Thermophysical Properties of Cold- and Vacuum Plasma-Sprayed Cu-Cr-X Alloys, NiAl and NiCrAlY Coatings I: Electrical and Thermal Conductivity, Thermal Diffusivity, and Total Hemispherical Emissivity **S. V. Raj** 

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## Thermophysical Properties of Cold- and Vacuum Plasma-Sprayed Cu-Cr-X Alloys, NiAI and NiCrAIY Coatings I: Electrical and Thermal Conductivity, Thermal Diffusivity, and Total Hemispherical Emissivity

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This two-part paper reports the thermophysical properties of several cold- and vacuum plasma-sprayed monolithic Cu- and Ni-based alloy coatings. Part I presents the electrical and thermal conductivity, thermal diffusivity, and total hemispherical emissivity data, while Part II reports the specific heat capacity data for these coatings. Metallic copper alloys and stoichiometric NiAl and NiCrAlY coatings were fabricated by either the cold spray or the vacuum plasma spray deposition processes for thermal property measurements between 77 and 1223 K. The temperature dependencies of the thermal conductivities, thermal diffusivities, electrical conductivities, and total hemispherical emissivities of these cold- and vacuum-sprayed monolithic coatings are reported in this paper. The electrical and thermal conductivity data correlate reasonably well for Cu-8%Cr-1%Al, Cu-23%Cr-5%Al, and NiAl in accordance with the Wiedemann–Franz (WF) law although a better fit is obtained using the Smith–Palmer relationship. The Lorentz numbers determined from the WF law are close to the theoretical value.

Keywords	aerospace, cold and vacuum plasma spray, copper
	alloy coatings, NiAl coatings, NiCrAlY coatings,
	thermophysical properties

### 1. Introduction

The availability of good-quality thermophysical data is a key for simulating the performance of engineering components and formulating theoretical models to gain fundamental insights into material behavior. The necessity for generating highquality data is more critical for aerospace components especially when two or more different materials are bonded to each other as in the case of coatings deposited on substrates.

Combustion liner materials in a liquid hydrogen (LH<sub>2</sub>)fueled rocket engine experience extreme conditions due to a combination of environmental and thermomechanical effects, where the combustion flame temperatures in the chamber interior are about 3600 K, whereas the backside of the 1-mmthick liner wall experiences cryogenic temperatures of 20 K (Ref 1-6). Copper and its alloys have been used as combustor liner materials in these regenerative rocket engines because of their high thermal conductivity to enable efficient heat transfer from the combustion flame to preheat the cryogenic LH<sub>2</sub> flowing in the cooling channels. The GRCop-84 (Cu-8(at.%)Cr-4%Nb) copper alloy is a potential candidate material to replace the currently used NARloy-Z copper alloy combustor liners in the next generation of reusable launch vehicles (RLVs) due to its superior properties (Ref 7-9). However, uncoated copper alloy liners undergo environmental degradation due to a combination of the spallation of the copper oxide scale and "blanching," which consists of repeated oxidation of the copper matrix and subsequent reduction of the oxide scale (Ref 6). The application of protective coatings on GRCop-84 and other copper alloy substrates can minimize or eliminate many of the problems experienced by uncoated liners and significantly extend their operational lives in RLVs. The use of protective coatings is likely to increase component reliability, reduce depot maintenance turnaround times, and lower operational cost for using RLVs. In addition, the use of a suitable top coat to act as a thermal barrier can allow the engine to run at higher temperatures with a corresponding increase in thermal efficiency. As a result, several types of ceramic (Ref 1, 5) and metallic (Ref 10-16) coatings have been advocated as protective coatings for copper alloy liners. It was demonstrated that CuCrAl and NiCrAlY coatings deposited by either the cold spray (CS) or the vacuum plasma spray (VPS) techniques are potentially viable coatings for GRCop-84 combustion liners (Ref 14, 17-21).

However, the use of protective coatings on a substrate results in the development of residual stresses whenever the coated component experiences significant variations in temperature, such as during processing and thermal cycling conditions, in actual service. Therefore, it is essential that realistic finite element analysis (FEA) be conducted to give credence to the viability of these coated liners during use in RLVs in order to predict the performance of these coatings and to gain insights into the nature and magnitudes of the residual stresses.

The reliability of these modeling analyses requires the generation of high quality of thermophysical data in addition to mechanical properties data. However, thermophysical data for these sprayed coatings are either limited or nonexistent in the temperature range of interest for use in RLVs. Although

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thermal conductivity data of vacuum plasma-sprayed NiCrAlY alloys (Ref 22-25) and NiAl (Ref 26) have been previously reported in the literature, these properties are sensitive to compositional and processing variables. Similarly, although the thermal conductivities of copper alloys have been reported in early investigations (Ref 27-31), and more recently on the Cu-0.01 to 1.0 (at.%)Cr alloys (Ref 32), there are virtually no data available on the CS and VPS copper alloys investigated in the present paper except for GRCop-84 (Ref 7, 9). Thus, it is essential that thermophysical data be generated on protective coatings sprayed under processing conditions and for compositions similar to those developed for spraying the GRCop-84 liners in order to ensure the design models are reliable. Thermal expansion data for several VPS coatings investigated in the present study were reported earlier (Ref 33), while the elastic moduli data for CS and VPS coatings were reported elsewhere (Ref 34). The objectives of this two-part paper are to report the thermophysical data generated on CS and VPS Cu-Cr, CuCrAl, NiAl, and NiCrAlY coating alloys as a function of absolute temperature, T, varying between 77 and 1223 K. Part I presents the electrical and thermal conductivity, thermal diffusivity, and total hemispherical emissivity data, while Part II reports the specific heat capacity data for these coatings. It has been necessary to divide the papers in this manner due to the nature of the analyses of the data. For example, Part I presents electrical and thermal conductivity since they are related to metallic systems, whereas the analyses of the specific heat data in Part II are related to thermodynamic parameters.

### 2. Experimental Procedures

### 2.1 Alloy Composition and Processing

The nominal compositions of the alloy powders investigated in this research were Cu-8(wt.%)Cr, Cu-26(wt.%)Cr, Cu-8(wt.%)Cr-1%Al, Cu-23(wt.%)Cr-5%Al, Ni-31.5(wt.%)Al (NiAl), and Ni-17(wt.%)Cr-6%Al-0.5%Y (NiCrAlY). Details of the powder suppliers and fabrication methods were reported earlier (Ref 33-35). Monolithic coatings,\* typically 175-250 mm long and 19-25 mm thick, were fabricated by spraying the powders on rotating aluminum or steel mandrels either by the CS process or by the VPS method, respectively. The Cu-23%Cr-5%Al coatings were cold-sprayed at ASB Industries, Inc., Barberton, OH (Ref 17, 35). The Cu-8%Cr, Cu-8%Cr-1%Al, NiAl and NiCrAlY coatings were deposited by the vacuum plasma spray method at Plasma Processes, Inc., Huntsville, AL (Ref 33). The coated mandrels were hot isostatically pressed (HIP) between 1073 and 1273 K under argon gas pressures varying between 100 and 210 MPa for times varying between 1 and 4 h. In addition, a Cu-17(wt.%)Cr-5%Al alloy was prepared by arc-melting the appropriate mixtures of Al, Cr and Cu chunks or pellets (Ref 20). In this case, the button melt was flipped several times to homogenize the composition of the molten metal before being drop cast into a copper die cavity 12.7 mm dia.  $\times$  50 mm long. The alloy was homogenized annealed at 1223 K for 24 h under flowing argon to minimize elemental segregation. Specimens were machined from the sprayed cylinders by electrodischarge

machining (EDM). For baseline comparisons, density and thermophysical property measurements were also made on a hot-extruded GRCop-84 disk.

### 2.2 Thermophysical Measurements

The thermophysical property measurements reported in this paper were conducted at the Thermophysical Properties Research Laboratory, Inc. (TPRL), West Lafayette, IN under contract. Details of the techniques for measuring several of the thermal properties reported in this paper are described elsewhere (Ref 36). Table 1 gives the specimen dimensions for each thermal property measurement technique. The bulk density,  $\rho_d$ , of each specimen was calculated from its geometry and mass. High-temperature thermal diffusivity,  $\alpha$ , was measured between 295 and 1223 K under high vacuum using the laser flash techniques in accordance with ASTM E1461 (Ref 37). The front face of the disk specimen was heated by a short laser burst from a Korad K2 laser apparatus and the resulting temperature rise at the back face was recorded and analyzed by a computerized system. Constant pressure specific heat,  $C_{\rm p}$ , measurements on these monolithic coatings are reported in Part II (Ref 38). The high-temperature thermal conductivity,  $K_{\rm T}$ , of the specimen was calculated from the relationship  $K_{\rm T} = \alpha \rho_{\rm d} C_{\rm p}$ . While the laser flash method of determining  $K_{\rm T}$  is indirect, thermal conductivity of a NiCrAlY monolithic coating was also measured directly and dynamically using a laser beam of a known heat flux and measuring the front and back face temperatures on a 25.4 mm diameter × 3.1 mm thick disk specimen in order to compare the two sets of data. Details of this measurement technique are described elsewhere (Ref 39).

Low-temperature thermal conductivity,  $\lambda$ , and electrical resistivity,  $\rho$ , of the specimens were determined by the modified Kohlrausch method, which measures the product,  $\lambda \rho$ . The thermal conductivity measurements were taken between 80 and 458 K in vacuum. Details of the technique and the methods used for separating  $\lambda$  and  $\rho$  from the measurements are described elsewhere (Ref 36). Briefly, the method involves passing a direct current through the specimen to heat it while cooling the ends with liquid nitrogen. Radial heat losses were minimized by surrounding the specimen with an external heater with its center temperature maintained at the sample's midpoint temperatures. These test conditions ensured that a steady-state parabolic temperature profile was maintained along the axis of the specimen. Three thermocouples located at the specimen ends, designated as 1 and 3, and at its midpoint, designated as 2, were used as both voltage and temperature probes. Thus,

$$\lambda \rho = \frac{(V_3 - V_1)^2}{4[2T_2 - (T_1 + T_3)]};$$
 (Eq 1)

$$\rho = \frac{(V_1 - V_3)A}{iL_{13}},$$
 (Eq 2)

where  $V_j$  and  $T_j$  are voltages and absolute temperature readings from the *j*th thermocouple (j = 1, 2, or 3), respectively, *A* is the specimen cross-sectional area, *i* is the current through the specimen, and  $L_{13}$  is the distance between the end thermocouples, 1 and 3. The voltage and temperature data from the three thermocouples and the magnitudes of *i* were fed to a computerized data acquisition system, which enabled Eq 1 and 2 to be solved to evaluate  $\lambda$  and  $\rho$  for different sets of equilibrium conditions.

<sup>\*</sup>The term "monolithic coatings" is used in a generic manner in this paper to distinguish cold- and vacuum plasma-sprayed powders from cast or extruded alloys.

### Table 1 Dimensions of specimens used for different measurements

Property	Measurement technique	Specimen dimensions, mm
Density	Mass and geometric volume	12.7 dia. $\times$ 1.5 to 5.0 thick (disk); 12.8 width $\times$ 12.8 width $\times$ 2.0 thick (square)
Electrical resistance/thermal conductivity (low temperature)	Kohlrausch method	88.9 long $\times$ 4.8 width $\times$ 2.5 thick
Total hemispherical emissivity	Heat balance (ASTM 835-06)	254 long $\times$ 4.8 width $\times$ 2.5 thick
Thermal conductivity/thermal diffusivity (high temperature)	Laser flash method (ASTM E1461)	12.7 dia. $\times$ 1.5 to 5.0 thick
Measurements were conducted at TPRL, West Lafayette, IN		

The total hemispherical emissivity,  $\varepsilon_{\rm H}$ , was measured between 373 and 1223 K using a multi-property apparatus equipped with long vertical optical windows in accordance with ASTM 835-06 (Ref 40). The specimen was mounted between two electrodes and heated under high vacuum by passing a direct current through it. The power dissipated over a small central region of the specimen was determined by measuring the product, V·i, where V is the voltage, and the absolute temperature of the specimen midpoint,  $T_{\rm mid}$ . In order to make measurements at the lower temperatures, the specimen was surrounded by liquid nitrogen (LN<sub>2</sub>)-cooled copper shield with its interior surface painted black. The magnitude of  $\varepsilon_{\rm H}$  was calculated from

$$\varepsilon_H = \frac{V \cdot i}{P_{\rm c} L \sigma \left(T_{\rm mid}^4 - T_0^4\right)},\tag{Eq 3}$$

where  $P_{\rm c}$  is the circumference of the specimen, *L* is the distance between voltage probes,  $\sigma$  is the Stefan–Boltzmann constant, and  $T_0$  is the ambient temperature.

### 3. Results and Discussion

#### 3.1 Density and Microstructures

Table 2 shows the values of the bulk densities for several metallic monolithic coatings processed by different spraying techniques. The GRCop-84 and Cu-17%Cr-5%Al specimens were tested in the as-extruded and arc-melted conditions, respectively. The VPS Cu-26Cr (V2-02-27A) (Fig. 1a) and VPS NiCrAlY (V2-02-27E) (Fig. 1b) monolithic coatings had a significant amount of porosity, and this fact is reflected in this batch having lower densities than material from batches V2-03-524 (VPS Cu-26%Cr) (Fig. 1c) and V2-03-528 (VPS Ni-CrAlY) (Fig. 1d), which were nearly 100% dense with little or no significant amount of porosity (Table 1). The other coatings were close to 100% dense (Fig. 1e). It is noted that the microstructures of VPS Cu-8%Cr, Cu-26%Cr, and Cu-8%Cr-1%Al are similar with a distribution of  $\alpha$ -Cr precipitates in either an  $\alpha$ -Cu or  $\alpha$ -(Cu,Al) matrix, respectively, whereas the  $\alpha$ -Cu matrix in extruded GRCop-84 is strengthened by fine Cr<sub>2</sub>Nb precipitates. The volume fraction of the  $\alpha$ -Cr precipitates is higher in VPS Cu-26%Cr compared to the VPS Cu-8%Cr alloy. The microstructure of the as-cast Cu-17%Cr-5%Al alloy was reported elsewhere (Ref 20), where the  $\alpha$ -(Cu,Al) matrix contained a dispersion of  $\alpha$ -Cr dendrites.

### 3.2 Thermal Diffusivity

Figure 2 shows the comparison of the temperature dependencies of  $\alpha$  for extruded GRCop-84, VPS Cu-8%Cr, VPS Cu-

26%Cr, VPS Cu-8%Cr-1%Al, as-cast Cu-17%Cr-5%Al, and CS Cu-23%Cr-5%Al. The magnitudes of  $\alpha$  vary between  $5\times10^{-5}$  and  $1\times10^{-4}$  m<sup>2</sup>/s at 300 K for these materials. A close examination of the data reveals that the thermal diffusivity data for the VPS Cu-8%Cr, VPS Cu-26%Cr, and hot-extruded GRCop-84 specimens show a gradual decrease with increasing temperature, whereas the curve for the VPS Cu-8%Cr-1%Al coating initially increases gradually with increasing temperature until about 800 K before decreasing with continued increase in temperature to thermal diffusivity values close to those of Cu-8%Cr, Cu-26%Cr, and GRCop-84. The two sets of data for the VPS Cu-26%Cr monolithic coatings differ from each other significantly since batch V2-02-27B is significantly more porous (Fig. 1a) than batch V2-03-524 (Fig. 1c), and therefore, it has a lower thermal diffusivity. The thermal diffusivity of the as-cast Cu-17%Cr-5%Al alloy increases slightly with increasing absolute temperature from  $\alpha \sim 2.0 \times 10^{-5} \text{ m}^2/\text{s}$  at 296 K to  $\alpha \sim 2.9 \times 10^{-5} \text{ m}^2/\text{s}$  at 1223 K with the magnitudes of  $\alpha$  being significantly lower than those for the other copper alloys. As expected, the magnitudes of  $\alpha$ for the CS Cu-23%Cr-5%Al coating are similar during the heatup and cool-down portion of the cycle within the limits of experimental scatter. The data were regression-fitted empirically using the polynomial Eq 4

$$\alpha = A_{\alpha} * T^4 + B_{\alpha} * T^3 + C_{\alpha} * T^2 + D_{\alpha} * T + E_{\alpha}, \qquad (\text{Eq 4})$$

where  $A_{\alpha}$ ,  $B_{\alpha}$ ,  $C_{\alpha}$ ,  $D_{\alpha}$ , and  $E_{\alpha}$  are regression coefficients and  $R_{d}^{2}$  are coefficients of determination (Table 3).

The thermal diffusivity of VPS NiAl is almost independent of temperature with the magnitudes of  $\alpha \sim 1.8 \times 10^{-5}$  to  $1.9 \times 10^{-5}$  m<sup>2</sup>/s between 296 and 1223 K (Fig. 3). In contrast, the thermal diffusivity of the VPS NiCrAIY coating increases with increasing temperature from about  $2 \times 10^{-6}$  m<sup>2</sup>/s at 296 K to  $5 \times 10^{-6}$  m<sup>2</sup>/s at 1223 K. Interestingly, despite the differences in the porosity content, the magnitudes of  $\alpha$  for the two batches of VPS NiCrAIY are nearly identical. Table 3 shows the magnitudes of the regression coefficients and  $R_d^2$  for the monolithic VPS NiAl and the two batches of VPS NiCrAIY coatings.

### 3.3 Thermal Conductivity

Figure 4 shows the variation of  $K_{\rm T}$  as a function of absolute temperature for extruded GRCop-84, VPS Cu-8%Cr, two batches of VPS Cu-26%Cr, VPS Cu-8%Cr-1%Al, as-cast Cu-17%Cr-5%Al, and CS Cu-23%Cr-5%Al. In addition, the temperature dependencies of  $\lambda$  for VPS Cu-8%Cr-1%Al and CS Cu-23%Cr-5%Al are also shown in the figure. The magnitudes of  $K_{\rm T}$  are represented by the left-hand axis, while the data for  $\lambda$  are represented by the right-hand axis as denoted by the arrows. It is important to note that despite the fact that

### Table 2 Magnitudes of room-temperature bulk density of different sprayed monolithic coatings

Nominal coating composition(a)	Batch ID	Processed condition	Bulk density(b), kg/m
Cu-8(at.%)Cr-4%Nb	GRCop-84	Extruded	8945
Cu-8(wt.%)Cr	V2-03-134	VPS	8598
Cu-26(wt.%)Cr(c)	V2-02-27B	VPS	5450
Cu-26(wt.%)Cr	V2-03-524	VPS	5826
Cu-8(wt.%)Cr-1%Al	V2-05-27	VPS	8546
Cu-17(wt.%)Cr-5%A1	8	As-cast	7688
Cu-23(wt.%)Cr-5%Al	Cu-23Cr-5Al	CS	7575
Ni-50(at.%)Al	V2-03-166	VPS	5826
Ni-17(wt.%)Cr-6%Al-0.5%Y(c)	V2-02-27E	VPS	7161
Ni-17(wt.%)Cr-6%Al-0.5%Y	V2-03-528	VPS	7711

(a) All compositions are in wt.% except those for GRCop-84 and NiAl for which the compositions are reported in at.% as per convention

(b) Calculated from the ratio of the mass to the geometric volume of the specimen(c) These specimens had a lot of porosity. All other sprayed specimens were close to 100% density



**Fig. 1** Microstructures of vacuum plasma-sprayed monolithic coatings: (a) Cu-26%Cr (V2-02-27A); (b) Ni-17%Cr-6%Al-0.5%Y (V2-02-27E); (c) Cu-26%Cr (V2-03-524); (d) Ni-17%Cr-6%Al-0.5%Y (V2-03-528); (e) Cu-8%Cr (V2-03-134); and (f) stoichiometric NiAl (V2-03-143)



Fig. 2 Temperature dependences of the thermal diffusivities of extruded GRCop-84, VPS Cu-8%Cr, VPS Cu-26%Cr (V2-02-27B and V2-03-524), VPS Cu-8%Cr-1%Al, as-cast Cu-17%Cr-5%Al (8), and CS Cu-23%Cr-5%Al during the heat-up and cool-down cycle

Table 3 Regression coefficients for the temperature dependence of thermal diffusivity described by Eq 4

Material	$A_{\alpha}, \mathrm{m}^2/\mathrm{K}^4$ s	$B_{\alpha}$ , m <sup>2</sup> /K <sup>3</sup> s	$C_{\alpha}, \mathrm{m}^2/\mathrm{K}^2$ s	$D_{\alpha}, \mathrm{m}^2/\mathrm{K} \mathrm{s}$	$E_{\alpha}, \mathrm{m}^2/\mathrm{s}$	$R_{\rm d}^2$
GRCop-84 (extruded) (296 $\leq T \leq 1223$ K)	$-1.5 \times 10^{-16}$	$3.8 \times 10^{-13}$	$-3.6 \times 10^{-10}$	$1.3 \times 10^{-7}$	$7.7 \times 10^{-5}$	0.9977
Cu-8%Cr (V2-03-134) (296 $\leq T \leq 1223$ K)	$-9.5 \times 10^{-17}$	$2.2 \times 10^{-13}$	$-\ 1.8\times 10^{-10}$	$3.0 \times 10^{-8}$	$1.0 \times 10^{-4}$	0.9999
Cu-26%Cr (V2-02-27B) (296 $\leq T \leq 1223$ K)	$-2.6 \times 10^{-17}$	$5.1 \times 10^{-14}$	$-3.3 \times 10^{-11}$	$-1.7 \times 10^{-9}$	$4.1 \times 10^{-5}$	0.9993
Cu-26%Cr (V2-03-524) (296 $\leq T \leq 1223$ K)	$-5.6 \times 10^{-17}$	$1.3 \times 10^{-13}$	$-1.1 \times 10^{-10}$	$7.5  imes 10^{-9}$	$8.8 \times 10^{-5}$	0.9999
Cu-8%Cr-1%Al (V2-05-27) (296 $\leq T \leq 1223$ K)	$-4.8 \times 10^{-17}$	$1.5 \times 10^{-13}$	$-2.2 \times 10^{-10}$	$1.5 \times 10^{-7}$	$1.8 \times 10^{-5}$	0.9989
Cu-17%Cr-5%Al (as-cast) (8) (296 $\leq T \leq 1223$ K)	$-3.4 \times 10^{-17}$	$1.0 \times 10^{-13}$	$-1.4 \times 10^{-10}$	$9.5 \times 10^{-8}$	$1.3 \times 10^{-6}$	0.9989
Cu-23%Cr-5%Al- (CS) (heat-up) (296 $\leq T \leq 1223$ K)	$-7.3 \times 10^{-17}$	$2.3 \times 10^{-13}$	$-2.9 \times 10^{-10}$	$1.6 \times 10^{-7}$	$-8.6 \times 10^{-6}$	0.9987
NiAl (V2-03-166) (296 $\leq T \leq 1223$ K)	$3.2 \times 10^{-18}$	$-1.2 \times 10^{-14}$	$1.2 \times 10^{-11}$	$-1.1 \times 10^{-9}$	$1.8 \times 10^{-5}$	0.9889
Ni-17%Cr-6%Al-0.5%Y (V2-02-27E) (296 $\leq T \leq 1223$ K)	$-4.5 \times 10^{-18}$	$6.7 \times 10^{-15}$	$-1.4 \times 10^{-12}$	$1.6 \times 10^{-9}$	$2.4 \times 10^{-6}$	0.9975
Ni-17%Cr-6%Al-0.5%Y (V2-03-528) (296 $\leq T \leq 1223$ K)	$-5.1 \times 10^{-18}$	$1.1 \times 10^{-14}$	$-7.8 \times 10^{-12}$	$5.3 \times 10^{-9}$	$1.9 \times 10^{-6}$	0.9993

 $K_{\rm T}$  and  $\lambda$  were determined by two different techniques, the two sets of data match very nicely for both VPS Cu-8%Cr-1%Al and CS Cu-23%Cr-5%Al.

The values of  $K_{\rm T}$  decrease with increasing *T* for the VPS Cu-8%Cr and for the low-porosity VPS Cu-26%Cr coatings (V2-03-524), whereas  $K_{\rm T}$  increases slightly up to 673 K for extruded GRCop-84 before decreasing with increasing *T* when T > 673 K. The magnitudes of  $K_{\rm T}$  vary between about 345 W/m/K at 296 K and about 245 W/m/K at 1223 K for the VPS Cu-8%Cr coating. The values of  $K_{\rm T}$  for the VPS Cu-26%Cr coating (V2-03-524) are significantly lower varying between about 285 W/m/K at 296 K and 210 W/m/K at 1223 K. As expected, the presence of porosity in the VPS Cu-26%Cr batch V2-02-27B significantly decreases the thermal conductivity of VPS Cu-26%Cr by factors of 3.4 and 2.9 at 296 and 1223 K, respectively, compared to batch V2-03-524. In this case, the

magnitude of  $K_{\rm T}$  decreases from about 85 W/m/K at 296 K to about 72 W/m/K at 1223 K. The value of  $K_{\rm T}$  for the extruded GRCop-84 at 296 K is about 315 W/m/K, but increases to values similar to those for the VPS Cu-8%Cr coating above 673 K. In the case of Cu-8%Cr-1%Al,  $\lambda$  increases from about 100 W/m/K at about 92 K to about 179 W/m/K at 395 K, while  $K_T$  increases from about 165 W/m/K at 296 K to about 235 W/m/K at 1223 K. The magnitudes of  $K_{\rm T}$  for the as-cast Cu-17%Cr-5%Al increase from about 64 W/m/K at 296 K to about 116 W/m/K at 1223 K. These values are close to the magnitudes of K<sub>T</sub> for the CS Cu-23%Cr-5%Al coating for which  $K_{\rm T}$  varies between about 65 W/m/K at 296 K to about 97 W/m/K at 1223 K. As shown in Fig. 4, the magnitudes of  $\lambda$ for the CS Cu-23%Cr-5%Al vary from about 32 W/m/K at about 90 K to about 80 W/m/K at about 459 K, and these data are in very good agreement with the values of  $K_{\rm T}$ .



Fig. 3 Temperature dependences of the thermal diffusivities of stoichiometric VPS NiAl and two VPS Ni-17%Cr-6%Al-0.5%Y (V2-02-27E and V2-03-528)



Fig. 4 Temperature dependences of the low ( $\lambda$ ) and high thermal conductivities ( $K_T$ ) for as-extruded GRCop-84, VPS Cu-8%Cr, VPS Cu-26%Cr (V2-03-524), VPS Cu-8%Cr-1%Al, Cu-17%Cr-5%Al (as-cast), and CS Cu-23%Cr-5%Al. The low-temperature thermal conductivity data for VPS Cu-8%Cr-1%Al and CS Cu-23%Cr-5%Al are denoted by the horizontal arrows

Table 4 Regression coefficients for the temperature	dependence of temper	ature thermal conduc	tivity described by E	q 5		
Material	$A_{ m K}$ or $A_{ m k},$ W/m ${ m K}^5$	$B_{ m K}$ or $B_{\lambda},$ W/m ${ m K}^4$	$C_{ m K}$ or $C_{ m k},~ m W/m~ m K^3$	$D_{ m K}$ or $D_{ m \lambda},$ W/m $ m K^2$	$E_{ m K}$ or $E_{ m k},$ W/m K	$R_{ m d}^2$
GRCop-84 (extruded) (296 $\leq T \leq 1223$ K)	$-7.4 \times 10^{-10}$	$2.0  imes 10^{-6}$	$-2.1 \times 10^{-3}$	$9.6 \times 10^{-1}$	170.0	0.9808
$Cu-8\%Cr$ (V2-03-134) (296 $\leq T \leq 1223$ K)	$-5.2 imes 10^{-10}$	$1.4 \times 10^{-6}$	$-1.4 \times 10^{-3}$	$5.6 imes10^{-1}$	266	0.9996
$Cu-26\%Cr$ (V2-02-27B) (296 $\leq T \leq 1223$ K)	$-2.1 imes 10^{-10}$	$6.4  imes 10^{-7}$	$-7.1  imes 10^{-4}$	$3.2 imes 10^{-1}$	388	0.9951
$Cu-26\%Cr$ (V2-03-524) (296 $\leq T \leq 1223$ K)	$ 8.2 imes 10^{-10}$	$2.4  imes 10^{-6}$	$-$ 2.5 $ imes$ $10^{-3}$	1.0	140	0.9982
$Cu-8\%Cr-1\%Al$ (V2-05-27) (296 $\leq T \leq 1223$ K)	$-7.7 \times 10^{-11}$	$3.2  imes 10^{-7}$	$-5.4 imes 10^{-4}$	$4.7 imes10^{-1}$	693	0.9994
$Cu-8\%Cr-1\%Al$ (V2-05-27) (92 $\leq T \leq 395$ K)	$-1.1 \times 10^{-8}$	$1.2  imes 10^{-5}$	$-5.0 imes10^{-3}$	1.2	137	0.9998
Cu-17%Cr-5%Al (as-cast) (8) (296 $\leq T \leq 1223$ K)	$-9.9 \times 10^{-11}$	$3.4  imes 10^{-7}$	$-4.6 imes10^{-4}$	$3.4 imes 10^{-1}$	-5.21	0.9987
$Cu-23\%Cr-5\%Al$ (CS) (296 $\leq T \leq 1223$ K)	$-2.1  imes 10^{-10}$	$6.9  imes 10^{-7}$	$ 8.9 imes10^{-4}$	$5.4 imes10^{-1}$	- 34.3	0.9996
$Cu-23\%Cr-5\%Al$ (CS) (90 $\leq T \leq 459$ K)	$1.4  imes 10^{-9}$	$-1.3 \times 10^{-6}$	$2.8 imes 10^{-4}$	$1.5 imes 10^{-1}$	17.0	0.9997
NiAl (V2-03-166) (296 $\leq T \leq 1223$ K)	$1.0 \times 10^{-11}$	$-3.8 \times 10^{-8}$	$2.6  imes 10^{-5}$	$2.6  imes 10^{-2}$	48.3	0.9984
NiAl (V2-03-166) (82 $\leq T \leq 399$ K)	$-4.3 \times 10^{-9}$	$4.8 \times 10^{-6}$	$-2.0 imes10^{-3}$	$4.2 imes 10^{-1}$	8.99	0.9989
Ni-17%Cr-6%Al-0.5%Y (V2-02-27E) (296 $\leq T \leq 1223$ K)	$-6.3 \times 10^{-11}$	$1.6 \times 10^{-7}$	$-1.5 imes 10^{-4}$	$6.7  imes 10^{-2}$	-1.24	0.9983
Ni-17%Cr-6%Al-0.5%Y (V2-03-528) (296 $\leq T \leq 1223$ K)	$-6.3 \times 10^{-11}$	$2.0 imes 10^{-7}$	$-2.0  imes 10^{-4}$	$1.0  imes 10^{-1}$	-6.69	0.9998
Note: The subscripts K and $\lambda$ are for high and low temperature	e thermal conductivities, re	sspectively				

The  $K_{\rm T}$  and  $\lambda$  data for the copper alloys shown in Fig. 4 were regression-fitted using the polynomial Eq 5

$$K_{\rm T}$$
 or  $\lambda = A_{\rm i} * T^4 + B_{\rm i} * T^3 + C_{\rm i} * T^2 + D_{\rm i} * T + E_{\rm i}$ , (Eq 5)

where  $A_i$ ,  $B_i$ ,  $C_i$ ,  $D_i$ , and  $E_i$  are regression coefficients and the subscript *i* is either *K* or  $\lambda$  for high- and low-temperature conductivity, respectively.\*\* Table 4 gives the values of the regression coefficients, the corresponding magnitudes of  $R_d^2$ and the temperature ranges for which the regression parameter is valid.

The approximate similarity in the magnitudes of  $K_{\rm T}$  for VPS Cu-8%Cr and extruded GRCop-84 observed in Fig. 4 suggests that the differences in the processing conditions, precipitate composition (i.e., Cr<sub>2</sub>Nb in GRCop-84 and α-Cr in Cu-8%Cr), and precipitate size and morphology do not significantly affect the high-temperature thermal conductivity of these alloys. Increasing the Cr content from 8 to 26% decreases the hightemperature conductivity of the Cu-Cr alloys to some extent, but the presence of large amounts of porosity in the microstructure significantly decreases  $K_{\rm T}$  by a large amount. Interestingly, the addition of 1%Al to the Cu-8%Cr alloy results both in a considerable decrease in thermal conductivity at the lower temperatures and in the nature of its temperature dependence. Increasing the Al content to 5% further decreases the thermal conductivity of the Cu-Cr alloys irrespective of processing conditions and Cr content. Since the magnitudes of  $K_{\rm T}$  are approximately similar for the porous VPS Cu-26%Cr (V2-02-27B), as-cast Cu-17%Cr-5%Al, and CS Cu-23%Cr-5%Al, it appears that both matrix voids and Al atoms in solid solution scatter the lattice phonons and electrons more significantly than the Cr<sub>2</sub>Nb precipitates in the extruded GRCop-84 and the  $\alpha$ -Cr precipitates in the VPS Cu-8%Cr and Cu-26%Cr.

Figure 5 shows temperature dependences of  $K_{\rm T}$  and  $\lambda$  for VPS NiAl and the two batches of VPS NiCrAlY determined by the laser flash technique. In addition, thermal conductivity data on VPS NiCrAlY (V2-03-528) from the dynamic laser measurement method are also shown in the figure. Comparison of Fig. 4 and 5 reveals that these Ni-based coatings exhibit much lower thermal conductivities than the copper alloys. The values of  $\lambda$  for NiAl increase from about 33 W/m/K at 82 K to about 56 W/m/K at 399 K, while  $K_T$  increases from about 57 W/m/K at 296 K to about 72 W/m/K at 1223 K. At 300 K,  $\lambda \sim 51$  W/m/K for NiAl and this value is slightly lower than the room temperature magnitude of  $K_{\rm T}$ . In the case of NiCrAlY (V2-03-528), the magnitude of  $K_{\rm T}$  increases from about 11 W/ m/K at 296 K to about 30 W/m/K at 1223 K. The second NiCrAlY batch (V2-02-27E), which had considerably more porosity (Fig. 1b), exhibits similar values of  $K_{\rm T}$  between 296 and 1073 K, but attains an approximately constant value of  $K_{\rm T}$  ~ 24 W/m/K at and above 1073 K. Interestingly, the magnitudes of  $K_{\rm T}$  determined by the dynamic method are lower than those determined by the laser flash method for NiCrAlY (V2-03-528). The precise reason for this difference in the two sets of data is unclear. Clearly, unlike in the case of Cu-26%Cr (Fig. 4), the presence of voids in the NiCrAlY did not significantly affect the magnitudes of the measured  $K_{\rm T}$  below 973 K presumably because NiCrAlY has much lower thermal

<sup>\*\*</sup>Although the individual values of  $K_{\rm T}$  are derived from the values of  $\alpha$  and  $C_{\rm P}$  at each temperature, it is important to note that the purposes of the empirical regression equations such as Eq 5 are solely to identify the lowest order polynomial equations that accurately represent the data shown in Fig. 2, 3, 4, and 5 despite an inconsistency in the algebraic exponents.





Fig. 5 Temperature dependences of the low ( $\lambda$ ) and high thermal conductivities ( $K_T$ ) for stoichiometric VPS NiAl and two VPS Ni-17%Cr-6%Al-0.5%Y (V2-02-27E and V2-03-528) measured by the laser flash method. NiCrAlY (V2-03-528) (GRC) refers to the data obtained by the direct dynamic measurement technique



Fig. 6 Comparison of the temperature dependence of the high-temperature thermal conductivity of extruded GRCop-84 reported in the present investigation with those for extruded (Ref 7) and VPS (Ref 9) GRCop-84

conductivity than Cu-26%Cr. Above 973 K, the effect of porosity became more significant as the curve for NiCrAlY batch V2-02-27E tends toward a constant value of  $K_{\rm T}$  independent of temperature. Table 4 shows the values of regression coefficients and  $R_{\rm d}^2$  for the nonlinear regression fits to the data shown in Fig. 5 using Eq 5.

### 3.4 Comparison with High-Temperature Thermal Conductivity Literature Data

Other than GRCop-84, there appear to be no prior literature data reported on the Cu alloys investigated in the present study. Figure 6 shows the comparison of the present data on  $K_{\rm T}$  with those reported for extruded (Ref 7) and VPS (Ref 9) GRCop-

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Fig. 7 Comparison of the temperature dependence of the high-temperature thermal conductivity of VPS NiAl reported in the present investigation with those for single-crystal NiAl (Ref 43)



Fig. 8 Comparison of the temperature dependence of the high-temperature thermal conductivity of VPS Ni-17%Cr-6%Al-0.5%Y reported in the present investigation and in the literature (Ref 25, 26)

84. Since there was significant batch-to-batch scatter in the reported values of  $K_{\rm T}$  for extruded GRCop-84, the line in Fig. 6 represents the weighted regression equation for all the data published by Ellis and Keller (Ref 7). The VPS data represent those reported for the -325 mesh powder lot (Ref 9). The present data are in reasonable agreement with the literature data within the large scatter band reported in the literature (Ref 7).

Figure 7 shows the comparison of the temperature dependence of  $K_{\rm T}$  reported in the present investigation for VPS NiAl with those reported for single-crystal NiAl (Ref 41). Above 773 K, the two sets are in agreement within about 10%. The present observations are significantly lower than those reported for single-crystal NiAl below 773 K, where the two sets of data increasingly deviate from each other with decreasing temper-



Fig. 9 Temperature dependencies of the electrical resistivity for VPS Cu-8%Cr-1%Al, CS Cu-23%Cr-5%Al, and VPS NiAl. The solid lines through the data represent linear regression fits to the data. The literature data on Cu are also shown (Ref 54)



Fig. 10 Variation of  $(\rho - \rho_0)$  with  $(T - T_0)$  for VPS Cu-8%Cr-1%Al, CS Cu-23%Cr-5%Al, and VPS NiAl. The regression lines represent the fit of Eq.8 to the experimental data

ature presumably due to scattering at extrinsic defects, such as grain and splat boundaries, impurities, and voids, in the thermally sprayed coating.

Figure 8 shows the comparison the three sets of data reported in the present paper with those reported by Holmes

and McKechnie (Ref 24, 25) on VPS Ni-17%Cr-6%Al-0.5%Y. An examination of Fig. 8 reveals that the values of  $K_{\rm T}$  determined in the present investigation are comparable to those reported by Holmes and McKechnie (Ref 24, 25) below 573 K, but the deviation between the present data and those reported

### Table 5 Values of $\beta$ and $R_d^2$ determined by fitting Eq 8 to the data shown in Fig. 10

Material	<i>T</i> <sub>0</sub> , K	$\rho_0, \Omega$ m	β, Ω m/K	$R_{\rm d}^2$
Cu-8%Cr-1%Al	307.8	$5.0 \times 10^{-8}$	$1.73 \times 10^{-3}$	0.99864
Cu-23%Cr-5%Al	299.2	13.1 × 10 <sup>-8</sup>	$1.15 \times 10^{-3}$	0.99973
NiAl	300.0	15.4 × 10 <sup>-8</sup>	$2.47 \times 10^{-3}$	0.99728

Table 6	Values of $\beta_1$ ,	$\beta_2, \beta_3, \text{ and}$	l <i>R</i> <sub>d</sub> <sup>2</sup> d	etermined b	y fitting	Eq 9	9 to the	e data shown	in Fig.	. 10
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Material	$T_0(K)$	$ ho_0~(\Omega~m)$	β <sub>1</sub> (Ω m/K)	$\beta_2 \ (\Omega \ m/K^2)$	$\beta_3 (\Omega m/K^3)$	$R_{\rm d}^2$
Cu-8%Cr-1%Al (VPS) Cu-23%Cr-5%Al (CS) NiAl (VPS)	307.8 299.2 300.0	$5.0 \times 10^{-8}$ $13.1 \times 10^{-8}$ $15.4 \times 10^{-8}$	$\begin{array}{c} 1.6\times10^{-3}\\ 1.1\times10^{-3}\\ 2.1\times10^{-3} \end{array}$	$\begin{array}{c} 3.6\times10^{-8}\\ 4.0\times10^{-8}\\ -1.3\times10^{-6} \end{array}$	$5.0 \times 10^{-9}$ $9.0 \times 10^{-10}$ $4.2 \times 10^{-9}$	0.99997 0.99978 0.99999



Fig. 11 Plot of the ratio of the low-temperature thermal conductivity to electrical conductivity against absolute temperature for VPS Cu-8%Cr-1%Al, CS Cu-23%Cr-5%Al, and VPS NiAl. The regression lines represent the fit of Eq 10 to the experimental data

by Holmes and McKechnie (Ref 24, 25) increases with increasing temperature, where the values reported in this paper are significantly higher. One plausible reason for the observed differences in  $K_{\rm T}$  is that there were large differences in the density of pores. The measured density of the VPS NiCrAIY investigated by Holmes and McKechnie (Ref 24, 25) was about 5500 kg/m<sup>3</sup>, which is much lower than the values shown in Table 2 by 30-40%, thereby indicating a significantly more porous coating than those studied in the present investigation. This observation is consistent with the fact that batch V2-02-27E, which was more porous (Fig. 1b) than batch V2-03-528 (Fig. 1d), exhibits lower values of  $K_{\rm T}$  above 973 K (Fig. 5). The close agreement in the magnitudes of  $K_{\rm T}$  below 573 K for all the coatings, and below 973 K for the two batches studied in the present investigation, suggests that the dominant thermal conductivity mechanism is sensitive to the density of voids only at high temperatures. Since thermal conductivity in metallic alloys are mainly determined by electron mobility (Ref 42-48), it is reasonable to conclude that the observed lower values of  $K_{\rm T}$  observed in more porous batches of the Cu-26%Cr and NiCrAIY coatings are due to electron–porosity scattering.

### 3.5 Temperature Variation of Electrical Resistivity

Figure 9 shows the variation of the electrical resistivity with absolute temperature for VPS Cu-8%Cr-1%Al, CS Cu-23%Cr-5%Al, and VPS NiAl between about 100 and 500 K with the linear regression fit represented by the solid lines. The slopes of these regression lines are depicted in the figure. The figure also shows literature data on Cu for comparison (Ref 52). The electrical resistivities of these three coatings are higher than those of Cu. The resistivity of the Cu-8%Cr-1%Al coating, which is significantly lower than that of Cu-23%Cr-5%Al and NiAl, varied between  $3.0 \times 10^{-8} \Omega$  m at 92.9 K and  $5.7 \times 10^{-8} \Omega$  m at 394.9 K. In comparison, the electrical

### Table 7 Values of $L_0$ and $R_d^2$ determined by fitting Eq 10 to the data in Fig. 11

Material	$L_0 (W\Omega/K^2)$	$R_{ m d}^2$
Cu-8%Cr-1%Al (VPS)	$2.70 \times 10^{-8}$	0.9841
Cu-23%Cr-5%Al (CS)	$2.79 \times 10^{-8}$	0.9833
NiAl (VPS)	$2.64 \times 10^{-8}$	0.9977

Table 8 Values of  $L_0$ , B, and  $R_d^2$  determined by fitting Eq 11 to the data in Fig. 11

Material	$L_0 (W\Omega/K^2)$	<i>B</i> (WΩ/K)	$R_{\rm d}^2$
Cu-8%Cr-1%Al (VPS)	$\begin{array}{c} 2.42 \times 10^{-8} \\ 2.49 \times 10^{-8} \\ 2.56 \times 10^{-8} \end{array}$	$6.88 \times 10^{-7}$	0.9996
Cu-23%Cr-5%Al (CS)		$8.28 \times 10^{-7}$	0.9994
NiAl (VPS)		$2.01 \times 10^{-7}$	0.9990



Fig. 12 Temperature dependence of total hemispherical emissivity for VPS Cu-8%Cr, VPS Cu-26%Cr (V2-03-524), VPS Cu-8%Cr-1%Al, and VPS NiAl (V2-03-166). The effect of oxidation on  $\varepsilon_{\rm H}$  is shown for the Cu-8%Cr coating

resistivity,  $\rho_{Cu23Cr5Al}$ , of the Cu-23%Cr-5%Al coating varied between  $9.9 \times 10^{-8} \Omega$  m at 90.7 K and  $1.6 \times 10^{-7} \Omega$  m at 458.7 K. Similarly, the values of electrical resistivity,  $\rho_{NiAl}$ , for the NiAl coating varied between  $6.6 \times 10^{-8} \Omega$  m at 82.4 K and  $1.8 \times 10^{-7} \Omega$  m at 398.6 K. Since the electrical resistivity of NiAl exhibits a stronger temperature variation than Cu-23%Cr-5%Al, the two plots cross each other at about 200 K so that  $\rho_{NiAl} < \rho_{Cu23Cr5Al}$  when T < 200 K.

Matthiessen's rule states that the electrical resistivity can be expressed as (Ref 42-48)

$$\rho = \rho(T) + \rho_c, \tag{Eq 6}$$

where  $\rho(T)$  is temperature-dependent component of electrical resistivity due to electron-phonon scattering and  $\rho_c$  is the temperature-independent residual electrical resistivity due to electron-impurity scattering by impurities of a dilute concentration, c. Since Matthiessen's rule is not always observed, an additional term is often added to Eq 6 (Ref 42, 43, 46)

$$\rho = \rho(T) + \rho_c + \Delta \rho(c, T), \tag{Eq 7}$$

where  $\Delta\rho(c,T)$  accounts for the deviation between the experimental data and Eq 6. Above the Debye temperature,  $\theta_D$ , for a nonmagnetic metal or alloy, the temperature dependence of  $\rho(T)$ , which is due to electron–phonon scattering, is generally expressed as (Ref 28, 31, 42, 43, 45, 46, 49)

$$\rho(T) = \rho_0 (1 + \beta(T - T_0)), \tag{Eq 8}$$

where T is the absolute temperature,  $T_0$  is the reference temperature,  $\rho_0$  is the resistivity at  $T_0$ , and  $\beta$  is the temperature coefficient of the resistivity. The linear temperature dependence given by Eq 8 is not always followed, and in this case, empirical polynomial fits are used (Ref 45, 49, 50). It is

Material	Surface finish	т	£0	$R_{\rm d}^2$
Cu-8%Cr	Polished	0.0002	0.0232	0.9999
Cu-8%Cr	Lightly oxidized	0.0003	0.0294	0.9992
Cu-8%Cr	Heavily oxidized	0.0005	0.0770	0.9999
Cu-26%Cr	As-machined	0.0003	0.2854	0.8400
NiAl (second run)	As-machined	-0.000001	0.4002	0.0016



Fig. 13 Comparison of the predicted values of  $\varepsilon_{\rm H}$  by the Davisson–Weeks model [57] (Eq 14) with the experimental data for VPS Cu-8%Cr-1%Al and VPS NiAl (V2-03-166)

noted that other electron scattering mechanisms are important at  $T < \theta_D$ , where  $\rho(T) \propto T^n$  with n = 2, 3, or 5 depending on the characteristics of the electron scattering mechanism predicted by the Bloch–Grüneisen equation (Ref 44, 46, 51).

Figure 10 shows the variation of  $(\rho - \rho_0)$  with  $(T - T_0)$  for VPS Cu-8%Cr-1%Al, CS Cu-23%Cr-5%Al, and VPS NiAl, where the experimental values of  $\rho_0$  and  $T_0$  for each alloy are given in Table 5.<sup>†</sup> The values of  $\beta$  shown in Table 5 were determined by fitting Eq 8 to the experimental data. The corresponding values of  $R_d^2$  are also shown in Table 5. A close examination of Fig. 10 reveals that the linear temperature dependence of  $(\rho - \rho_0)$  predicted by Eq 8 is closely matched by the data for the two copper alloys, whereas the data for NiAl significantly deviate from the linear regression line represented by Eq 8. Since nonlinear temperature dependencies of  $\rho(T)$  are predicted by the Bloch–Grüneisen theory (Ref 44, 46, 51), Eq 9 was used to fit the data shown in Fig. 10.

$$\rho(T) = \rho_0 \Big( 1 + \beta_1 (T - T_0) + \beta_2 (T - T_0)^2 + \beta_3 (T - T_0)^3 \Big),$$
(Eq 9)

where  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  are temperature coefficients of resistivity. Table 6 gives the values of  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ , and  $R_d^2$ . It is clear through a comparison of the values of  $R_d^2$  in Tables 5 and 6, Eq 9 fits the data in Fig. 10 much better than Eq 8 especially for NiAl. These observations suggest that other electron scattering processes (e.g., electron–electron scattering) may have contributed to the experimental measurements in addition to the high-temperature electron–phonon scattering mechanism.

#### 3.6 Application of the Wiedemann–Franz law

Typically, for  $T >> \theta_D$ , the Wiedemann–Franz law is followed by a large number of metallic materials, where the carriers for electrical and thermal conduction are valence electrons (Ref 28, 31, 43, 45, 47, 48, 52). The law states that

$$\frac{\lambda}{\sigma_{\rm e}} = L_0 T, \tag{Eq 10}$$

where  $\sigma_e$  (= 1/ $\rho$ ) is the electrical conductivity and  $L_0$  is the Lorentz number with a theoretically derived constant Sommerfeld value of  $2.45 \times 10^{-8}$  WΩ/K<sup>2</sup> (Ref 43, 45, 47, 52). However, for  $T < < \theta_D$ , the Lorentz number is no longer a universal constant and less than  $2.45 \times 10^{-8}$  WΩ/K<sup>2</sup> (Ref 45).

Equation 10 suggests that the ratio  $\lambda \sigma_e$  increases linearly with T. Figure 11 confirms this linear relationship, and Table 7 lists the values of  $L_0$  determined by fitting Eq 10 to the data. The experimental magnitudes of  $L_0$  are  $2.64 \times 10^{-8} \text{ W}\Omega/\text{K}^2$  for

<sup>&</sup>lt;sup>†</sup>A plot of  $(\rho - \rho_0)$  against  $(T - T_0)$  essentially cancels the contribution of  $\rho_c$  to  $\rho$ .

VPS NiAl,  $2.70 \times 10^{-8}$  for VPS Cu-8%Cr-1%Al, and  $2.79 \times 10^{-8}$  WΩ/K<sup>2</sup> for CS Cu-23%Cr-5%Al. These values are higher than the theoretical Sommerfeld value by about 8 to 14%, but compare very well with values reported for metals (Ref 43, 48, 52). Equation 10 assumes that  $L_0$  is not dependent on temperature. In reality, deviations from the form of Eq 10 have been reported and discussed in detail in the literature (Ref 28, 29, 31, 43, 48, 52).

Smith and Palmer (Ref 28) empirically analyzed their data using Eq 11

$$\frac{\lambda}{\sigma_{\rm e}} = L_0 T + B,\tag{Eq 11}$$

where *B* is a constant. Later developments in the theory of heat conduction resulted in other forms of Eq 11 (Ref 31):

$$\frac{\lambda}{\sigma_e} = L_0 T - C T^n, \tag{Eq 12}$$

where C is a constant and  $-1 \le n \le 0$  in Eq 12 (Ref 31). The values of  $L_0$  and B determined by fitting Eq 11 to the data shown in Fig. 11 are tabulated in Table 8. A comparison of Tables 7 and 8 reveals that the magnitudes of  $R_d^2$  are higher, thereby indicating that Eq 11 is a better fit to the data than Eq 10. Clearly, the constant *B* in Eq 11 is identified with  $(-CT^n)$  in Eq 12. Since the experimental values of B shown in Table 8 are independent of absolute temperature, it suggests that  $n \sim 0$  so that C = -B.

### 3.7 Temperature Dependence of the Total Hemispherical Emissivity

Figure 12 shows the temperature dependence of  $\varepsilon_{\rm H}$  for vacuum plasma-sprayed Cu-8(wt.%)Cr, Cu-26(wt.%)Cr, Cu-8(wt.%)Cr-1%Al, and NiAl monolithic coatings. Also shown are the effects of oxidation on the magnitudes of  $\varepsilon_{\rm H}$  for the Cu-8(wt.%)Cr coating.<sup>‡</sup> The data for heavily oxidized (Ref 53) and electropolished (Ref 54) Cu are also shown. The linear regression lines for each set of data are shown in the figure.<sup>§</sup> An examination of Fig. 12 reveals that  $\varepsilon_{\rm H}$  increases linearly with increasing T for the VPS copper alloy coatings, but it is essentially independent of temperature for VPS NiAl. This temperature dependence of  $\varepsilon_{\rm H}$  is well represented by

$$\varepsilon_{\rm H} = mT + \varepsilon_0,$$
 (Eq 13)

where *m* and  $\varepsilon_0$  are regression coefficients listed in Table 9 for each coating and surface condition. The Cu-8%Cr coating with a polished surface exhibits the lowest values of  $\varepsilon_{\rm H}$  varying from 0.103 at 373 K to 0.220 at 920 K. After lightly oxidizing the surface,  $\varepsilon_{\rm H}$  increases to 0.143 at 373 K and 0.309 at 920 K with a corresponding increase in the magnitude of m (Table 9). In comparison, a heavily oxidized surface results in significant increases in the magnitudes of  $\varepsilon_{\rm H}$  and m (Table 9). In this case,  $\varepsilon_{\rm H}$  increases from 0.257 at 373 K to 0.517 at 920 K. In comparison, the magnitudes of  $\varepsilon_{\rm H}$  varied from 0.489 at 753 K to 0.621 at 1194 K for the Cu-26%Cr coating. Interestingly, the data for the heavily oxidized Cu8%Cr coating and that for Cu-26%Cr are similar above 750 K presumably because the surface oxides are similar in composition. The values of  $\varepsilon_{\rm H}$  for electropolished Cu increased from 0.009 at 179 K to 0.024 at 820 K (Ref 54). The reported values of  $\varepsilon_{\rm H}$  for heavily oxidized Cu varied from 0.49 at 592 K to 0.85 at 1035 K (Ref 53).

In contrast,  $\varepsilon_{\rm H}$  was not significantly dependent on absolute temperature for the NiAl coating with  $\varepsilon_{\rm H} \sim 0.4$  between 395 and 1225 K. Since NiAl forms an Al<sub>2</sub>O<sub>3</sub> surface layer, it is worth noting that a constant value of  $\varepsilon_{\rm H} \sim 0.4$  between 590 and 810 K was reported for oxidized Al specimens (Ref 53). The magnitudes of  $\varepsilon_{\rm H}$  for electropolished Al increased from about 0.01 at about 150 K to about 0.04 at about 750 K (Ref 54).

The Davisson and Weeks (DW) model (Ref 55) predicted that  $\varepsilon_{\rm H}$  in metals is related to electrical resistivity through Eq 14.

$$\varepsilon_{\rm H} = 0.751 * (\rho T)^{0.5} - 0.632 * (\rho T) + 0.670 * (\rho T)^{1.5} - 0.607 * (\rho T)^2.$$
(Eq 14)

Figure 13 shows the comparison of the predicted values of  $\varepsilon_{\rm H}$  from Eq 14 with the experimental data determined for Cu-8%Cr-1%Al and NiAl with as-machined surfaces. As is evident from Fig. 13, the predictions of the DW model (Ref 55) do not agree with the experimental data, where the predicted values are much lower than the experimental data by more than a factor of seven. Presumably, this difference may be due to the fact that the DW model assumes a pristine metallic surface and does not account for the progressive oxidation of the alloy at high temperatures.

### 4. Summary and Conclusions

This paper reports the temperature dependencies of electrical and thermal conductivities, thermal diffusivities, and total hemispherical emissivities between 77 and 1200 K for several VPS or CS copper alloy, NiCrAlY and NiAl monolithic coatings. Data are also presented for extruded GRCop-84 and an as-cast Cu-17%Cr-5%Al. In general, the thermal conductivities of GRCop-84, Cu-8%Cr, and Cu-26%Cr tend to decrease with increasing temperature although this trend was only observed above 673 K for the GRCop-84 alloy. In contrast, the thermal conductivities of the Cu-Cr-Al, NiCrAlY, and NiAl coatings increased with increasing temperature. As expected, the presence of porosity in the VPS Cu-26%Cr and NiCrAlY coatings decreased the thermal conductivities of these coatings, where the thermal conductivity of the NiCrAlY coating was sensitive to porosity only above 973 K. The magnitudes of the thermal conductivity for extruded GRCop-84 and VPS NiCrAlY reported in the present investigation were larger than those reported in the literature. The electrical resistivity increased with increasing temperature for the VPS Cu-8%Cr-1%Al, CS Cu-23%Cr-5%Al, and VPS NiAl coatings. It is demonstrated that the electrical resistivity data for the three coatings are best represented by a third-order polynomial equation. Although the Wiedemann-Franz law was a reasonable fit for the  $\lambda/\sigma_{\rm e} - T$  data and the experimentally determined Lorentz numbers compared reasonably well with values reported in the literature, it is demonstrated that the Smith-Palmer equation was a better fit to the data. The magnitude of

<sup>&</sup>lt;sup>‡</sup>The specimen was somewhat oxidized prior to measurement, but the surface started brightening as it was heated under high vacuum. Thus, the emissivity measurements were taken with the surface in three different conditions. The terms "heavily oxidized," "lightly oxidized," and "bright" are used in a qualitative sense to indicate the relative conditions of the surface.

<sup>&</sup>lt;sup>§</sup>The regression lines for NiAl are only for the open symbol data.

 $\epsilon_{H}$  increased linearly with increasing temperature for the VPS Cu-8%Cr and Cu-26%Cr coatings, but it was essentially independent of temperature for VPS NiAl. It was observed that  $\epsilon_{H}$  increased with the degree of oxidation consistent with the observations in the literature for oxidized Cu.

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