PHYSICAL-CHEMICAL PRINCIPLES OF GROUP IV INTERMETALLIDE-HYDRIDE ADDITIVE CONCENTRATION IN TITANIUM AND CHROMIUM CARBIDE BASED COATING ESTIMATION

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Introduction

While choosing intermetallide-hydride concentration in carbide coating we proceeded from dissociation end product properties at high temperatures. The following data have been taken into consideration: number of phases in Zr-Ti-C, Ni-Ti-C, Cr-Ti-C, Fe-Ti-C, Fe-Cr-C etc. systems. Such characteristics as fusion temperature, constancy, homogeneity range, structure, mass transfer mechanism in acid and monoxide medium have been investigated.

Results and Discussion

The research aimed at working out new technological process of plasma coating application by means of activating and finishing additives on group IV metal hydride basis. Titanium and chromium compound carbides with nichrome connective, high corrosion resistance, thermal conductance, homogeneity and approaching steel thermal corrosion coefficient have been chosen as a coating basis.

Choosing materials for plasma coating application on 12Х1МФ boiler pipes it is necessary to take into account a set of characteristics considering exploitation conditions. These requirements are partially met, in terms of thermophisical requirements, by self-fluxing alloys [1], containing nickel, chromium and boron carbides, non-stochiometric composition silicon. However, they are not highly corrosion resistant and tent to endurance failure.

Zr and Hf are good finishing elements, which can be infused from their intermetallide-hydrides. In Ukraine "Zircon" company is producing iron and nickel based intermetallides. Zr and Hf additive number has been chosen on the basis of double and triple Ni-Zr, Ni-Hf, Ti-Zr-C and Cr-Zr-C alloy charts.

The advantages of a new technological process are determined by the right choice of activating composition and correlation of components of the given system for plasma spraying. The advantages of technology with Ti, Zr or Hf with Fe intermetallide-hydride additives are in the fact that such TiC-Cr_3C_2-NiCr plus hydride heterogeneous alloy under gas-thermal spraying can consume heat excess that evolves while generating hydrogen on reducing process. Earlier [2] we gave grounds for necessity of 75 mass % Ni-Cr connection infusions in carbides, because under plasma spraying of TiC-Cr_3C_2 coating without nichrome additives formed phase grain increase can be observed.

Suggested new coating composition [3] of TiC-Cr_3C_2-NiCr heterogeneous system with group IV hydride infusion consists of finishing components dissolving only on the phase grain boundaries. It has good qualities owing to its individual component characteristic preserving. This being mentioned earlier in the research [2]. Sprayed layers of this carbide alloy depending on the composition (having Ti or Zr, Hf and their mixture intermetallide-hydrides) can have the required set of technological properties as a result of additivity of separate phase component properties.

Process efficiency is conditioned by the fact that melting phase component (Cr-Ni eutectic) is retained in interstice of NiC- Cr_3C_2 hard array owing to capillary pressure. This characteristic is determined by phase disengagement boundary state. It can be adjusted by varied hydride to carbide correlation. However, 1:30 correlation increase determines interstice coagulation formation. 1:9 correlation is optimum in this case.

There have been given results of coating microstructure analysis experiment data, received by applying new technological plasma spraying process using group IV hydrides.

While studying TiC-Cr_3C_2-NiCr coating material structures we have discovered that carbide grain size influences the diffusion speed.

Phase balance in TiC-Cr-C triple system confirms the received experimental data on $Zr_{k\alpha}$ and $Hf_{k\alpha}$ accommodation in coating surface on the TiC(Cr_3C_2) carbide grain boundary. While finishing TiC-Cr_3C_2-NiCr coating finishing element oxycarbides, which increase their corrosion resistance in steam generating unit at temperatures > 12000C, can be formed.

We have taken into consideration the fact that component chemical potential gradients are the driving force of ion and electron chemical diffusion in coating exploitation conditions, that is, in carbides and oxycarbides they are conditioned by gradient of non-stoichiometricity degree.

Still during the first stage of spraying process under gas-chemical stream influence a sample surface temperature gradient can be formed. These phenomena bring additional contribution to the element diffusion on phase boundaries.

We have used main transport equation for thermal diffusion case [4]. Here, assuming independent motion of different particles for K-particle blast in chemical and thermal fields, this transport equation looks as follows:

$I_{k=-}(D_k \cdot N_k/KT)\ (\Delta\mu_k + q_k\Delta\varphi)$, where:

I_k – particle stream density

D_k – component random diffusion coefficient;

N_k – particle interstice number;

K – defect forming reaction balance constant;

T – absolute temperature;

$\Delta\mu_k$ – potential gradient referring to one particle;

q_k – particle charge;

$\Delta\varphi$ - electrostatic potential alteration.

Thus, the study of phase composition of TiC-Cr_3C_2- (Ni-Cr) based coverings with FeH_xHf additives after oxidation has shown the formation of the following oxide and oxycarbide phases: Fe_2Zr_2O, $FeHf_2O$, ZrC_xO, HfC_xO, $NiCr_2O_4$. $NiCr_2O_4$ spinel being stable at temperature >1200^0C has protective qualities.

According to estimations zirconium and hafnium are finishing elements that are more reactive to oxygen than TiC and Cr_3C_2 carbides.

Interstices formed in carbide coating are filled with $NiCr_2O_4$, zirconium and hafnium oxycarbides. Thus, oxygen has limited dissolution in coating carbide alloy. Coating stability increase after intermetallide-hydride finishing is based on the same principle.

References

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