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Meet Our New Colleagues

This column presents selected currently graduating Ph.D. students in the thermal spray field from around the world. Students planning to graduate in the area of thermal spray within the next 3 to 6 months are encouraged to submit a short description (1 to 2 pages, preferably as Word document) of the projects they performed during their studies to Jan Ilavsky, JTST Associate Editor, address: Argonne National Laboratory, Advanced Photon Source, 9700 S. Cass Ave., Argonne, IL, 60439; e-mail: JTST.Ilavsky@aps.anl.gov. After limited review and corrections and with agreement of the student's thesis advisor, selected submissions will be published in the upcoming issues of JTST.

Studies on the Hot Corrosion Behavior of HVOF Coatings on Some Ni- and Fe-Base Superalloys

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The presented research program aims at evaluating the hot corrosion behavior of high-velocity oxyfuel (HVOF) sprayed coatings on five types of superalloys, with the objective to protect the boiler superheaters and reheaters so they can be used at temperatures significantly higher than in the existing steam-generating systems. Four types of commercial available feedstock materials—Cr_3C_2-NiCr, NiCrBSi and Stellite-6 in the powder form, and Ni-20Cr in the wire form—were used for spraying coatings on Ni- and Fe-base superalloys using a Hipojet-2100 HVOF system for powder spraying and a Hijet-9600 HVOF system for wire spraying.

The hot corrosion behavior of the bare and HVOF coated superalloys was studied in the simulated molten salt (Na_2SO_4-60%V_2O_5) environment under cyclic conditions. The molten salt studies were performed in the laboratory tube furnace for 50 cycles; each cycle consisted of 1 h heating at 900 °C followed by 20 min cooling. In order to establish an understanding for the behavior of these coatings and bare superalloys in the actual working conditions where these coatings are intended to be used, the specimens were exposed to platen superheater zone of the coal-fired boiler for 1000 h at Guru Nanak Dev Thermal Power Plant, Bathinda, Punjab, India, under cyclic conditions. Each cycle consisted of 100 h exposure to the boiler environment followed by 1 h cooling.

As-sprayed coatings as well as corrosion products were characterized by using the combined techniques of optical microscopy, microhardness testing, x-ray diffractometry (XRD), scanning electron microscopy/energy-dispersive analysis (SEM/EDAX), and electron probe microanalyzer (EPMA).

Results

Main conclusions from this study are:

- All the coatings were successfully deposited by HVOF process on the given Ni- and Fe-base superalloys using liquid petroleum gas (LPG) as a fuel. All the coatings exhibited dense structure with layered morphology consisting of flat splats with average porosity less than 2% and surface roughness in the range of 4-6 μm. The thickness for all the coatings was limited to 250-300 μm in the present study to ensure integrity of the coatings. The thicker coatings were found to disintegrate by themselves.
- It has been established that the HVOF sprayed Ni-20Cr wire coating is a technically viable and effective alternative to the HVOF sprayed Ni-20Cr powder coating.
- The Cr_3C_2-NiCr, NiCrBSi, and Ni-20Cr coatings revealed the formation of nickel-base fcc structure as the principal phase, whereas Co-base fcc has been identified as the principal phase in the case of Stellite-6 coating.
- All the coatings have imparted resistance to hot corrosion in the molten salt environment for all the substrate superalloys. The overall protective behavior of the coatings in this environment on different superalloys used in the present study has been found in the following sequence: Ni-20Cr > Cr_3C_2-NiCr > NiCrBSi > Stellite-6. All the coated superalloys have followed nearly parabolic behavior up to 50 cycles, and their parabolic rate constants are found to be significantly less than bare alloys. The coatings showed good adherence to their respective substrates during the exposure.
- The coatings have successfully imparted the hot corrosion resistance to the superalloys in the boiler environment also and showed no thickness loss due to spallation during experimentations. The coatings have shown the following trend of hot corrosion resistance on different superalloys in the boiler environment: Ni-20Cr > Stellite-6 > NiCrBSi > Cr_3C_2-NiCr.
- The hot corrosion resistance of all the coatings under study, in both the environments, has been attributed mainly to the formation of oxides both at the splat boundaries and at the surface of the coatings. The scale developed on the surface of all the coated superalloys, after exposure to both the environments, consists of protective oxides mainly of Cr, Si, and Ni, and their spinels containing Ni-Cr and/or Co-Cr type mixed oxides.
- It has been established that with the progress of corrosion, the splat boundaries of the coatings are more active in imparting the overall hot corrosion resistance as compared to rest of the coating regions. In both the environments, the oxide scale has preferentially formed at the splat boundaries due to oxidation of active elements of the coatings. The Ni- and Co-rich splats of the coatings are mostly in an unoxidized state.
- Additionally, the very low porosity and the flat splat structure of the HVOF sprayed coatings have also contributed to enhanced hot corrosion resistance, as this is the desired structure when the coatings have to perform in corrosive environment at higher temperature. The distance from the coating surface to coating/substrate interface along the splat boundaries increases significantly in case of a flat splat structure.

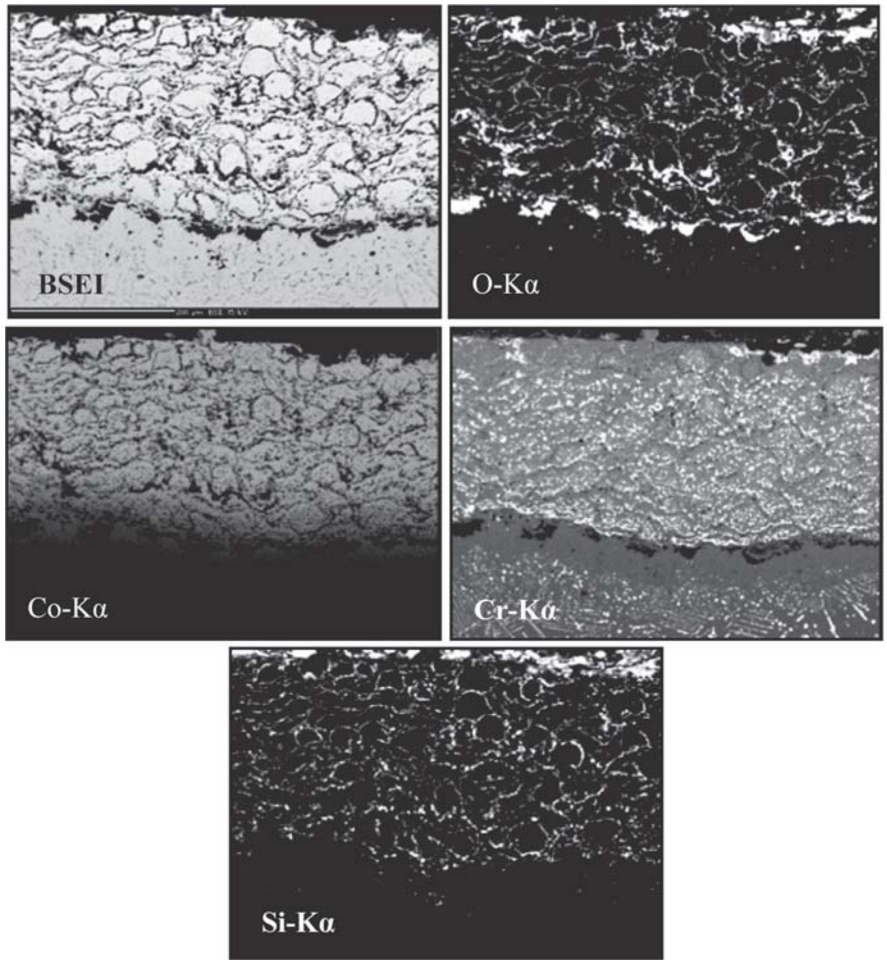

Fig. 1 Backscattered electron image (BSEI) and x-ray mappings across the cross section of a Stellite-6 coated superalloy after 1000 h exposure to platen superheater zone of the coal-fired burner at 900 °C

- The superior performance of the Ni-20Cr coating is mainly attributed to the formation of oxides of Ni and Cr and their spinel at the topmost part of the scale, and the selective oxidation of Cr to form stringers or globules at the splat boundaries or in pores.
- The relatively higher oxidation of the Cr_3C_2-NiCr coating as compared to the Ni-20Cr coatings in the molten salt environment has been attributed to the presence of higher amount of Cr, which leads to the formation of a thick network of Cr_2O_3 around the Ni-rich splats. The relatively poor performance of Cr_3C_2-NiCr coating in the boiler environment is ascribed to the formation of thickest oxide of Cr due to longer exposure time (1000 h), resulting in more spallation of the scale due to difference in the coefficient of thermal expansion of the oxides, the coating, and the substrates.
- Comparatively lower corrosion resistance of the NiCrBSi coating as compared to the Ni-20Cr and Cr_3C_2-NiCr coatings in molten salt environment is ascribed to lower content of Cr (15%) in its basic composition. However, the better hot corrosion resistance of NiCrBSi coating as compared to the Stellite-6 coating has been attributed to the presence of Si and B, as they promote the selective oxidation of the protective scale-forming elements resulting in the formation of a continuous scale in the initial corrosion stage and improve the adherence of the outer scale to the coating in the subsequent hot corrosion process. In contrast to the molten salt environment, the NiCrBSi coated superalloys have shown relatively lesser hot corrosion resistance than the Stellite-6 coated superalloys in the boiler environment. The continuous silicon oxide layer that has been formed at the topmost part of the scale in the molten salt (Na_2SO_4-60%V_2O_5) environment could not form in the boiler environment due to fluxing actions of the low melting point alkali-iron trisulfates $(Na,K)_3Fe(SO_4)_3$ compounds (melting point 552 °C).
- The relatively least hot corrosion resistance of the Stellite-6 coating in molten salt environment is due to the presence of more porosity and larger size globules in the coating. However, this coating performed better in the boiler environment due to the formation of thick oxides of Cr and Si, and spinels of Co-Cr and Ni-Cr at the boundaries of Co-rich splats due to longer exposure time, which blocked the penetration of oxygen and other corrosive species into the substrates (Fig. 1). Further, the formation of Co-Cr spinel ($CoCr_2O_4$) also has a beneficial effect as $CoCr_2O_4$ spinel blocks the diffusion activities through the cobalt oxide (CoO) by suppressing the further formation of CoO.
- All the coated superalloys have shown higher rate of hot corrosion during initial cycles of exposure, and thereafter the corrosion rate decreases and finally stabilizes. Initially, the oxygen permeates inward along the splat boundaries and pores, and causes rapid oxidation. Subsequently, these oxides plug/seal all possible diffusion paths in the coatings, thereby blocking or slowing down the penetration of aggressive species. The corrosion is then confined mainly to the surface of the coatings, thus resulting in the corrosion rate to reach a steady state.
- The degradation of bare superalloys in the boiler environment has been attributed to the dissolution of the protective oxides due to fluxing actions of the low melting-point alkali-iron trisulfate compounds.
- In both the environments, the base superalloys have affected the performance of different coatings due to outward diffusion of the substrate elements into the coatings at high temperature. The base superalloys affected the hot corrosion behavior of the coatings significantly in the boiler environment, whereas their effects are relatively less in the laboratory conditions.
- The Ni-20Cr coating using wire as feedstock materials has given the best

performance on all the substrates under study in both the environments and is, therefore, recommended as the best coating for the given conditions. The (Ni-20Cr)-Superfer 800H and (Ni-20Cr)-Superni 75 coating/substrate combinations have the highest hot corrosion resistance in the molten salt and coal fired boiler environments, respectively.

- Based on the findings of the present study, all the coatings under study are recommended for applications to superheater and reheater tubes of the boilers for protecting them against corrosive environments for high-temperature applications.

Publications

Research papers published in the "referred journals" out of this investigation are:

- T.S Sidhu, S. Prakash, and R.D. Agrawal, State of the Art of HVOF Coating Investigation—A Review, *Marine Technol. Soc. J.,* 2005, **39**(2), p 55-66
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- T.S. Sidhu, S. Prakash, and R.D. Agrawal, Hot Corrosion Studies of HVOF NiCrBSi and Stellite-6 Coatings on a Ni-Based Superalloy in an Actual Industrial Environment of a Coal Fired Boiler, *Surf. Coat. Technol.,* Corrected proofs available online
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