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Highly reflective silver mirror under annealing and hydrothermal exposure

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The highly reflective Ag-based thin-film coating for the ITER optical diagnostic mirror was tested under annealing at 250−310 °C and steam exposure. The Ag grain growth triggered by elevated temperature was identified as the main reason for the deterioration of the coating reflectivity and structure. The $SiN_x/(SiO_x/SiN_x)^2$ nanolaminate barrier composition over the Ag layer was found to effectively suppress the corrosive effect of steam.

Keywords: surface degradation, silver mirrors, annealing, corrosion.

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The in-vessel part of the collection optics of the ITER tokamak Divertor Thomson Scattering (DTS) diagnostic system under development consists of seven large-size mirrors divided into two channels with five consecutive reflections in each channel. The optical transmission of this system under operational loads should be maintained during the entire ITER lifecycle (20 years) at the ≥ 0.5 level in the 540−1100 nm band. This requires that the specular reflection coefficient of all mirrors, except for the „first" one, be at least $R = 0.9$ [1]. Unlike the "first" mirror, which is subject to contamination by eroding first wall material fluxes and erosion by fast particle fluxes, the operating conditions of subsequent "second" mirrors potentially allow the use of thin-film coatings for which $R \geq 0.9$ can be achieved. The major identified operational risks for coatings in the ITER vacuum vessel are: multiple thermal cycling at 70−250°C and hydrothermal corrosion at 30−250 °C following a cooling water steam ingress accident.

The harsh operating conditions limit the list of materials applicable for optical surfaces inside the ITER vacuum vessel. Well researched in this capacity Rh, Mo, and stainless steel have $R \leq 0.8$. Multilayer interference dielectric coatings [2] show high effectiveness, but their application for large-size DTS mirrors is associated with significant technological difficulties.

Highly reflective thin-film coatings based on Ag have been studied for many years and successfully used in optical devices operating in corrosive environments or under thermal loads: geophysical, astronomical, orbital optics, solar energy [3]. The most resistant of the coatings of this kind mentioned in the literature consist of a reflective Ag layer and interface layers of NiCr or $NiCrN_x$ protected by a barrier composition of one or more transparent dielectric layers [4,5]. The anticorrosion performance of coatings of this structure is driven by the defect-free and inert functioning of its barrier composition. [6]. The barrier function is greatly enhanced by the use of so-called nanolaminates — a large number of thin layers [7]. Known studies on the hydrothermal corrosion resistance of Ag-based optical coatings with barrier protection have been conducted at temperatures not exceeding 100 °C, while the polycrystalline Ag film is subject to degradation due to grain growth at temperatures approaching the ~ 0.36 melting point ($0.36T_m \approx 170$ °C) [8].

This study explores three types of Ag-based reflective coatings with NiV interface layers and nanolaminate barrier compositions (see table). All layers were deposited using a radio-frequency magnetron on a Ø20 mm substrate made of 316L(N)-IG steel polished to a RMS roughness of $S_q \sim 3$ nm. The total thickness of the barrier composition was 30 nm in each case. The samples were annealed in vacuum and then exposed in water steam with a temperature profile simulating an ITER [9] steam ingress accident and shown in Fig. 1, *a*.

The specular reflectance (Fig. 1, *b*) of samples *A* and *B* in the band 500−900 nm before the tests was higher than that of sample *C* but unlike the latter, it decreased by $\sim 8-10$ %, as a result of the tests, while that of sample *C* decreased by 2.5 %.

The scanning electron microscopy (SEM) revealed the most common coating defects that occurred after the tests: 1) continuous delamination of the barrier structure; 2) local ruptures of the barrier structure with subsequent corrosion of the Ag layer; 3) grain growth in the polycrystalline Ag layer with formation of voids between grains, as well as formation of individual large and extra large grains (up to 1 μm) but without continuous destruction of the barrier coating.

Clear continuous delamination of the barrier structure occurred only on the sample *A* (inset in Fig. 2). Local

Silver mirror coating designs investigated

Sample	Coating Design	Layer Thickness, nm	Annealing Mode
A *B*	Substrate/NiV/Ag/NiV/SiN_x Substrate/NiV/Ag/NiV/SiN_x/SiO_x/SiN_x	50/190/0.5/30 50/190/0.5/10/10/10	310 °C, 3 h
C	Substrate/NiV/Ag/NiV/SiN_x/$(SiO_x/SiN_x)^2$	$50/120/0.5/6/(6/6)^2$	250 °C, 5 h

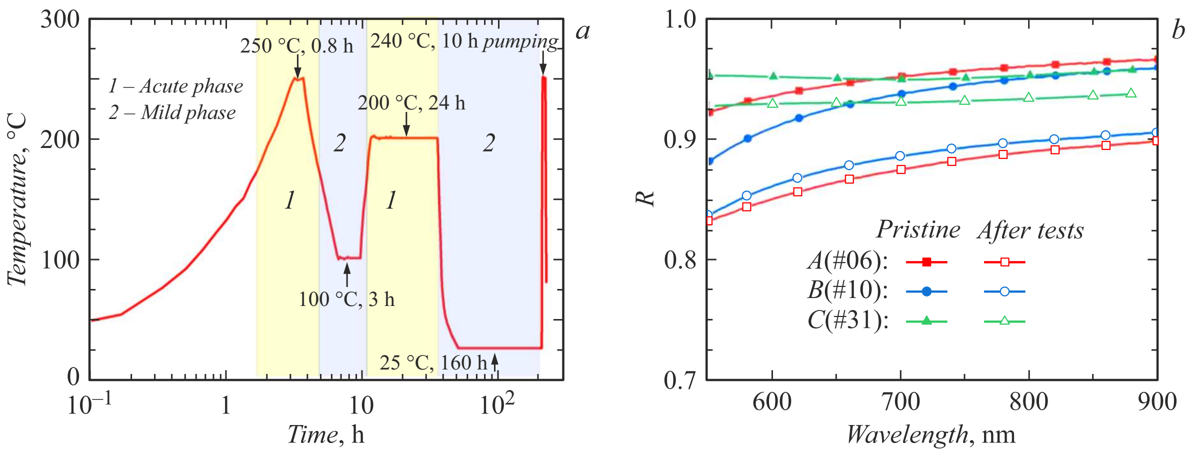

Figure 1. *a* — temperature profile of mirror exposure to water steam, simulating a steam ingress accident in ITER; *b* — spectral characteristic of the specimen specular reflectance of *A*, *B*, *C* before and after testing.

barrier structure ruptures were observed on samples *A* and *B*, while they were not detected on sample *C* even at the locations of large Ag grains. The authors believe that the multilayer barrier composition better relaxes tangential stresses caused by temperature rise at the interface with the Ag layer due to the difference in the coefficients of thermal linear expansion and growth of grains [10]. Furthermore, the increase in the number of interfaces increases the resistance of the structure to through-growth defects stemming from coating deposition [11].

The reason for the appearance of local defects (Fig. 2, *a*) can be both the development of cracks initially present in the barrier coating and its damage due to stresses caused by the growth of individual extra-large Ag grains or desorption of working gas accumulated in the Ag film during the deposition process. Individual Ag particles of size $\sim 1\,\mu$m were also found on the surface of the Ag layer before the tests and are apparently microdroplets of magnetron target material arising from the action of micro-arcs on its surface in the deposition process. The corrosion processes near the local defects are confirmed by traces of Cl and S registered near them with the energy dispersive spectrometer.

The growth of Ag grains at elevated temperature was observed both on the surface (Fig. 2, *b*) and in volume. On samples *A* and *B*, which were annealed at 310 °C, this effect was more pronounced than on sample *C*, which was annealed, although longer, but at 250 °C (by a factor of ~ 2 for samples *A*and *B* and by a factor of ~ 1.5 for sample *C* according to the results of XRD analysis). The increase in roughness and voids formation on the Ag surface led to a decrease in specular reflectivity [12]. The area of such defects is ~ 5 % of the *B* sample surface area, which is comparable to the magnitude of the decrease in reflectance and much larger than the area occupied by although large but localized defects on sample *A*. There are almost no voids on sample *C* which can be explained by the fact that annealing temperature affects grain growth more strongly than time. Disruption of the barrier structure can lead to oxygen access, which increases the surface diffusion rate of Ag by a factor of 100 [13], and thus, like elevated temperature, increases the grain growth rate.

The mechanism of thermodynamic suppression of polycrystal grain growth by grain-boundary segregation of impurity has recently been actively investigated. Grain-boundary segregation of impurity in a polycrystal — the excess of its concentration in grain boundaries over the concentration in the grain — is a strongly pronounced phenomenon in the Ag(Ni) [14] system. The introduction of Ni impurity occurs either from the interface layers containing it or by co-deposition Ag : Ni. Known theoretical models of this phenomenon predict that Ni is one of the elements whose introduction into Ag polycrystal enables suppression the growth of its grains [14]. However, as the annealing duration increases, Ni will diffuse into the deeper grain boundaries, and its concentration may not be sufficient to suppress the growth of near-surface grains. There is also a possibility of Ni precipitation, i.e. formation of crystalline Ni grains (Fig. 2, *c*), which will lead to a decrease in its concentration in the segregated state and weakening of the effect of suppression of Ag grain growth.

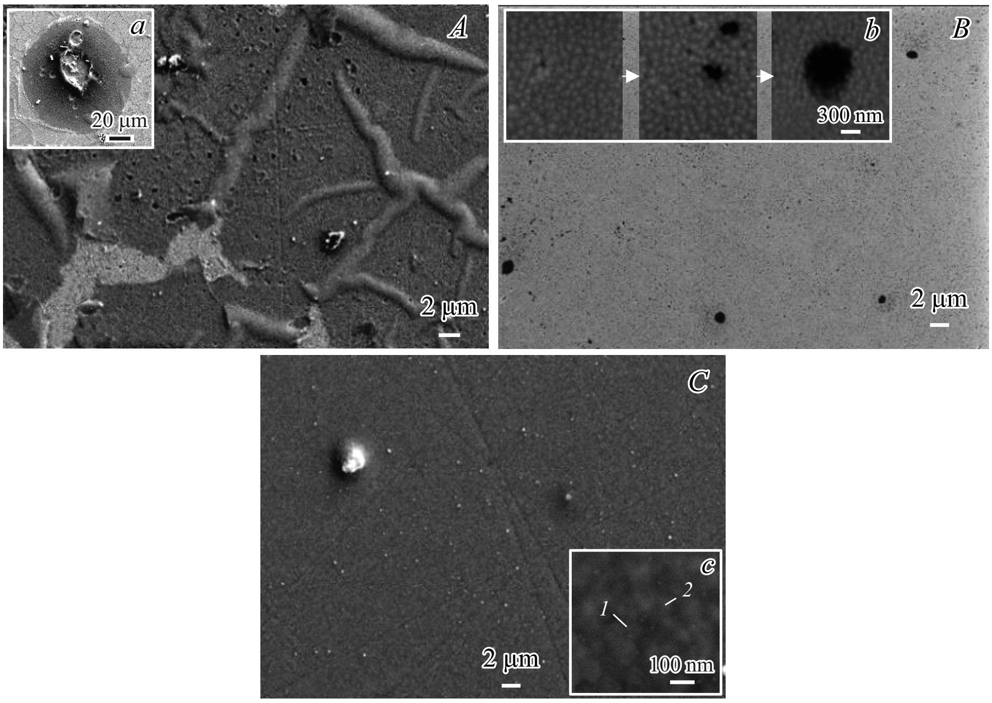

Figure 2. SEM image of the surface of samples *A*, *B* and *C* after testing. In insets: *a* — local rupture of the barrier structure with corrosion of the Ag layer; *b* — evolution of voids in the Ag layer with growth of grains; *c* — spherical particles (*1*) of size ~ 20 nm at the grain boundaries of Ag (*2*).

The range of phenomena observed as a result of coating samples tests of is quite wide. Further studies should seek to isolate them: for example, to perform diagnostics after the acute phase of exposure ($T > 170\,^\circ$C) and several times during the longer „quiet" phase (Fig. 1, *a*), as well as to study the effect of the described factors on the coating layers separately.

The authors argue that Ag grains growth is the most difficult factor to mitigate in barrier layer degradation. The nanolaminate barrier composition seems to be preferable for applications under cyclic thermal stresses.

For the next cycle of research, the coating plant is being upgraded to reduce the partial pressure of O in the residual atmosphere, the theoretical model of Ni segregation in Ag is being developed [15] to determine its optimal concentration, and the technological methods of its introduction into the polycrystalline Ag film are being investigated.

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Conflict of interest

The authors declare that they have no conflict of interest.

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