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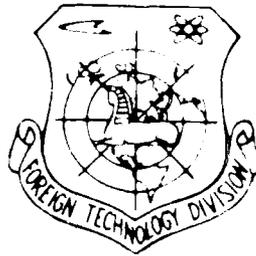
FOREIGN TECHNOLOGY DIVISION



INVESTIGATION OF GAS CORROSION OF NICKEL ALLOYS AND
THEIR PROTECTIVE COATINGS

by

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<p>ABSTRACT (U) The gas corrosion resistance of ZhS6-K and EP-99 alloy specimens was studied under conditions similar to those under which gas-turbine blades made of these alloys operate. The sulfur content of the diesel fuel, the velocity of the gas stream and the temperature of the combustion were varied, and in some cases salty water or sea water was injected into the gas stream. It was found that the sulfur content of the diesel fuel did not significantly affect either the rate or the nature of corrosion of the specimens. However, the injection of droplets of salty water or sea water considerably decreased the corrosion resistance of the specimens. Specimens with two-component diffusion coatings covered with protective layers had very high corrosion resistance. Their weight loss due to corrosion was 6-15 times lower than that of noncoated specimens.</p>				

INVESTIGATION OF GAS CORROSION OF NICKEL ALLOYS AND THEIR PROTECTIVE COATINGS

K.I. Lutsenko

(Odessa)

The problems of corrosion of metals and alloys in gases and media containing sulfur gases have recently acquired particular importance in connection with the extensive use of high-sulfur liquid fuels in technology. At temperatures above 800-900°C, the corrosion resistance of many alloys whose mechanical characteristics adapt them for work at these temperatures is found to be inadequate [3].

Tests of specimens and alloys used to make gas-turbine buckets are run on equipment that does not fully duplicate the working conditions of the products. As a rule, laboratory-test specimens are in a medium at static equilibrium, so that it is impossible to take account of the influence that may be exerted on corrosion rate by gas-flow head and increased surface roughness, which is a major factor in determining the aerodynamic characteristic of the buckets [1, 2].

As a rule, marine gas turbines use diesel fuel. However, almost no research has been done on the corrosion stability of nickel-base alloys and their protective coatings under the conditions imposed by the combustion products of this fuel. The literature sheds little light on the problem of gas corrosion of chromium-nickel alloys in the presence of SO₂ at elevated temperatures. There are no data at all from study of these alloys under the conditions of accidental entry of sea, river and rain spray into the gas-turbine induction system - something that occurs frequently in practice as a result of the large amounts of air drawn by gas turbines from the environment.

To ensure that specimens would be tested under conditions similar to those under which the buckets of gas-turbine engines work, an erosion-corrosion testing machine that permits wide-range regulation of the composition and flow rate of the combustion products and the temperature and velocity of the gas flow, as well as injection of salted and sea water into the combustion chamber, was built following a proposal of K.V. Olisevich.

The first stage of the study provided for investigation of

the alloys ZhS -K and EP-99 to determine corrosion stability in a gaseous stream of combustion products of diesel fuels with increased and reduced sulfur contents. Specimens of these alloys were weighed before and after testing to within 0.0001 g. The preliminary conclusion as to degree of corrosion was drawn from the weight difference and the external appearance of the part. However, the specimen weight change is not an unequivocal index to stability, especially for coated specimens, because of the varying volatilities of the oxides of elements. After the tests, therefore, microstructural studies were made to determine the surface state of the specimens and the distribution of corrosion into the interior. The scale and the points of failure of the specimens were also subjected to x-ray structural analysis.

The test procedure provided for testing at various gas-flow speeds and chemical compositions at temperatures of 800-1300°C, with injection of salt water for times adequate to obtain characteristic corrosion failures.

One of the important objectives was to obtain surface corrosion damage within a relatively short time because of the large number of specimens with their wide variety of coatings. For this reason, the continuous-testing time was less than 30 h.

The specimens were enclosed in cartridges in such a way that one of the sides of the specimen was protected from active onflow and was situated in a zone of stagnant gas flow. This provided for protection of thermocouples from premature burnout and made it possible to study the influence of the corroding gases on the alloy in their stagnation zone. The mounted specimen was washed intensively by a stream of gaseous diesel-fuel combustion products containing sea-water vapor, solid particles of salts, and their new chemical compounds with the combustion products. A stop watch was used to establish the dripping frequency of the water (observations through the sighting window of the metering unit).

To determine the influence of NaCl on the corrosion process more precisely, experiments were conducted under the same conditions, but with the sea water replaced by distilled water containing dissolved NaCl in the amount present in solid sea-water residue.

To complete the picture of the influence of solid-residue salts on the gas-corrosion process of the alloys, experiments were conducted without water injection, with ground solid sea-water residue and NaCl and MgCl₂ injected directly into the gas flow.

Color photography was used in classifying the corrosion-damage types by color. It was noted that specimens of ZhS6-K alloy, which had sustained severe corrosion damage, were dark green and had little damage. Specimens whose diffusion coatings were preserved were orange and dark orange. Color photography also brings out the "engraving" of the surface damage better because of the light-and-dark gradations.

Surface roughness was measured in studying the scale. During the initial phase of corrosion, the combustion products blister

out on the surface, a phenomenon that can be used to mark the onset of the damage. Specimens with diffusion coatings have lower finish classes after testing because of microscopic cracks and blisters in the protective film. It is possible to determine these changes if surface roughness is measured before and after the tests, followed by comparison of the finish classes and the recorded roughness profiles.

Specimens of the ZhS6-K and EP-99 alloys were subjected to tests (lasting 30 h) at 800-1000°C with brief heating to 1300°C for 1.5 h. The variation of the gas-flow velocity, angle of attack, and the excess-air ratio and the substitution of high-sulfur (up to 0.81% S) for low-sulfur diesel fuel did not make it possible to obtain characteristic specimen damage. As a result, a thin, tough layer of scale formed and did not peel off. Traces of edge burning and gas erosion were observed. The metallographic examinations established a difference in the nature of oxidation at the grain boundaries and down the depth of the damage. Chemical analysis indicated less sulfur in the specimen scale than in bucket scale. Subsequent experiments were therefore conducted with water injection into the combustion-chamber air intake.

After 15 h of testing at 800°C, the layer of scale that had formed was separated, and layer-type corrosion began, with the appearance of small blisters. The microscope showed porosity at the points of scale formation, and the surface was black with a dense white deposit. The back of the specimen had been corrosion-damaged over 0.5 of its area. Metallographic examinations showed surface cracks resulting from corrosion on all three specimens. On the last specimen, a layer of a nonmetallic phase and grain-boundary oxidation extending to a depth of 100-150 μm were detected.

At 900°C, the specimen showed a severely corroded surface after the tests. The scale that formed peeled off, exposing a green blister-speckled surface with deep gouges resulting from pitting damage to the alloy. Layerwise destruction of the upper layer with pitting was clearly visible under the microscope. A dark scale had formed on the back of the specimen and some of it had crumbled. The specimen-thickness measurements made before and after removal of scale showed a thickness decrease of 0.5-0.55 mm. Microscopic examination showed severe corrosion of the surface, with the damage extending to a depth of 300-500 μm . The damaged layer consisted of three zones: a) an outer, nonmetallic phase 100-140 μm deep; b) a nonmetallic phase along grain boundaries to a depth of 200-400 μm ; c) aggregates of nonmetallic point inclusions arrayed parallel to the surface. Dealloying had occurred to a depth of 300-500 μm , and microhardness was down (170-200 daN/mm²). There was no intermetallic punctate phase.¹ The phase composition of the damaged layer was NiO and Me₃O₄. The depths of all three zones of the damaged layer decreased proportionally with decreasing rate of water injection. The surface damage found on the EP-99 alloy specimens under these conditions was 9-10 times less severe than that on the specimens of ZhS6-K alloy. However, the phase composition and the pattern of the damage corresponded to those of turbine buckets that had actually been used. Injection of water containing NaCl showed that the damage was similar to that described earlier as resulting from the use of sea water. The penetration of the

damage was down 15-20%. Also worthy of note is the fact that increasing the test time in either case (tests with sea water and salted water) has little effect on the pattern and depth of the damage, while the test time, other conditions the same, was the principal factor for ZhS6-K foundry alloy.



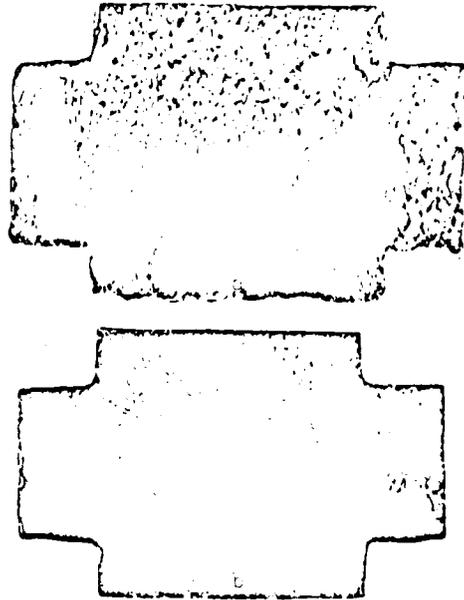
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Fig. 1. Specimens after testing on laboratory machine (2×): a) ZhS6-K alloy; b) EP-99 alloy.

Substitution of a diesel fuel with a sulfur content of 0.1% for fuel containing less than 0.74% sulfur produced no substantial differences in the intensity and nature of corrosion even at this temperature.

To determine the influence of sea-water solid-residue salts on the gas corrosion of ZhS6-K and EP-99 alloys, specimens were tested for 15 h at 900°C. The gas-flow parameters were left the same. Solid sea-water residue was fed into the gas stream in ground form in an amount (per unit of time) equal to the amount present in the sea water. After the tests, the specimens showed no distinct external signs of corrosion damage. Metallographic examination showed damage with a pattern similar to that for specimens tested with brine- and salted-water injection. However, the depth of the damage was 5-6 times smaller on ZhS6-K alloy specimens than on the same specimens when tested with brine injection. A similar pattern was observed for EP-99 alloy.

Thus, it was ascertained (Fig. 1) as a result of the gas-corrosion tests run on ZhS6-K and EP-99 nickel-base alloys that the



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Fig. 2. Specimens with thermal-diffusion coatings after tests: a) failed; b) did not fail.

use of high-sulfur fuel with sharp variations in gas-flow temperature did not result in intensive surface corrosion. This confirms the high corrosion stability of the alloys at elevated temperatures and fuel sulfur contents below 0.81%. Low corrosion stability of the alloys was noted when droplets of brine and salted water were admitted into the gas stream.

A surface-damage pattern similar to that observed on gas-turbine buckets that have run for several hundred hours under operating conditions was obtained on specimens subjected to short-term tests (10-15 h). A method for testing specimens with diffusion coatings was improved and given its final form during the process of the tests.

Superficially, the corrosion patterns on specimens tested in the gas stream from combustion of diesel fuels with various sulfur contents are also similar. Finally, comparison of microstructure photographs of specimens after testing under the same conditions but with injection of equal quantities of salted (NaCl) water repeats the same damage pattern.

However, differences in the rates of the alloys' corrosion processes are indicated by the results of the specimen tests, the tabulated weight-change data, the depth of the damage and its zone distribution.

Characteristic surface damage was obtained on ZhS6-K alloy

specimens on the laboratory machine with injection of sea water whose solid salt residue represents 0.023% of the weight of the air and fuel used at 900°C over at least 10 h.

During tests on specimens with thermal-diffusion protective coatings, the state of the surface was followed continuously and the times at which stains, blisters, deposits and corrosion products appeared were recorded.

In comparing the weight losses of the uncoated and coated specimens that were tested, it should be noted that the loss of weight per unit area decreases by a factor of 6-15 for satisfactory coatings, and that an increase in weight is observed for coatings with good characteristics.

Determination of surface finish by measuring roughness and comparing roughness profiles showed that the surface finish is lowered by 1-2 GOST classes on specimens with coatings that performed well in the test.

Two-component diffusion coatings with successive application of protective layers showed high corrosion stability under these conditions, and the best of them were recommended for industrial testing (Fig. 2).

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Footnote

- 3 ¹The department of metals technology and metallography of OPI developed the protective-coating technology and performed the metallographic examinations (microstructural and x-ray).