

Thermophysical Properties of Cold and Vacuum Plasma Sprayed Cu-Cr-X Alloys, NiAl and NiCrAlY Coatings Part 2: Specific Heat Capacity

S.V. Raj
Glenn Research Center, Cleveland, Ohio

NASA STI Program . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program plays a key part in helping NASA maintain this important role.

The NASA STI Program operates under the auspices of the Agency Chief Information Officer. It collects, organizes, provides for archiving, and disseminates NASA's STI. The NASA STI Program provides access to the NASA Technical Report Server—Registered (NTRS Reg) and NASA Technical Report Server—Public (NTRS) thus providing one of the largest collections of aeronautical and space science STI in the world. Results are published in both non-NASA channels and by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counter-part of peer-reviewed formal professional papers, but has less stringent limitations on manuscript length and extent of graphic presentations.
- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., “quick-release” reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.
- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or co-sponsored by NASA.
- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

For more information about the NASA STI program, see the following:

- Access the NASA STI program home page at <http://www.sti.nasa.gov>
- E-mail your question to help@sti.nasa.gov
- Fax your question to the NASA STI Information Desk at 757-864-6500
- Telephone the NASA STI Information Desk at 757-864-9658
- Write to:
NASA STI Program
Mail Stop 148
NASA Langley Research Center
Hampton, VA 23681-2199



Thermophysical Properties of Cold and Vacuum Plasma Sprayed Cu-Cr-X Alloys, NiAl and NiCrAlY Coatings Part 2: Specific Heat Capacity

S.V. Raj
Glenn Research Center, Cleveland, Ohio

National Aeronautics and
Space Administration

Glenn Research Center
Cleveland, Ohio 44135

Acknowledgments

The experimental measurements were conducted by the Thermophysical Properties Research Laboratory, Inc. (TPRL), West Lafayette, Indiana, under contract, and these contributions are gratefully acknowledged. This paper was published in the Journal of Engineering Materials and Performance and can be found at <https://link.springer.com/article/10.1007/s11665-017-3012-0>.

Trade names and trademarks are used in this report for identification only. Their usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

Level of Review: This material has been technically reviewed by technical management.

Available from

NASA STI Program
Mail Stop 148
NASA Langley Research Center
Hampton, VA 23681-2199

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
703-605-6000

This report is available in electronic form at <http://www.sti.nasa.gov/> and <http://ntrs.nasa.gov/>

Thermophysical Properties of Cold and Vacuum Plasma Sprayed Cu-Cr-X Alloys, NiAl and NiCrAlY Coatings

Part 2: Specific Heat Capacity

S.V. Raj
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Abstract

Part I of the paper discussed the temperature dependencies of the electrical resistivities, thermal conductivities, thermal diffusivities and total hemispherical emissivities of several vacuum plasma sprayed (VPS) and cold sprayed copper alloy monolithic coatings, VPS NiAl, VPS NiCrAlY, extruded GRCo-84 and as-cast Cu-17(wt.%)Cr-5%Al. Part II discusses the temperature dependencies of the constant pressure specific heat capacities, C_p , of these coatings. The data were empirically regression-fitted with the equation:

$$C_p = AT^4 + BT^3 + CT^2 + DT + E$$

where T is the absolute temperature and A , B , C , D and E are regression constants. The temperature dependencies of the molar enthalpy, molar entropy and Gibbs molar free energy determined from experimental values of molar specific heat capacity are reported. Calculated values of C_p using the Neumann-Kopp (NK) rule were in poor agreement with experimental data. Instead, a modification of the Neumann-Kopp rule was found to predict values closer to the experimental data with an absolute deviation less than 6.5%. The specific molar heat capacities for all the alloys did not agree with the Dulong-Petit law, and $C_p > 3R$, where R is the universal gas constant, were measured for all the alloys except NiAl for which $C_p < 3R$ at all temperatures.

1.0 Introduction

As noted in Part I (Ref. 1), an evaluation of the thermophysical properties of materials is important both for gaining a fundamental understanding of material behavior, as well as in engineering applications, such as structural design of components and systems. Environmental and thermal barrier protective metallic coatings designed for aerospace applications, such as reusable launch vehicle (RLV) combustion liners, turbine blades and vanes, are commonly deposited by conventional cold and vacuum plasma spray processes. The deposition of these coatings on the substrates results in the development of residual stresses which can affect the performance and durability of the coating-substrate system. In the case of aerospace applications, modeling the heat transfer behavior and stress analyses of the coating-substrate system is crucial for predicting component performance and life. Part I discussed the microstructures, densities and temperature dependencies of electrical resistivity, thermal conductivity, thermal diffusivity and total hemispherical emissivity of several vacuum plasma sprayed (VPS) and cold sprayed (CS) copper alloy monolithic coatings, VPS NiAl, VPS NiCrAlY, extruded GRCo-84 and as-cast Cu-17(wt.%)Cr-5%Al. The objective of Part II is to report the constant pressure specific heat capacities, C_p , of these materials as a function of absolute temperature, T .

2.0 Experimental Procedures

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), Ni-17(wt.%)Cr-6%Al-0.5%Y (NiCrAlY). Monolithic coatings¹ were sprayed on mandrels either by cold (CS) or vacuum plasma spray (VPS) methods. Details of the powder suppliers and fabrication methods were reported earlier (Refs. 2, 3, and 4), and summarized in Part I (Ref. 1). In addition, extruded GRCop-84 and an as-cast Cu-17(wt.%)Cr-5%Al alloy were also investigated. The batch I.D.s used in this paper are given in Table II in Part I (Ref. 1).

As noted in Part I (Ref. 1), the thermophysical property measurements reported in Parts I and II were conducted at the Thermophysical Properties Research Laboratory, Inc. (TPRL), West Lafayette, Indiana, under contract. Constant pressure specific heat was measured between 295 and 1223 K using a standard Perkin-Elmer Model DSC-2 Differential Scanning Calorimeter using sapphire as the reference material in accordance with ASTM E1269 (Refs. 5 and 6), where the sapphire and the experimental specimens were subjected to an identical heat flux. The differential powers required to heat both the reference and the experimental specimens at identical rates were recorded by a computerized data acquisition system. The specific heat of the experimental specimen was calculated from the known specific heat of sapphire, masses of the sapphire standard and specimen, and the differential power.

3.0 Results and Discussion

3.1 Constant Pressure Specific Heat Capacities of Copper Alloys

Figure 1 shows the variations of the experimental values of C_P with T 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 broken line represents the magnitudes of C_P for Cu calculated from the equation published by Lewis and Randall (Ref. 7). In all cases, the magnitudes of C_P increases with increasing values of absolute temperature. An examination of Figure 1 reveals that the data fall into two categories. First, the values of C_P for all the alloys except CS Cu-23%Cr-5%Al are clustered in a narrow range close to those for copper (Ref. 7) with the maximum deviation of about 13.5% for Cu-8%Cr-1%Al occurring at 1223 K. Thus, $(C_P)_{Cu} \sim 386 \text{ J/kg}\cdot\text{K}$ at 295 K for Cu and $(C_P)_{Cu} \sim 477 \text{ J/kg}\cdot\text{K}$ at 1223 K (Ref. 7). In comparison, $(C_P)_{Cu8Cr1Al} \sim 413 \text{ J/kg}\cdot\text{K}$ at 295 K increasing to $(C_P)_{Cu8Cr1Al} \sim 541 \text{ J/kg}\cdot\text{K}$ at 1223 K. Second, the magnitudes of C_P for CS Cu-23%Cr-5%Al coating exhibits an increasing deviation from the clustered data for the other alloys with increasing temperature. In this case, $(C_P)_{Cu23Cr5Al} \sim 434 \text{ J/kg}\cdot\text{K}$ at 295 K and $(C_P)_{Cu8Cr1Al} \sim 602 \text{ J/kg}\cdot\text{K}$ at 1223 K.

A fourth order NASA polynomial equation² given by Equation (1) was used to regression fit the data shown in Figure 1 (Refs. 8, 9, and 10).

$$C_P = A * T^4 + B * T^3 + C * T^2 + D * T + E \text{ (J/kg}\cdot\text{K)} \quad (1)$$

where A , B , C , D and E are the regression constants. Table I gives the magnitudes of these coefficients for the copper alloys shown in Figure 1 as well as the corresponding coefficients of determination, R_d^2 for each material. It was confirmed that the regressed values and the experimental data were in excellent agreement for all the alloys.

¹ 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.

² It is noted that the NASA polynomial equation was a better fit to the experimental data than the other commonly used empirical equation $C_P = E_1 + D_1 * T + C_1/T^2$ (Ref. 7).

Figure 2 compares the temperature dependencies of C_p for VPS GRCop-84 (Ref. 11) with those for extruded GRCop-84 reported in the present paper. The two sets of data are in excellent agreement irrespective of the processing method.

TABLE I.—REGRESSION COEFFICIENTS DETERMINED BY FITTING EQUATION (1) TO THE EXPERIMENTAL DATA SHOWN IN FIGURE 1 AND FIGURE 2, AND THE CORRESPONDING VALUES OF R_d^2

Material	A, J/kg•K ⁵	B, J/kg•K ⁴	C, J/kg•K ³	D, J/kg•K ²	E, J/kg•K	R_d^2
GRCop-84 (Extruded)	-1.8×10^{-11}	2.4×10^{-7}	-4.6×10^{-4}	0.39	302.0	0.9989
Cu-8%Cr (V2-03-134)	-1.2×10^{-10}	4.4×10^{-7}	-5.9×10^{-4}	0.42	306.8	1.0000
Cu-26%Cr (V2-02-27B)	-5.4×10^{-10}	2.1×10^{-6}	-2.6×10^{-3}	1.40	171.8	0.9986
Cu-26%Cr (V2-03-524)	-9.3×10^{-10}	2.9×10^{-6}	-3.2×10^{-3}	1.50	167.0	0.9970
Cu-8%Cr-1%Al (V2-05-27)	3.3×10^{-10}	-7.8×10^{-7}	7.2×10^{-4}	-0.23	436.1	0.9997
Cu-17%Cr-5%Al (as-cast) (8)	5.6×10^{-11}	5.8×10^{-8}	-2.7×10^{-4}	0.28	354.0	0.9936
Cu-23%Cr-5%Al-heat up (CS)	4.0×10^{-10}	-9.4×10^{-7}	7.8×10^{-4}	-0.15	435.4	0.9949
Cu-23%Cr-5%Al-cool down (CS)	9.0×10^{-11}	-1.2×10^{-7}	1.9×10^{-5}	0.19	366.8	0.9999
NiAl (V2-03-166)	-3.1×10^{-11}	1.4×10^{-7}	-2.9×10^{-4}	0.36	466.3	0.9998
Ni-17%Cr-6%Al-0.5%Y (V2-02-27E)	-1.3×10^{-9}	4.1×10^{-6}	-4.4×10^{-3}	2.10	140.1	0.9964
Ni-17%Cr-6%Al-0.5%Y (V2-03-528)	-1.2×10^{-9}	4.3×10^{-6}	-5.2×10^{-3}	2.60	313.4	0.9999

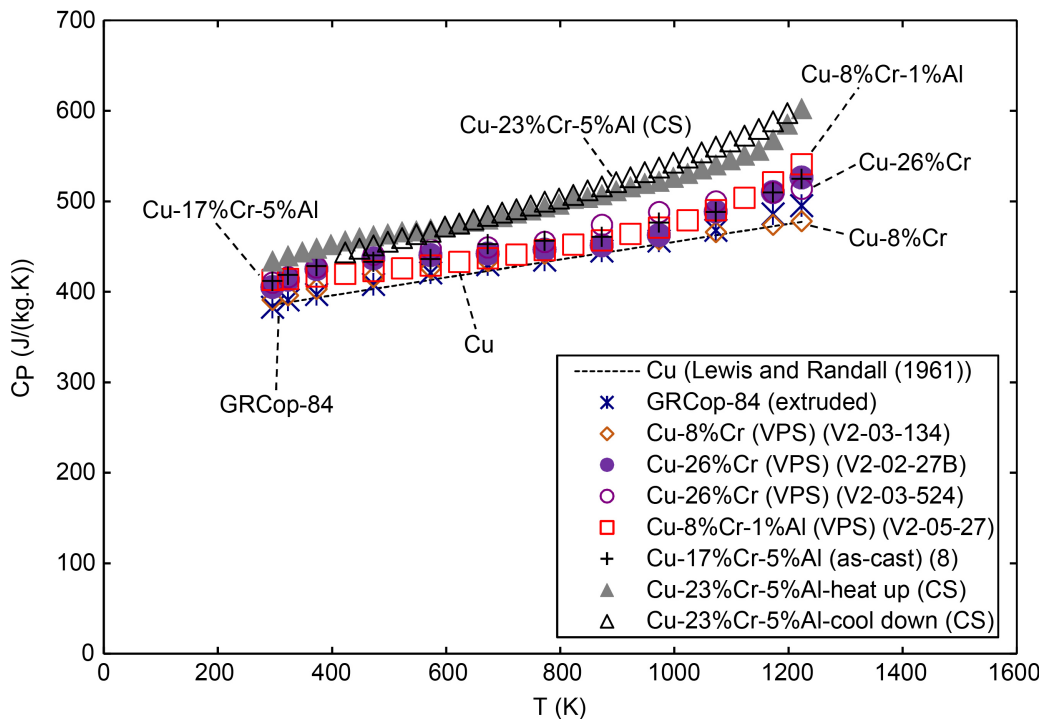


Figure 1.—Temperature dependencies of the specific heat capacities for extruded GRCop-84, and VPS Cu-8%Cr, VPS Cu-26%Cr (V2-03-524), VPS Cu-8%Cr-1%Al, as-cast Cu-17%Cr-5%Al, and CS Cu-23%Cr-5%Al.

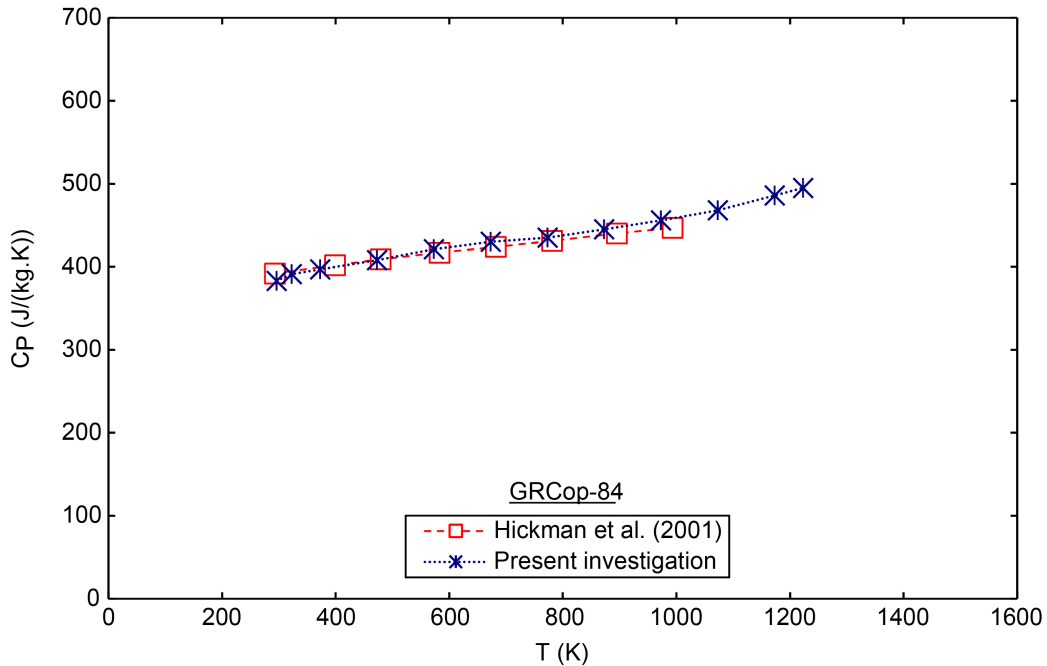


Figure 2.—Comparison of the temperature dependencies of the specific heat capacities for extruded GRCop-84 determined in the present investigation with those reported for VPS GRCop-84 (Ref. 8).

3.2 Constant Pressure Specific Heat Capacities of Nickel Alloys

Figure 3 shows the variation of C_p with T for VPS NiAl and the two batches of VPS NiCrAlY. The literature data for Ni (Ref. 12) and stoichiometric NiAl single crystal (Ref. 13) are also included. As shown in Figure 3, the data for single crystal NiAl (Ref. 13) and polycrystalline VPS NiAl are in excellent agreement increasing from 550 J/kg•K at 295 K to 650 J/kg•K at 1223 K. This suggests that C_p is insensitive to processing method, grain size and crystal orientation in stoichiometric NiAl. The values of C_p for NiAl are higher than those for VPS NiCrAlY below 973 K, and at nearly all temperatures, for Ni (Ref. 12). The C_p data for both batches of VPS NiCrAlY are almost identical at and below 973 K but the two sets deviate above 973 K with the values for C_p increasing significantly with increasing absolute temperature for the denser batch of NiCrAlY (V2-03-528). The values of C_p are also higher than those for NiAl above 973 K. Overall, the magnitudes of C_p for NiCrAlY (V2-03-528) increases from 455 J/kg•K at 295 K to 789 J/kg•K at 1223 K. The regression coefficients were determined by fitting Equation (1) to the data for VPS NiAl and VPS NiCrAlY, and the values of these coefficients and their corresponding R_d^2 are given in Table I. Figure 4 compares the specific heat capacities of the copper and nickel-based alloys investigated in the present investigation. The specific heat capacities of NiAl and NiCrAlY are larger than those for the copper coating alloys and GRCop-84 substrate.

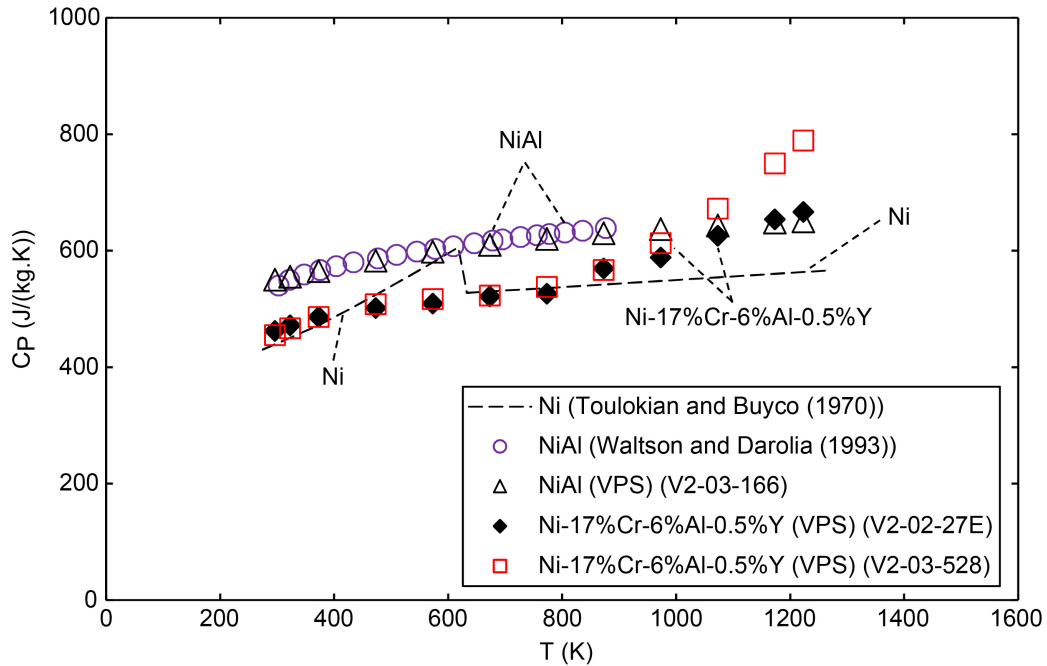


Figure 3.—Temperature dependencies of the specific heat capacities for VPS NiAl and VPS Ni-17(wt.)Cr-6%Al-0.5%Y. The present data are compared with literature data on Ni (Ref. 9) and NiAl single crystal (Ref. 10).

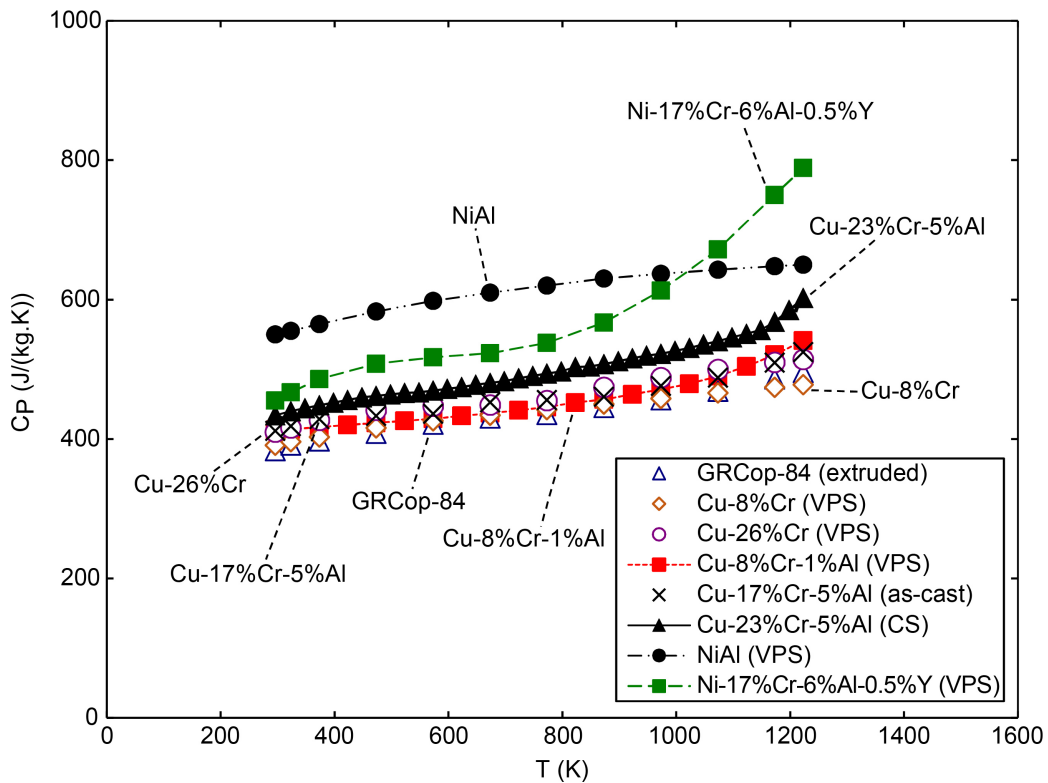


Figure 4.—Comparison of the specific heat capacities for extruded GRCop-84, VPS Cu-8%Cr, VPS Cu-26%Cr (V2-03-524), VPS Cu-8%Cr-1%Al, as-cast Cu-17%Cr-5%Al, CS Cu-23%Cr-5%Al, VPS NiAl (V2-03-166) and Ni-17(wt.)Cr-6%Al-0.5%Y (V2-03-528).

3.3 Comparison of the Experimental Data With the Neumann-Kopp Rule

The empirical Neumann-Kopp (NK) rule is often used to estimate the heat capacities of compounds formed from their constituent elements with some degree of success although several deviations have been noted in the literature (Refs. 7, 14, 15, 16, and 17). In the case of alloys formed by mixing M elements, the NK rule states that the specific heat capacity of the alloy, $(C_P)_{NK}$, is given by

$$(C_P)_{NK} = f_1 * C_1 + f_2 * C_2 + f_3 * C_3 + \dots + f_N * C_M \quad (2)$$

where f_i is the atom percent of the i^{th} element with a specific heat capacity, C_i , and $i = 1, 2, 3, \dots, M$.

Figure 5 and Figure 6 compare the temperature dependencies of the experimental,³ $(C_P)_{\text{expt}}$, and predicted values using Equation (2) for the copper and nickel-based alloys studied in the present investigation. For the copper alloys, $(C_P)_{NK} > (C_P)_{\text{expt}}$ at most temperatures, where the absolute deviations⁴ varied between 0.5 and 14% depending on absolute temperature; however, the values of $(C_P)_{NK} \sim (C_P)_{\text{expt}}$ for the Cu-23%Cr-5%Al within an absolute deviation of 5% (Figure 5). The magnitudes of $(C_P)_{NK} \gg (C_P)_{\text{expt}}$ for NiAl and NiCrAlY with the absolute deviations varying between 18 and 44% for NiAl and 8 and 12% for NiCrAlY, respectively (Figure 6). In contrast, Brandt et al. (Ref. 18), who observed that the absolute deviations varied between 0.22 and 11.99% for a Ni-9.94(at.%) Al alloy, concluded that the agreement between the experimental and the predicted values were reasonable.

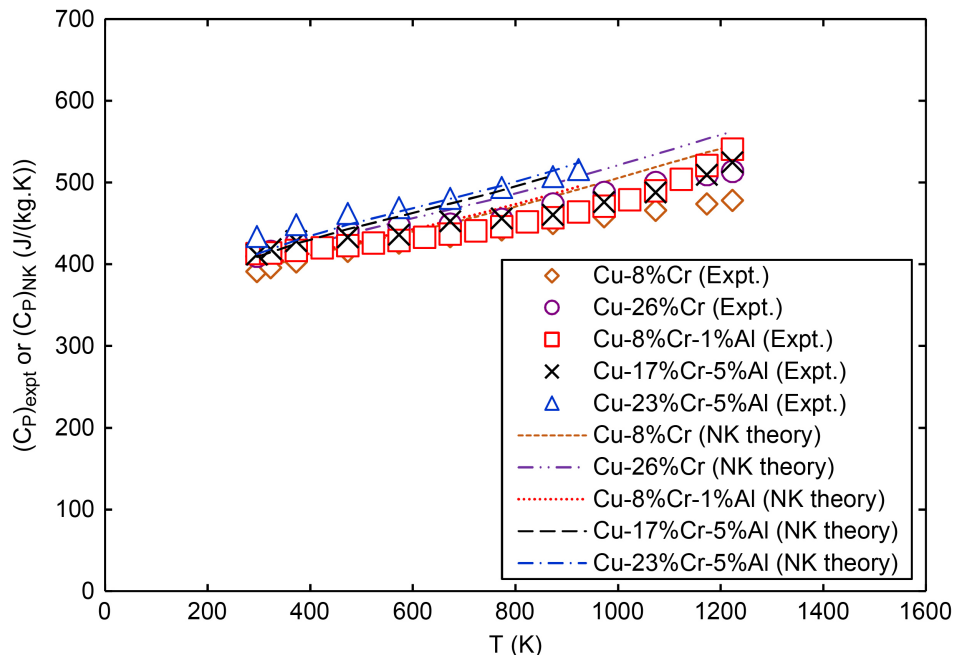


Figure 5.—Comparison of the experimental, $(C_P)_{\text{expt}}$, and calculated Neumann-Kopp, $(C_P)_{NK}$, specific heat capacities for extruded GRCop-84, and VPS Cu-8.%Cr, VPS Cu-26%Cr (V2-03-524), VPS Cu-8%Cr-1%Al, as-cast Cu-17%Cr-5%Al, and CS Cu-23%Cr-5%Al.

³ Although C_P was used to describe the experimental data in Figure 1 to Figure 4, the term $(C_P)_{\text{expt}}$ is used in Figure 5 to Figure 7 specifically to distinguish the experimental data from the values calculated using Equation (2). It is noted that the experimental data shown in Figure 5 to Figure 7 are identical to those shown in Figure 1 to Figure 4.

⁴ The deviation was defined as $((C_P)_{NK} - (C_P)_{\text{expt}})/(C_P)_{\text{expt}}$. Only absolute values are reported.

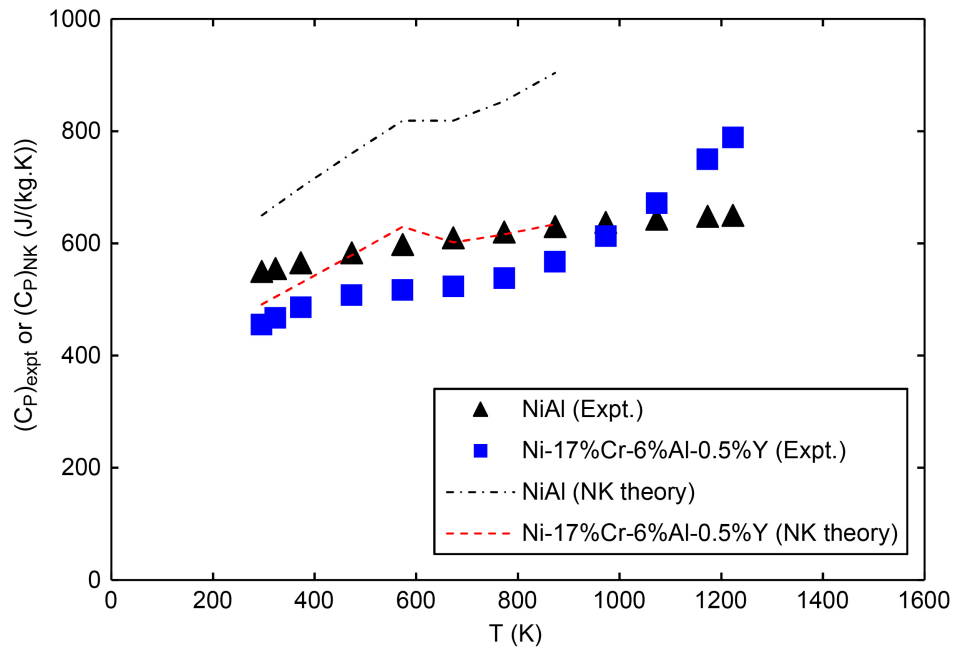


Figure 6.—Comparison of the experimental and calculated Neumann-Kopp specific heat capacities for VPS NiAl and VPS Ni-17(wt.%)Cr-6%Al-0.5%Y (V2-03-528).

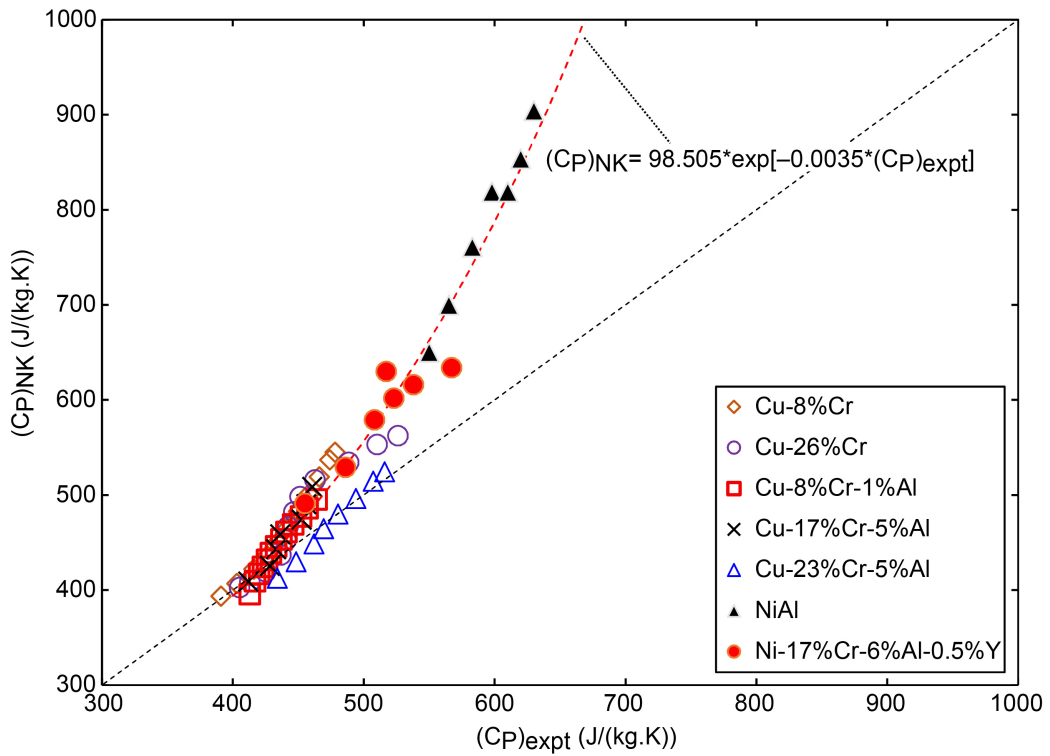


Figure 7.—Plot of the calculated Neumann-Kopp specific heat capacity against the experimental specific heat capacity showing the extent of deviation from the 45° line for the different alloys.

A plot of $(C_P)_{NK}$ against $(C_P)_{\text{expt}}$ provided additional insights into the extent of disagreement between the predicted and the experimental values (Figure 7). It is noted that the broken line at 45° in Figure 7 represents the case when $(C_P)_{NK} = (C_P)_{\text{expt}}$. An examination of Figure 7 reveals that the predicted values determined from Equation (2) are generally significantly larger than the experimentally measured values of C_P except in a narrow region, where the symbols are close to the 45° line. However, as noted earlier, the agreement between the experimental and the predicted values is reasonably good for the CS Cu-23%Cr-5%Al coating within 5%.

A close examination of the data shown in Figure 7 suggests that it may be possible to fit a single curve through the data for all the materials reported in the present paper. A regression fit revealed that $(C_P)_{NK}$ and $(C_P)_{\text{expt}}$ correlate very well through Equation (3):

$$(C_P)_{NK} = 98.505 * \exp[-0.0035 * (C_P)_{\text{expt}}] \text{ (J/kg}\cdot\text{K)} \quad (3)$$

with a $R_d^2 = 0.9516$. Rearranging the terms in Equation (3), the magnitudes of C_P for an alloy or a compound with i elements with known values of C_i , where $(C_P)_{NK}$ is calculated from Equation (2), can be estimated from

$$C_P = 288.68 * \ln\left(\frac{98.505}{(C_P)_{NK}}\right) \text{ (J/kg}\cdot\text{K)} \quad (4)$$

The absolute deviation, $|\Delta|$, between the values estimated from Equation (4) and the experimental measurements of C_P for the materials shown in Figure 7 varied between 0.1 and 6.5%. Despite this excellent agreement, it is cautioned that the general validity of Equation (4) for estimating the magnitudes of C_P for other materials needs to be proven.

3.4 Comparison With the Dulong-Petit Law

Figure 8 plots the specific molar heat capacity against absolute temperature for the copper alloys, NiAl and NiCrAlY investigated in this study. The atomic weight data used for calculating the molar masses were obtained from Zumdahl (Ref. 19). The experimental data lie to right of the vertical broken line at 295 K. The symbols to the left of this line represent the calculated values of C_P determined from empirical polynomial equations fitted to the experimental data. In order to ensure that $C_P = 0$ at $T = 0$ K,⁵ the fitting equation used had the form

$$C_P = A_1 * T^4 + B_1 * T^3 + C_1 * T^2 + D_1 * T \text{ (J/mol}\cdot\text{K)} \quad (5)$$

where A_1 , B_1 , C_1 and D_1 are regression constants (Table II). The lower and upper horizontal broken lines represent values of $C_P = 3R$ and $4R$, respectively, where R is the universal gas constant.

The Dulong and Petit law states that $C_V = 3R = 24.9 \text{ J/mol}\cdot\text{K}$, where C_V is the specific heat capacity of constant volume, and R is the universal gas constant (Refs. 7, 14, 15, and 19). Since the molal volume of a solid does not change very much under 1 atm. pressure, $C_P \approx C_V$ (Refs. 7, 14, 20, and 21). An examination Figure 8 reveals that except for VPS NiAl, the experimental values of $C_P > 3R$ for all the copper alloys and VPS NiCrAlY. In fact, $C_P \geq 4R$ above 1000 K for Cu-23%Cr-5%Al and NiCrAlY. The fact that $C_P > 3R$ at high temperatures is consistent with reported observations in the literature (Refs. 7, 14, and 21). In the case of VPS NiAl, $C_P < 3R$ at all temperatures but approaches $3R$ above 1100 K.

⁵ Since the specific heat measurements were not conducted between 0 and 295 K, the form of the Equation (3) has to be consistent with theories on low temperature specific heat capacities. In the absence of experimental data, Equation (3) is provided to enable the estimation of design parameters of the RLV combustion chamber in the cryogenic range.

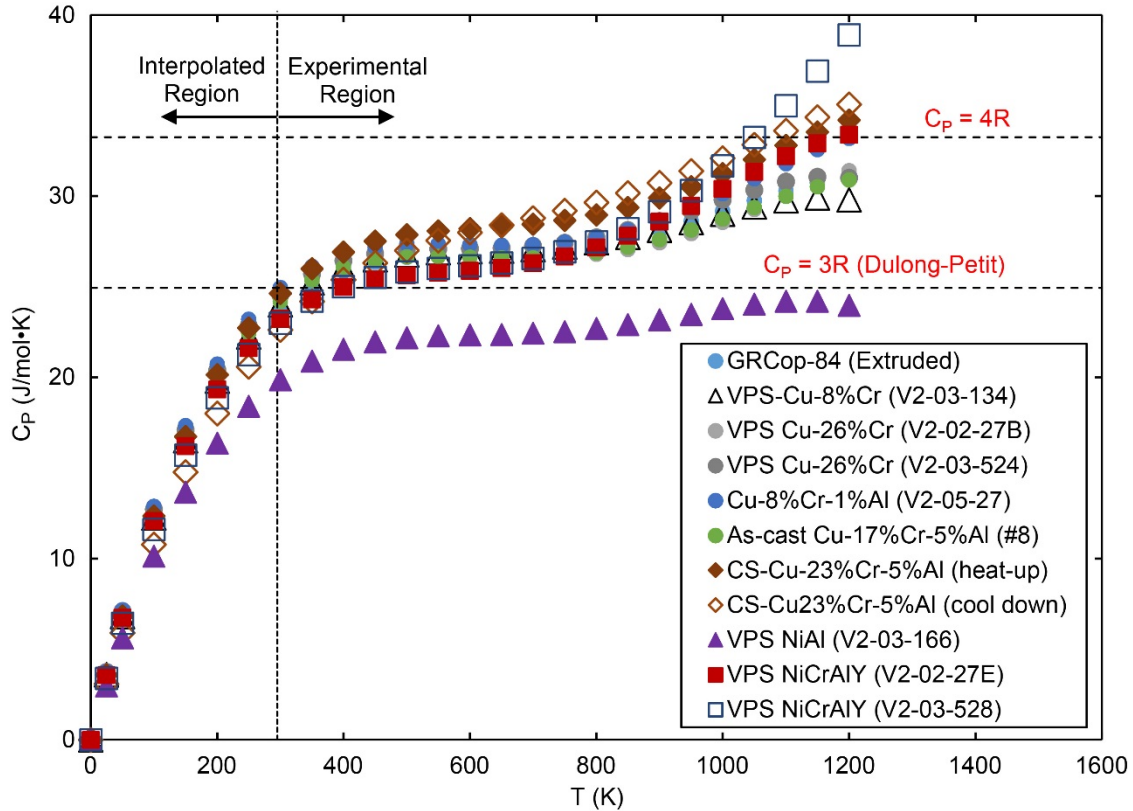


Figure 8.—Plot of the specific molar heat capacity against the absolute temperature for the copper alloys, NiAl and NiCrAlY alloys. The experimental data lie to the right of the vertical broken line, while the symbols to the left of this line are interpolations of the regression equations to the experimental data. The two horizontal broken lines represent values of $C_p = 3R$ or $4R$.

TABLE II.—REGRESSION COEFFICIENTS DETERMINED BY FITTING EQUATION (3) TO THE EXPERIMENTAL DATA SHOWN IN FIGURE 1 AND FIGURE 2, AND THE CORRESPONDING VALUES OF R_d^2

Material	A, $\text{J/mol}\cdot\text{K}^5$	B, $\text{J/mol}\cdot\text{K}^4$	C, $\text{J/mol}\cdot\text{K}^3$	D, $\text{J/mol}\cdot\text{K}^2$	R_d^2
GRCop-84 (Extruded)	-8.1×10^{-11}	2.6×10^{-7}	-3.0×10^{-4}	0.15	0.9998
Cu-8%Cr (V2-03-134)	-8.8×10^{-11}	2.8×10^{-7}	-3.1×10^{-4}	0.15	0.9998
Cu-26%Cr (V2-02-27B)	-7.6×10^{-11}	2.6×10^{-7}	-3.1×10^{-4}	0.15	0.9999
Cu-26%Cr (V2-03-524)	-9.8×10^{-11}	3.1×10^{-7}	-3.4×10^{-4}	0.16	0.9999
Cu-8%Cr-1%Al (V2-05-27)	-9.0×10^{-11}	3.0×10^{-7}	-3.3×10^{-4}	0.16	0.9997
Cu-17%Cr-5%Al (as-cast) (8)	-8.5×10^{-11}	2.8×10^{-7}	-3.2×10^{-4}	0.15	0.9998
Cu-23%Cr-5%Al (CS) (heat up)	-7.6×10^{-11}	2.5×10^{-7}	-3.0×10^{-4}	0.15	0.9998
Cu-23%Cr-5%Al (CS) (cool down)	-5.3×10^{-11}	1.9×10^{-7}	-2.3×10^{-4}	0.13	1.0000
NiAl (V2-03-166)	-7.3×10^{-11}	2.3×10^{-7}	-2.6×10^{-4}	0.12	0.9998
Ni-17%Cr-6%Al-0.5%Y (V2-02-27E)	-9.6×10^{-11}	3.0×10^{-7}	-3.2×10^{-4}	0.15	0.9999
Ni-17%Cr-6%Al-0.5%Y (V2-03-528)	-6.6×10^{-11}	2.4×10^{-7}	-2.8×10^{-4}	0.14	1.0000

3.5 Evaluation of the Temperature Dependencies of Enthalpy, Entropy and Gibbs Free Energy

The changes in enthalpy, ΔH_T , entropy, ΔS_T , and Gibbs free energy, ΔG_T , were calculated for $0 \leq T \leq 1200$ K using Equation (3), and for simplicity, assuming that the standard reference thermodynamic state is at $T = 0$ K.⁶ The thermodynamic relationships are given by (Refs. 7, 14, and 21):

$$\Delta H_T = H_T = \int_0^T C_P dT \quad (6)$$

$$\Delta S_T = S_T = \int_0^T \frac{C_P}{T} dT \quad (7)$$

$$\Delta G_T = G_T = \Delta H_T - T * \Delta S_T \quad (8)$$

Figure 9 to Figure 11 show the temperature dependencies of ΔH_T , ΔS_T , and ΔG_T evaluated from Equations (6) to (8). Once again, the vertical broken lines in the figures denote the experimental and the interpolated regions. The enthalpies for the copper alloys, as well as for VPS NiCrAlY, are extremely close and indistinguishable in Figure 9 between 0 and 1223 K. At 1200 K, the lowest value of $\Delta H_T \approx 29.3$ kJ/mol in this band is for VPS Cu-26%Cr and the highest value of $\Delta H_T \approx 31.0$ kJ/mol is for CS Cu-23%Cr-5%Al. The enthalpy curve for VPS NiAl falls below those for the copper alloys and VPS NiCrAlY and increasingly deviates away from the other curves with increasing absolute temperature (Figure 9). At 1200 K, the magnitude of $\Delta H_T \approx 24.2$ kJ/mol for NiAl. The enthalpy increases with absolute temperature for all the materials.

The molar entropy increases at a decreasing rate with increasing absolute temperature for all the alloys studied in the present investigation (Figure 10). The values of ΔS_T for the copper alloys and VPS NiCrAlY fall within a relatively narrow band with a maximum spread of about 4.5 J/mol. The maximum and minimum values of 73.8 and 69.0 J/mol occur at 1200 K for VPS Cu-8%Cr-1%Al and CS Cu-23%Cr-5%Al (cool-down), respectively. The average maximum value of ΔS_T for the other alloys at 1200 K is 71.3 J/mol. The data for ΔS_T for VPS NiAl well below this band with the maximum value of about 58.7 J/mol occurring at 1200 K.

The Gibbs free energy decreases with increasing absolute temperature (Figure 11). The lowest value of ΔG_T at 1200 K is for VPS Cu-8%Cr-1%Al, which was estimated to be about -58.3 kJ/mol. The highest magnitude of ΔG_T at 1200 K was for VPS NiAl with an estimated value of about -46.3 kJ/mol.

⁶ It should be noted that this assumption allows the calculation of the absolute values H_T , S_T and G_T rather than ΔH_T , ΔS_T , and ΔG_T .

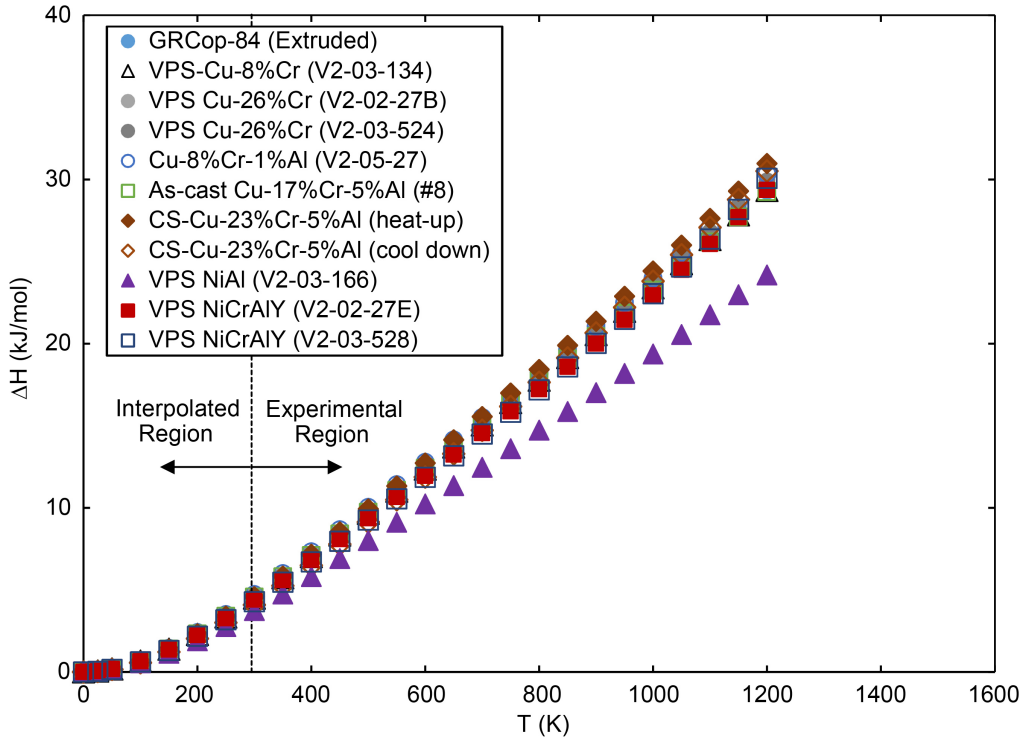


Figure 9.—Plot of the calculated values of the molar enthalpy against the absolute temperature for variously processed copper alloys, VPS NiAl and VPS NiCrAlY alloys. The calculated values from the experimentally measured C_p data lie to the right of the vertical broken line, while the symbols to the left of this line are based on interpolated values of C_p .

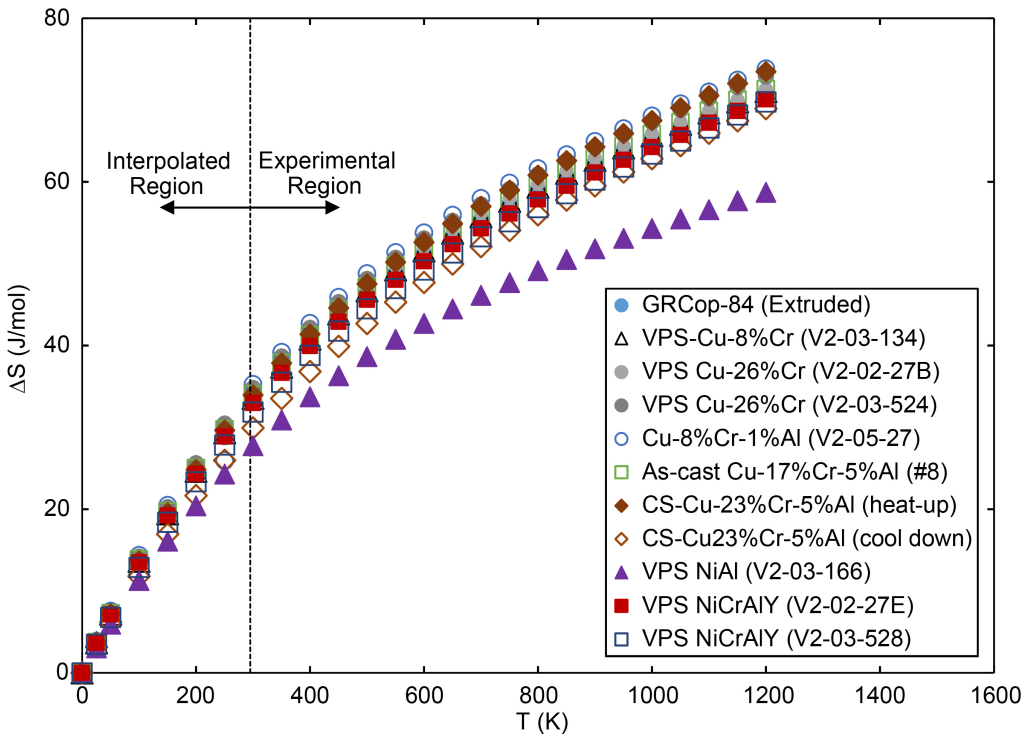


Figure 10.—Plot of the calculated values of the molar entropy against the absolute temperature for variously processed copper alloys, VPS NiAl and VPS NiCrAlY alloys.

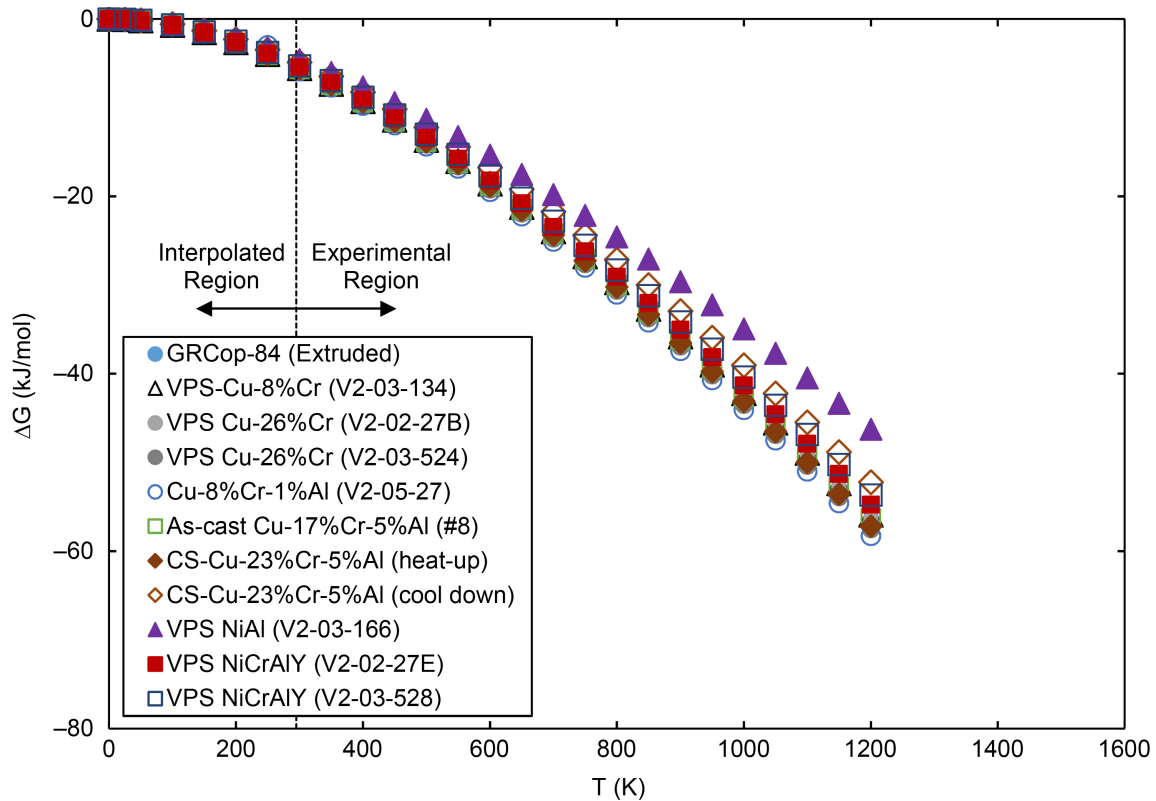


Figure 11.—Plot of the calculated values of the Gibbs molar free energy against the absolute temperature for variously processed copper alloys, VPS NiAl and VPS NiCrAlY alloys.

4.0 Summary and Conclusion

The temperature dependencies of the constant pressure specific heat capacities, C_p , of several vacuum plasma sprayed (VPS) and cold sprayed copper alloy monolithic coatings, VPS NiAl, VPS NiCrAlY, extruded GRCop-84 and as-cast Cu-17(wt.%)Cr-5%Al are discussed. The magnitudes of C_p increased with increasing temperature for all the alloys with the data falling within a narrow scatter band for most of the Cu-Cr alloys but well separated for the NiAl and NiCrAlY coatings. The data were well represented by empirical polynomial equations, and the evaluated values of the regression coefficients are reported. The experimental data did not agree with values calculated from the empirical Neumann-Kopp rule. Instead, a modification of the Neumann-Kopp rule was found to predict values closer to the experimental data with an absolute deviation less than 6.5%. The molar specific heat capacities for the alloys did not agree with the Dulong-Petit law. Instead, the magnitudes of $C_p > 3R$, where R is the universal gas constant, at all temperatures for all the alloys except VPS NiAl for which $C_p < 3R$. The values of molar enthalpy, molar entropy and Gibbs molar free energy calculated from the molar specific heat capacities are reported for the investigated alloys.

References

1. S.V. Raj, Thermophysical properties of cold and vacuum plasma sprayed Cu-Cr alloys, NiAl and NiCrAlY coatings Part I: Electrical and thermal conductivity, thermal diffusivity, and total hemispherical emissivity, *J. Eng. Mater. Perform.* 2017, **vol. 26, 11**, p. 5472-5480. <https://link.springer.com/article/10.1007/s11665-017-3012-0>; NASA/TM—2017-219715.

2. S.V. Raj and A. Palczer, Thermal expansion of vacuum plasma sprayed coatings, *Mater. Sci. Eng. A*, 2010, **A 527**, p. 2129-2135.
3. S.V. Raj, R. Pawlik and W. Loewenthal, Young's moduli of cold and vacuum plasma sprayed metallic coatings, *Mater. Sci. Eng. A*, 2009, **A 513-514**, p. 59-63.
4. J. Karthikeyan, Development of oxidation resistant coatings on GRCo-84 substrates by cold spray process, NASA/CR—2007-214706, 2007, NASA Glenn Research Center, Cleveland, OH.
5. Thermophysical Properties Research Laboratory, Inc., <http://www.tprl.com/services.html>.
6. ASTM Standard E1269, Standard test method for determining specific heat capacity by differential scanning calorimetry, *ASTM Annual Book of Standards*, vol. 14.02, ASTM International, West Conshohocken, PA, 2004.
7. G.N. Lewis and M. Randall, *Thermodynamics*, 2nd ed., McGraw-Hill, New York, NY, 1961, p. 66.
8. D.O. Allison, Polynomial approximations of thermodynamic properties of arbitrary gas mixtures over wide pressure and density ranges, 1972, NASA TN D-6862, National Aeronautics and Space Administration, Washington, D.C.
9. J.R. Andrews and O. Biblarz, Temperature dependence of gas properties in polynomial form, NPS67-81-001, 1981, Naval Postgraduate School, Monterey, CA.
10. B.J. McBride, S. Gordon and M.A. Reno, Coefficients for calculating thermodynamic and transportation properties of species, 1993, NASA TM 4513, National Aeronautics and Space Administration, Washington, D.C.
11. R. Hickman, T. McKechnie and R. Holmes, Material properties of vacuum plasma sprayed Cu-8Cr-4Nb for liquid rockets, *37th Joint Propulsion Conf.*, Salt Lake City, UT, 2001, American Institute for Aeronautics and Astronautics, Washington, D.C.
12. Y.S. Touloukian and E.H. Buyco, Specific Heat: Metallic elements and alloys, *Thermophysical Properties of Matter*, vol. 4, 1970, p. 146-152, IFI/Plenum, New York, NY.
13. W.S. Walston and R. Darolia, Effect of alloying on physical properties of NiAl, *High-Temperature Ordered Intermetallic Alloys V*, (eds. I. Baker, R. Darolia, J.D. Whittenberger and M.H. Yoo, 1993, **vol. 288**, p. 237-242, *MRS Symposium Proceedings*, Materials Research Society, Pittsburgh, PA.
14. L.S. Darken and R.W. Gurry, *Physical Chemistry of Metals*, 1953, McGraw-Hill, New York, NY.
15. R.A. Swalin, *Thermodynamics of Solids*, John Wiley, 1962, New York, NY.
16. J. Valencia and P.N. Quested, Thermophysical properties, *ASM Handbook*, 2008, **vol. 15**, p. 468-81.
17. J. Leitner, P. Vonka, D. Sedmidubsky and P. Svoboda, Application of Neumann-Kopp rule for the estimation of heat capacity of mixed oxides, *Thermochim. Acta*, 2010, **497**, p. 1-13.
18. R. Brandt, L. Pawlowski, G. Neuer and P. Fauchais, Specific heat and thermal conductivity of plasma sprayed yttria-stabilized zirconia and NiAl, NiCr, NiCrAl, NiCrAlY, NiCoCrAlY coatings, *High Temp. High Pressures*, 1986, **18**, p. 65-77.
19. S.S. Zumdahl, *Introductory Chemistry*, 5th ed., 2004, Houghton Mifflin Co., Boston, MA.
20. N.F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, 1958, Dover, N.Y., NY.
21. H. Wang, R. Lück and B. Predel, Heat capacities of intermetallic compounds in the iron-titanium system, *Z. Metall.*, 1993, **84**, p. 230-236.

