ABSTRACT

The potential use of nanostructured surface protective coating with alumina–zirconia (ASZ) and alumina–(yttria) zirconia (A-YSZ) ceramic nanocomposites is attracting attention towards different corrosion environments to protect metal alloy specimens. The stable t-zirconia phase is most important in both ASZ and A-YSZ nanocomposites coating as it provides the required physico-chemical and thermomechanical properties at both room and high temperatures. The use of ASZ and A-YSZ composites as nanostructured thermal barrier coatings (TBCs) is considered as they generally undergo a severe coating degradation due to their transition of tetragonal t-zirconia into m-phase in both high temperature oxidation and molten salt hot corrosion atmosphere.

Ultimately, it is inevitable to realise the structural volume expansion results on the deformation of TBCs in corrosion environments. To prevent the structural failure of TBCs, a promising and active multiphase structural nano phase composite with stable structural phase and reduced nanocrystalline size is essentially required. In the proposed thesis, an attempt has been made to develop silicate based TBCs using Al₂O₃–ZrO₂ and Al₂O₃–(Y₂O₃)ZrO₂ nanocomposites as nanofillers in silica sol for better surface protective coating.

Eutectic Al₂O₃–ZrO₂ (ASZ) 70:30 (wt. %) and Al₂O₃–(Y₂O₃)ZrO₂ (A-YSZ) 67:3:30 (wt. %) nanocomposites are obtained from their nitrate precursors through hot-air spray pyrolysis. The characteristics of both ASZ and A-YSZ eutectic composites are comprehensively studied in terms of structural phase, crystallite size, particle size, surface area, and chemical composition, morphology, and thermomechanical properties. The observed XRD pattern results show that the stabilization of stable tetragonal t-ZrO₂ phase exists in both ASZ and A-YSZ matrices up to 1773 K.
Nevertheless, the m-ZrO\(_2\) phase exists in ASZ from 1373 K onwards while the same is absent in A-YSZ with only presence of \(\alpha\)-alumina at 1773 K. As a result of amorphous phase, the crystallite size of t-zirconia can effectively be inhibited in pseudo eutectic A-YSZ composite than in ASZ, which is observed in the range of 9–47 and 6–65 nm, respectively. The structural phase transition of both ASZ and A-YSZ from their amorphous phase into crystalline phases is correlated by thermal analysis. The indentation tests on ASZ and A-YSZ nanocomposites before and after sintering show that the hardness and elastic modulus of A-YSZ composite are enhanced when compared with those of ASZ. The observed textural properties of Al\(_2\)O\(_3\)–ZrO\(_2\) and Al\(_2\)O\(_3\)–(Y\(_2\)O\(_3\))ZrO\(_2\) nanocomposites from their experimental results are proposed for surface protective coating applications.

Amorphous nano-Al\(_2\)O\(_3\)–ZrO\(_2\) and Al\(_2\)O\(_3\)–(Y\(_2\)O\(_3\))ZrO\(_2\) filled silica sol are prepared individually, which are used as multilayer nanostructured TBCs on SS 316L, namely SSC and SSCY specimens. Thermal stability of both SSC and SSCY TBCs are investigated in terms of direct heat treatment, isothermal cyclic oxidation, and hot corrosion molten salt (50 V\(_2\)O\(_5\) + 25 Na\(_2\)SO\(_4\) + 25 NaCl) wt. % at different temperatures such as 1073, 1173, and 1273 K for 100 h. The XRD patterns of SSC and SSCY specimens for the heat-treated and hot corrosion tested specimens show the stable structure of t-ZrO\(_2\), Al\(_2\)SiO\(_5\), and ZrSiO\(_4\) with the addition of Y\(_2\)SiO\(_5\) for SSCY specimen.

The most striking m-ZrO\(_2\) phase is absent during high temperature heat treatment and molten salt hot corrosion. The microstructured images of SSC and SSCY heat treated specimens showed dense and crack free surface coating with randomly presented porosity. However, the molten salt deposited specimens at 1273 K showed the surface deformation with crack and patches. After heat treatment, BET surface area of SSC and SSCY is found to be decreased in coating in the range of 185–1.55 and 634–493 m\(^2\)g\(^{-1}\) along with crack splats.
The rate of cyclic oxidation in TBCs increases with an increase over a wide range of temperatures and resulted in cyclic high oxidation resistance than the hot corrosion. Thus, the cyclic high temperature oxidation rate for SSC and SSCY specimen is, respectively, in the range of $0.001-0.066$ and $0.001-0.012$ Kg m$^{-2}$ whereas the hot corrosion rate is in the range of $0.015-0.724$ and $0.003-0.029$ Kg m$^{-2}$. The results of the nanoindentation test show that the average hardness ($H$) and reduced elastic modulus ($E_r$) values of SSC coating are approximately in the range of $15.49 \pm 0.16$ to $18.43 \pm 0.30$ and $75.43 \pm 0.29$ to $68.30 \pm 0.46$ GPa, respectively. The same for the SSCY specimen are respectively in the range of $16.36 \pm 0.03$ to $21.67 \pm 0.02$ GPa and $70.01 \pm 0.07$ to $62.87 \pm 0.09$ GPa. After molten salt test, $H$ and $E_r$ values of SSCY specimen reduced in the range of $14.88 \pm 0.12$ to $14.04 \pm 0.29$ GPa and $75.81 \pm 0.30$ to $92.80 \pm 0.21$ GPa, respectively. The observed nanostructured silicate based TBCs provide better protection to SS specimen from high temperature corrosion.

Multilayer anticorrosive coating of epoxy polyamide (EP) resin and mixture of $\text{Al}_2\text{O}_3$–$\text{ZrO}_2$ nanoparticles in epoxy polyamide resin (NEP), respectively, are applied on SS 316 L specimens. The performance of EP and NEP coated samples is comprehensively characterised in terms of surface topography, morphology, structural phase, chemical composition, thermal stability, thermal conductivity, thermal diffusivity, and elastic properties. The in-situ SPM and AFM images are used to explore the formation of $\text{Al}_2\text{O}_3$–$\text{ZrO}_2$ nanofiller in the EP matrix. After acid immersion (10 % $\text{H}_2\text{SO}_4$) of both EP and NEP samples for 48 h, the SPM and AFM microstructure images show that the NEP coated sample maintains its original surface feature with existing passive layer formation whereas EP coated sample shows surface deterioration and deformation. This shows that $\text{Al}_2\text{O}_3$–$\text{ZrO}_2$ nanofiller can be used to improve the desirable properties in the host epoxy matrix.
The observed results show that the production of Al$_2$O$_3$–(Y$_2$O$_3$)ZrO$_2$ amorphous nanocomposite can provide the stable structural phase stability and crystalline size effect at elevated temperature than that of Al$_2$O$_3$–ZrO$_2$ composite. The same is proposed for high temperature structural coating applications. In addition, the development of silicate based TBCs can arrest the high temperature oxidation hot corrosion with the absence of m-ZrO$_2$ phase from t-ZrO$_2$ stabilised Al$_2$O$_3$–ZrO$_2$/SiO$_2$ and Al$_2$O$_3$–(Y$_2$O$_3$) ZrO$_2$/SiO$_2$ TBCs. In addition, the incorporation of Al$_2$O$_3$–ZrO$_2$ nanofiller in epoxy polyamide matrix also improves the anticorrosion properties.