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Emissivity Enhancement Coatings for Thermophotovoltaic (TPV) Radiator Applications

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Abstract

Ten emissivity enhancing coatings (ZrO_2 + 18% TiO_2 + 10% Y_2O_3, Cr_2O_3, ZrC, Fe_2TiO_5, $ZrTiO_4$, ZrO_2 + 8% Y_2O_3 + 2% HfO_2, TiC, TiC + 5% Al_2O_3 + 5% TiO_2, ZrB_2, and ZrB_2 + 10% $MoSi_2$) deposited on Mo, Nb, and Haynes 230 substrates were evaluated for potential use in Themophotovoltaic (TPV) Radiator Applications. Emissivity testing of as-coated and annealed coupons indicate that 5 of the 10 Vacuum Plasma Spray (VPS) coating candidates have promise ((ZrO_2 + 18% TiO_2 + 10% Y_2O_3, ZrC, Fe_2TiO_5, $ZrTiO_4$, ZrO_2 + 8% Y_2O_3 + 2% HfO_2). Four of the ten coatings have emissivity values that are too low to be of further interest (TiC, TiC + 5% Al_2O_3 + 5% TiO_2, ZrB_2, and ZrB_2 + 10% $MoSi_2$). The final coating was mostly Cr_2O_3, and exhibited excessive evaporation during vacuum annealing with a significant decrease in emissivity. Base metal powder, which was added to the bond layer of all coatings to improve coating adhesion, was detected in the top layer of the coatings. Differences in reactive interaction between the base metal powder and coating during vacuum annealing produced varying changes in emissivity. A small decrease in emissivity was observed for the ZrC coating deposited on niobium, which agrees with the limited interaction between the niobium base metal particles and the ZrC coating detected in SEM/EDS examinations. A large decrease in emissivity was observed for the ZrC coating deposited on Haynes 230, and significant interaction between the base metal particles and ZrC coating was observed.

INTRODUCTION

The thermophotovoltaic (TPV) radiator must conduct heat away from a high temperature heat source and emit photons in a specific wavelength range to cells for conversion to electrical power. Some radiator design concepts involve high pressure coolant. Two important material properties for a TPV radiator are creep strength and emissivity. In order to provide high power density levels, emissivity values of 0.9 or higher are desirable for a TPV radiator. Since many candidate radiator materials with the desired creep strength have a low emissivity ($\epsilon \sim 0.1$ to 0.4), blackbody emissivity enhancement coatings are being evaluated for use in TPV radiator applications.

EXPERIMENTAL PROCEDURE

Ten Vacuum Plasma Spray (VPS) deposited coatings from the Thermal Spray Laboratory at the State University of New York at Stony Brook (SUNY) (ZrO_2 + 18% TiO_2 + 10% Y_2O_3, Cr_2O_3, ZrC, Fe_2TiO_5, $ZrTiO_4$, ZrO_2 + 8% Y_2O_3 + 2% HfO_2, TiC, TiC + 5% Al_2O_3 + 5% TiO_2, ZrB_2, and ZrB_2 + 10% $MoSi_2$) were deposited on Mo, Nb, and Haynes 230 substrates. The coatings were deposited in 2 layers to a nominal total coating thickness of 2-3 mils: (1) 1 mil thick bond coat consisting of a 50/50 mixture of substrate powder (molybdenum, niobium, or Haynes 230) and coating powder, and (2) 1-2 mil thick top coat of coating powder. The substrate powder additions were made to improve coating adhesion and minimize differences in coefficient of thermal expansion (CTE) between the coating and substrate. Multiple component coatings were produced by blending the constituent compound powders prior to VPS deposition.

In order to evaluate coating stability for TPV radiator application, the VPS coatings were annealed in vacuum ($< 10^{-5}$ torr) for 500 hours at 1100°C. Emissivity measurements were made at NASA-Lewis in Cleveland, Ohio on the same coupon in the as-coated condition and post-annealed condition. Emittance values obtained from NASA Lewis are achieved by measuring reflectance at low temperature with the assumption of zero transmittance (emittance = 1 - reflectance), and then using an algorithm to calculate a value at high temperatures. The NASA

Lewis emittance value is a total-hemispherical measurement, which means that emissivity is measured at $\lambda = 0$ to 10 μm and at 0° to 90° solid angle to the substrate. Emissivity measurements of the as-coated specimens were also made in the radiator screening test stand at our laboratory. Emissivity measurements in the radiator screening stand are obtained directly at temperature at a narrow wavelength (2.0 to 2.6 μm) and only normal to the substrate (90° solid angle).

RESULTS AND DISCUSSION

Comparison of emissivity data measured at NASA-Lewis and radiator screening stand for as-coated ZrC and $ZrTiO_4$ coupons deposited on molybdenum in Figure 1 indicates a difference of about 10%. The relative differences in values between ZrC and $ZrTiO_4$ are comparable for the NASA-Lewis and the radiator screening stand. The coupons measured at NASA-Lewis and the radiator screening stand were not identical, but were from the same batch of coated substrates. The emissivity values from NASA-Lewis exhibit little temperature dependence while the emissivity values measured in the radiator screening stand increase as a function of temperature. Differences in the emissivity values obtained at NASA-Lewis and the radiator screening stand are attributed to the differences in the measurement techniques.

Emissivity measurements made at 1100°C in the radiator screening stand for the ten VPS coatings and POCO Graphite and Hexoloy SA SiC are compared in Table 1. Assuming the emissivity values for POCO Graphite and Hexoloy SA SiC represent satisfactory values, promising coating candidates are identified on a comparative basis. Six as-coated candidates (ZrO_2 + 18% TiO_2 + 10% Y_2O_3, Cr_2O_3, ZrC, Fe_2TiO_5, $ZrTiO_4$, ZrO_2 + 8% Y_2O_3 + 2% HfO_2) are the most promising candidates due to their emissivity values being close to POCO Graphite and Hexoloy SA SiC.

Following vacuum annealing, large decreases in emissivity were observed for the Cr_2O_3 coatings, with the largest decrease observed for the Cr_2O_3 coating deposited on niobium, see Figure 2. SEM/EDS examinations of the as-coated surface in Figure 3 show that the Cr_2O_3

coating contains chromium and oxygen at levels consistent with chromium-oxide (Cr_2O_3). The smooth flat region with the high BSE contrast in Figure 3a was determined to be niobium, and these niobium "splat" particles were frequently observed on the as-coated coupon. These niobium particles are likely substrate powder from the bond layer that was kicked up into the top layer of the coating during the VPS deposition process. Cr_2O_3 is generally volatile at temperatures above 1000°C, which explains the large decrease in emissivity and high weight loss in Figure 3. The surface of the coatings in Figure 3b was very porous after vacuum annealing from Cr_2O_3 evaporation, and the substrate powder regions also exhibited some porosity. Higher niobium contents were detected on the coating surface after vacuum annealing, which likely results from Cr_2O_3 evaporation and surface diffusion of niobium. Due to evaporation, a Cr_2O_3 coating is not a viable candidate.

Figure 4 shows that only small decreases in emissivity were observed after annealing for the ZrC coating deposited on molybdenum and niobium, while large decreases in emissivity were observed for the ZrC coating deposited on Haynes 230. Niobium base metal powder was observed in the ZrC coating deposited on niobium. Figure 5 shows that there was little interaction between the niobium base metal particles and the ZrC coatings after vacuum annealing. A higher density of base metal powder particles was observed in the ZrC coating deposited on Haynes 230, but SEM/EDS analysis detected higher levels of elements not associated with Haynes 230 (niobium, molybdenum, iron, sulfur, silicon, titanium, and calcium), see Figure 6a. A greater amount of reactive interaction between these metal powder particles and the ZrC coating was observed after vacuum annealing in Figure 6b for the ZrC coating deposited on Haynes 230. The reaction between the ZrC coating and these metallic powder particles likely produces the large decrease in emissivity observed for the ZrC coatings deposited on Haynes 230.

CONCLUSION

Differences in as-coated emissivity values from NASA-Lewis and radiator screening stand are attributed to the differences in measuring technique.

These results show that 5 of the 10 VPS coating candidates provided by SUNY have promise for radiator applications ((ZrO_2 + 18% TiO_2 + 10% Y_2O_3, ZrC, Fe_2TiO_5, $ZrTiO_4$, ZrO_2 + 8% Y_2O_3 + 2% HfO_2). Four of the ten coatings have emissivity values that are too low to justify further consideration (TiC, TiC + 5% Al_2O_3 + 5% TiO_2, ZrB_2, and ZrB_2 + 10% $MoSi_2$). The Cr_2O_3 coating exhibited an unacceptable level of evaporation during vacuum annealing.

Base metal powder particles, which were added to the bond layer to improve coating adhesion, were detected in the top layer of the coatings. The composition of these metallic inclusions is specific for a coating/substrate combination. Differences in reactive interaction between the base metal powder particles and coating during vacuum annealing produces variable changes in emissivity. Only a small decrease in emissivity was observed for the ZrC coating deposited on niobium, which agrees with the limited interaction between the niobium base metal particles and the ZrC coating detected by SEM/EDS examinations. A large decrease in emissivity was observed for the ZrC coating deposited on Haynes 230, and significant interaction between the base metal particles and ZrC coating was observed.

Acknowledgments

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Table 1 : Comparison of emissivity values measured in the radiator screening stand at 1100°C for candidate VPS coatings from SUNY and POCO graphite and Hexoloy SA SiC.

Coating	Substrate	Normal Spectral Emissivity at 1100°C
ZrO_2 + 18% TiO_2 + 10% Y_2O_3	Molybdenum	0.89
POCO Graphite	None	0.86
Cr_2O_3	Molybdenum	0.85
Hexoloy SA SiC	None	0.85
ZrC	Molybdenum	0.82
Fe_2TiO_5	Molybdenum	0.80
$ZrTiO_4$	Molybdenum	0.77
ZrO_2 + 8% Y_2O_3 + 2% HfO_2	Molybdenum	0.76
TiC	Molybdenum	0.65
TiC + 5% Al_2O_3 + 5% TiO_2	Molybdenum	0.65
ZrB_2	Molybdenum	0.63
ZrB_2 + 10% $MoSi_2$	Molybdenum	0.61

Results (Blackbody Emitters)

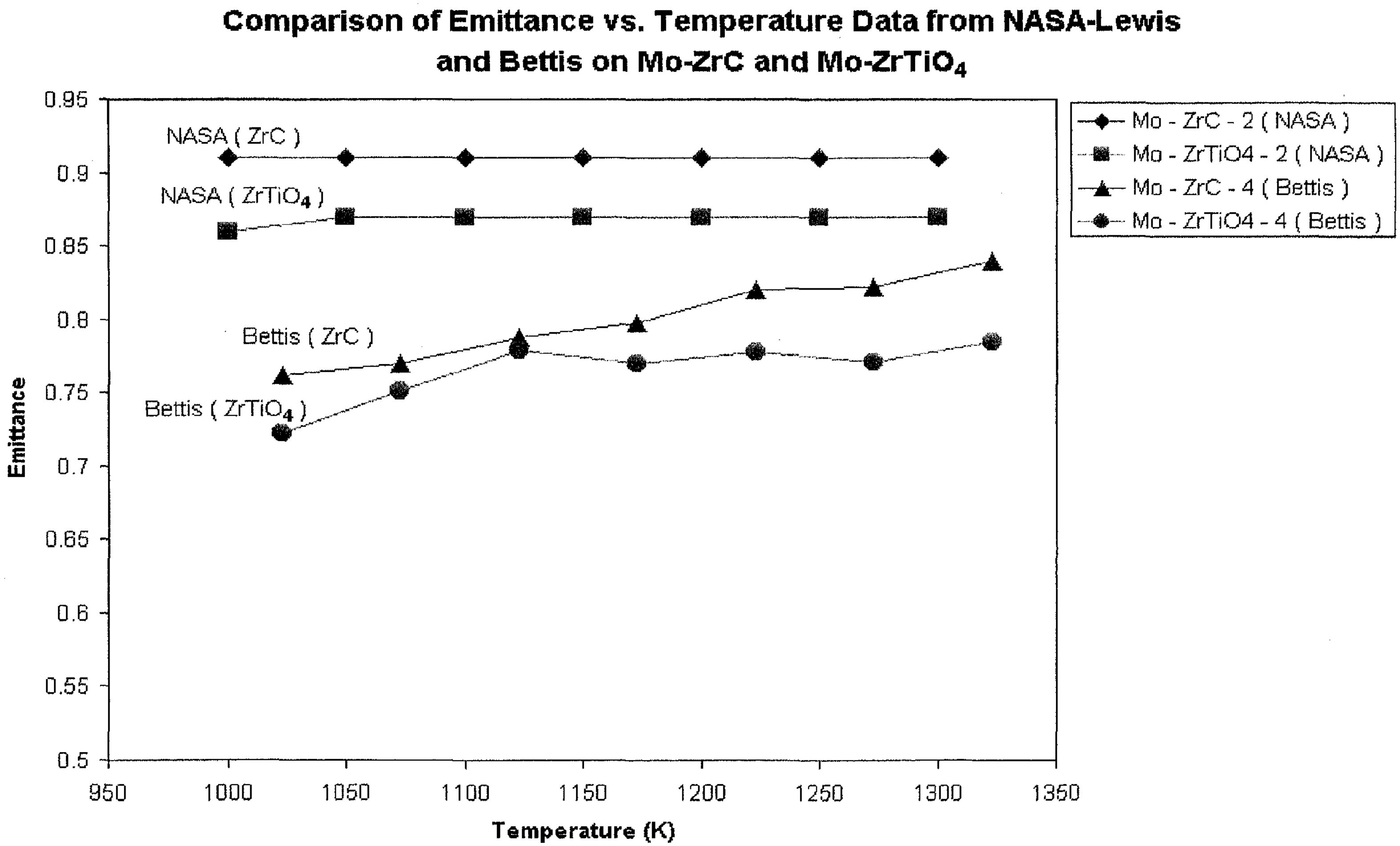


Figure 1. Comparison of emittance vs. temperature for data on ZrC and $ZrTiO_4$ coatings obtained from NASA-Lewis (Mo-ZrC-2 and Mo-ZrTiO4-2) and the radiator screening stand (Mo-ZrC-4 and Mo-ZrTiO4-4). The coatings were all deposited on molybdenum, and are in the as-deposited condition.

Results (Blackbody Emitters)

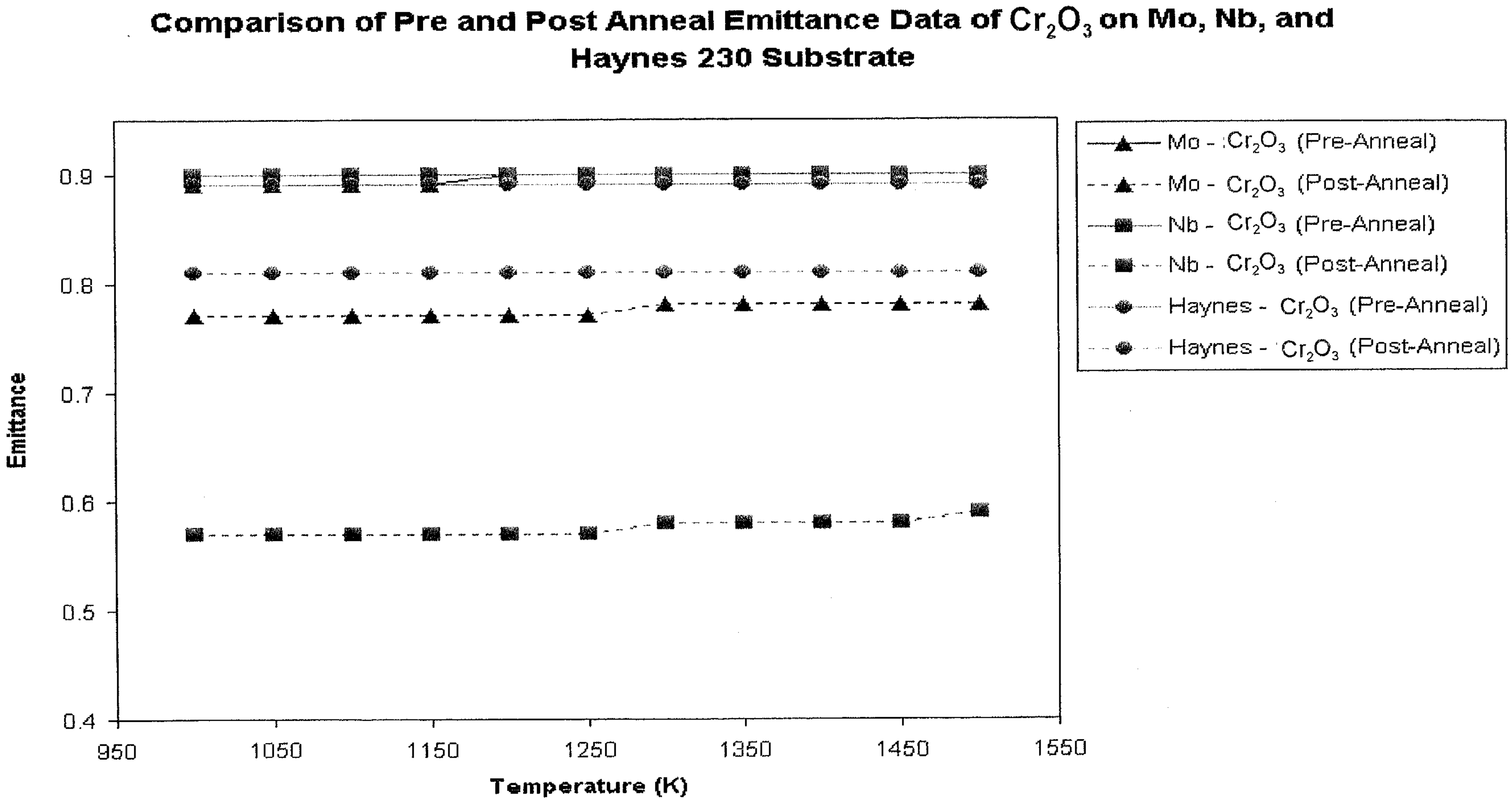
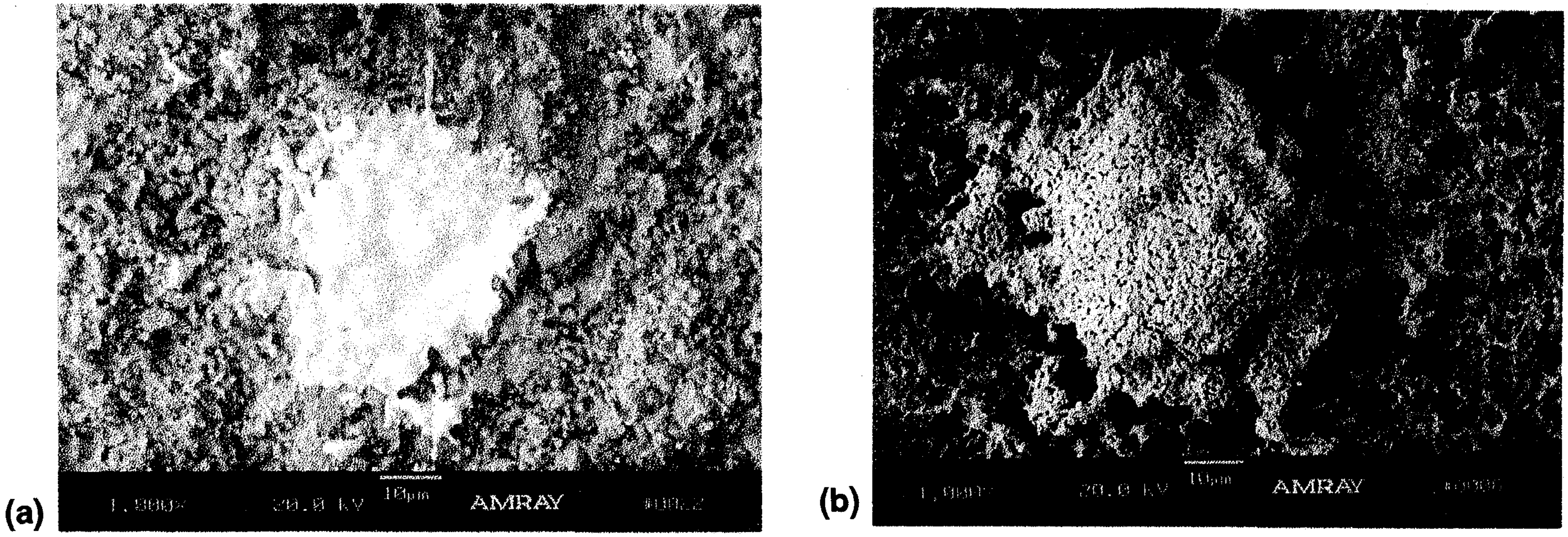


Figure 2 : Comparison of pre- and post-anneal emittance data obtained from NASA-Lewis for the Cr_2O_3 coating deposited on a Mo (blue triangles), Nb (red squares), or Haynes 230 (green circle) substrate.

Scanning Electron Microscopy Micrographs (BSE ; 1000X)



(a) Nb - Cr_2O_3 (As Coated)

Emittance : 0.90

Weight : 7.32173g

(b) Nb - Cr_2O_3 (Post-Annealed)

Emittance : 0.58 (1400K)

Weight : 7.27903g (~1400K; for 500 hrs)

Figure 3 : SEM micrographs of the surface of the Cr_2O_3 coating deposited on Nb: (a) surface of as-deposited coating, and (b) surface of coating after vacuum annealing at 1100°C for 500 hours.

Results (Blackbody Emitters)

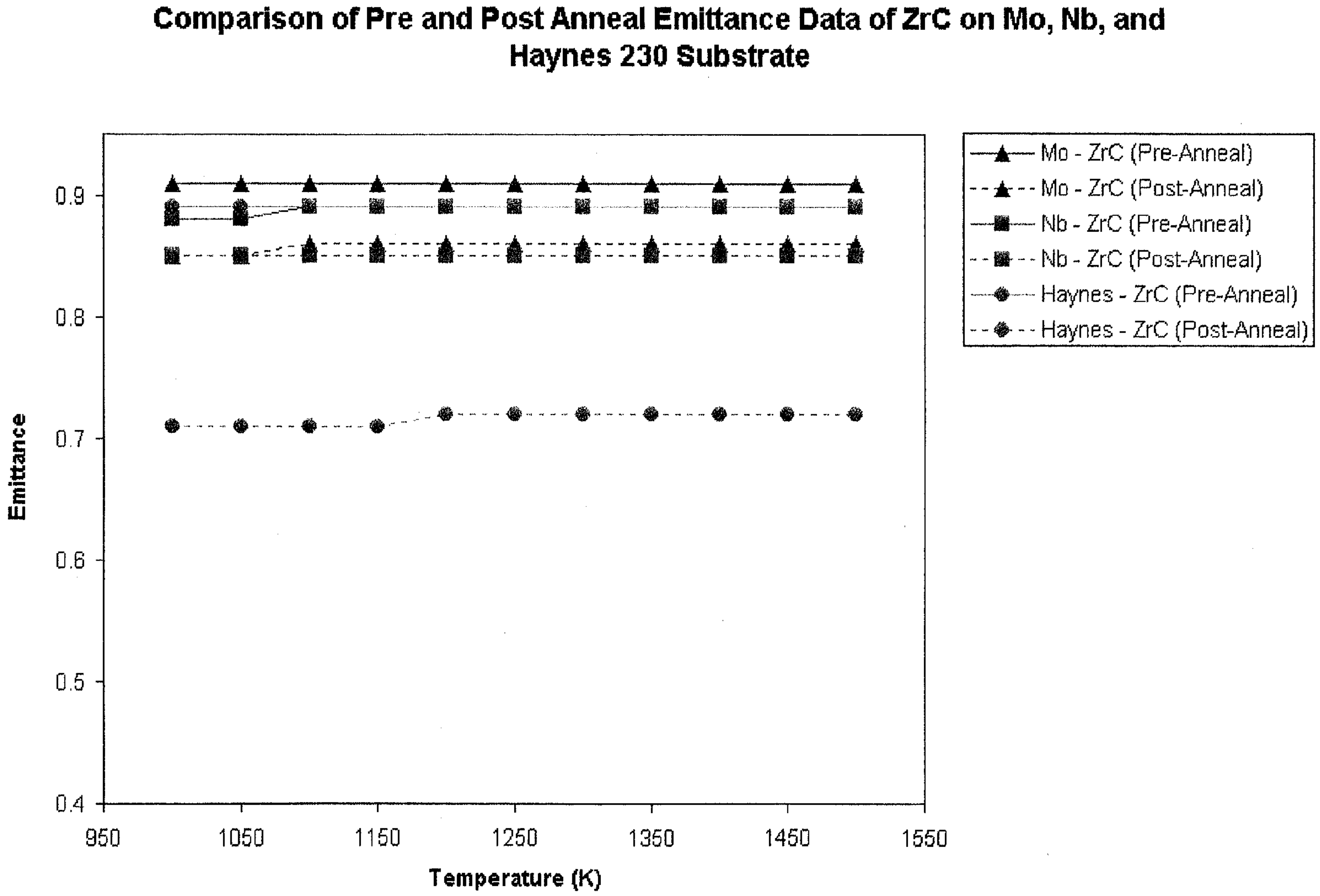


Figure 4 : Comparison of pre- and post-anneal emittance data obtained from NASA-Lewis for the ZrC coating deposited on a Mo (blue triangles), Nb (red squares), or Haynes 230 (green circle) substrate.

EDS : Nb - ZrC (Post-Annealed)

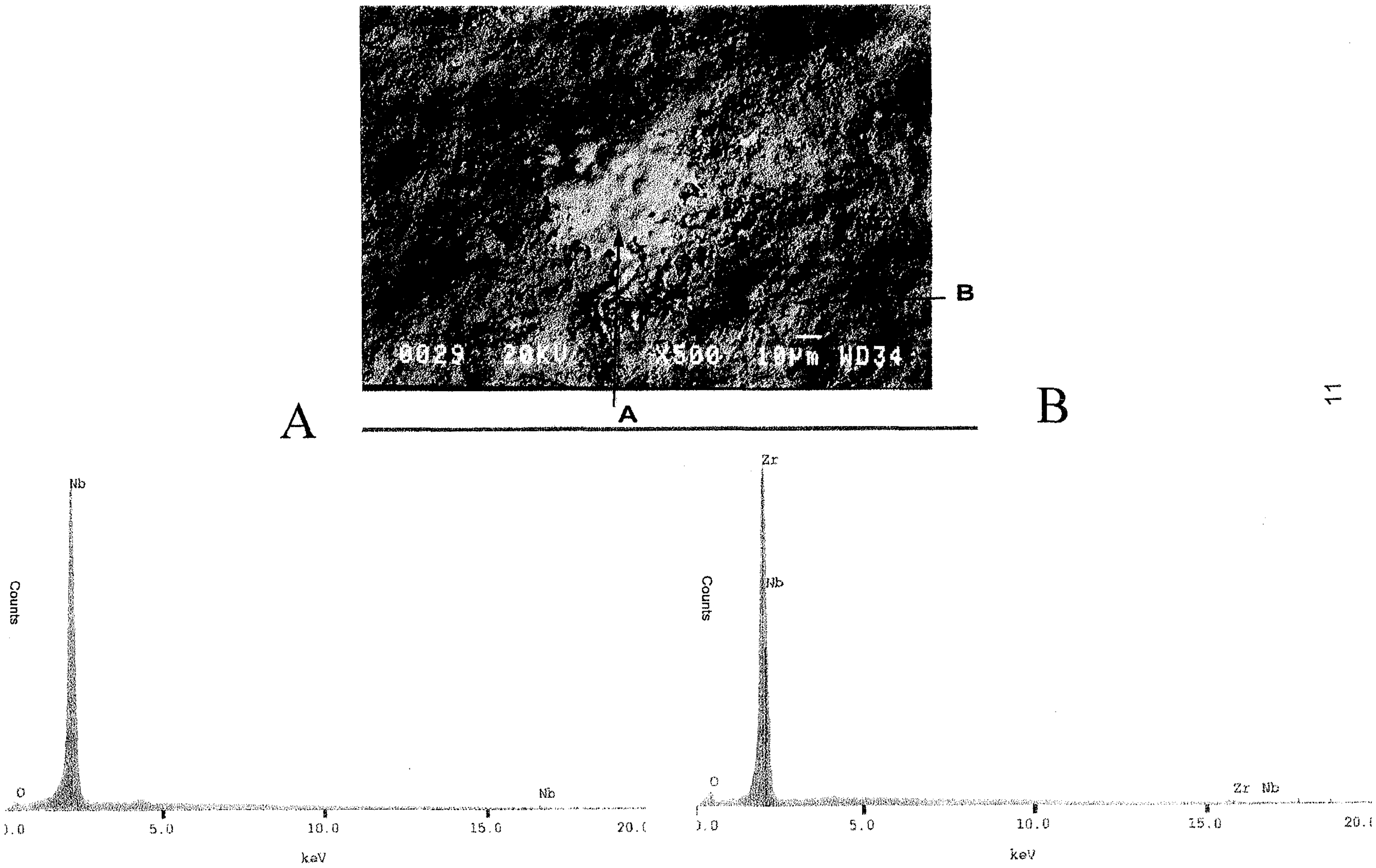
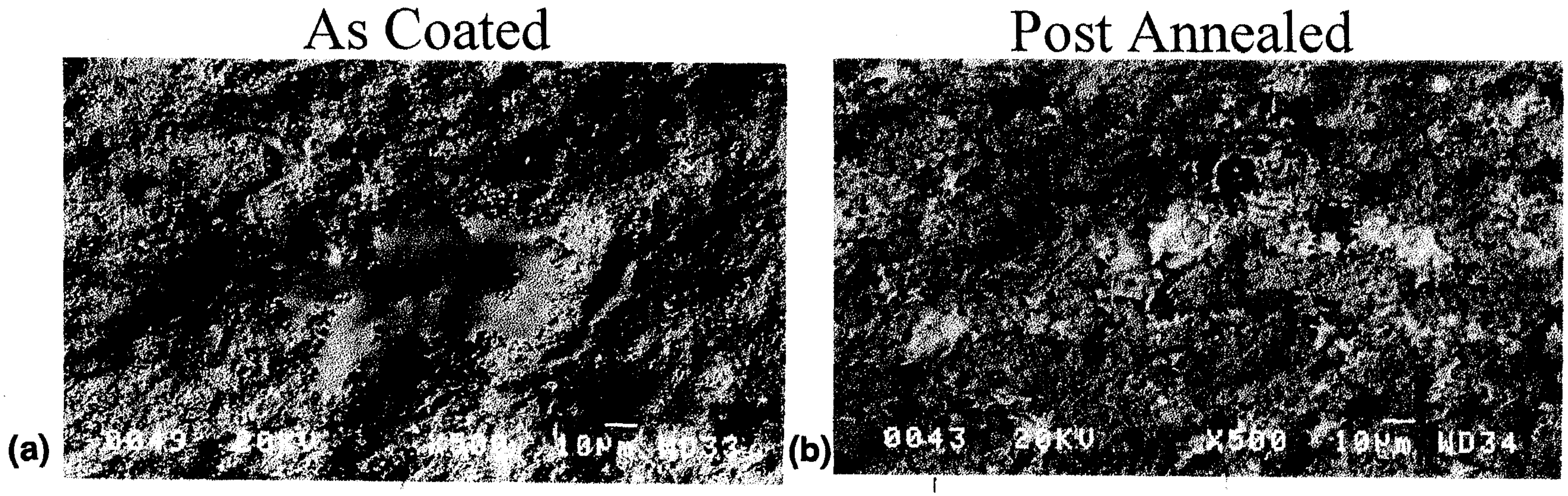


Figure 5 : SEM micrographs of the surface of the ZrC coating deposited on Nb after vacuum annealing at 1100°C for 500 hours with EDS spectra taken from two regions.

EDS : Haynes 230-ZrC


As Coated

Post Annealed

As Coated		
Major	Minor	Traces
Ni	Mo	Fe
Cr	Nb	S
	Zr	Si
		Ti
		Ca

Post Anneal		
Major	Minor	Traces
W	Ni	Fe
	Cr	S
	Zr	

Figure 6 : SEM micrographs of the surface of the ZrC coating deposited on Haynes 230 with a table of EDS results for substrate powder: (a) surface of as-deposited coating, and (b) surface of coating after vacuum annealing at 1100°C for 500 hours.