas about an excess carbide phase in high-purity iron-carbon alloys of the Damascus steel type are incomplete. Until now, it has not been possible to determine the nature of these carbide formations.

By analyzing work in the field of ancient Damascus steel arms [5–11], the authors have concluded that in some Damascus steel specimens part of the excess cementite has an unusual nature of origin, differing from excess phases of

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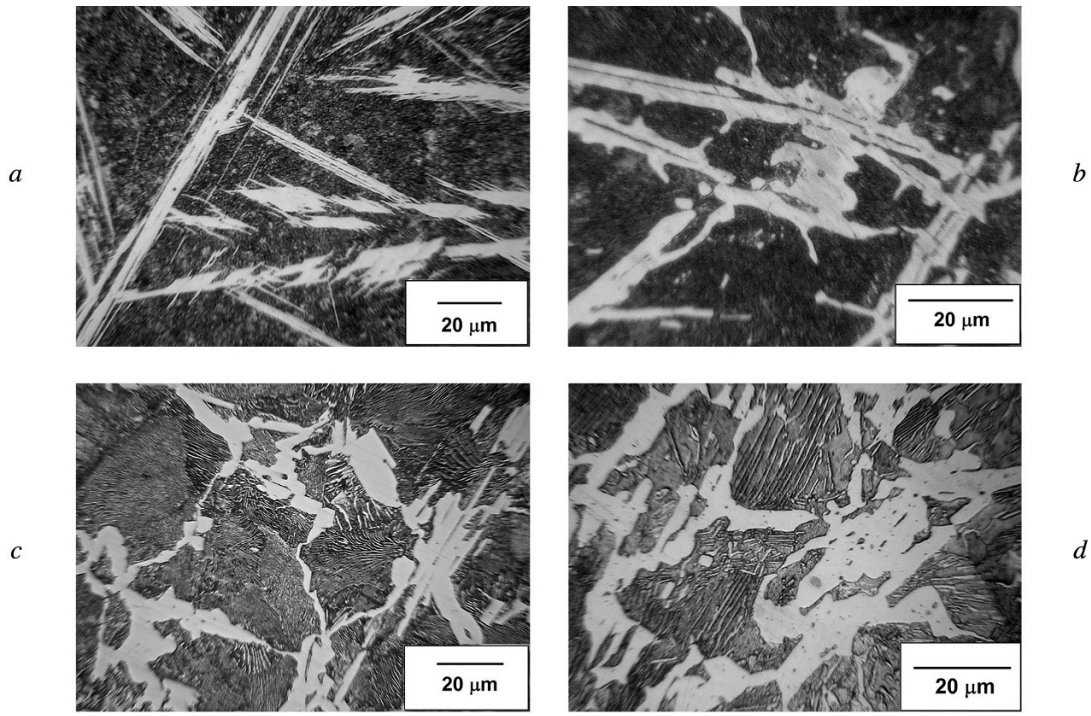


Fig. 1. Morphology of alloy BU22A excess cementite: *a*) vacuum melting, air cooling; *b*) annealing at 700°C, soaking for 2 h; *c*) annealing at 1100°C, soaking for 2 h; *d*) annealing at 1150°C, soaking for 2 h.

secondary cementite, ledeburite cementite, and primary cementite in iron-carbon alloys. A morphological feature of this cementite includes the anomalous coarseness of excess carbides, having the shape of irregular octahedral and prisms, which from our point of view are more similar to angular carbides in ledeburite steels [12].

The aim of this work is establishment of the nature and reasons for the formation of excess anomalously coarse angular carbides in Damascus steel. A question about the nature of angular carbides of faceted shape is one of the most interesting and important in the problem being analyzed. It is not only scientifically, but practically important.

The nature of angular carbides has been studied most in alloy steels of the ledeburite class. Carbide inhomogeneity of steels is connected with dendrite liquation during ingot solidification. Golikov [13] noted that with an increase in degree of dendrite liquation eutectic inclusions become more important. With hot deformation of alloyed ledeburite, it is broken down with formation of accumulations of coarse carbides of angular shape, which is not so different from areas of deformed metastable ledeburite. In [14], from results of a number of experiments it has been proposed that angular carbides form as a result of elimination of a eutectic network and has a similar structure and composition. In view of this, it has been concluded that angular carbides are products of incomplete spheroidization. Anomalously coarse angular carbides should be rounded with prolonged isothermal annealing. Morphological stability has been revealed in [15] for angular carbides of ledeburite steels during annealing. An increase in annealing duration led to coarsening of carbide particles, and, most importantly, to their gradual faceting. In the opinion of the authors, angular carbides are triangular prisms, that is a simpler shape of growing crystals of hexagonal syngony. In [16], the main types of carbide phase transformations in three-component systems Fe–C–*M* (*M* is carbide-forming element) have been summarized. Angular prismatic carbides form in eutectic by recrystallization of metastable complexes of the M_6C and M_3C types in stable carbide formations of types MC, M_2C, and M_7C_3 with a hexagonal structure. In fact, this approach to resolving the problem of studying the nature of angular carbides in the region of alloyed ledeburite steels is most suitable from our point of view.

The nature of anomalously large angled carbides in the region of unalloyed carbide steels has been studied in high purity alloys with a carbon content in the region of white cast iron. The object studied was high-carbon alloy BU22A,

containing 2.25% C; 0.065% Si; 0.024% Mn; 0.002% P; 0.004% S, and all of the rest of the elements in hundredths or thousandths of a percent. The alloy was prepared in a vacuum furnace in the scientific production base of the Bardin TsNIIchermet. Alloy chemical composition was monitored by an optical-emission spectrometer of type ARL 3460. In grading the alloy, letters and figures signify the following: BU is carbon Damascus steel containing not more than 0.1% manganese and silicon (each individually), 22 is average weight fraction of carbon (2.25 wt.%); A is high-quality alloy with a sulfur and phosphorus content not above 0.03% (each individually). Structural studies were conducted by means of a METAM PB-21-2 optical microscope in the magnification range ×50–1100. More fundamental studies were carried in a Carl Zeiss EV050 XVP electron microscope using an EDS X-Act microanalyzer. Phase analysis was carried out in an ARL XTRA diffractometer. Diffraction patterns of specimens were recorded using copper x-ray tube as a source of x-radiation with a voltage of 40 kV and current of 40 mA. Analysis of specimens was performed in reflected geometry without monochromatization of the incident and reflected radiation. The average value of fixed energy dispersion Si(Li)-detector peak wavelength was: $\lambda = 0.15406$ nm. Diffraction patterns were recorded repeatedly in a time regime with a step $\Delta 2\theta = 0.02°$ and 0.05°.

Due to a high degree of melt supercooling, excess phase in original specimens of alloy BU22A is in the form of Widmanstatten cementite platelets with a volume fraction of about 20% (Fig. 1*a*). Clearly defined areas with ledeburite eutectic are not observed, which provides a basis for concluding that the limited saturation of primary austenite crystals with carbon occurs during melt solidification. As a result of this, alloy with a carbon content corresponding to white cast iron solidifies as high-carbon steel.

Deformation by forging this alloy is connected with certain difficulty. Plates of Widmanstatten cementite, due to structural features, facilitate alloy embrittlement, and it is subject to crack formation and damping during forging. This is explained by the fact that Widmanstatten cementite platelets exhibit anisotropic properties. The length of platelets may reach more than 200 μm, whereas the width comprises only about 7–10 μm, and platelet consists of individual layers with a thickness of about 0.6–1.0 μm. The number of layers in plates varies from one to several tens. The authors in [17] consider that the boundary between layers is enriched with dislocation type microdefects. During deformation by forging in areas there is an increase in dislocation density, cementite platelets separate into individual blocks and bars, splitting over zones of layer contact. A morphological feature of this cementite is the less favorable for operating properties for tool steels and a globular shape of secondary excess cementite [18].

In order to understand how high-carbon alloy BU22A is converted into Damascus steel, starting materials with a structure of Widmanstatten cementite were previously heat treated. Specimen heating for treatment was performed in a SNOL 6/11 laboratory chamber furnace. Heat treatment and structural parameters of specimens after annealing are given in Fig. 1*b–d*.

During annealing at 700°C for 2 h, the structure of alloy BU22A does not undergo phase transformations. In the pearlite matrix, there is a reduction in residual stresses, arising after melt solidification. It has been shown in [12] that at this temperature at the surface of Widmanstatten cementite plates projections start to appear in the form of tongues (see Fig. 1*b*). The opening angle of tongue projections is about 60°, and their presence is connected with separation of Widmanstatten cementite plates into parts, connected with the start of carbide spheroidization. The mechanism of thermal separation of cementite is similar to that described in [19].

The higher the annealing temperature, the more rapid is thermal separation of cementite platelets. With heating to 1100°C and soaking for 2 h, the excess phase has the form of coarse cementite precipitates with a size of 5–30 μm, predominantly arranged over boundaries of previous austenite grain (see Fig. 1*c*). Metallographic indications make it possible to identify them as metastable ledeburite [13]. Doubts in structural identification of metastable ledeburite are included if a specimen of ally BU22A is heated to more than 1147°C with which it starts to melt. Within the microstructure shown in Fig. 1*d*, phases are clearly developed that in external appearance are reminiscent of ledeburite colonies. A typical morphological feature of metastable ledeburite is the fact that compared with lamellar and honeycomb ledeburite of white cast iron it contains within its structure a smaller number of micropores and has less defined layering, i.e., with respect to composition it is not altogether ledeburite, but is still not angular carbide.

In essence, alloy BU22A becomes Damascus steel during isothermal exposure on annealing, which leads not only to separation of cementite platelets but also to their limitation. Specimens of alloy BU22A in an original condition have a structure of excess phase in the form of metastable ledeburite (Fig. 2*a*). After annealing at 1100°C with isothermal exposure for 15 min

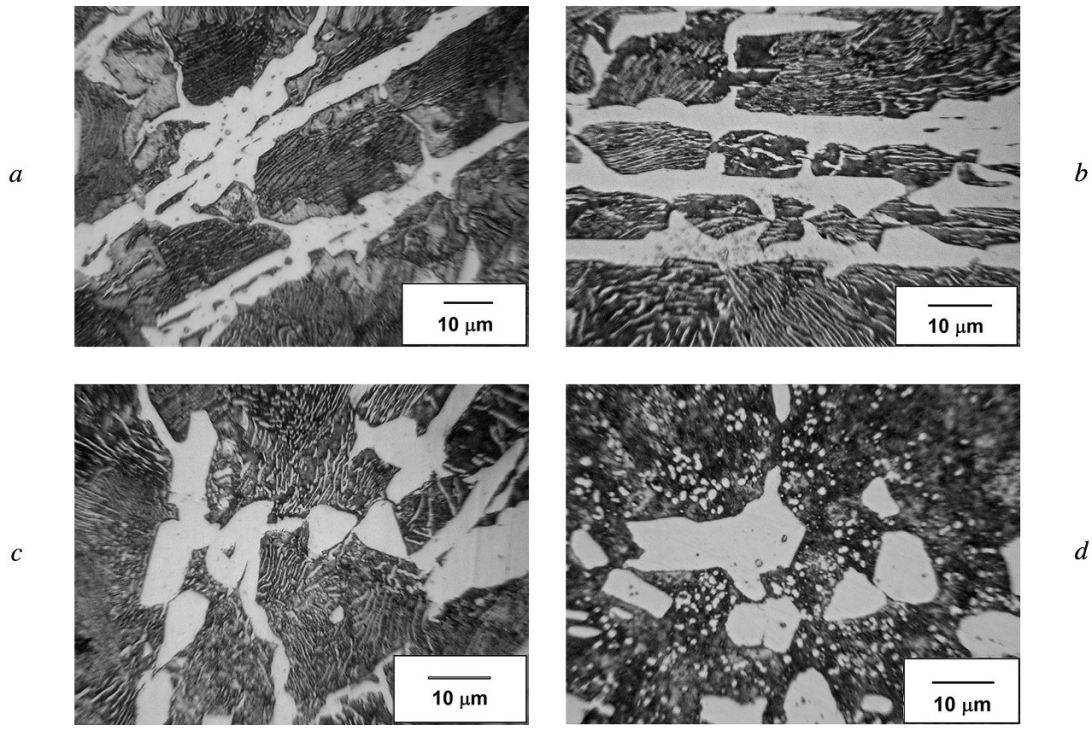


Fig. 2. Alloy BU22A excess cementite morphology: *a*) original alloy structure (metastable ledeburite); *b*) annealing at 1100°C, soaking for 15 min; *c*) annealing at 1100°C, soaking for 15 h; *d*) forging in the range 850–650°C, 12 reheats.

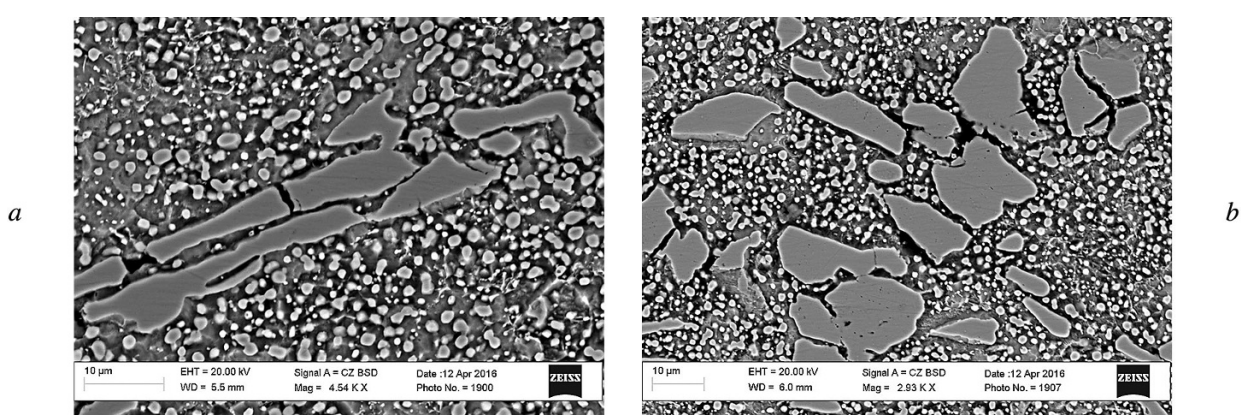


Fig. 3. Alloy BU22A excess cementite morphology (SEM) after forging I the range 850–650°C: *a*) two reheats (carbide fragmentation); *b*) 12 reheats (faceted carbides).

(Fig. 2*b*) and 15 h (Fig. 2*c*) as a result of metallographic studies by the authors it has been established that the duration of isothermal exposure is an integral part of excess carbide faceting. On heating to 1100°C and soaking for 15 min, the growth of angular projections in the form of tongues commences, along previous austenite grain boundaries (see Fig. 2*b*). With an increase in exposure time to 15 h, angular projections on cementite platelets are capable of separating forming isolated carbides arranged unevenly within the matrix of the lamellar pearlite (see Fig. 2*c*). Part of the excess carbide has an irregular triangular prismatic shape. New faceted angular carbides form as a rule within the original metastable ledeburite colonies, and therefore they are called "eutectic" [20], by analogy with faceted angular carbides in alloyed ledeburite steels.

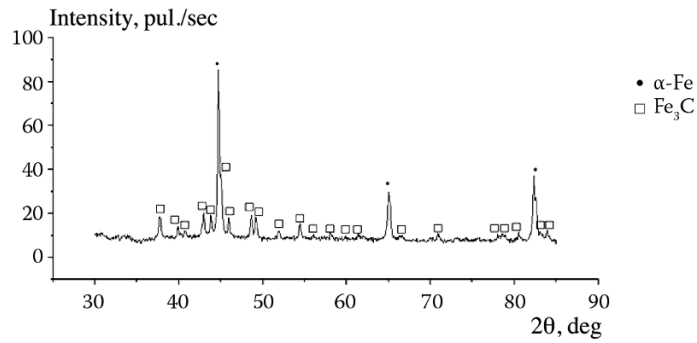
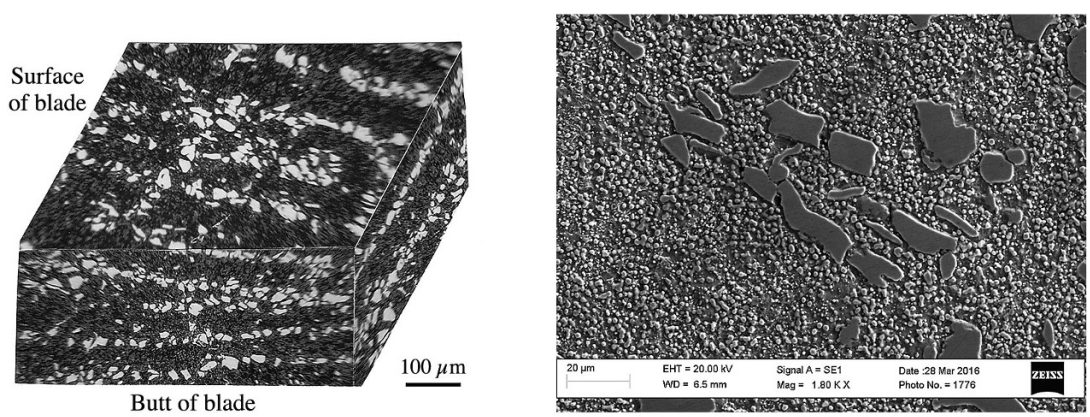


Fig. 4. x-Ray diffraction pattern of a specimens of alloy BU22A prepared by forging in the range 850–650°C; 12 reheats (excess phase is faceted carbide).



a *b*

Fig. 5. Alloy BU22A excess cementite morphology: *a*) carbide inhomogeneity within the Damascus steel blade structure; *b*) eutectic carbides in sorbite matrix (SEM).

Deformation of alloy BU22A in the range 850–650°C accelerates the formation of angular eutectic carbide. The structure is a globular sorbite matrix with irregularly distributed eutectic carbide of angular shape (see Fig. 2*d*). In the first stages of alloy BU22A deformation, the main complication consists in the break-up of metastable ledeburite colonies into parts. At first, there is formation of an austenitic matrix. Metastable ledeburite formations are under the action of normal compressive stresses of austenite and shear strain stresses. As noted in [21], during deformation around and within carbide conglomerates defects accumulate in the form of dislocations. When the dislocation density reaches a critical value, there is fragmentation of carbide by shear over adjacent matrix sub-boundaries (Fig. 3*a*). During subsequent forging deformation, carbide conglomerates break down into individual fragments in areas of dislocation accumulation that is often confirms the traditional view of angular carbide formation [22].

Intermediate prolonged heating for forging facilitates coarsening of angular carbides (Fig. 3*b*). The coalescence of eutectic carbide is reduced to diffusion transfer of carbon atoms through an austenite solid solution. Eutectic cementite grain growth proceeds as a result of interphase boundary migration. Eutectic carbides of angular shape grow due to the finer residues of secondary cementite particles. The coalescence of eutectic carbide is strengthened with prolonged high-temperature exposure. As a result of this, there is decarburization of the matrix due to anomalous growth of angular carbides. A similar process has been observed by the authors in [6, 23] during annealing of specimens cut from a Damascus steel blade. It should be noted that during coalescence eutectic angular carbides retain a faceted shape, whereas as a rule secondary excess carbides are spheroidized.

All this points to the development of either a new carbide with a hexagonal close-packed lattice of the Fe_7C_3 type, or a special shape of cementite formed with an orthorhombic closely-packed lattice of the Fe_3C type. Alloys having hexagonal carbides of the Fe_7C_3 type within their structure should exhibit lower magnetization, which corresponds to the lower relative concentration of iron within these carbides compared with cementite. However, we have not encountered experimental work confirming this assumption. Therefore, a requirement arose for phase analysis of eutectic carbides of triangular prismatic morphology. Phase analysis was performed in a ARL XTRA x-ray diffractometer with the Novosibirsk State Technical University (NGTU). In order to reduce the effect of a ferrite matrix, a previously polished BU22A specimen was given prolonged chemical etching in 4% alcoholic solution of nital (HNO_3). At the surface of a test specimen, carbides of different configuration appeared. Analysis of diffraction patterns (Fig. 4) showed that the main phases in BU22A alloy are ferrite and cementite. Other phases were not detected by us, which agrees with the data in [24]. Due to the interference of secondary cementite matrix line imposition, this x-ray phase analysis did not permit specific identification of angular shaped eutectic carbides. At this stage of research, it is only possible to talk reliably about the fact that we have observed cementite of special morphology.

Conclusion. It has been established that the main phases in the structure of alloy BU22A, in which there are excess carbides in the form of faceted crystals of angular shape, are ferrite (α-Fe) and cementite (Fe_3C). In alloys of the BU22A type, excess carbide with respect to amount and size is not uniformly distributed within the volume of a sorbitic matrix (Fig. 5*a*). The structure of the sorbitic matrix is ferrite with uniformly distributed cementite within it, whose particles have a regular round or oval shape (without clearly defined angles) about 0.2 μm in diameter (Fig. 5*b*). It has been shown that deformed alloys of the BU22A type with respect to carbon content are in the region of white cast irons, and they do not contain within their structure broken ledeburite. A pattern of carbon inhomogeneity entirely consists of eutectic angular carbides of irregular triangular prismatic morphology with a size of 5–20 μm (se Fig. 5*b*). From the collection of data provided about the structure of alloy BU22A, it may be specified as a tool unalloyed steel of the carbide class [25], similar with respect to structural features with die steel of the X12 type (GOST 5950) and high-speed steel of the type R9 (GOST 19265), differing from them only by the nature of excess carbide phase.

REFERENCES

1. Yu. G. Gurevich, "Classification of Damascus steel from macro- and microstructure," *MiTOM*, No. 2(620), 3–7 (2007).
2. V. R. Nazarenko, V. F. Yankovskii, M. A. Dolginskaya, and P. N. Yakovenko, "Damascus steel: myths and reality," *MiTOM*, No. 6, 36–37 (1992).
3. L. B. Arkhangel'skii, *Damascus Steel Secrets*, Metallurgiya, Moscow (2007).
4. I. N. Taganov, "Setting the legend of Damascus steel," *Kalashnikov, Oruzhie, Boepr., Snar.*, No. 11, 92–97 (2009).
5. P. P. Anosov, "Damascus steel," in: *Russian Scientists – Metallurgists*, A. M. Nakhimov and A. G. Rakhstadt (eds.), GNTI Mash. Lit., Moscow (1951), pp. 38–112.
6. I. S. Gaev, "Damascus steel and cotemporary iron-carbon alloys," *MiTOM*, No. 9, 17–24 (1965).
7. F. N. Tavadze, B. G. Amaglobeli, G. V. Inanishvili, and T. V. Eterashvili, "Electron microscope study of Damascus steel," *Soobsh. AN SSSR*, **113**, No. 3, 601–604 (1984).
8. V. M. Schastlivtsev, V. N. Urtsev, A. V. Shmakov, et al., "Damascus steel structure," *FMM*, **114**, No. 7, 650–657 (2013).
9. O. D. Sherby and J. Wadsworth, "Damascus steel," *Sci. Amer.*, **252**, No. 2, 112–120 (1985).
10. J. D. Verhoeven, A. H. Pendray, and E. D. Gibson, "Wootz Damascus steel blades," *Mater. Characteriz.*, No. 37, 9–22 (1996).
11. M. R. Barnett, A. Sullivan, and R. Balasubramaniam, "Electron backscattering diffraction analysis of an ancient Wootz steel blade from Central India," *Mater. Characteriz.*, No. 60, 252–260 (2009).
12. D. A. Sukhanov, L. B. Arkhangelsky, N. V. Plotnikova, and N. S. Belousova, "Morphology of excess carbides Damascus steel," *J. Mater. Sci. Res.*, 5, No. 3, 59–65 (2016).
13. I. N. Golikov, *Dendrite Liquation in Steel*, Metallurgizdat, Moscow (1958).

14. L. S. Kremnev and V. K. Zaboletskii, "Coarse carbides in high-speed steel structure," *MiTOM*, No. 1, 54–56 (1969).
15. Yu. N. Taran, P. F. Nizhnikovskaya, and E. N. Pogrebnoi, "Nature of angular carbides in high-speed steel," *MiTOM*, No. 10–13 (1974).
16. P. F. Nizhnikovskaya, "Carbide transformations in eutectic iron-carbon alloys," *Metally*, No. 6, 105–110 (1982).
17. Yu. N. Taran and V. I. Novik, "Structure of white cast iron cementite," *Lit. Proizv.*, No. 1, 34–38 (1967).
18. N. V. Plotnikova, *Role of Cementite Morphology in Providing Structural Strength in Carbon Hypereutectoid Steels: Auth. Abstr. Dissert. Cand. Techn. Sci.*, Novosibirsk (2004).
19. A. A. Baranov, K. P. Bunin, M. F. Evsyukov, and M. I. Pritomanova, "Mechanism of cementite crystal separation during spheroidizing annealing," *MiTOM*, No. 6, 19–23 (1969).
20. D. A. Sukhanov and L. B. Arkhangel'skii, "Damascus steel microstructure," *Metallurg*, No. 9, 112–115 (2015).
21. P. F. Nizhnikovskaya, "Structure and ductility of iron-carbon alloys of the eutectic type," *MiTOM*, No. 9, 5–9 (1984).
22. Yu. A. Geller, *Tool Steels*, Metallurgiya, Moscow (1968).
23. V. M. Schastlivtsev, V. Yu. Gerasimov, and D. P. Rodionov, "Structure of three gold-like Damascus steels," *FMM*, **106**, No. 2, 182–188 (2008).
24. A. M. Parshin and N. B. Kirillov, "Role of Fe_3C carbide distribution in Damascus steel," in *Alloy Radiation Damage and Properties*, A. M. Parshin and A. N. Tikhonov (eds.), Politekhnika, St. Petersburg (1995), pp. 32–40.
25. D. A. Sukhanov, "Damascus steel – unalloyed carbide class steel," *Metallurg*, No. 2, 93–96 (2014).