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# Influence of impurities contained in fuel and air on sulfide corrosion of turbine blades of the gas turbine engine

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**Abstract:** In the process of improving gas turbine engines (GTE), increasing the resource and efficiency, there is a constant increase in temperature and pressure of the working fluid. Turbine elements are subjected to high thermomechanical loads and continuous exposure from the aggressive environment. These impacts are especially significant for the working blades of the first stages of the turbine, located in the area of the highest temperatures. One of the most serious types of damage in this case is the corrosive effect on the working blade from the combustion gases entering the flow part of the turbine. The TS-1 fuel used on an aircraft contains sulfur compounds in its composition – elemental sulfur and mercaptans, which in the combustion process, together with sodium and potassium in the air, leads to an aggressive effect on the material of the turbine blade. To ensure the long-term operation of the turbine blades of the turbine at the gas temperature at the turbine inlet up to 800...850 °C, the content of these products in both fuel and air is limited according to the regulatory and technical documentation. However, it is not yet possible to exclude them completely. The presence of sulfur compounds on the turbine blades of the GTE causes sulfide corrosion. Therefore, the article considers the influence of impurities in fuel and air on the process of sulfide corrosion of the turbine blades material of the turbine. The mechanism of sulfur dissolution in metal oxides or protective coating is presented, as well as the diffusion of sulfur oxide from the coating surface into its depth. The reason for the influence of sodium chloride contained in the air on the corrosion of nickel alloy or the protective coating applied on it has been established. The influence of vanadium in the fuel on the corrosion rate is given. In order to increase the efficiency of the turbine blades when exposed to such an aggressive environment, it is proposed to use a new coating formed from an aqueous suspension and allowing the introduction of chromium into the coating, which provides a higher durability of such a coating in comparison with serial aluminide coatings. The introduction of chromium is ensured by an exothermic reaction occurring during the formation of the coating during heat treatment.

**Key words:** sulfur, sulfide corrosion, atomic lattice, protective coating, corrosion processes, impurities, nickel alloy.

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# Влияние примесей, содержащихся в топливе и воздухе, на сульфидную коррозию лопаток турбины газотурбинных двигателей

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**Аннотация:** В процессе совершенствования газотурбинных двигателей (ГТД), повышения ресурса и коэффициента полезного действия (КПД) происходит постоянный рост температуры и давления рабочего тела. Элементы турбины подвергаются высоким термомеханическим нагрузкам и непрерывному воздействию со стороны агрессивной среды. Эти воздействия особенно существенны для рабочих лопаток первых ступеней турбины ГТД, находящихся в области наиболее высоких температур. Один из самых серьезных видов повреждений в данном случае – коррозионное воздействие на рабочую лопатку со стороны газовых продуктов сгорания, поступающих в проточную часть турбины. Применяемое на воздушном судне (ВС) топливо ТС-1 содержит в своем составе сернистые соединения –элементарную серу и меркаптаны, что в процессе сгорания совместно с находящимися в воздухе натрием и калием приводит к агрессивному воздействию на материал рабочей лопатки турбины ГТД. Для обеспечения длительной работы лопаток турбины ГТД при температуре газа на входе в турбину до 800…850 °С содержание данных продуктов как в топливе, так и в воздухе, согласно нормативно технической документации, ограничивают. Однако исключить их полностью пока нет возможности. Присутствие соединений серы на лопатках турбины ГТД вызывает протекание сульфидной коррозии. Поэтому в статье рассматривается влияние примесей в топливе и воздухе на процесс протекания сульфидной коррозии материала лопаток турбины ГТД. Представлен механизм растворения серы в оксидах металла или защитного покрытия, а также диффузия оксида серы с поверхности покрытия в его глубь. Установлена причина влияния содержащегося в воздухе хлористого натрия на коррозию никелевого сплава или применяемого на нем защитного покрытия. Приводится влияние находящегося в топливе ванадия на скорость коррозии. С целью увеличения работоспособности рабочих лопаток турбины ГТД при воздействии такой агрессивной среды предлагается применение нового покрытия, формируемого из водной суспензии и позволяющего ввести в состав покрытия хром, что обеспечивает более высокую долговечность такого покрытия в сравнении с серийными алюминидными покрытиями. Введение хрома обеспечивается за счет экзотермической реакции, протекающей в процессе формирования покрытия при термической обработке.

**Ключевые слова:** сера, сульфидная коррозия, атомная решетка, защитное покрытие, коррозионные процессы, примеси, никелевый сплав.

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# Introduction

Different types [1, 2] of coating are developed and used in purpose of GTE turbine performance increase.

Analysis of the gas turbine engine blade protective coating use, along with laboratory tests allows us to distinguish the two specific areas of their damage while use and testing, depending on the temperature – that is 650…850 °C and up to 1050 °C [2–6]. There are moderate corrosion processes in 900…1050 ˚C temperature interval due to use of protective coating and $Al_2O_3$ – $Cr_2O_3$, highly protective from gas corrosion, on it.

Combustion products and ash sediment corrosion impact [4, 6, 7, 8] (fig. 1) is a type of turbine engine blade protective coating damage, which decreases their performance.

External inspection of blades after running hours shows us, that there is a blast of pinpoint lodgment mainly on blade pressure side (colour

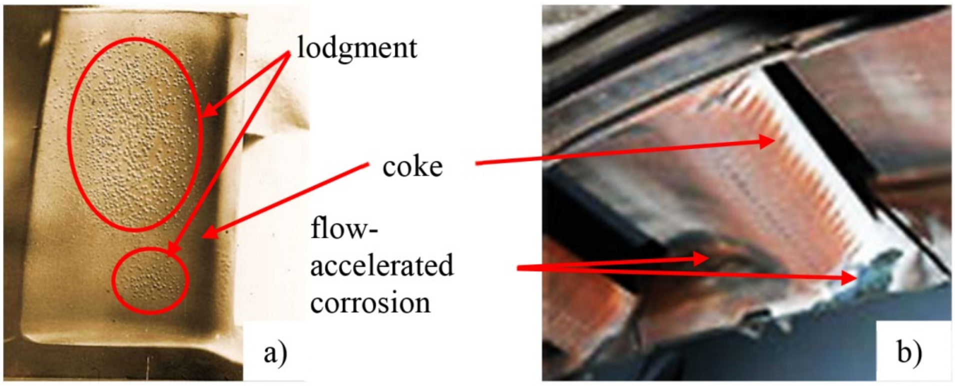

**Fig. 1.** The appearance of the working (a) and nozzle (b) blades after operating time 10671 hours

from light up to dark brown) (fig. 1, *a*) on the blade web surface. Flow-accelerated damage of protective coating, along with coke ash lodgment (fig. 1, *b*) is detected on nozzle cluster blades due to aggressive gas flow.

There is local lodgment on blasts, which work on fuel of high sulfur concentration, generally consisting of $Na_2SO_4$ (≈74%). Such lodgment is a basic sulfide corrosion reagent, whether there is no lodgment, then there is no corrosion.

It should be mentioned, that due to high temperature impact turbine gas atmosphere and impurements on GTE turbine blades, which lead to their intensive corrosion, are highly oxidizing, increasing the corrosion rate [9–11].

Presence of sulfur compounds in combustion gases or in turbine blade lodgment is a main condition for sulfide corrosion. Thus, it is meaningful to observe the mechanism of sulfur introduction in metal crystalline grid or oxides on its surface, which will help us understand, what actions it is necessary to take in order to decrease sulfide corrosion impact.

## Results and discussion

Let us consider approximate impurities, which lead to corrosion, and their sources in combustion chamber, in order to understand turbine blade sulfide corrosion mechanism while maintenance.

Sodium chloride is a basic compound, which leads to sulfide corrosion, invading combustion chamber along with the air [4, 6, 12]. This is particularly evident while aircraft operation in coastal areas and above the sea [13].

Sulfur and alkalic metals, as main corrosion agents, may invade GTE combustion chamber along with the fuel. Fuel may be polluted with sodium chloride whether water invades it. Vanadium, chlorum, lead, hydrocarbon or their compound [6, 12, 14] may also occur in GTE combustion chamber along with the fuel, which accelerates corrosion processes.

Covering, which protective feature is aluminum and chrome oxide – $Al_2O_3$ and $Cr_2O_3$ cyclization, is applied onto turbine blades in order to prevent high temperature oxidation. Therefore, sulfur invades oxide crystalline grid while combustion in finely crushed forms and influences the hole cyclization, in other words, defect balance [15].

Nickel oxides [1, 5] are cycled on blade surface while operation when covering protective features are exhausted and nickel is diffused into covering. In this case sulfur is implied into anion nickel oxide subbarray decreasing vacant electron hole concentration and increasing hole concentration. This can be described with an equation:

$$^1/_2\, S_2 \rightleftarrows S_0^{**} + V_{Ni}^{//} \tag{1}$$

or

$$^1/_2\, S_2 + O_2 + 2h \rightleftarrows S_0^{**} + {}^1/_2\, O_{2,} \tag{2}$$

where $S_0^{**}$ – is an electropositive sulfur atom, entered in place of oxygen ion;

$h$ – vacant electron hole;

$V_{Ni}^{//}$ – bivalent cation tie-up.

Besides that, sulfur can be entered in interstitialcy oxide space, not influencing crystalline grid defects.

Wagner presented the oxidation theory in 1930s [16] and found out, that sulfur diffusion rate in polycrystal nickel and cobalt oxides is an order of magnitude higher than in monocrystals of 1000 °C temperature and more [17, 18].

It is necessary to find out diffusion of sul-fur and sodium chloride, in other words, mechanism of their dilution in oxides, in purpose of protective coating development, with ability of long-term work in their aggressive impact conditions.

Condition which should be complied in purpose of sulfur diffusion:

$$P_{S_2}^{//} > P_{S_2}^{/}, \tag{3}$$

where $P_{S_2}^{//}$ и $P_{S_2}^{/}$ – partial sulfur pressures on calx-gas and calx-metal faze border respectively. Equation (3) will be complied in case of complying the following inequation:

$$P_{S_2}^{/} > \exp\left(\frac{2\Delta G_3^0}{RT}\right), \qquad (4)$$

where, $\Delta G_3^0$ – thermodynamical potential, $R$ – gas constant, and $T$ – absolute temperature.

It can be said, that alloy-determined sulfur diffusion is possible whether:

$$P_{S_2}^{//} > \exp\left(\frac{2\Delta G_3^0}{RT}\right). \qquad (5)$$

Sulfur dioxide $SO_2$ molecule diffusion runs on bead borders, through micro-breaks, cavings in a calx. While diffusion sulfur dioxide reacts with calx metal and metal activity will increase with moving further. Therefore, partial oxygen pressure will decrease with moving further to metal border. Consequently, sulfur compound may cycle under the calx even while low sulfur steam pressure [18]. Such a process shows us the opportunity of the rapid nickel alloy damage, containing the traces of sulfur dioxide.

Water steams invade the GTE gas track along with sulfur combustions, containing sea salt, which sodium chloride *NaCl* [12] is a basic component of, leading to nickel alloy corrosion rate increase.

In case of sodium chloride presence in a fuel or in air, invading GTE, and in sulfur oxide presence with $t_m$ ≈885 °C there are the compounds in combustion products:

$$4NaCl + 2SO_2 + O_2 + + 2H_2O \rightarrow 2Na_2SO_4 + 4HC1 \qquad (6)$$

$$NaCl + H_2O \rightarrow NaOH + HCl \qquad (7)$$

While GTE operation the sodium natrium particles collapse on turbine blades surface and sulfate.

Protective coverages [1, 5] on GTE turbine blades cycle the aluminum and chrome dioxides – $Al_2O_3$ and $Cr_2O_3$. Sodium natrium practically does not interact with aluminum dioxide. It cycles volatile products, leading to slick bulbing and damage, with chrome dioxide, along with chrome-containing alloys. Nevertheless, coverages with chrome oxide $Cr_2O_3$ are sodium chloride resistant.

The main reason of sodium natrium influence is chemical reactions running:

$$Cr_2O_3 + 6NaCl + O_2 = = 3Na_2CrO_4 + 2CrCl_2 \qquad (8)$$

$$Cr_2O_3 + 2NaCl + {}^1/_2\, O_2 = = NaCrO_4 + CrO_2Cl_2 \qquad (9)$$

Volatile chloride and oxychloride cycling increases with higher temperatures, leading to more chloride natrium impact on nickel alloy corrosion.

Vanadium impurity influences on corrosion rate increase. Compounds, which can cycle while vanadium-containing fuel combustion, depending on temperature:

– vanadium trioxide (melting point $t_m$ = 1970 °C):

$$4V + 3O_2 \rightarrow 2V_2O_3 \qquad (10)$$

– vanadium tetroxide ($t_{пл}$ = 1970 °C):

$$2V_2O_3 + O_2 \rightarrow 2V_2O_4 \qquad (11)$$

– vanadium pentoxide ($t_{пл}$ = 675 °C):

$$2V_2O_4 + O_2 \rightarrow 2V_2O_5 \qquad (12)$$

Mechanism of vanadium impact on corrosion process in common is in oxide slick damage, increasing its porosity and oxidation rate due to $V_2O_5$ influence, along with diffusion flow increase through chrome oxide and sodium natrium influence.

The following protective coating damage mechanism on turbine blades is confirmed with the research conducted by the authors. The blades (fig. 1, *a*) of GTE turbine at gas-pumping station were analyzed. The metallographic research of working blades in maximum lodgment areas (fig. 1, *a*) after operation and baseline protective coating (fig. 2).

As we can see, there is a corrosion of AZH-8 coverage surface in local lodgment areas. Protective coating corrosion is of frontal (areal) character at 500…700 mkm distance under local saline lodgment layers. In case of pitting layer affection

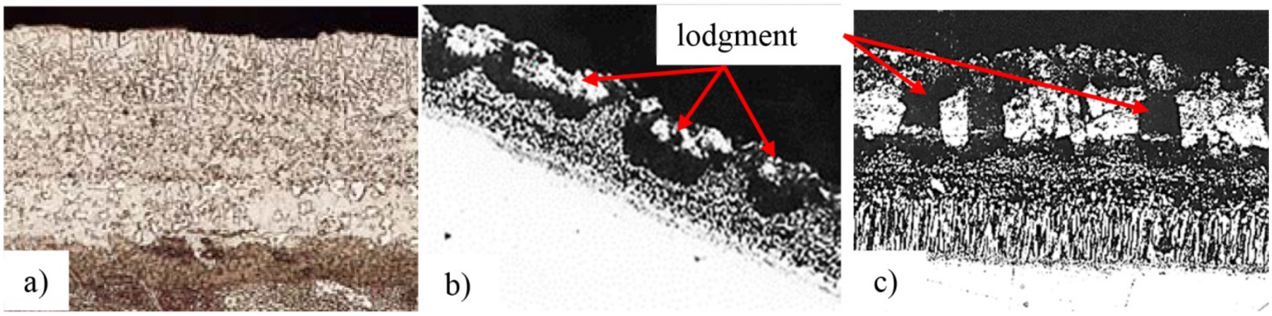

**Fig. 2.** The microstructure of the coating AZH-8 on the blade before operating time (a) and with an operating time of 10671 hours on the side of the trough (b) and the back (c)

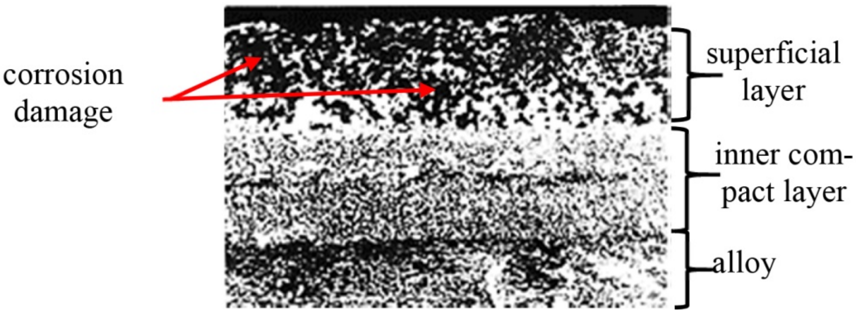

**Fig. 3.** Microstructure of AZH-8 coating after laboratory tests for sulfide corrosion

there is a wedge shaped corrosion spreading in depth of the coverage.

Such a character of AZH-8 coverage corrosion is also confirmed with sulfide corrosion laboratory tests (fig. 3).

As we can see in Figure 3, saline corrosion has invaded only 50% of coverage depth and stopped before the NiCrTaWAlSiHfY pattern, which is more corrosion resistant, than the outside zone of β- and γ/-fazes, formed while chrome aluminizing.

The results of the research confirm the above-mentioned mechanism of protective coverage damage due to impurities combustion products impact in fuel and air and aggressive atmosphere impact on GTE working blades.

The laboratory tests for sodium natrium impact on differently gained protective coverages were conducted. Chrome alumined (ChA) coverage, mass used in aircraft construction, formed in bulk solid with gas circulation (CCA) method was applied on nickel alloy samples. The research of the new coverage, formed of a water suspension of excessive chrome content – 10…13% was conducted as an alternative to the following coverages. There is an exothermal reaction while thermo vacuum annealing in a new coverage, which has allowed us to imply chrome in coverage [19, 20].

The sea salt water dilution, containing 58% NaCl, 26,5% $MgCl_2$, 9,8% $Na_2SO_4$, 2,8% $CaCl_2$, 1,6% KCl, 0,5% $NaHCO_3$, 0,2% KBr was applied on ZhS6U samples. Every sample was soaked in the following dilution for no less than 3 times and was dried outdoors within 15 minutes. Afterwards the samples were weight in purpose of salt mass overweight, which was about 5 ± 1 mg/cm$^2$. The tests were conducted with 1100 °C temperature, and the calx quantity in crucibles (fig. 4).

The results of the research showed us, that the coverages may be set in the following sequence from the resistance (change of the appearance) up to corrosion (in descending order): NPH, CCA, HA (fig. 4). The samples were weight along with the crucibles in purpose of estimation by calx quantity in a crucible. There was a insignificant white-coloured calx quantity in NPH crucible. Apparently, this is a crumbled salt with a insignificant quantity of corrosion

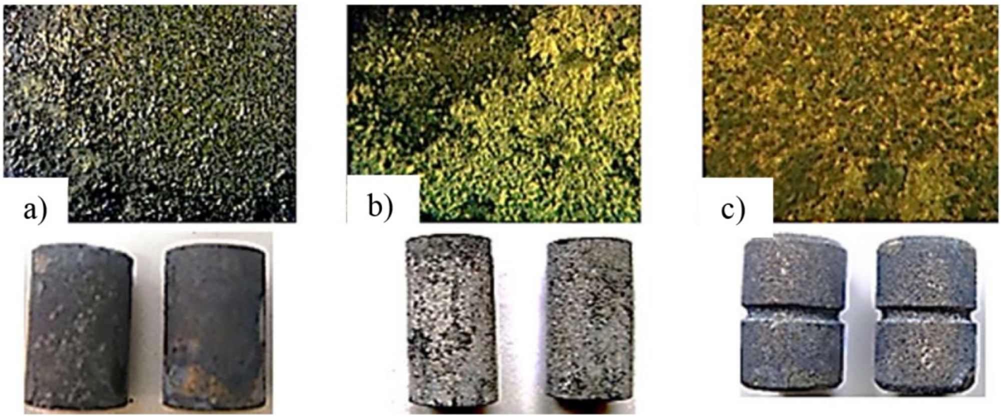

**Fig. 4.** Surface structure and general appearance of samples from the alloy ZhS6U with protective coatings: *a* – HA, *b* – CCA, *c* – NPH after salt corrosion for 100 hours at a temperature of 1100 °C

products. There is more dark and large size calx in CCA and HA coverage crucibles.

The research confirms the above-mentioned (formula 8 and 9) sodium natrium impact on protective coverage. Implication of about 10% of chrome allows to increase its resistance to gas corrosion, due to $Cr_2O_3$ protective oxide slick cycling, along with aggressive combustion products resistance.

## Conclusions

1. It is possible to increase GTE turbine blade working capacity, working in an aggressive gas flow for a long time, using the protective coverage, allowing to decrease their tendency to corrosion. The working capacity of coverages on the blades depends on many factors and first of all on their pattern.

2. The mechanism of protective coverage and metal destruction due to dilution and diffusion of sulfur, invading the turbine blade protective coverage from fuel, in the coverage depth is presented according to the conducted research.

3. The laboratory tests allowed us to determine the impact of sodium natrium in the air, invading the turbine blade surface along with the combustion products, on the corrosion destruction of the protective coating.

4. The presence of sulfur, sodium natrium and vanadium in combustion products leads to corrosion rate increase.

5. Chrome alloy addition to coverage increases corrosion resistance, consequently, allowing us to increase their longevity while working with aggressive combustion products.

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