POSTER

ANTIOXIDATIVE PROTECTIVE COATINGS FOR CARBON MATERIALS

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INTRODUTION

To increase the high-temperature strength and moisture resistance of carbon-carbon articles used in the space technology,electrothermal equipment (heaters, heat-insulating lining),metallurgy (crucibles for metal melting), NIIGrafit has development a slip glass-silicide coating which ensures a durable exploitation of the articles at temperatures of 1500-1600 oC in air flow and in rarefied air atmospheres [1].

Plasma spraying is a method which ensure coating local areas of articles as well as protecting large-size articles as a whole. A technology has been developed for plasma spraying refractory metal oxides (ZrO_2, TiO_2, Al_2O_3, Cr_2O_3, etc.) onto carbon materials.

The slip-baking coatings are characterized by processability,usefulness for large-size intricate articles, apparatus simplicity for their applying.

NIIGrafit has developed a number of formulations which ensure the exploitation of carbon articles up to 1700 oC.

EXPERIMENTAL RESULTS AND DISCUSSION

As a result of the investigations a composition is proposed for applying coatings onto siliconized CCM based on high-melting borosilicate glass doped with $MoSi_2$.The borosilicate glass is SiO_2 doped with B and Al oxides.The service temperature increase of the coating is attained via introducing into the glass of a more high-melting and high-temperature resistant $MoSi_2$ retaining its properties up to 1700 oC.The high temperature resistance of $MoSi_2$ is attributed to the availabillty of a gas-tight stable glassy (amorphous) silica film. The presence of B and Al oxides in the glass composition makes it possible to obtain a glassy gas-tight coating as a result of diffusion at HTT. Along with that B and Al oxides decrease the crystallization ability of SiO_2 and make the coating more stable in its properties,especially at high temperatures.

The main advantage of the glass-silicide coating is its high resistance to thermal cycling, which is conditioned by the fact that along with a good match between CTE of the coating and substrate, the coating material at a temperature at over 1150-1200 oC is a viscoelastic state leading to the relaxation of thermal stresses arising.The resulting coating has a low thermal conductivity (1.71 W/(m*K) at 20 oC) and good electroinsulating properties (ρ= 10^4 Ohm). The coating has been successfully used for protecting against oxidation of graphite and graphite-chamotte crucibles for melting noble metals, bronze, Al and Cu alloys.

The interaction between the coated articles and air flow under the medium pressure of 0.01-0.09 MPa has been investigated. The experiments were carried out on a high-frequency electrodelessm plasmatron VGU-2 at P=0.01-0.09 MPa, V_ℓ=130-205 m/s,H_e=17-25 MJ/kg,T_w=1000-2000 oC using discs of 30 mm in diameter and 9 mm long. The interaction of free subsonic streams of dissociated air and N2 with the glass silicide coating results in the latter degradation which is reflected in the change of optical properties, chemical composition, and the formation of pores. At P=0.01 MPa and the surface temperature T =1000-1500 oC, the mass loss rate changes insignificantly with temperature and equals 10^-5 kg/(m^2*s). Efforts to smoothly increase the surface temperature above 1500-1510 oC resulted in the sharp uncontrolled temperature rise up to 2000 oC. Following a 2-3 min active gas release from inside the molten coating,the temperature decreased to 1500 oC and the gas release stopped.As a result, the average (for 6 cycles, 10 min long each) mass loss rate increased up to 10^-4 kg/(m^2*s).

To reveal the abnormal gas release mechanism in the silicide glass coating,experiments were conducted in N2 flow there was no gas release effect and that the mass loss rate could be approximated by the Arrhenius relation G_w= A*exp(-B/T), the $G_w$value at P=0.01 MPa being somewhat higher than at P=0.09 MPa. There suggest that the major mass loss mechanism in this case seems to be the glass evaporation. Spectral studies of the boundary layer in the samples at T_w =1000-1500 oC showed that in the N2 flow MoI lines in the boundary layer spectrum were absent, whereas in the dissociated air flow intensive Mo lines were observed over the whole surface temperature range investigated.The gas release effect in the coating also was not found during testing in the air flow at P=0.09 MPa when the boundary layer was in equilibrium and atomic oxygen was virtually absent at the surface. Control experiments with a borosilicate coating containing no MoSi2 also showed no abnormal gas release both in N2 and air flows at all the pressures. Thus, the present effect in the coating is brough about by the exothermal interaction between MoSi2 and the atomic oxygen from the incoming flow. Hence at relatively low service temperatures (from 1000 to 1300 oC), the coating breakdown (sublimation) occurs through evaporating Si and B oxides. As the temperature increases, the coating material viscosity gets decreased which leads to releasing gas inclusions trapped below the coating in the carbon substrate.With the further temperature increase, an exothermal oxidation reaction between MoSi2 and O2 occurs inside the coating,accompained with a short-time temperature increase at the sample surface (up to 1800-1900 oC). The temperature at which the exothermal reaction starts depends on the substrate pore structure,the melt viscosity, and content of Al and B oxides.

CONCLUSIONS

Based on the investigation of the interaction mechanism between the coating material and air flow, the ways have been suggested: decrease or replacement with other heat-resistant materials of the MoSi2 phase in the coating composition; surface densification or porosity decrease in a substrate;decrease of the boron oxide content in the coating composition; substrate vacuum degasification during coating formation.The realization of the above directions has enabled us to create a modified glass silicide coating that provides an efficient operation of parts up to 1600 oC.The major advantages of these coatings are as follows:service temperature as high as 1500-1600 oC; stress relaxation due to the plastic state at high temperatures; good CTE match between coating and substrate;self-healing of small defects under service conditions;simple technology;the possibility of applying coatings onto large-size parts (up to 2 m) of intricate configuration.

REFERENCE

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