



## **INFLUENCE OF PHOSPHORUS IMPURITY ON THE STRUCTURE AND NATURE OF THE DESTRUCTION OF THE GENUINE DAMASCUS STEEL**

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### **Abstract:**

*It is established that the ancient knife blade belongs to the Eastern group of Indo-Persian steel type genuine Damascus steel with a pattern of "Kara-Taban", which literally means black-shiny. The methods of spectral, x-ray phase and optical analysis show that the genuine Damascus steel is a high-purity non-alloy high-carbon steel with a high content of phosphorus. It is revealed that phosphorus, having a high segregation coefficient of impurity contributes to the process of segregation of carbon in the process of crystallization of crucible ingots. The main physical and chemical factors influencing morphology of structure formation of genuine Damascus steel are revealed. It is established the relationship between the structure and the nature of the destruction of the genuine Damascus steel under impact load.*

**Keywords:** *Damascus Steel; Wootz Steel; Indo-Persian Steel; Bulat.*

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### **1. Introduction**

Ancient blades from genuine Damascus steel along with a beautiful large external pattern, according to experts and fans of bladed weapons, have high strength, elasticity and abrasion resistance. The qualitative character of the determination of the operational properties of the ancient genuine Damascus steel, based on the desire to sell the product more expensive, prevails over the quantitative characteristics that are known to a narrow circle of researcher. Despite all the advances in modern metallurgy, there is a perception that of properties ancient genuine Damascus steel over high-quality modern tool steel.

The Austrian metallurgist Zschokke (1924), one of the first conducted research of ancient Damascus steel [1]. He subjected two daggers and four ancient sabres from genuine Damascus steel to chemical, mechanical and metallographic analysis, comparing their properties with the properties of blades specially made for him in Solingen. The obtained results led to a paradoxical conclusion that according to the static properties of the old blade from genuine Damascus steel is inferior to industrial blade steels. In his opinion, a huge impact on the decrease in mechanical

properties has impurities phosphorus, in a significant amount present in all studied samples genuine Damascus steel.

The main conclusions of article [1] confirmed to Professor Gaev (1956) [2], who studied the ancient blade Damascus steel of the XVIII century from the State Hermitage Museum. American researchers Verhoeven and Jones (1987) [3] considered several mechanisms for the formation of a heterogeneous structure in genuine Damascus steel associated them with an admixture of phosphorus and sulfur. Professor Taganov and Kalinin (2009) [4] did a great job in understanding the structure and properties of genuine Damascus steels, researching dozens of Indo-Persian blades assembled by expeditions of the Russian Geographical Society. The authors of the articles [5 - 8] have done a lot of work to understand the main technological processes taking place in the genuine Damascus steel.

The purpose of this work was a comprehensive study of the structure, chemical composition and nature of destruction of the blade from genuine Damascus steel with a large pattern, typical for the Indo-Persian period of the XVII – XIX centuries. The task was to establish the relationship between the structure and the nature of the failure of the genuine Damascus steel under dynamic load.

## 2. II. MATERIALS AND METHODS

For studies of the structure and properties of Damascus steel used a fragment of the tip of the knife length 50 mm. According to the shape and size of the pattern, it can be assumed that the blade belonged to the Eastern group of genuine Damascus steel such as "Kara-Taban", since after polishing and etching in 4% alcohol solution of nitric acid on the side surface of the blade showed a contrasting pattern with a Golden tint (Fig. 1).



Figure 1: Fragments of knife from genuine Damascus steel.

To facilitate the reference in the text of the article, let us denote the genuine Damascus steel as Ds15P. In the marking of the alloy, letters and figures mean the following: Ds - Damascus steel containing no more than 0.1% manganese and silicon (each separately): 15 – the average mass fraction of carbon (1.48 Mass. %); P – phosphorus with a mass fraction of at least 0.1%.

The chemical composition of the genuine Damascus steel was determined using a spectrometer type *ARL 3460*. Quantitative phase analysis and mass fraction of chemical elements in separate phases were carried out with the help of microstructure studies on a Scanning electron microscope *Carl Zeiss EV050 XVP* with the system of probe micro analyzer *EDS X-Act* and optical microscope series *METAM PB-21-2* in the range of magnification from 50 to 1100 crats. To reveal the peculiarities of the fine structure of faceted excess carbides, a Transmission electron microscope *FEI Tecnai G2 20 TWIN* was used.

The local stoichiometric composition of large carbide inclusions larger than 10  $\mu\text{m}$  was determined by means of probe micro analyzer *EDS X-Act* in combination with raster electron microscopy. The stoichiometric composition of carbon atoms in unalloyed carbides was described by the inequality  $25 < C < 35$  (atom %). This method allows estimating qualitatively in what range of concentrations of carbon atoms there are oblong rounded particles carbides in genuine Damascus steels.

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 ( $t = 4 \dots 9$  seconds.) with step  $\Delta 2\theta = 0.02$  and  $0.05$  degrees.

### 3. Results and Discussions

The chemical composition of the fragment sample of the Damascus knife contained about 1.48% of the carbon. In the sample there are practically no residues of deoxidation products silicon up to 0.082%, manganese up to 0.006% and aluminum up to 0.004%. The spectral method of chemical analysis revealed a reduced sulfur content to 0.005% and an overestimated phosphorus content of about 0.192%. This figure for phosphorus is ten times higher than the threshold for high-quality steels. All the other alloying elements did not exceeded thousandths of percent. Thus, the investigated fragment of the blade from genuine Damascus steel according to the modern classification is non-alloy high-carbon steel with a high content of phosphorus (Fig. 2).

Damascus steel	The content of chemical elements, %				
	C	Mn	Si	P	S
<b>Ds15P*</b>	1,48	0,006	0,082	0,192	0,005
*Deciphering the markings: <b>Ds</b> – Damascus steel; <b>15</b> – 1,45...1,54% carbon; <b>P</b> – 0,12...0,22% phosphorus					

Figure 2: The chemical composition genuine Damascus steel.

In the analysis of the chemical composition of genuine Damascus steel, special attention was paid to the detection of traces of alloying elements that could positively affect the mechanical properties. Found only two elements that were in hundredths of a percent: 0.011% vanadium and 0.015% cobalt. The low content of vanadium and cobalt could not significantly affect the morphology of the structural components of genuine Damascus steel.

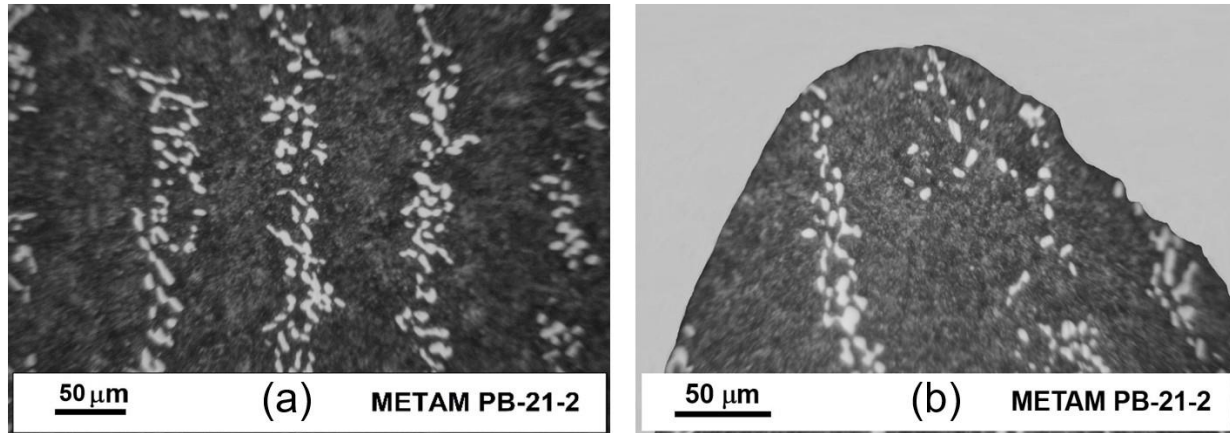
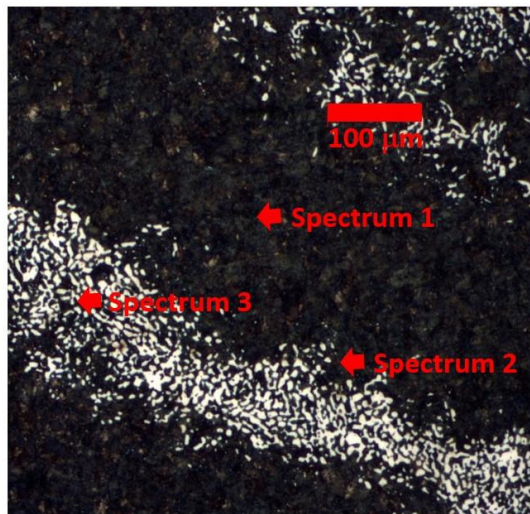


Figure 3: The microstructure of the genuine Damascus steel (Ds15P):  
a - longitudinal direction; b - transverse direction.

In the microstructure of the knife of the Damascus steel in the longitudinal direction (Fig. 3, a) and transverse direction (Fig. 3, b), observed a regular layered structure formed in the process of forging a knife blade. On a dark background of a matrix, the light intermittent layers with a thickness from 15 microns to 45 microns enriched with oblong rounded particles of cementite are visible. Density of carbide layers is from 10 to 15 pieces per 1.0 mm. Thickness of the dark gaps between the light carbide layers is in the range of 45 microns to 75 microns.



Spectrum	The content of chemical elements, %				
	C	Si	P	S	Fe
Spectrum 1	0,86	0,03	---	---	99,11
Spectrum 2	3,54	0,16	0,20	---	96,10
Spectrum 3	4,13	0,18	0,38	0,14	95,18

Figure 4: Analysis of dark and light bands of the genuine Damascus steel (Ds15P).

The chemical composition of light and dark bands in the fragment knife blade from Damascus steel was revealed by microprobe spectral analysis. Dark layers correspond to high-purity eutectoid steel containing about 0.86% carbon. Light layers, in terms of carbon content and amount of impurities, correspond to high-carbon white cast iron containing about 3.54...4.13% carbon. The distribution of chemical elements in the layers shown in Fig. 4. The analysis showed that in carbide layers there is an increased phosphorus content of about 0.38% and sulfur of about 0.14% (Spectrum 3). In the dark troostite layers, the amount of phosphorus gradually decreases to 0.2%

(Spectrum2) and zero in the middle part of troostite layer (Spectrum1). Quantitative analysis of the distribution of phosphorus layers, allows establishing the basic laws of crystallization of the crucible ingot. Thus, genuine Damascus steel Ds15P (Indo-Persian steel) born with significant chemical heterogeneity in during the crystallization of the crucible ingot.

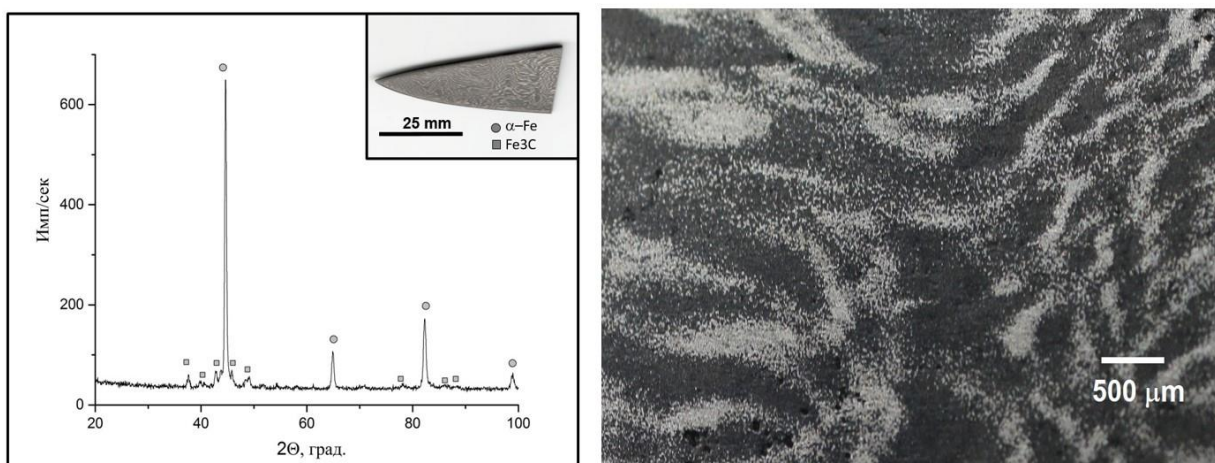


Figure 5: X-ray diffraction diagram and macrostructure of genuine Damascus steel (Ds15P).

Method x-ray diffraction in structure genuine Damascus steel discovered only ferrite and cementite with clear predominance of the diffraction peaks of the ferrite. The volume ratio between ferrite and cementite is not possible to determine due to the imposition of all the diffraction lines of ferrite on the diffraction lines of cementite (Fig. 5). Intermediate phases of the type of iron phosphide ( $Fe_3P$ ) or residual austenite ( $\gamma-Fe$ ) that can be formed in the process of crystallization of the crucible ingot, by the method of x-ray phase analysis did not reveal. Thus, genuine Damascus steel type Ds15P consists of two phases: ferrite ( $\alpha-Fe$ ) and cementite ( $Fe_3C$ ).

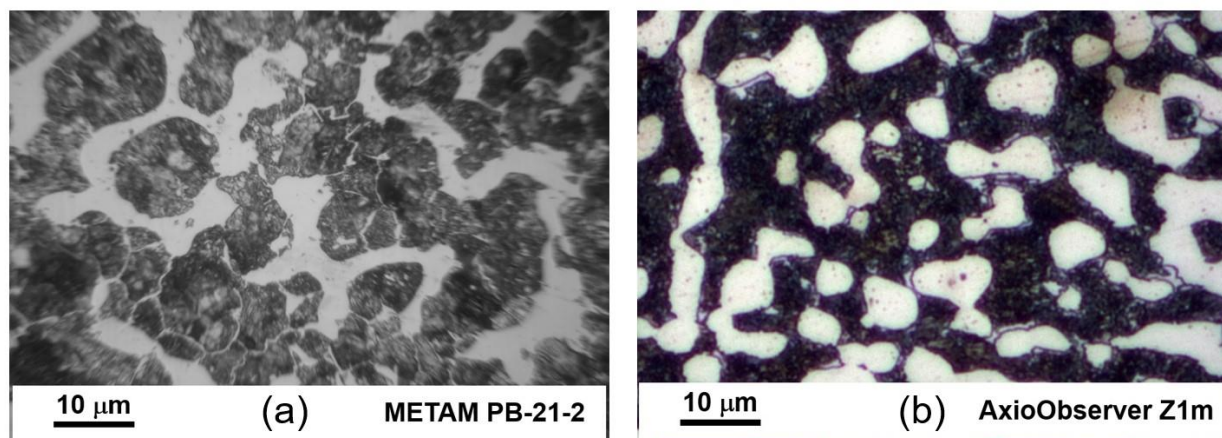


Figure 6: The microstructure of the genuine Damascus steel (Ds15P):  
a - after crystallization of the crucible ingot; b - after forging of the crucible ingot.

Phosphorus contributes to the process of segregation of carbon during the crystallization of the ingot (Fig. 6, a). During long-term isothermal exposure (about 1200 °C) formed metastable

structures with excess carbides phases. During the forging process at a temperature of heating below the  $A_{cm}$  (about 860...880 °C) is the destruction of metastable structures with the formation of carbides elongated shape (Fig. 6, b).

Oblong excess carbides on morphological grounds are reminiscent of an oval pebbles with a thickening in the middle part. The size of the carbides in the cross section are about 3...4  $\mu\text{m}$  in the longitudinal cross section does not exceed 9...12  $\mu\text{m}$ , axis ratio is 1/3. The chemical composition of the separated excess carbides showed that they are somewhat overestimated carbon values of about 7.06% (Spectrum1 in Fig. 7), in comparison with cementite (6,67% C), which indicates the imperfection of the crystal lattice of these carbide formations.

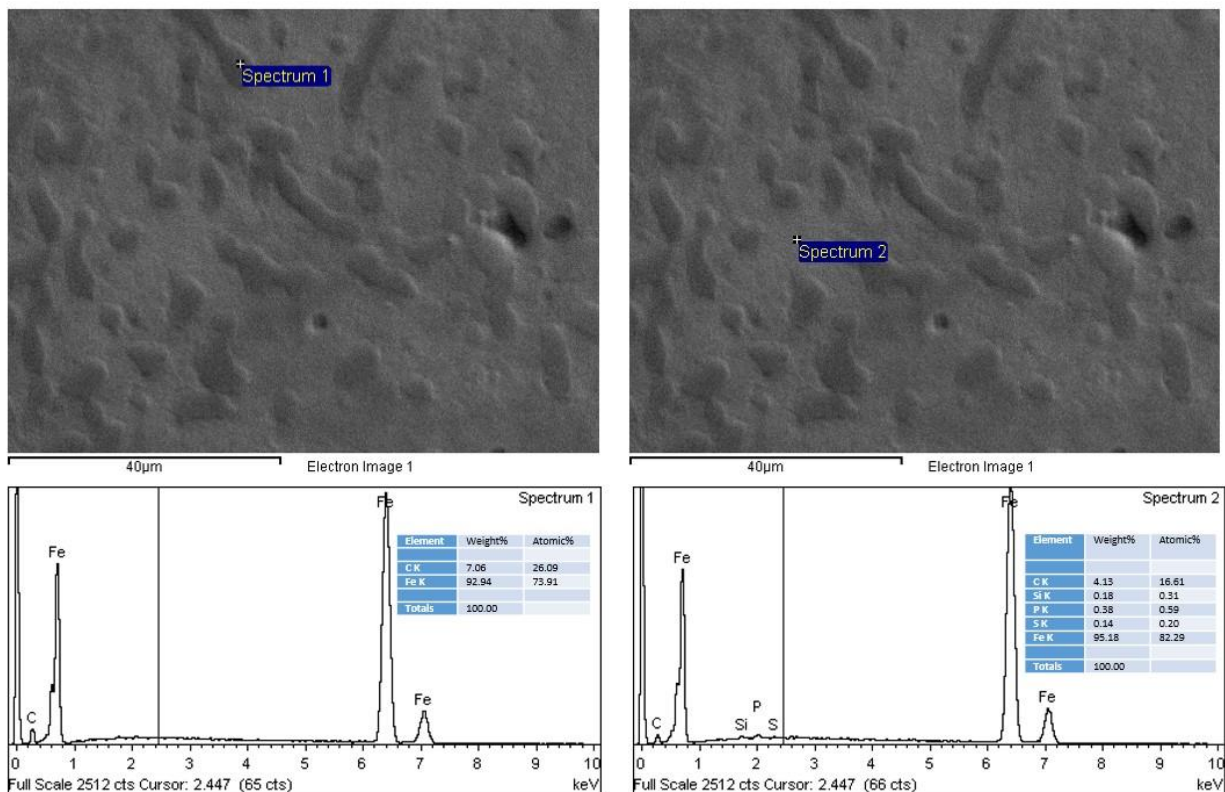


Figure 7: Stoichiometric composition of excessive oblong carbides (Spectrum 1 - carbides) and of iron matrix (Spectrum 2 - matrix).

Microprobe analysis revealed the chemical composition of the dark matrix in the carbide layers (Spectrum 2 in Fig. 7). The increased phosphorus content of the 0.38%, silicon 0.18% and sulfur 0.14% indicates that genuine Damascus steel (Ds15P) was born with significant chemical heterogeneity in the crystallization process. Phosphorus contributes to the process of segregation of carbon in the spaces between dendrites austenite. In these areas, in the process of crystallization of ingot, are formed of carbides education, which in the process of forging and heat treatment are transformed into carbides oblong form.

With the help of Scanning electronic microscopy revealed that, the excess of elongated carbides consist of several smaller carbide particles. These excess carbide particles are spherical shape with

an average diameter of 2.0...3.0  $\mu\text{m}$  (Fig. 8, a). Thus, excessive carbides of an oblong form, most likely, are a consequence of incompleteness of process of coagulation at their secondary allocation from austenite during plastic deformation forging.

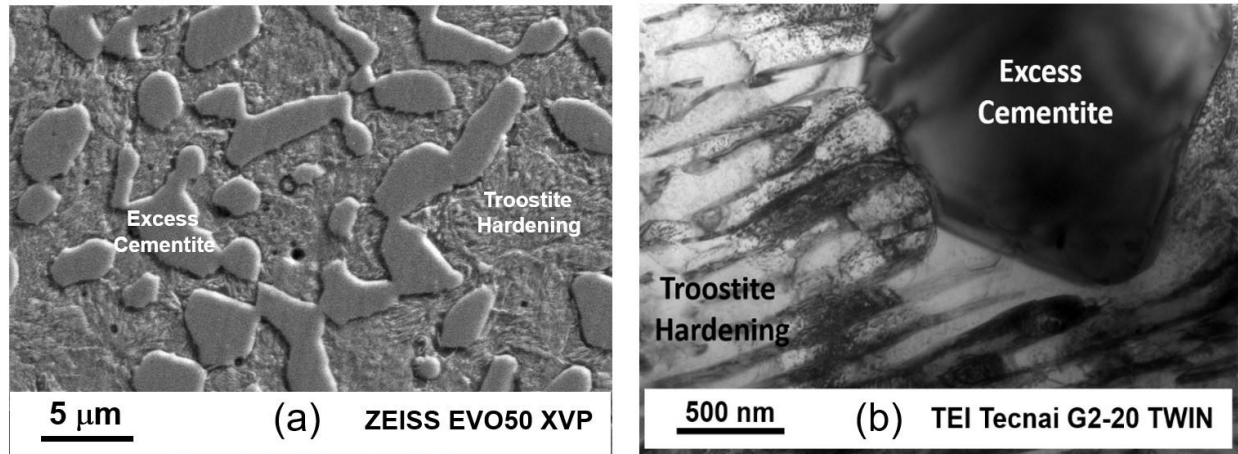


Figure 8: The microstructure of the genuine Damascus steel (Ds15P):  
a - Scanning electron microscope; b - Transmission electron microscope.

According to the transmission electron microscopy, it was found that the dark spaces of matrix of genuine Damascus steel is of the "troostite hardening" with an inter-plate distance of no more than 100 nm (Fig. 8, b). The "troostite hardening" is formed at the isothermal hardening in molten fat at the temperature 200  $^{\circ}\text{C}$ . Thus, the structure of genuine Damascus steel is constitute of the "troostite hardening" with irregularly placed in it by elongated particles of cementite, with the ratio of the axes of 1/3.

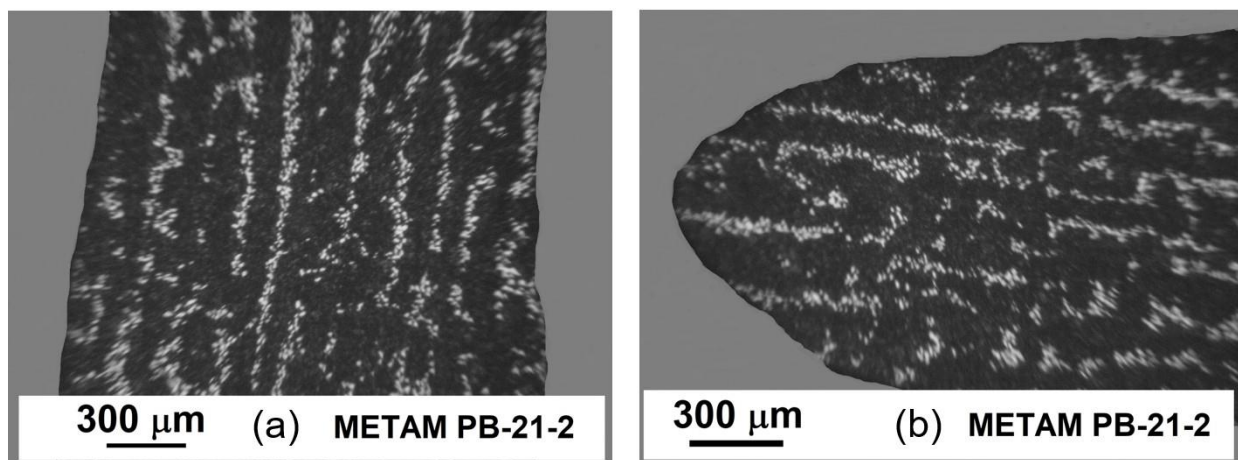


Figure 9: The macrostructure of the genuine Damascus steel (Ds15P):  
a - longitudinal direction; b - transverse direction.

The macrostructure of the fragment Damascus knife, visible on the front surface in the form of a "Kara-Taban" pattern, depends on the increased phosphorus content. Segregation of phosphorus and carbon impurities in the inter-axial portions of dendrites contributes to the development of

structural heterogeneity. After deformation forging, elongated dendritic axes and inter-axial portions, in the longitudinal (Fig. 9, a) and in transverse (Fig. 9, b) directions, form a set of layers consisting of oblong cementite carbides on dark background of matrix.

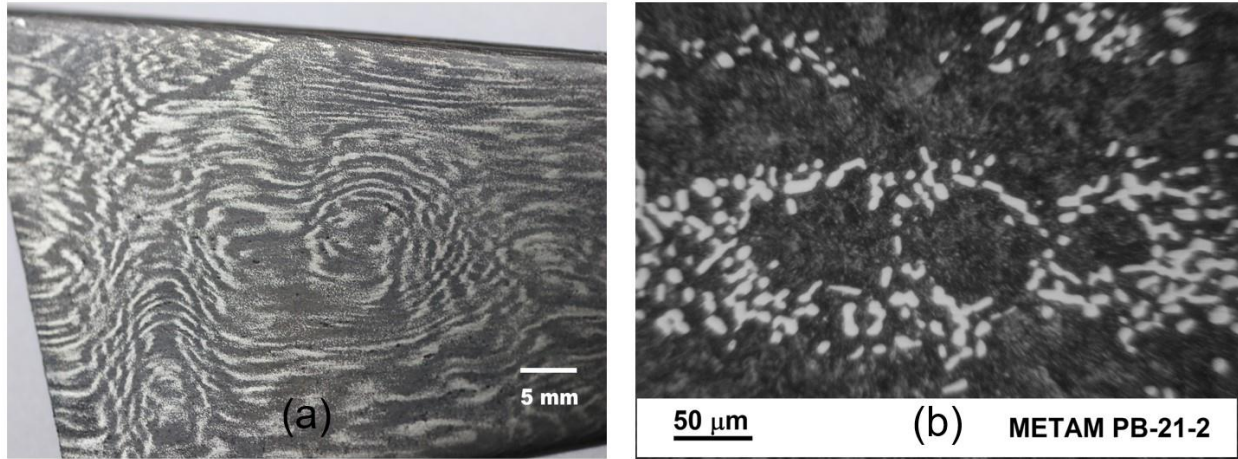


Figure 10: The structure of the front surface of the genuine Damascus steel (Ds15P):  
 a - macrostructure of the knifeblade; b - microstructure of the knifeblade.

In the process of forging on the front surface of the knife blade from Damascus steel are formed areas of concavity and convexity, resembling a topographic contour (Fig. 11). Approximately the local maximum (convexity) and the local minimum (concave), the contour of carbide inhomogeneity acquires elliptical forms, and in the vicinity of the geometric saddle the contour of carbide inhomogeneity is a set of hyperbolic lines. After polishing and etching on the front surface of the knife blade appears of carbides inhomogeneity on a dark background "troostite hardening", resembling pattern "Kara-Taban" ("black-shiny") (Fig. 10, a - b).

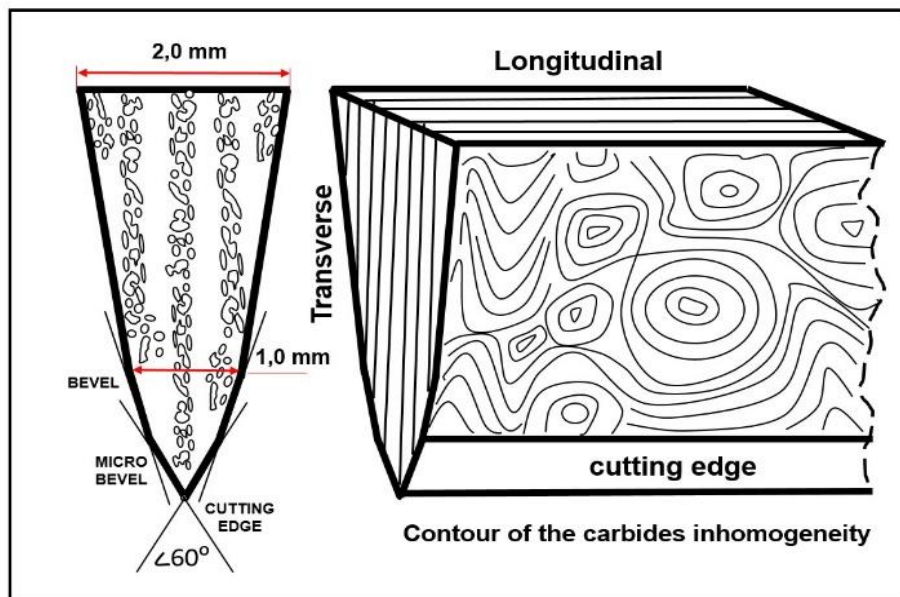


Figure 11: Structural scheme of the knifeblade of the genuine Damascus steel



The transverse part of the knife blade, as well as the butt of the blade (longitudinal direction) has a layered structure (Fig. 9). Closer to the cutting edge of the blade there is observed no more than 5 pieces of carbide layers. Closer to the butt of the blade is observed from 10 to 15 carbide layers. On the cutting edge of the blade, the thickness of the carbide layers and troostite layers the same as on the butt of the blade. The cutting edge of a blade are formed of the layers excess carbides and troostite (Fig. 11). On the cutting edge are formed "micro-saw» from structural elements of Damascus steel, such as of the troostite layer and carbide layers. The cutting process of the "micro-saw" is that the troostite layer wears out faster than carbide layer, that ensuring the effect of self-sharpening.

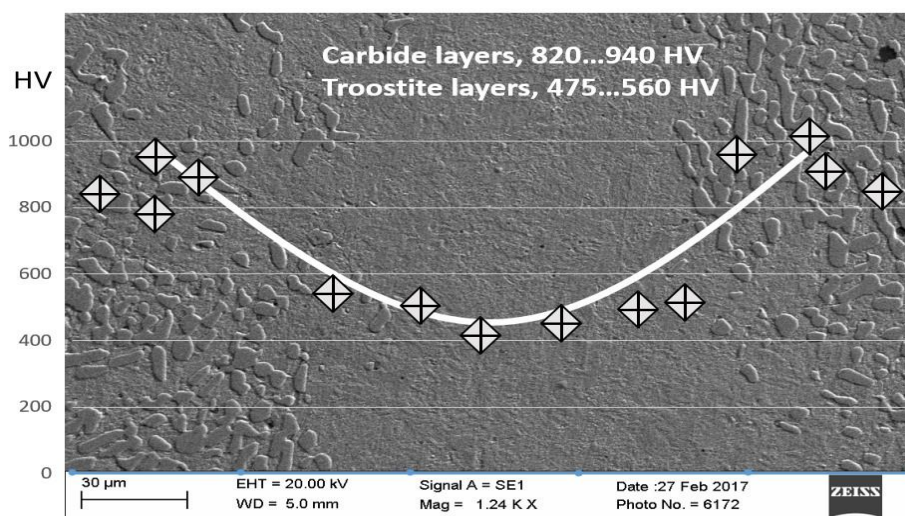


Figure 12: Diagram of the microhardness genuine Damascus steel (Ds15P).

Microhardness in the carbide and troostite layers confirms the effect of self-sharpening of the blade edge. The diagram of distribution of values of micro hardness on layers is given in Fig. 12. The wide range of hardness data in the troostite layer is related to the uneven distribution of dissolved phosphorus. Phosphorus distorts the crystal lattice of the solid solution, which contributes to the strengthening of the ferrite in the troostite colonies. The lowest hardness is observed in the middle of the troostite layer 390...420 HV, where phosphorus impurity is minimal. In the transition zone, at the edge of the troostite layer of micro hardness increases to critical values, reaching almost 580 HV. As a result, the average hardness in troostite layers is 475...560 HV.

In carbide layers, due to the heterogeneity of the distribution of oblong carbides in the troostite matrix, hardness depends not only on the increased phosphorus content, but also from the damping effect of the diamond pyramid. An oblong carbide particle is capable of being pressed into a softer matrix, showing undervalued hardness values. If the oblong carbide particle is hidden under the troostite matrix is observed the effect of damping the diamond pyramid, which leads to an overestimation of the hardness data of the troostite. As a result, the average hardness in carbide layers is 820...940 HV, which is consistent with the data of Gaev (770...1000 HV) [2] and Taganov (average 800 HV) [4]. The integral Rockwell hardness on the knife's butt does not exceed 48 HRC, on the cutting edge of the knife blade reaches 54 HRC. With such hardness of the knives from genuine Damascus steel has a maximum elasticity and good wear resistance at the cutting edge.

According to the shape of the fracture obtained from the impact destruction of the genuine Damascus steel, it is possible to identify the details of the wavy fracture typical of the intracrystalline cleavage. Wavy fracture represents the steps between different local cleavage facets directed along the slip plane. The height of the steps wavy fracture indicates the relationship of impact angle to the direction of cleavage facets within the colony of troostite. We can assume that the cleavage facet, which does not contain wavy fracture, is likely oriented at right angles to the main axis of the impact. Thus, the appearance of a wavy fracture gives us information about the direction of crack propagation during impact.

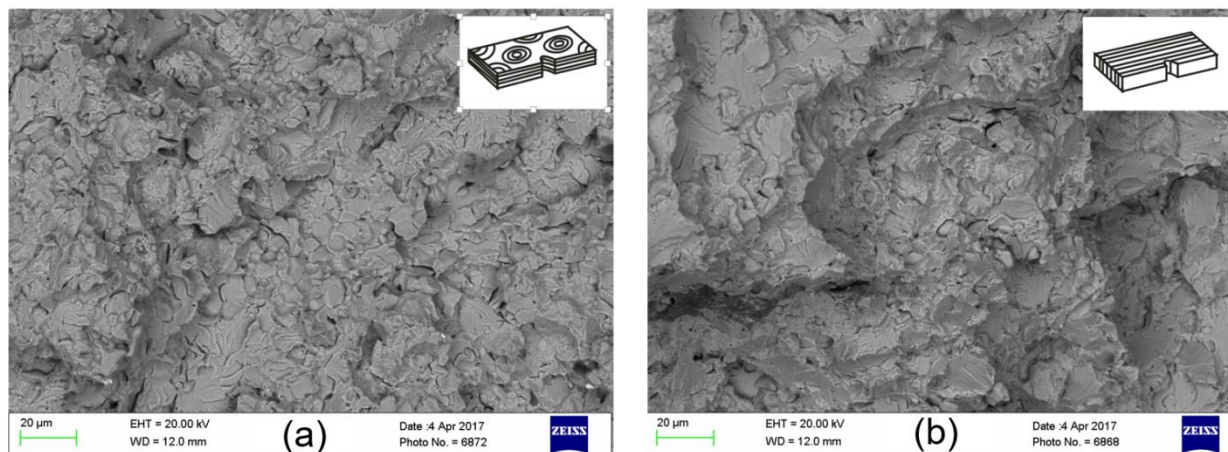


Figure 13: Fractures genuine Damascus steel Ds15P:

a – branching of the crack(longitudinal direction); b – inhibition of cracks(frontdirection).

Wavy fracture changes its orientation, if the path of the crack found in excess oblong carbides. The trajectory of the main crack will depend on the morphology and the number these of excess oblong carbides and their distributions in the troostite matrix.

The crack branching along the carbide and troostite layers in the longitudinal direction impact of the sample from genuine Damascus steel, reducing the energy of crack growth due to the separation of its front (Fig. 13, a). The mechanism of intra-layer cracking is realized, forcing the crack to move in each separate layer.

At front direction fracture of the sample, barriers are formed on the way of crack front propagation in the form of local laminations, which provide full stress relaxation (Fig. 13, b). In front of the main crack front at the interface of carbide and troostite layers is formed, the trap is able to stop her. For further destruction of the sample requires the emergence of new microcracks on the surface of the layer, which requires additional energy. As a result, the resistance to destruction in the front direction increases by 20...25% compared to the longitudinal direction of the impact destruction.

#### 4. Conclusion

Pattern type "Kara-Taban" in genuine Damascus steel is a consequence of carbides heterogeneity obtained in the process of technological operations.

In the chemical composition of most of the Eastern Indo-Persian steel (genuine Damascus steel) there is an admixture of phosphorus (tenths). For a more complete flow of the process of segregation of impurities, ingot (wootz) long annealed in the furnace at temperatures 1200...1250 °C at least 5...6 hours. Under such isothermal annealed, the solidus line, in the diagram iron-carbon is shifted to the left up to the eutectoid point corresponding to 0.8% carbon. Axial areas of austenite dendrites are released from impurities up to hundredths and thousandths percent, which leads to an increase in deformation plasticity under normal forging conditions. Interdendritic intervals are saturated with excess carbon and low-melting phosphide elements, contributing to the formation of eutectic compounds similar in texture and composition to white cast iron. The crystallization point in the inter-axial sections dendritic is reduced below the eutectic line corresponding to a temperature of 1147 °C. Further cooling of the crucible ingot can take place in an accelerated mode.

Forging of the annealed crucible ingot occurs at a temperature above lines Acm at 30...50 °C. The proof of this statement is the complete absence in the structure genuine Damascus steel of the fragments arising from the crushing of the excess carbide phase in the process of low-temperature forging. Low speed of diffusion of phosphorus in austenite matrix contributes to the slow decay of the resulting segregation of carbon in interdendritic intervals, which can significantly increase the temperature of heating for forging, without loss of carbide heterogeneity. Thus segregation of the impurities of phosphorus and carbon in inter-axial portions of the dendrites is formed of parallel layers (fibers), consisting of an oblong (elongated) carbides of cementite and high-purity layers (matrix) of troostite hardening.

The negative influence of phosphorus impurity on the ductility and fracture toughness at negative temperatures with increasing carbon content is widely known. Back in the early XI century Persian thinker Al-Biruni [9] wrote, "bulat cannot stand the cold (Russian) winters and breaks on impact". This quote proves that the Eastern blacksmiths in the pursuit of beauty of the pattern Indo-Persian steel neglected indicators of the structural strength of the blades due to weather conditions. When the content of phosphorus about 0.2% most of the Eastern genuine Damascus steel is not only fragile (cold brittleness), but also hot brittleness, that is, crumble under a hammer while them forging.

Today, on the basis of ancient Indo-Persian blades from genuine Damascus steel has developed a new class high-purity alloys such as Damascus steels ledeburite class type BU16A, BU22A and BU27A [10 - 14], as well as malleable white cast iron type B24A (WCI24HQ) and B27A (WCI27HQ) [15-16], cleared of all impurities. Non-alloy carbon high-purity alloys, having in its structure more heat-resistant eutectic carbides of faceted shape can rightly be considered modern Wootz steels (BULATS).

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