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STUDY OF THE INFLUENCE OF STRUCTURAL HERITAGE AND OPERATING CONDITIONS ON THE DURABILITY OF SAFETY VALVE SPRINGS FROM STEEL 50KHFA

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Abstract. The reasons for the premature failure of a spring made of steel 50KhFA, which operated in the safety valve of the column's head part of the flare facility, were investigated using analytical chemistry, energy dispersive analysis, macro- and microstructural analysis, electron microscopy, macro- and electron fractography, phase chemical and X-ray structural analysis, hardness and microhardness tests and reductive heat treatment according to the regime recommended for safety valve springs in the standard process documentation and reference literature. The influence of non-metallic inclusions, such as carbides, their chemical composition, shape, and distribution on the operational properties of springs from steel 50KhFA has been investigated. Information on the characteristic external signs, typical micro damages, and the mechanism of destruction during low-temperature hydrogen sulfide corrosion of steel 50KhFA with the most dangerous accompanying process – hydrogenation was obtained. The analysis of the research results showed that the premature failure of the spring is due to both technological heredity and contact with the working environment not envisaged by the project.
Keywords: steel 50KhFA, spring, safety valve, failure, fracture, low-temperature hydrogen sulfide corrosion, cracking, failure mechanism

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1. Introduction

The continuity of equipment operation in the oil refining industry depends on the reliability of safety valves, of which springs are the most important part.

The durability and reliability of springs are laid down at the design stage and must be ensured by the manufacturing technology, quality control, and operating conditions [1,2]. During operation the condition of the safety valve and springs is diagnosed in the manner and volumes provided for by the current regulatory documents, for example, IPKM-05 "Procedure for the operation, revision, and repair of safety valve springs and membrane safety devices of oil refining and petrochemical enterprises of the Ministry of Industry and Energy of Russia".

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However, there have been cases of premature failure of safety valve springs during the operations of refineries. The issues of investigating the damageability of safety valve springs during the operation of oil refineries are covered in the literature to a lesser extent in comparison with the issues of damageability of equipment and pipelines. Moreover, literary sources mainly provide descriptions of the results of fractographic studies of springs [3-10]. Meanwhile, there is mostly no information on the use of other no less informative methods of laboratory research of broken springs. Therefore, the development of a laboratory testing methodology for safety valve springs for establishing the causes of premature failure, the results of the study of the physical and mechanical properties of the metal obtained during its implementation, and the development of recommendations for safe operation in the oil refining industry are of certain scientific interest and have practical significance.

2. Subjects and methods of research

The investigated safety valve springs were made of steel 50HFA, intended for helical cylindrical springs for valve compression. The material of the safety valve springs must have high operational properties, such as elastic limit, endurance limit, and relaxation resistance. The subject of the study is the springs of the SPPK 4r 200-16 (17S7nzh) safety valve installed at the outlet of the column into the flare system of one of the primary oil refining units, which collapsed after 6 years of operation and 6 operating cycles with a design life of at least 30 years and an average operating time failure 360 cycles. The operating temperature of the valve was 51°C, and the pipeline operating environment was C1-C2 hydrocarbon gas with a mass fraction of hydrogen sulfide 0.02%.

To determine the causes of springs failure classical research methods and modern equipment were used, as well as modeling of the initial structural and mechanical condition of the spring material before operation by means of reductive heat treatment. During the study, the following were carried out: visual and measurement control, chemical analysis of the steel composition, energy-dispersive X-ray spectroscopy (EDS) of metal in local areas and corrosion deposits on the surface of the spring, macro- and microstructural analysis, macro- and electron fractography, phase chemical and X-ray structural analysis, hardness and microhardness tests and reductive heat treatment according to the regime recommended for safety valve springs in the standard process documentation and reference literature [11,12]: quenching at 860±10°C and medium tempering at 420±10°C.

Metallographic studies were carried out using a complex of software and hardware for microstructure analysis of the surface of solids based on an optical microscope, as well as a scanning electron microscope for identification of structural components and study of their morphology, mutual orientation, determination of the presence of modified structures in surface layers and defects. The chemical composition of steel and carbide analysis of the metal were determined by analytical methods using a spectrophotometer, an automatic titrator, and an express analyzer for carbon. X-ray structural analysis was carried out on an X-ray apparatus. Microhardness was measured using a microhardness tester with a load of 100 g, and the hardness was measured using the Rockwell method. In addition to the study of the physical and mechanical properties of the metal, a study of corrosion deposits from the surface of the spring was carried out.

3. Results and discussion

The investigated fragment of the spring is shown in Fig. 1a. Visual inspection showed that the number of spring turns, the outer diameter, the diameter of the rod, and other dimensions corresponded to the original parameters of the spring according to the manufacturer's specification. The protective coating on the surface of the spring was damaged in the form of swelling, flaking, side wear, and corrosion (Fig. 1b, 5).

a b

Fig. 1. Fragment of spring after failure: a – fracture surface; b – defects in the protective coating

The chemical composition of the spring's metal, given in Table 1, corresponds to steel 50HFA according to GOST 14959-2016 [13].

Table 1. Results of the analysis of the chemical composition of the spring's metal

Material	Mass fraction of elements, %						
	C	Si	Mn	Cr	V	S	P
Spring	0.517	0.32	0.55	0.97	0.103	0.0053	0.019
Steel 50KhFA GOST 14959-2016	0.46-0.54	0.17-0.37	0.50-0.80	0.80-1.10	0.10-0.20	≤0.025	≤0.025

The hardness of the test samples (Table 2) is lower than the recommended by the regulatory documentation and reference literature. After the heat treatment carried out by the quenching and medium tempering regime, according to the recommendations of ST TsKBA 030-2006 [11] and reference literature [12], the hardness became within permissible limits, which indicates a non-optimal heat treatment regime used during the production of the spring. Low hardness may indicate a decrease the in elastic limit, relaxation resistance, and endurance limit. However, during the audit shortly before the failure during the test for threefold compression of the spring, no deformations were found, which indicates the preservation of its elastic properties. The endurance limits for bending σ_{-1} and torsion τ_{-1} can be roughly estimated by the characteristics of static strength, for example, Brinell hardness, using relations (1) and (2) given in the reference literature [14,15]:

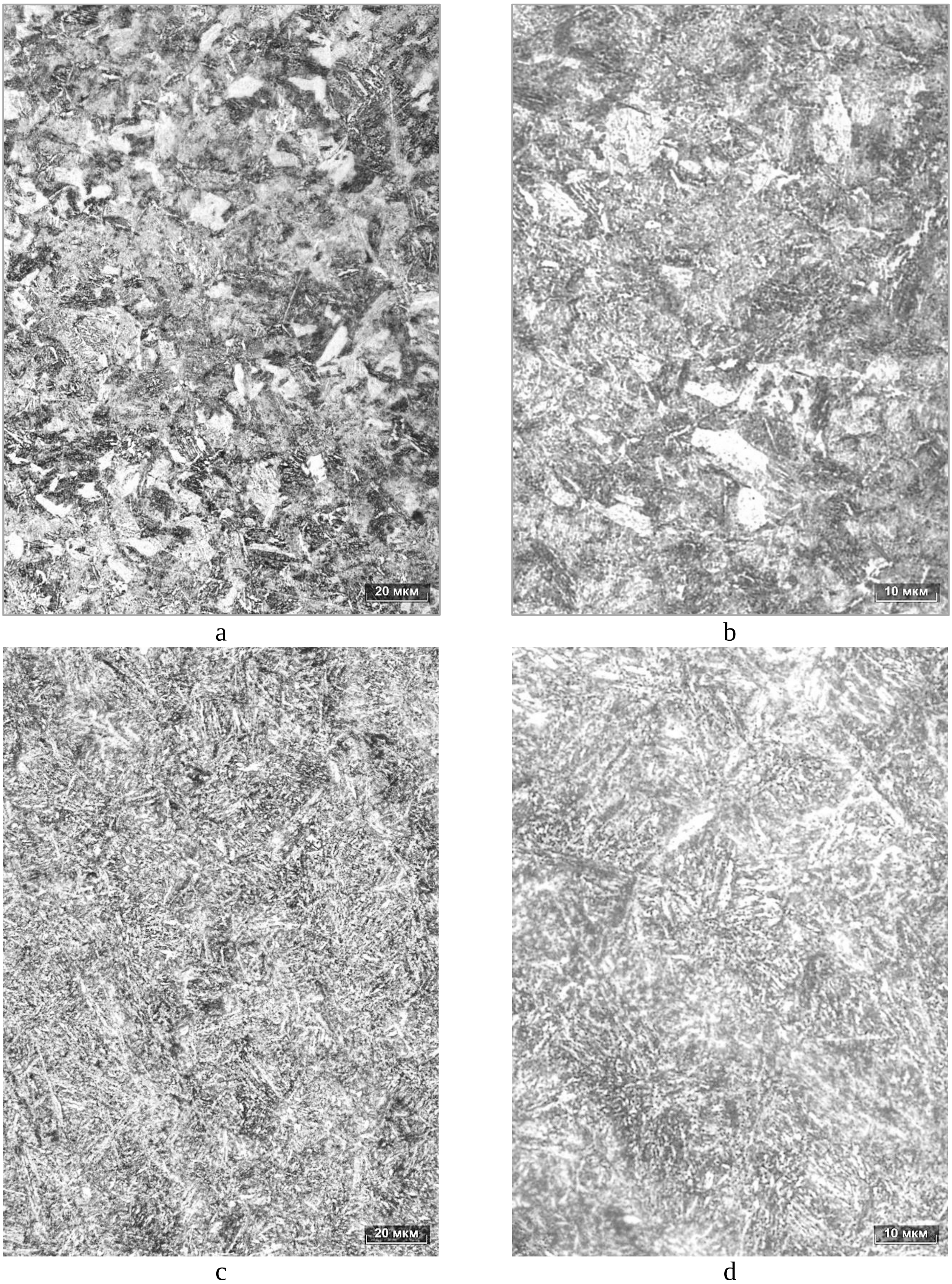
$$\sigma_{-1} = 0.18\ HB, \quad (1)$$

$$\tau_{-1} = (0.50 \ldots 0.65)\ \sigma_{-1}\ . \quad (2)$$

An approximate estimation according to formulas (1) and (2) shows that the endurance limits of the metal after operation were approximately 1.2 times lower than the endurance limits after reductive heat treatment, while the calculated value of τ-1 after the operation (410-500 MPa) turned out to be lower than the value given in the reference literature [15] for the recommended heat treatment regime (519 MPa).

Despite the spring's low hardness, it is still exceeded the limiting values of 20-22 HRC, at which steel does not expose to hydrogen sulfide stress cracking [16], which is important due to the presence of hydrogen sulfide in the working environment.

The microstructure of metal with the different fineness of special carbides (Table 3), which manifests itself in areas with different etching on the microsection (Fig. 2 a, b) and visible on SEM images at ×25000 (Fig. 3 a), as well as the orientation along martensite indicated quenching and medium tempering. The presence of bright polyhedral grains with carbide precipitates and low hardness (Table 2) indicated an insufficient heating temperature or a low cooling rate during quenching with the formation of regions of non-martensitic structures. After reductive heat treatment, the structure became more homogeneous (Fig. 2 c, d).



a b

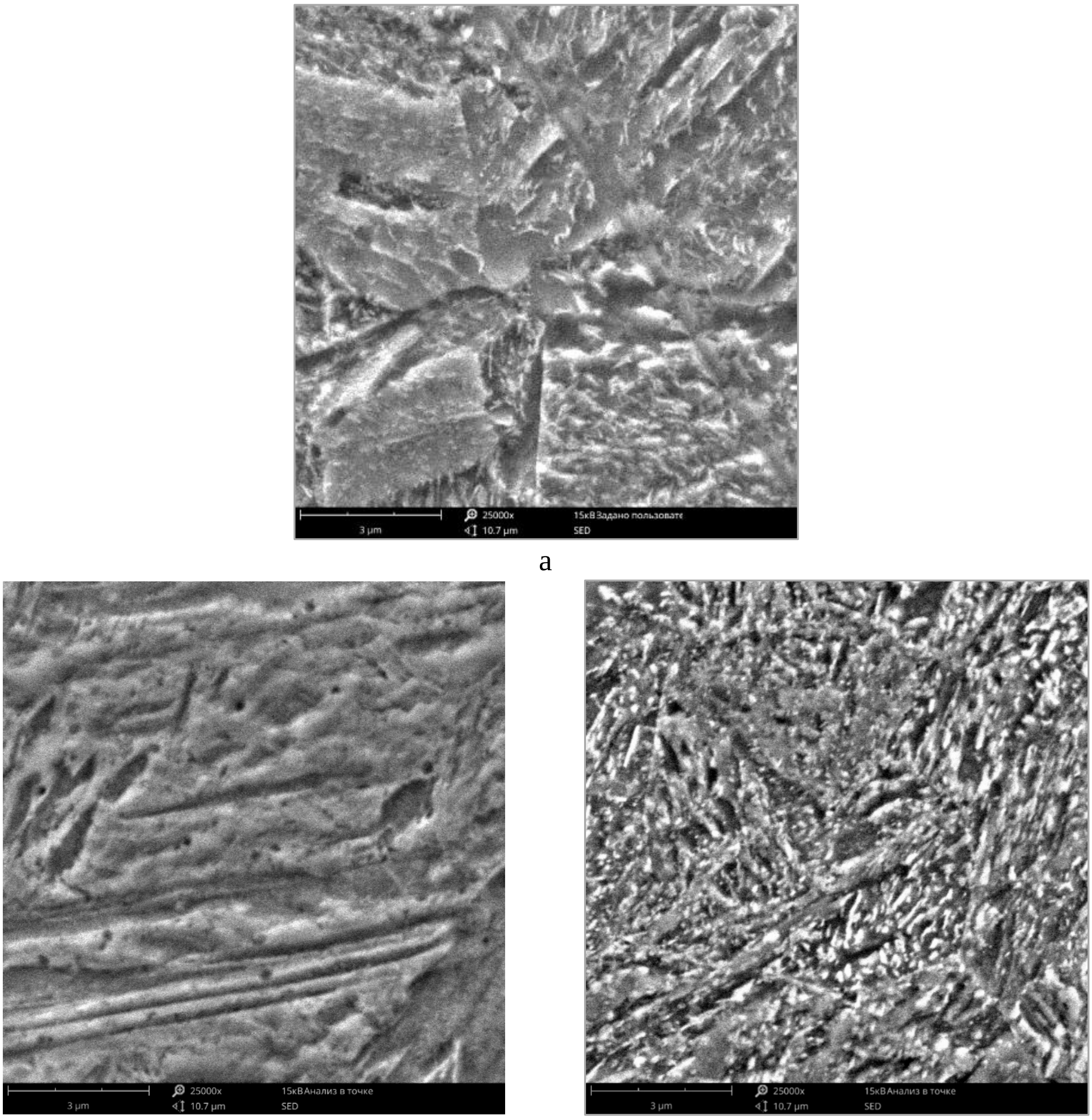
c d

Fig. 2. The microstructure of the spring's metal after the operation (a, b) and after heat treatment (c, d): a, c – ×500; b, d – ×1000

Table 2. Results of the springs hardness testing

Material	Hardness HRC	
	After operation	After reductive heat treatment
Investigated spring, 50KhFA	38-45 (40.8) *	46-51 (48)
Steel 50KhFA GOST 13764-86 [17]	44.0-51.5	
Steel 50KhFA ST TsKBA 030-2006 [11]		
Steel 50KhFA [14]	42-49	
Steel 50KhFA [12]	44-49	

Note: * - mean values in brackets



a

b

c

Fig. 3. Morphology of the carbide phase in the spring's metal, x25000, SEM image: a – after operation; b – after operation + quenching: c – after operation + quenching + tempering

A comparison of the morphology of the carbide phase before (Fig. 3 a) and after (Fig. 3 c) reductive heat treatment showed that the initial material had a lower distribution density of carbides with a predominance of lamellar precipitates. After the reduction heat treatment, the structure was dominated by round-shaped carbides with a size of 0.1 μm. It should be noted that the presence of carbides in the form of plates is not a defect and it's typical for spring steel after quenching and medium tempering, in contrast to coagulated carbides after high tempering, which reduces the elastic properties of springs.

The results of the phase X-ray diffraction analysis of the spring's metal (Table 3) indicated that the main type of carbide was a carbide Me_7C_3, in particular $(Cr, Fe)_7C_3$, typical for steel 50KhFA in the condition after medium tempering and operation at 51°C [18]. Vanadium carbides were absent in the carbide deposit because their precipitation usually occurs at a higher tempering temperature (above 500°C) [19]. Therefore, the embrittlement of the spring's metal due to the possible precipitation of fine vanadium carbides during tempering did not occur.

Table 3. Results of carbide analysis

Material	Mass fraction of elements, %				The relative content of the Cr in carbides, %	Carbide type
	Carbide precipitate			Solid solution		
	Fe	Cr	Σ	Cr		
50KhFA	2.198	0.071	2.269	0.899	7	Me_7C_3

Phase chemical analysis showed that only 7% of chromium turns into carbides, and the rest remained in a solid solution, which, along with carbide and dislocation hardening mechanisms, provides a solid solution mechanism for steel hardening. However, the total chromium content in steel of 0.98% cannot provide corrosion resistance in the working environment of the safety valve in question, which entails the need to protect against the working environment falling on its surface via a high-quality seal of the detachable valve connections and a protective coating that turned out to be damaged.

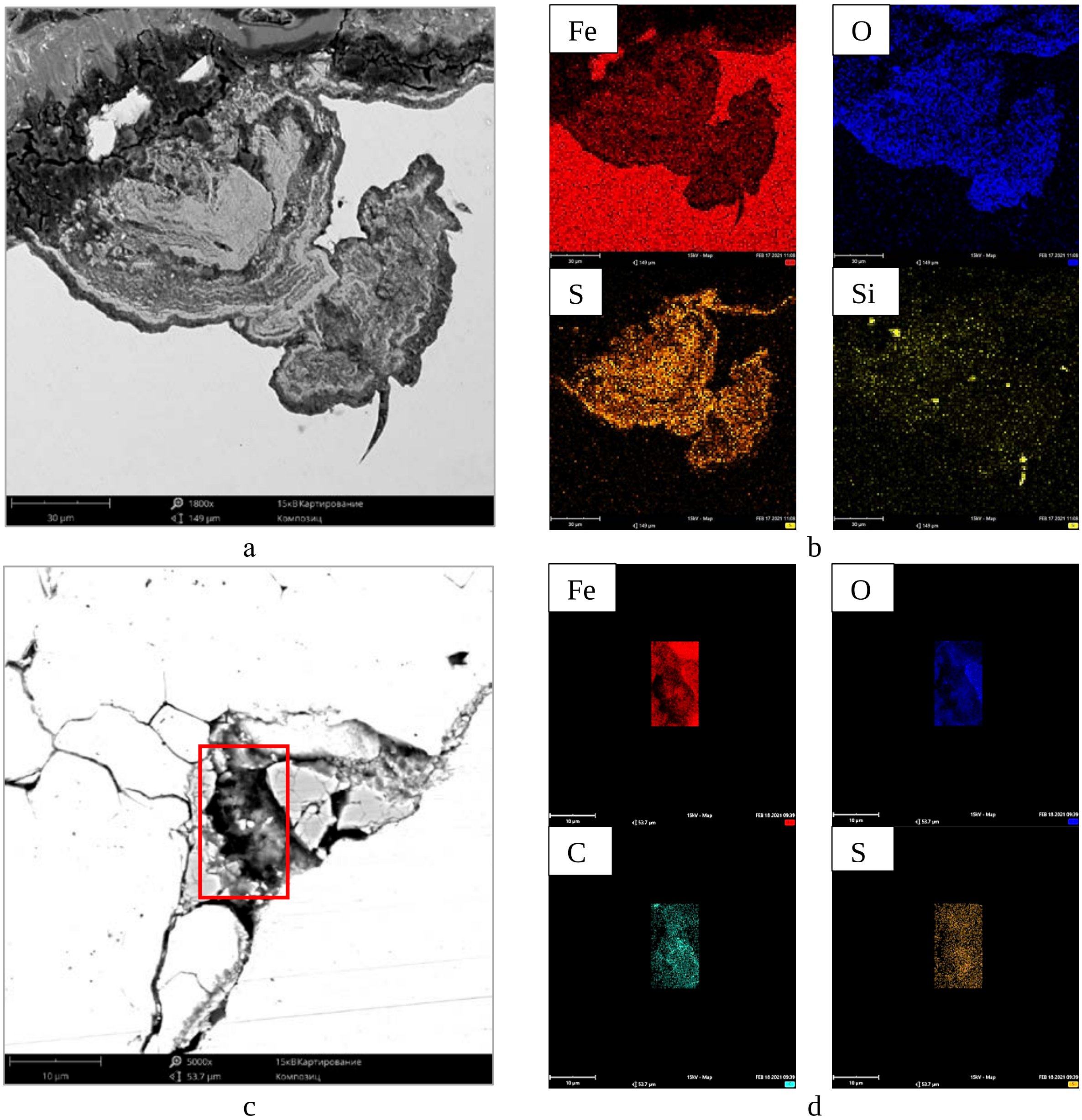
In the study of the macro- and microstructure of the samples, a decarbonized layer with a depth of 0.056-0.1 mm was revealed, which was formed, probably, during technological operations of spring production. The minimum values of the metal microhardness, measured by the cross-section of the rod, corresponded to the zone of the decarbonized layer (Table 4). Since most of the elastic elements work in torsional conditions, when the maximum stresses fall on the surface layer, the presence of a soft decarbonized layer contributed to the damage to the surface under the protective coating and the formation of crack origin.

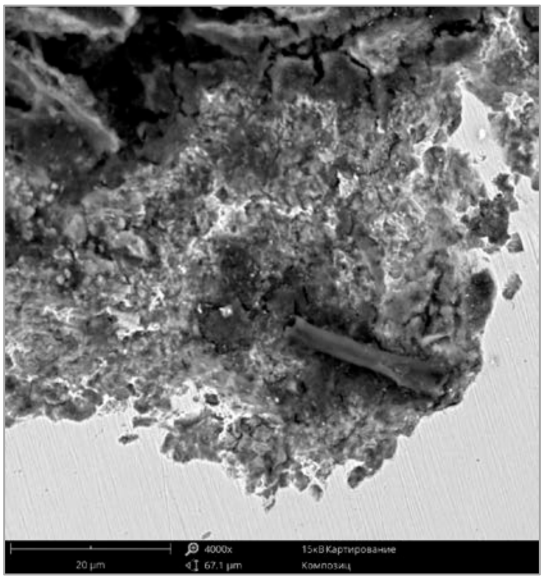
Table 4. Microhardness of metal measured on microsection

Microhardness $HV_{0,1}$		
Microsection edges	The central part of the microsection	Decarburized layer
30.5-42.6 (38.2) *	30.0-37.8 (35.3)	18.2-21.4 (20.2)

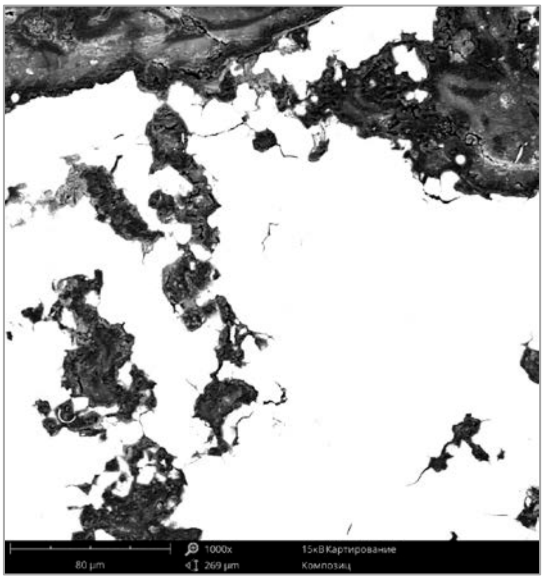
Note: * - mean values in brackets

The study of the microstructure in the places of damage to the protective coating, revealed during visual and measurement control, showed the presence of multiple surface microdefects of the metal in the form of ulcerative damage and penetrating of corrosion products into the deep layers of metal (up to 1/3 of the rod section), as well as the destruction of metal near non-metallic inclusions and cracking mainly along the boundaries of primary austenite grains (Fig. 4). Analysis of the distribution of chemical elements in cavities and cracks (Fig. 4 a-d) indicated a significant content of sulfur and oxygen, which indicated the occurrence of low-temperature hydrogen sulfide corrosion. The propagation of damage along with the structural elements and the morphology of cracks on microsections after etching with a 4% of HNO_3 solution are shown in Fig. 5, from which it can be seen that cracks propagate not only along the boundaries of primary austenite grains, where the largest precipitates of carbides are located but also along the interphase boundaries of oriented plates of carbides, pores in the matrix of the solid solution are also visible (Fig. 5 a, b). The smallest micropores up to 0.5 μm in martensite, which were not eliminated by quenching during the reduction heat treatment (Fig. 3 b), were also found on microsections cut away from the surface of the spring, which may be due to the presence of hydrogen in the steel formed during low-temperature hydrogen sulfide corrosion.





e



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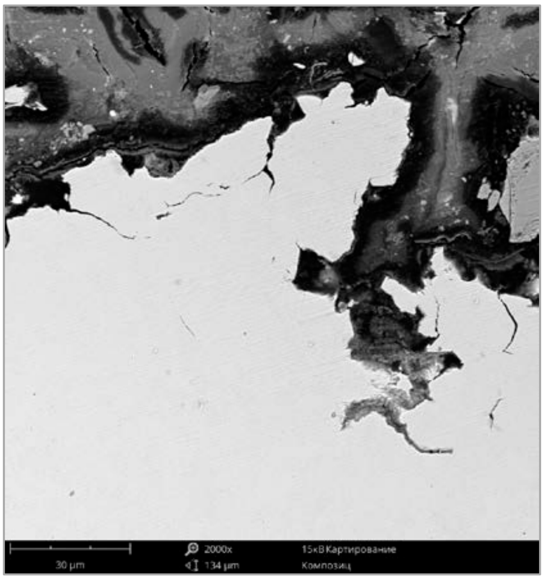
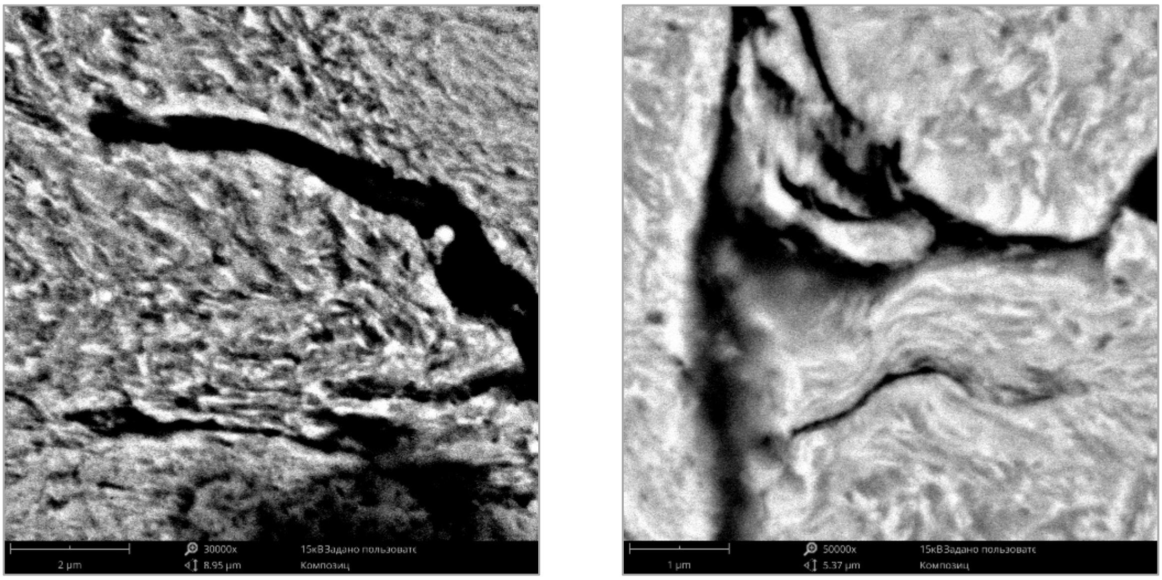


g

Fig. 4. Defects in the spring's metal at the crack origin, not etched:
a, c – analyzed surface; b, d – element distribution map; e – destruction of metal at sulfide;
f, g – cracks and penetration of corrosion products into the deep layers of the metal

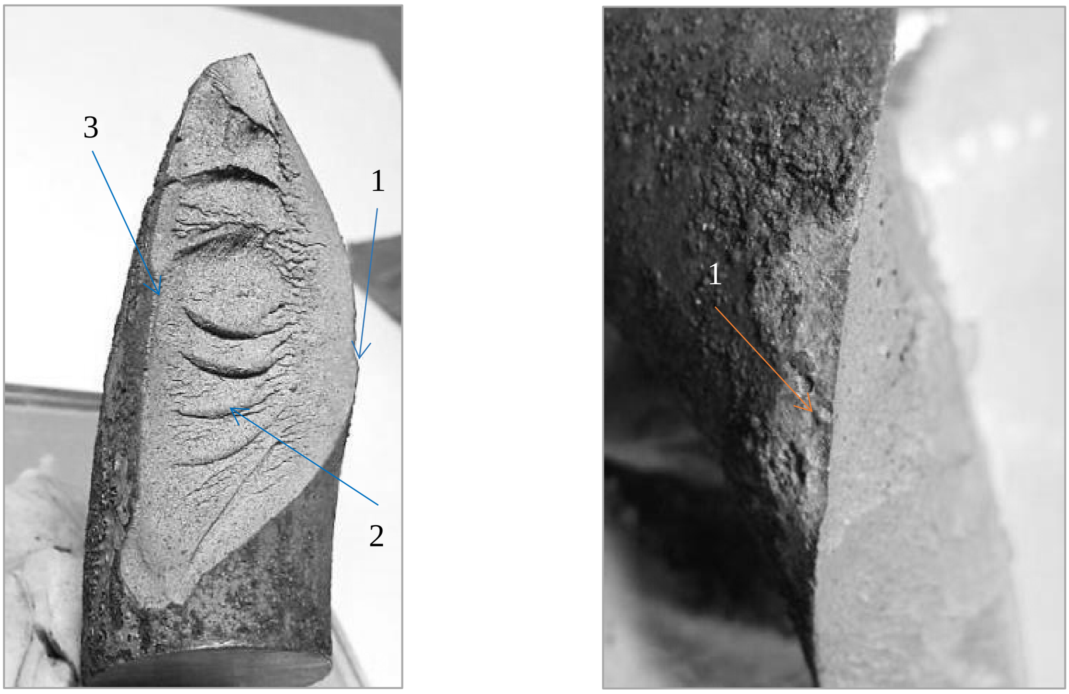
Figure 5 b shows that when the cracks form an almost closed loop, the metal is deformed under hydrogen pressure with the subsequent formation of cavities that reduce the resistance to operational loads and lead to failure.

Fractographic research has established that the fracture is matte, dark gray in color. The fracture surface was oriented at an angle of 45° to the axis of the rod and perpendicular to the direction of action of the maximum tensile stresses during torsion, in the central part there was a concavity characteristic of quasi-brittle materials [20]. The macrogeometry of the fracture indicates the formation of fracture during the workloads. According to the macrostructure, the spring's fracture was characterized by the following successive zones: first – zone of crack origin with smooth relief, second – zone of failure crack propagation with ratchet marks, and third – fast fracture zone with less rough areas (Fig. 6). At the crack origin, determined by the convergence of ratchet marks, and located on the outer surface of the spring between the small and large turn radius, there was a loss of protective coating, as well as ulcerative damage on the surface (Fig. 6).



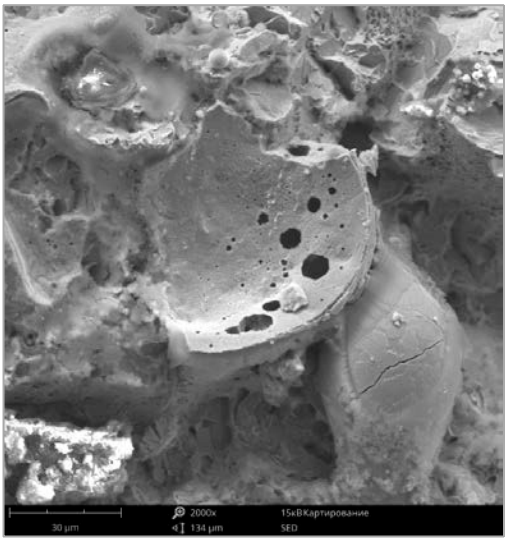
a b

Fig. 5. View of cracks after etching: a – × 30000, b – × 50000

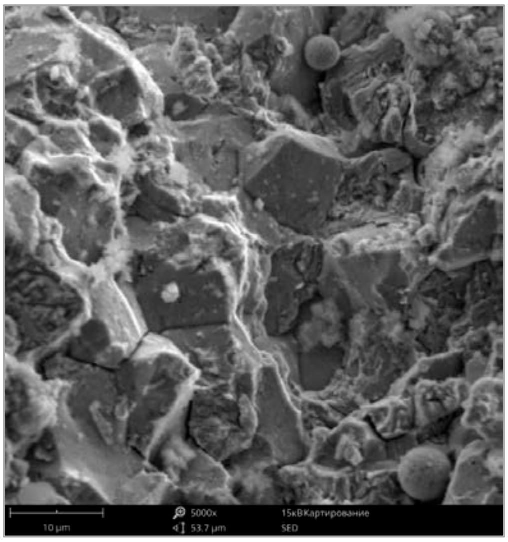


а б

Fig. 6. General view of the fracture of the spring:
1 – crack origin; 2 – failure crack propagation zone; 3 – fast fracture zone



a



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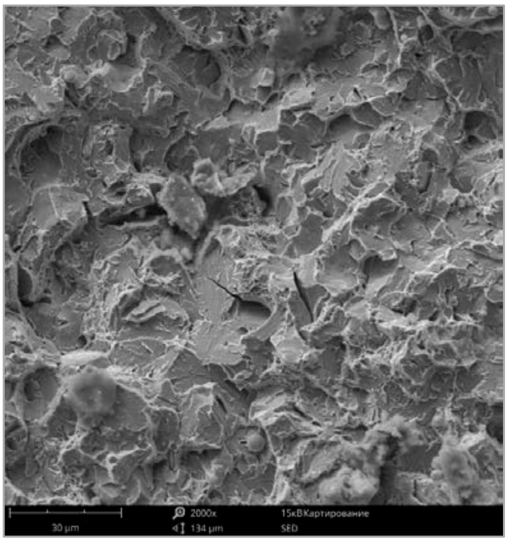

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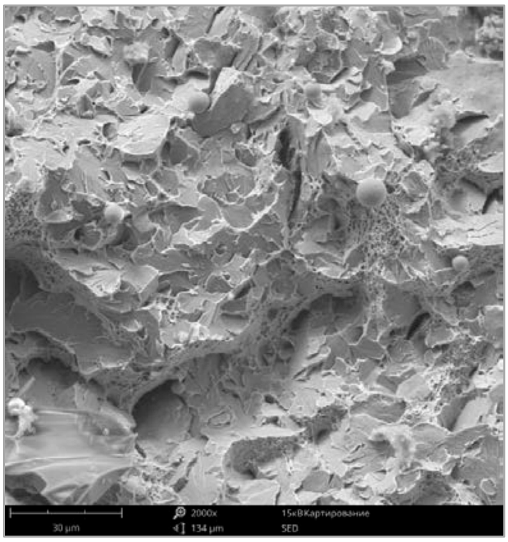
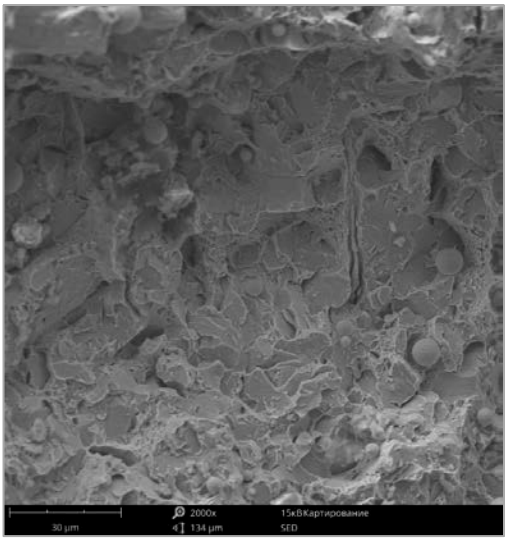


d



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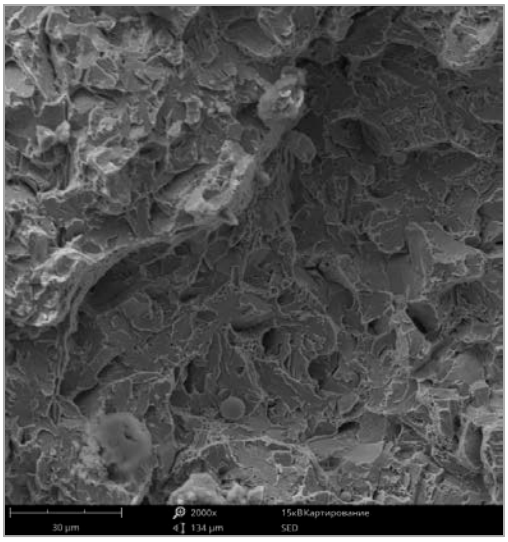

f

Fig. 7. Electron fractography of the spring's failure surface:
a, b – crack origin; c, d – failure crack propagation zone, zone of ratchet marks,
e, f – fast fracture zone

According to electron-fractographic studies, corrosion products were present in the crack origin coinciding with the place of damage to the coating, in the decarbonized surface layer there were open cavity-bubbles, bubbles with cracks (Fig. 7 a), non-metallic inclusions, intergrain facets, and cracks characteristic of corrosion damage were observed (Fig. 7 b). In the zone of failure crack propagation (Fig. 7 c, d) there were facets of cleavage and quasi cleavage, splitting by non-metallic inclusions, as well as pores typical for slow cracking under the influence of hydrogen [4,20-22]. The fracture surface in the ratchet marks zone was formed by facets of intercrystalline fracture with alternating quasi-cleavage and some areas of the dimple fracture. The fast fracture zone was characterized by facets of intergranular, transcrystalline fracture with areas of dimple fracture (Fig. 7 e, f). Thus, the propagation of the crack along the body of the spring proceeded by the mixed brittle-ductile mechanism.

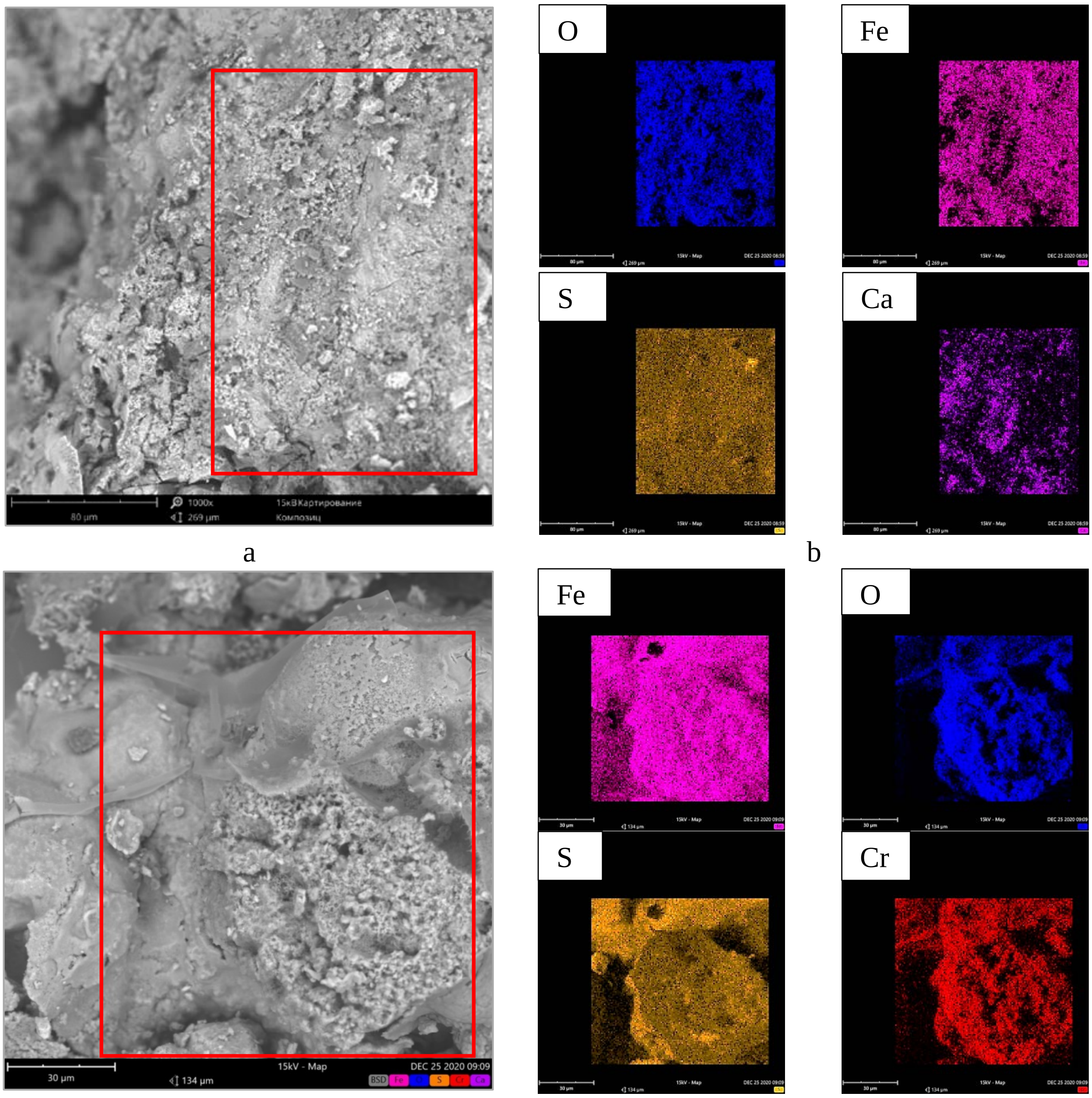

Fig. 8. Results of EDS of corrosion deposits from the metal surface:
a, c – analyzed surface; b, d – element distribution map

Using EDS corrosion deposits collected from the surface of the spring were investigated (Fig. 8), on the basis of the results of which it can be argued that the environment is highly aggressive, the deposits mainly consist of iron sulphides FeS, oxide compounds of iron and sulfur, as well as particles containing a large number of chemical elements represented by pigments and fillers included in the composition of the protective coating.

Thus, the summation of the results of the study allowed us to conclude that the cause of the spring failure was low-temperature hydrogen sulfide corrosion. The most dangerous concomitant process of low-temperature hydrogen sulfide corrosion is the hydrogenation of steel, which is confirmed by the presence of blistering under the deposits. Such blistering is the result of the presence in the cavities of either hydrogen sulfide itself or hydrogen released during the reaction of hydrogen sulfide with iron. Hydrogen, diffusing deep into the steel, accumulates in places within crystal lattice defects and non-metallic inclusions, eventually forming internal pores and causing the development of microcracks, which ultimately lead to the creation of significant internal stresses and embrittlement of the metal. The presence of moisture in the working environment significantly accelerated low-temperature hydrogen sulfide corrosion and hydrogen saturation of steel, thereby accelerating its embrittlement.

4. Conclusions

1. A comprehensive method has been developed for determining the causes of the safety valve spring's failure using standard and special research methods, including reductive heat treatment.

2. Analysis of the results of metal research showed that premature failure of the safety valve spring is due to technological heredity (alloying system that does not provide corrosion resistance in the hydrogen sulfide environment, non-optimal heat treatment regime with the formation of a structure corresponding to insufficient hardness, strength, reduced fatigue resistance, low corrosion resistance of the surface of the rod with the presence of a decarburized layer, insufficient protection of the spring against corrosion by the protective coating) upon contact with the working environment not provided for by the project.

3. Based on the results of the analysis of corrosion deposits, it was revealed that the environment is highly aggressive, the deposits mainly consist of iron sulfides FeS, oxide compounds of iron and sulfur, as well as particles containing a large number of chemical elements represented by pigments and fillers included in the protective coating, and the cause of the spring failure was low-temperature hydrogen sulfide corrosion.

4. It has been established that at low-temperature hydrogen sulfide corrosion of steel 50KhFA, blistering and ulcerative damage are formed on the surface of the spring with the penetration of corrosion products into the spring's metal. The destruction of the metal occurs at non-metallic inclusions, along the boundaries of the primary austenitic grains, where the largest carbides are located, as well as along the interphase boundaries of the oriented carbide plates. When cracks form an almost closed loop, the metal is deformed under the pressure of hydrogen, followed by the formation of cavities that reduce resistance to operating loads and lead to failure. The solid solution contains multiple micropores up to 0.5 μm in size, which cannot be closed by reductive heat treatment. The information obtained on the characteristic external signs, typical microdamages, and the mechanism of failure during low-temperature hydrogen sulfide corrosion of steel 50KhFA with the most dangerous concomitant process – hydrogenation can be used by researchers in the diagnosis of spring failure.

5. On the basis of the studies carried out, a set of measures was recommended to improve the reliability and prevent the failure of safety valve springs operating in similar conditions: hardness measurement during receipt inspection, periodic visual measurement control, capillary, and magnetic particle inspection; monitoring the condition of the sealing surfaces; ensuring the quality of valve assembly after repair and alignment of the parts installation; the use of protective covers – bellows made of 08Cr18Ni10Ti steel or more

corrosion-resistant for similar springs, which do not allow penetration of aggressive environment to the surface of the spring.

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