DOI: 10.17580/cisisr.2019.01.12

ANALYSIS OF CHEMICAL COMPOSITION OF DAMASK BLADES FROM THE COLLECTION OF THE MINING MUSEUM IN ST. PERTERSBURG MINING UNIVERSITY

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Key words:

metallurgy, damask steel, Pavel Anosov, X-ray photoelectron spectroscopy, Zlatoust, Tiflis, chemical composition, weapons, impurities.

ABSTRACT

The modern sensor base and tooling allow to evaluate and consider principally in the new way solving of any tasks and problems, connected with the technology of manufacture of unique materials that have been fabricated several centuries ago. Examination of such historical artifacts as damask steel products makes it possible to understand the features of the technological process of their fabrication and to make an adequate evaluation of the typical parameters of these unique steel products.

The researches were conducted with damask weapons from the collection of the Mining museum in St. Petersburg Mining University. These weapons have been fabricated in Tiflis in 1830–1832 and at Zlatoust armoury during XIX century. In general, this collection of cold arms includes 192 pieces. 24 damask blades were selected from it without handle forming, what allowed to take samples of material from a tang without damage of the blade surface and its decorated part.

Analytical investigation of chemical composition of damask blades was conducted based on the Center of Collective Usage (CCU) at the Mining university in the laboratory of analytical researches (LAR) using running X-ray photoelectron spectrometer XRF-1800 of Shimadzu production. Practically all examined samples were characterized by multi-component chemical composition, excluding the dagger fabricated by N. N. Anosov in 1836. The obtained results formed the common database that allows to determine belonging of a damask blade to the concrete place and date of manufacture, based on its chemical composition, region and time period.

Introduction

There are a lot of works devoted to investigations of damask steel and its production technology. Analysis of literary sources shows that today there is no definitive determination of cast damask steel or welded damask steel. In this work we suggest that damask steel is carbon steel with disordered pattern on the blade surface. The authors classify patterned steels by the method of their production proposed by S. N. Vlasov and A. S. Grishko [1]. According to this classification, the first group includes production technology of cast damask steels based on crucible melting. Such melting is characterized by the pattern on the blade surface, due to special crystallization of carbon melt. The second group includes production technology of welded damask steels based on connection of initially uniform steel plates using hammer welding. It is mentioned that the pattern of welded damask steel is more rhythmic and repeated in this case.

The Large Russian Encyclopedia (3rd edition, 1969–1978) separated the terms of damask steel and welded damask steel; however, the archives of the Mining museum dated 1830–1845, all examined material can be related to cast or welded damask steel, what corresponds with the titles in catalogue cards determined almost 190 years ago. The authors take this concept as the basis in this article.

Review of the recent researches of damask steel

The large amount of the works devoted to research of damask steel was published during last years in different countries. All these works (as domestic, as well as foreign) examined mainly chemical composition, microstructure, carbon content and nature of forming of damask steel properties [1–9, 11, 12, 14–17]. Investigations were conducted at different equipment and using different methods, i.e. non-destructive ones (such as spectroscopy, tomography, neutron diffraction etc.) [2–5, 10, 12]. As a result, the authors reached different conclusions. Those who have examined damask blades from Zlatoust armoury, concluded that only damask steel manufactured by Pavel Anosov meets all requirements to such material in chemical composition, pattern and metal structure [15].

However, essential part of weapons investigations is related to Indian and Persian region, where these favourite blades were fabricated. Authors of these works noted that damask steel includes, besides ferrum and carbon, also other elements — Cr, Si, S, P, Zn, As, Mn — in different percentage [2–5].

Aim of the research

Determination of the component chemical composition of solid samples of damask steel. Examination of possibility of relation between chemical composition of samples and date and region of damask steel production.

Analysis of the obtained results and formulation of proposals about possibility of creation of the common database for damask steel products.

Main tasks of the research

The main tasks of the research included determination of chemical composition of solid steel samples using running X-ray photoelectron spectrometer XRF-1800 of Shimadzu production.

Object of the research

24 pieces of damask steel weapons from Tiflis and Zlatoust (9 and 15 pieces respectively) we chosen, without handle forming.

Technique of researches. The researches were conducted on the base of the Centre of collective usage of the Mining university in the Laboratory of analytical investigations, under the leadership of V. G. Povarov. The running X-ray photoelectron spectrometer XRF-1800 of Shimadzu production was used. The samples for analysis were taken from tangs (the blades parts that were not processed and decorated) as powder, average sample mass made 100 mg.

Results of researches. Examinations for carbon content were not conducted in this work, unlike to other research works. Thereby we can't conclude (contrary to the above-mentioned specialists), if the researched blades can be considered as high-carbon steel or no. The obtained chemical composition of the examined samples is presented in the tables 1 and 3.

Tiflis. The results of investigations of the blades from Tiflis region are presented in the **Table 1**. All examined samples displayed multi-component chemical composition.

Nine items were examined: two of them were made by the master Geurg Eliazarov himself (Table 1, No. 1 and 2), two other items – by his son Kahraman Elaizarov (Table 1, No. 3 and 4), three items else were made by V. I. Yuzhakov, the master of Zlatoust factory (Table 1, No. 5–7), and two last items are the sword blades made by the master Karl Wolfertz, also from Zlatoust.

The results presented in the table 1 display that dispersion of the data on Fe content in Tiflis damask steels is rather essential – from 93.83 to 99.79%. Archive sources testify that iron and steel samples were delivered to Tiflis from Zlatoust, and partially local raw materials were used for fabrication of cold weapons [9]. Probably these factors had the effect on Fe content in damask steel.

Presence of different elements in the examined damask steels in addition to ferrum (such as calcium, aluminium, potassium, sodium, magnesium and titanium) can be explained by the features of chemical composition of the crucibles made from refractory clay and used for melting. All obtained results are characterized by higher content of silicium, aluminium and sulfur in comparison with the results of another work [14].

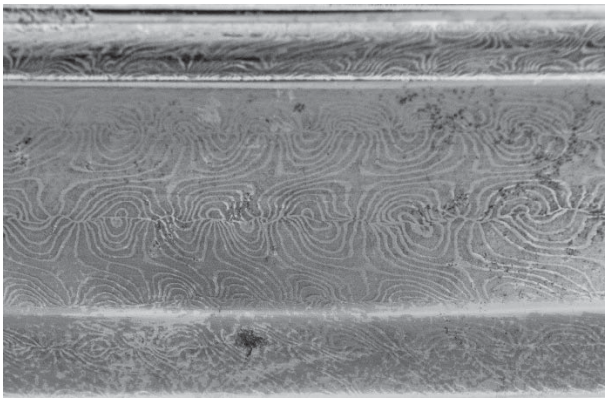
The authors can't confirm presence of increased phosphorus content in Tiflis damask steels as it was mentioned in this work [14]. The measured values for Tiflis vary in the range 0.04–0.1%. It is substantially different comparing with the blades made by G. Eliazarov with 0.14% of P (Table 1, No. 1) and by K. Wolfertz (Table 1, No. 8).

As concerns sulfur content, it can be contained in initial ore (as pyrite and marcazite), in fuel, in iron fines and scrap that were involved in the process of weapons fabrication. Sulfur is also transformed into ash after burning of sulfur-containing fuel. If we use coal as a fuel, it always contain non-combustible mineral impurities including calcium and magnesium carbonates $CaCO_3$ and $MgCO_3$ as well as gypsum, pyrite and rare elements. Sulfur content should not exceed 0.05% according to up-to-date requirements, but only 4 of the examined samples met these requirements, while other were characterized by exceeding the allowable value by several times.

Table 1. **Chemical composition of Tiflis damask steel blades**

No.	Year	Content, %												
		Fe	Cr	Ca	Si	Al	S	Cu	K	P	Cl	Na	Mg	Ti
1	1830	93.83	–	0.76	2.69	0.92	0.31	0.07	0.27	0.14	0.36	0.35	0.23	0.07
2	1830	95.94	–	0.69	1.32	0.48	0.19	–	0.28	0.10	0.18	0.20	0.17	0.14
3	1832	99.79	–	0.00	0.08	0.06	0.02	–	–	0.05	–	–	–	–
4	1832	98.47	–	0.09	0.58	0.47	0.17	0.08	0.07	0.05	–	–	–	–
5	1832	99.63	–	–	0.12	0.10	0.05	–	–	0.05	–	–	–	0.05
6	1832	99.77	–	0.01	0.08	0.10	0.03	–	–	–	–	–	–	0.02
7	1832	99.73	–	–	0.08	0.05	0.02	–	0.01	0.04	–	–	–	0.07
8	1832	97.94	0.05	0.05	0.82	0.63	0.06	0.09	–	0.12	0.14	–	0.10	–
9	1832	95.99	1.53	0.10	0.84	0.86	0.14	0.13	0.07	0.06	0.10	–	–	0.18

Table 2. **Fragments of damask steel blades of Tiflis period (1830–1832)**

Master	Year	Fragment
G. Eliazarov Court sword blade	1830	
K. Wolfertz Sword blade	1832	

Chromium was found only in two blades made by K. Wolfertz. Presence of this element in damask steel and essential dispersion of its percentage is evidently connected with impurities in the initial ore. The area of this ore mining is unknown.

Copper was found in the four samples from the examined nine. Copper content is connected with iron ore delivered from Zlatoust, it contains this chemical element.

Presence of manganese, arsenic, zinc and lead in the examined samples was not revealed, unlike the previous researches [2, 3, 11, 15].

In addition to the abovementioned chemical elements, chlorine was found in composition of the four samples (Table 1, No. 1, 2, 8, 9), it probably remained after surface pickling of blades. It is known that $FeCl_3$ was usually used for pickling of damask steel blades in the XIX century.

Images of several Tiflis blades with different surface pattern are presented in the **Table 2**.

Zlatoust armoury. Zlatoust armoury became famous worldwide in the XIX century owing to unequaled quality of manufactured cold weapons. P. P. Anosov was graduated from the Mining military school (cadet corps) and later worked more than 20 years at Zlatoust armoury; he was known as the author of the technology for production of high-quality cast and damask steel. Production of weapons reached the new level due to his efforts. Damask steel weapons fabricated according to the Anosov's developments [6, 12] occupied the especial place in the Zlatoust factory production range.

The combined **Table 3** includes the results of researches of damask steel samples at Zlatoust armoury during 1836–1880-ies. All examined samples have multi-

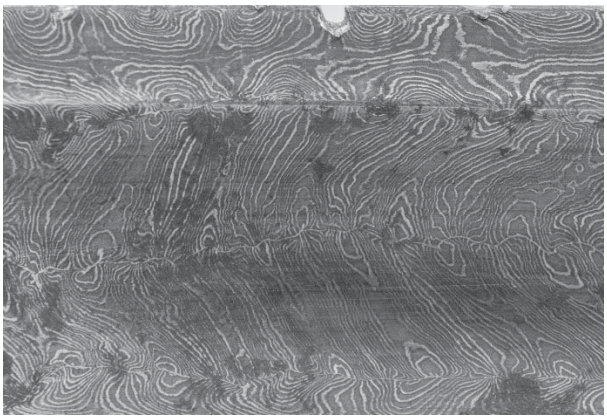
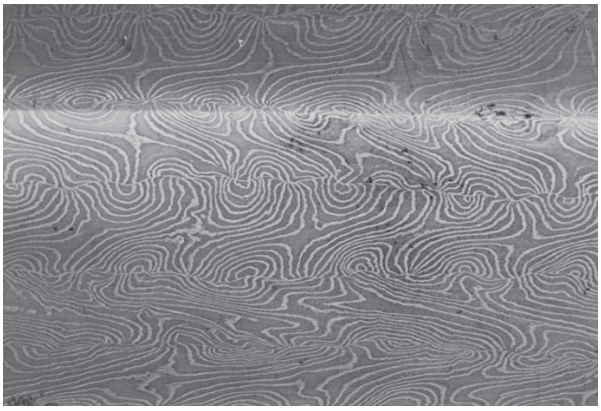
Table 3. **Chemical composition of Zlatoust damask steel blades**

No.	Year	Contents,%													
		Fe	Cr	Ca	Si	Al	S	Cu	K	P	Cl	Na	Mg	Ti	Pb
1	1836	99.72	0.15	0.13	–	–	–	–	–	–	–	–	–	–	–
2	1859	97.61	–	0.03	0.32	0.19	0.15	–	0.05	0.05	0.17	0.27	0.14	0.22	0.81
3	1872	99.01	–	0.02	0.12	0.06	0.10	0.06	0.02	–	0.21	0.12	–	–	0.28
4	1873	99.71	–	0.03	–	–	–	0.24	0.01	–	–	–	–	–	–
5	XIX c.	97.34	–	–	0.24	1.30	0.72	0.09	0.12	0.02	0.04	–	–	0.13	–
6	1879	98.99	0.14	0.02	0.22	0.32	0.11	–	0.04	0.02	–	–	0.13	–	–
7	1879	94.83	–	0.41	1.38	1.02	0.22	0.51	0.28	0.04	0.11	–	0.11	0.10	1.00
8	1879	90.81	–	0.56	3.44	1.93	0.28	0.54	0.74	0.05	0.13	0.35	0.17	0.09	0.92
9	1880	97.13	–	0,.59	0.47	0.25	0.22	–	0.26	0.05	0.69	0.17	0.11	0.06	–
10	1880	97.63	–	0.05	0.50	0.23	0.13	–	0.06	0.04	0.09	–	0.08	–	1.19
11	1880	98.72	–	0.01	0.32	0.29	0.16	0.11	0.04	0.02	0.06	0.18	0.07	–	–
12	1880	93.34	–	0.10	2.06	1.05	0.16	0.72	0.24	0.05	0.16	0.33	0.17	0.67	0.97
13	1880	97.86	–	0.02	0.35	0.18	0.09	0.11	0.04	0.02	0.10	0.23	0.10	0.24	0.65
14	XIX c.	99.26	–	0.03	0.16	0.07	0.09	–	0.03	0.02	0.07	0.18	0.06	0.03	–
15	XIX c.	98.72	–	0.04	0.19	0.07	0.10	–	0.03	0.02	0.07	–	0.15	–	0.61

component chemical composition excluding the dagger fabricated by N. N. Anosov in 1836. This sample includes only three elements: ferrum, chromium and calcium samples (Table 3, No. 1).

The results presented in the Table 3 display that dispersion of Fe content data for Zlatoust blades is rather essential — from 90.81 to 99.72%. The factory used iron ore mined in the nearest surroundings of the plant. Among these mines the following five large ones had the most importance: Orlovskiy, Tesminskiy, Taganaiskiy, Semibratskiy and Atlyanskiy. Hematite (hydro-goethite and limonite) and hydrohematite are considered as the main ore minerals forming ore from all deposits. Minor ore minerals are presented by pyrolusite, manganite, goethite, pyrite and magnetite. Copper can be also found in deposits, what was confirmed by chemical analysis of the examined samples. Ore from all deposits contains very small amounts of phosphorus (0.05%) and sulfur (0.025%), what stipulated high quality of the metal molten from these ores. Since the end of XIX century the main part of raw materials was delivered from Bakalskoe deposit.

Table 4. **Fragments of damask steel blades from Zlatoust armoury**

Master	Year	Fragment
K. Ibach, F. Lorch Sword blade	1859	
S. Fetisov Sword blade	1880	

It can be concluded on the base of the obtained data that dispersion of silicon, aluminium, calcium, magnesium, titanium, potassium and sodium content is rather large. It can be explained by the features of chemical composition of clay materials from the nearest deposits of refractory clays. Local clays were used for manufacture of crucibles that were applied for damask steel melting at Zlatoust armoury in XIX century [7, 13].

Zlatoust armoury is located in the South Ural region, and South Ural clays can be considered as kaolinite-hydromicaceous with montmorillonite and high-plastic in their mineral composition. They are also characterized by rather high content of Fe oxides (up to 3–6%). Magnetite, siderite, rutile, ilmenite and pyrite are also presented in these clays. Relative high content of Fe_2O_3 in clays is determined by usage of clay-type material mainly from the areas covered by residual soils of granodorites and more ferriferous rocks from the boundaries of Chelyabinsk granite massif. Chemical composition of such clay materials includes complicated mixtures of alumosilicates — compounds of silica (SiO_2) and alumina (Al_2O_3). Additionally to these main compounds, oxides of several metals: titanium, ferrum (Fe_2O_3), as well as calcium (CaO), magnesium (MgO) and alkali metals K_2O и Na_2O are included in small amounts composition of clay materials.

As concerns phosphorus content in damask steel, it does not exceed its concentration in ores and varies in the range 0.02–0.05%.

Ore contains up to 0.025% of sulfur, while sulfur content in the examined samples varies from 0.09 to 0.72%, what exceeds substantially the amount of this element in ore. Increased sulfur content in Zlatoust damask steel is caused, by the opinion of the authors, by pyrite presence in the ore, by quality of used coal, by addition of iron scrap and by billet powdering by iron fines.

Chromium presence was revealed only in 2 blades from 15 — in the dagger blade made by P. P. Anosov (Table 3, No. 1) and in sword blade by D. Ronzhin (Table 3, No. 6) with chromium content 0.15 and 0.14% respectively. It should be also mentioned that manganese presence was not found in the examined samples, as well as in Tiflis blades, unlike with the previous researches [14, 15].

Lead presence was displayed in 8 Zlatoust blades from 15. Its content varies in the range 0.28–1.19%, what can be considered as rather high value according to the modern standards. It is known [17] that special lead baths for blade quenching were used at Zlatoust armoury in the end of XIX — beginning of XX century for improvement of battle properties of cold weapons. It is evident that lead appearance in this case was determined by material of these baths, not by ore raw materials. As soon as this investigation includes analysis only of tangs, that were not

subjected to additional processing (such as polishing, pickling etc.) unlike other part of blades, in can be suggested that this factor could have the effect on decrease of content of this impurity. There was only one case of lead inclusion in damask blade (Table 1, No. 2) revealed in the collection of Tiflis weapons that was explained by ore impurity.

Images of several Zlatoust blades with different surface pattern are presented in the **Table 4**.

In addition to the above-described elements, the research displayed chlorine presence in the samples of Zlatoust weapons. This presence was revealed practically in the all examined objects, and its content varies rather widely – from 0.04 to 0.21%. Such high chlorine concentration is caused not only by the technology of blade pickling (as in the case with Tiflis damask blades), but also by chlorine transmission in the obtained damask steel from coal used as the main fuel at Zlatoust factory. Chlorine content in coal varies mainly in the range 0.015–0.15%. Chlorine contains also in coal organic mass as sorbent [5].

Conclusion

Analytical investigation of chemical composition of damask steel blades manufactured in XIX century in Tiflis and at Zlatoust armoury is conducted. The obtained results displayed absence of any chemical elements typical for damask steel blades from the definite regions, unlike previous researches devoted to Indo-Persian and Zlatoust weapon samples. All examined samples were characterized by multi-component chemical composition, excluding P. P. Anosov's dagger. At present time these results are sufficient to create the united common database that will allow to determine the concrete damask steel blade according to its chemical composition, region and time period. In this connection we think that further joint researches together with other museums and collectors are necessary for additional completion of this database.

The research was conducted within RF State Assignment, the theme "Forming of the united scientific-educational information complex based on complex examination of the unique collections and artifacts of the Mining museum", No. 5.12856.2018/8.9.

Acknowledgement

The authors express their gratitude to Dr. Chem. Vladimir G. Povarov, head of the laboratory of analytical researches (LAR) in the Center of Collective Usage (CCU).

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