Thermophysical properties of Ni-containing single-phase concentrated solid solution alloys

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Abstract

Temperature dependent thermophysical properties, including specific heat capacity, lattice thermal expansion, thermal diffusivity and conductivity, have been systematically studied in Ni and eight Ni-containing single-phase face-centered-cubic concentrated solid solution alloys, at elevated temperatures up to 1273 K. The alloys have similar specific heat values of 0.4 - 0.5 J·g⁻¹·K⁻¹ at room temperature, but their temperature dependence varies greatly due to Curie and K-state transitions. The lattice, electronic, and magnetic contributions to the specific heat have been separated based on first-principles methods in NiCo, NiFe, Ni-20Cr and NiCoFeCr. The alloys have similar thermal expansion behavior, with the exception that NiFe and NiCoFe have much lower thermal expansion coefficient in their ferromagnetic state due to magnetostriction effects. Calculations based on the quasi-harmonic approximation accurately predict the temperature dependent lattice parameter of NiCo and NiFe with less than 0.2% error, but underestimated that of Ni-20Cr by 1%, compared to the values determined from neutron diffraction. All the alloys containing Cr have very similar thermal conductivity, which is much lower than that of Ni and the alloys without Cr, due to the large magnetic disorder.

Keywords: Solid solution alloy, Thermophysical properties, Neutron diffraction, Chemical disorder

1. Introduction

Thermophysical properties, e.g. specific heat capacity, coefficient of thermal expansion (CTE), and thermal conductivity, of transition metal alloys are of broad interest from both practical and scientific perspectives. For example, thermal expansion is an important concern in engineering applications of alloys, since the thermal stress and strain induced from temperature variations can greatly impact their high-temperature processing, a particularly critical factor when the alloys are used as part of composite material [1]. The Invar behavior observed in Ni-65Fe and other Ni-Fe-based alloys has long made understanding thermal expansion in these alloys an important scientific challenge [2]. The temperature dependent specific heat is not only a factor in determining thermal conductivity, but also an indicator of phase transitions such as magnetic phase and other order/disorder transitions [3-5]. Control of thermal conductivity is required in many practical applications, and both low (e.g. as thermal barriers and thermoelectric materials) and high (e.g. in cooling system, cladding tube in nuclear engineering, or other places where thermal shock needs to be prevented) values could be required depending on the application fields. Furthermore, thermal conductivity is a necessary parameter in theoretical studies of defect evolution under irradiation or energy deposition process, especially in the molecular dynamic simulations using a two-temperature model [6, 7].

The development of single-phase concentrated solid solution alloys (SP-CSA), including high entropy alloys, in the past decade [8-11] has gained significant interest due to their outstanding corrosion and wear resistance [12, 13], good weldability [14], exceptional mechanical properties [15-17], potential enhancement in radiation tolerance [18], and unique physical properties [19-22]. The large application potential of these alloys makes knowledge of their thermophysical properties highly desirable. In contrast to traditional alloys, which usually consist of one principal element and are typically multiphase, SP-CSA contain 2-5 (or even more) principal alloying elements [23] while condensing as single-phase solid-solutions on simple underlying lattices (e.g. single phase face-centered cubic, FCC). A significant feature of this novel class of alloys is that they offer new opportunities for tailoring materials properties through

control of chemical complexity – changes in the number, type and concentration of alloying elements. Clearly, the notion of alloy design through control of chemical complexity not only greatly expands on traditional concepts of alloy design through microstructure modification but also raises challenges in understanding their intrinsic physical properties and opportunities of tuning them.

Recent studies have demonstrated that controlling compositional complexity of the Ni-containing FCC SP-CSAs can systematically tune their electrical and magnetic properties at low temperatures over wide ranges [19]. For example, the magnetic moment of Cr has been found anti-parallel to that of other elements when alloying with Ni, Co, and Fe, which generates large magnetic disorder, causes strong scattering of electrons, and induces high (residual) electrical resistivity in the complex alloys [19]. In some of the alloys in this family, e.g. NiCoCr, unique quantum critical behavior has been observed, and its Curie temperature and transport properties can be dramatically changed with varying Cr concentration [21]. Although certain aspects of thermal properties have been measured by individual studies in various binary alloys in the early days (relevant references will be discussed in Section 3) and in some high entropy alloys, e.g. NiCoFeCrAl (note: usually not single-phase solid solution) and NiCoFeCrMn more recently [24, 25], systematic studies on the thermophysical properties in SP-CSA with varying compositional complexity at elevated temperature have been limited.

In the present study, a family of Ni-containing SP-CSAs from elemental Ni to quinary alloys, including equiatomic NiCo, NiFe, NiCoFe, NiCoCr, NiCoFeCr, NiCoFeCrMn and NiCoFeCrPd, and non-equiatomic Ni-20Cr (since equiatomic NiCr is not a single-phase FCC solid solution [26]), were selected, and their thermophysical properties from 300 to 1273 K have been systematically investigated. The temperature dependent lattice parameter, constant pressure specific heat, and thermal diffusivity have been measured by neutron diffraction, differential scanning calorimeter (DSC), and laser flash technique, respectively. Moreover, the CTE and thermal conductivity of these alloys have then been derived and compared. First-principles calculations have been performed to evaluate the lattice parameter and the lattice contribution to

the specific heat in the three binary alloys along with NiCoFeCr.

2. Experiments and methods

2.1. Materials

Appropriate amounts of elemental (>99.9% pure) Ni, Co, Fe, Cr, Mn and Pd metals (from Atlantic Equipment Engineers, NJ USA and Alfa Aesar, MA USA) were mixed by arc-melting. Each arc-melted button was flipped and re-melted five times before drop-casting the melt into a copper mold. The as-cast ingots were then homogenized at 1473 K for 24 h, followed by water quenching. All the alloys have been experimentally determined to be single-phase solid solution with FCC crystal structure and the experimental details can be found elsewhere [26, 27]. Briefly, Fig. 1 shows the microstructure and X-ray diffraction results of the NiCoFeCrPd alloy as an example. The backscattered electron image only exhibits uniform grain structures and no secondary phase is observed. The Energy-dispersive X-ray spectroscopy (EDX) mapping further shows uniform elemental distribution. The X-ray diffraction pattern shown in Fig. 1c reveals only FCC peaks. These results confirm that the materials used in this study are single-phase solid solution alloys. The samples were then cut into various shapes using electro-discharge machining (EDM) to satisfy different characterization techniques.

2.2. Characterizations

The constant-pressure specific heats, C_p , were measured from 300 to 1000 K (to 1200 K for NiCoFe) using a Netzsch 404 C differential scanning calorimeter (DSC), following ASTM E 1269 using a sapphire standard. The samples were heated in a flowing argon atmosphere at a constant heating rate of 10 K/min. The samples experienced a full heating-cooling cycle before each measurement to rule out the exothermic reactions due to non-equilibrium cooling during the quench process [4, 28]. For each sample, at least two measurements were performed and the heat capacity error of 5% was estimated.

Cylindrical samples with nominal diameter of 12 mm and length of 20 mm were used for in-situ neutron diffraction measurements, conducted on the VULCAN Engineering Materials Diffractometer at the Spallation Neutron Source, Oak Ridge National Laboratory (SNS, ORNL)

[29]. The samples were heated by copper induction coils at a constant rate of 15 K/min, from 300 to 1273 K, and the average lattice parameter and its changes upon heating were determined from the single peak fit of (111), (200), (220), and (311) peaks.

Thermal diffusivity was measured using a laser flash technique following ASTM E1461, using a Netzsch LFA 457 laser flash apparatus. Cylindrical sample disks with 12.7 mm in diameter and ~3-6 mm in thickness were used for the measurements. Both flat surfaces of the sample disks were spray coated with colloidal graphite to increase the emissivity of the surfaces. Flowing argon was used as a purge gas to protect the samples from oxidation. The data were collected every 50 K from room temperature to 473 K, and every 100 K up to 1273 K during heating. A few temperature points were re-collected during cooling, which showed about the same value as during heating.

2.3. Calculation details

First-principles calculations were performed using the projector augmented wave (PAW) method [30] implemented in the Vienna *ab-initio* simulation package (VASP) [31, 32]. The generalized gradient approximation (GGA) exchange-correlation functional in the formalism of PBE [33] was employed.. The energy cutoff for the plane-wave expansion was set to 400 eV, and a Γ -centered Monkhorst-Pack k-point grid was used for the Brillouin zone integration. A 32-atom special quasi-random structure (SQS) [34] was used to optimize the volume and all the atomic positions of considered alloys. The relaxation was performed using 1st-order Methfessel-Paxton method along with $6 \times 6 \times 6$ k-point mesh, and the Hellmann-Feynman forces were converged to 0.005 eV/Å.

Quasi-harmonic approximation (QHA) was employed for the thermal expansion, and the phonon calculations were performed using the linear response method implemented in VASP. Depending on the specific materials, the magnetism is incorporated differently. For NiFe and NiCo, the ferromagnetic ground state was used throughout the relaxation and the phonon calculations, ignoring the magnetostriction effects. On the contrary, Ni-20Cr has been proven to be nonmagnetic experimentally [35], therefore, magnetism of this system was prohibited in our

calculations. To shed some light on the thermal behavior beyond the Curie temperature, several random collinear spin configurations were generated based on the SQS cells to model the phonon properties in the paramagnetic state. This is similar to the concept of the disorder local moment (DLM) state [36], but without sophisticated statistical averaging. Those DLM-like states are also applied to the NiFeCoCr alloys.

3. Results and discussions

3.1. Specific heat

The values of room temperature specific heat of all alloys tested are between 0.4 and 0.5 $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$, as shown in Fig. 2a and 2b, while their temperature dependence varies significantly. For Ni, NiFe and NiCoFe, sharp peaks are observed at 628, 780, and 995 K, respectively, which are attributed to the magnetic contribution to the specific heat, with peak temperatures indicating the Curie temperatures. The Curie temperature of NiCo is determined to be 1117 K by a separate DSC measurement (not shown here). These Curie points, as well as the values of specific heat of Ni and NiFe, agree well with the literatures [37-40].

For NiCoFeCrPd, a distinguishable but very small peak is observed at 374 K, as shown in the inset of Fig. 2b, which agrees with the Curie temperature determined by magnetization measurements [19]. This much smaller peak, compared to that in the alloys mentioned above, indicates a smaller enthalpy of magnetic ordering in NiCoFeCrPd, which might be related to its possible spin noncollinear ground state: the strong spin-orbit effects in Pd, along with the exchange frustration in the alloy, facilitate the spin canting. The magnetic phase transition of the other studied alloys containing Cr appears below 300 K [19], and thus no corresponding peaks were observed in this study.

Other than the Curie transition, endothermic reactions, shown as an abrupt increase in specific heat, were observed for all the alloys containing Cr, as well as for NiCoFe, within a transition temperature window of 750-950 K. All these curves were reproduced at least twice, the C_p – T curves from the second heating-cooling cycles are identical to those from the first cycles, and the

possible oxidation issue is then excluded.

Similar transitions regarding specific heat in the same temperature window in the alloys containing Ni and Cr have been reported, not only for the commercial alloys such as 617 [41], 600 [4], and Ni-Cr-Mo [42] systems, but also for the model alloys such as Ni-20Cr [41] and Ni-Fe-Cr [43]. Other thermal anomalies in physical (e.g. electrical resistivity) and mechanical properties (e.g. creep) in the Ni-Cr- containing alloys on the Ni-rich side have also been commonly observed [44, 45]. These unique behaviors have been generally termed as “komplex-” or K-state [46], the origin of which has been extensively studied over the decades experimentally and theoretically but still not yet fully clarified. A few of these studies attributed the K-state mainly to the development of long-range order, e.g. dispersed ordered Ni_2Cr domains in a random or disordered matrix [4, 44]. In contrast, many others believed that only short-range order occurs in the alloys with Cr concentration below ~25 at% [45, 47]. Short-range order in this family of alloys has been measured repeatedly using diffuse neutron [48, 49] and X-ray [50] scattering and theoretically studied by first-principles calculations [51].

The formation of a long-range ordered Ni_2Cr phase has been reported in Ni-Cr alloys after long-term (hundreds to thousands of hours) annealing at temperatures below 500-600 °C [44, 52]. The evidence of such long-range ordering in neutron diffraction patterns is the appearance of superlattice peaks [52], corresponding to a Mo_2Pt -type orthorhombic crystal structure. In the current study, however, the starting materials were water-quenched and the heating time during measurements were limited to a few hours. Neutron diffraction patterns from these materials do not show any sign of superlattice peaks. For example, Fig. 3 shows the representative neutron diffraction patterns of Ni-20Cr and NiCoFeCrMn alloys that only exhibit FCC peaks, indicating no detectable long-range ordered Ni_2Cr phase. In addition, with repeated measurements on each sample, the heat absorption in the transitions remained the same between each test cycle. Furthermore, a single crystalline Ni-20Cr sample grown using the floating-zone directional solidification method was also tested for comparison, and exhibited about the same C_p -T curve as the quenched polycrystalline samples. Therefore, the transitions in our specific heat

measurements are believed to be attributed to the short-range order/disorder transitions, while the detailed mechanism requires further investigations [41]. It needs to be emphasized that all the alloys containing Cr selected in this study exhibit a similar transition, from binary to quinary with Cr concentration from 20 to 33 at%, which implies that all Cr-contained alloys might exhibit short-range order. Interestingly, for the alloys without Cr (meaning that Ni-Cr related short range order is not possible), only NiCoFe alloy exhibits a similar transition around 750-800 K. Unfortunately, the current experiments and state of knowledge do not reveal the nature of this transition, a situation that will be revisited in future studies.

The specific heat of the Invar-type alloys (Ni-Fe-based) has been measured over the past decades with controversial results. Bendick *et al* [53]. observed an anomalous maximum at ~500 K in addition to the one at the Curie temperature for Ni-50Fe, and attributed this behavior to a Schottky-type anomaly assuming a two-level model. However, this anomaly was not observed by Tanji *et al* [54]. The studies by Hausch [55] on Ni-44Fe and by Orehotsky *et al.* [37] on Ni-55Fe also showed no additional peaks in this temperature range. Here our measurement disagrees with Bendick's but supports the results of others that no additional maximum exists at ~500 K.

The lattice contribution to the specific heats of NiCo, NiFe, Ni-20Cr, and NiCoFeCr has been calculated from first-principles. Since specific heat consists of lattice, electronic, and magnetic components, all the calculated results are smaller than the experimental results. The contribution from electrons is relatively small and usually approximately expressed as $C_e = \gamma T$, where γ is called the electronic specific heat coefficient [5]. The values of γ for NiCo and NiFe are both $\sim 7.2 \times 10^{-5} \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-2}$ [37] and the addition of the lattice and electronic contributions of these two alloys are plotted in Fig. 4a; the magnetic contributions are derived by subtracting these two contributions from the measured results. A lambda shape is observed as expected. The magnetic contribution is negligible in the low temperature regime, increases when approaching the Curie temperature, and vanishes at higher temperatures. For Ni-20Cr and NiCoFeCr, the electronic component can be derived from the difference between the experimental value and the calculated

lattice component, since the measurements were taken above the Curie temperature, as shown in Fig. 4b. The derived electronic specific heats of these two alloys are similar and are both linear with temperature; the estimated γ values are both $6.3 \times 10^{-5} \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-2}$, which is similar to that of NiCo and NiFe. Due to the unclear nature of the K-state transition, the contribution from each component after 800 K in Ni-20Cr and NiCoFeCr was not quantified.

3.2. Lattice parameter

The temperature-dependent lattice parameter is shown in Fig. 5a, from 300 to 1273 K, according to which the theoretical density as a function of temperature is then calculated. The lattice parameters are derived from the (200), (220), (111), and (311) peaks. An empirical formula in exponential form

$$L = L_0 + bT + c[\text{Exp}(-T / d) - 1] \quad (1),$$

where L and L_0 are the lattice parameters at temperature T and 0 K, respectively; b , c , and d are fitting parameters, can well describe the temperature dependence of lattice parameter for all these materials except NiFe and NiCoFe, in which magnetostriction effects may cause a significant change in thermal expansion [56]. Spline estimation is thus used to fit the curves for NiFe and NiCoFe. A similar form of Eq. 1, in which b , c , and d are correlated, has been used to describe the thermal expansion for some FCC steels [57] and NiCoFeCrMn [24] measured by dilatometer. Here, however, they need to be determined independently to reasonably fit the full set of alloys. All the fitting curves are shown as the solid lines in Fig. 5a.

The room temperature lattice parameters determined from our neutron diffraction measurement are in good agreement to the previous results based on X-ray diffraction [58]. In addition, the calculated densities at room temperature have little difference as compared with the experimental value; thus the deduced temperature-dependent density, ρ , is used in the calculation of thermal conductivity.

For the three binary alloys, NiCo, NiFe, Ni-20Cr, the temperature dependent lattice parameters

were calculated from first-principles, as shown in comparison with experiments in Fig. 5b. The calculated lattice parameters in NiFe and NiCo agree with the experimental values with an error less than $\sim 0.2\%$. On the contrary, for Cr containing alloys, PBE underestimate the lattice parameter of the supercells by 1%. This underestimation of the lattice spacing can be traced back to the antiferromagnetic spin alignment on Mn; GGA is less successful correcting the LDA overbinding problem for antiferromagnetic than ferromagnetic $3d$ metals, as shown in antiferromagnetic α -Mn, bcc-Cr, and γ -Fe [59].

The thermal expansion effect was evaluated by QHA, which is valid for systems without strong anharmonicity. Our cases presumably qualify due to the small mass disorder. As found in Fig. 5b, the calculated lattice parameter of NiFe increases faster with temperature than the experimental result. This is partially because QHA neglects the possible spin-phonon coupling, and thus it cannot capture the magnetostriction effect at elevated temperature. In addition, the thermal electronic effect was not included in the treatment since it is usually small compared with the vibrational effect. The entropy from the magnetism is also neglected in the free energy. Nevertheless, overall, this crude approximation provides reasonable predictions on lattice parameters and heat capacity.

The temperature dependent lattice parameter can provide information on the coefficient of thermal expansion, although some fine features, such as the peak of CTE right at the Curie temperature in Ni [60], cannot be captured. This is mainly due to the fact that the measured lattice parameters are bulk averaged over the temperature interval of 15 K, which is too large to properly capture such features [1]. Here the derived CTE value [61] of

$$\alpha = (1/L) dL/dT \quad (2)$$

is shown in Fig. 6. The CTE values of Ni, NiCo, NiCoCr, NiCoFeCr, and Ni-20Cr are very similar, while that of NiCoFeCrMn is slightly higher but follows the same trend. In contrast, the CTE of NiFe and NiCoFe are apparently lower in their ferromagnetic state due to the spontaneous volume magnetostriction (although not close to zero as the case of typical Invar

alloys such as Ni-65Fe [2]), and sharply increase beyond the Curie point. In the paramagnetic regime, the CTE of NiFe and NiCoFe become similar to the other alloys. Such temperature dependence of CTE in NiFe is similar to what has been observed in the dilatometer measurements [56].

3.3. Thermal diffusivity and thermal conductivity

The thermal diffusivity, D , and the derived [25] thermal conductivity using

$$\kappa = D\rho C_p \quad (3)$$

are shown in Fig. 7a and 7b, respectively. Below the Curie temperature, the thermal diffusivity and conductivity of the alloys that do not contain Cr are significantly larger than those of the alloys containing Cr, although smaller than those of pure Ni. This is mainly attributed to the fact that the electrical resistivity of the alloys without Cr is much smaller than that of Cr containing alloys, giving them larger electronic thermal conductivity [19]. The four systems that do not contain Cr also have negative coefficient of temperature dependence of thermal diffusivity/conductivity below the Curie temperature that is attributed to the fast increase of electrical resistivity according to the Wiedemann-Franz relationship

$$\kappa_e = LT/\rho, \quad (4)$$

where κ_e is the electronic thermal conductivity, ρ is the electrical resistivity, and L is the Lorentz constant [62].

A minimum in thermal diffusivity can be clearly seen around the Curie temperatures of the four Cr-free samples although the temperature interval is somewhat large, after which the thermal diffusivities increase with increasing temperature. Such minima have been commonly observed in magnetic metals and alloys in the past (e.g. Ni [63], Fe [64], Gd [65], Ni-Fe [62], and Ni-Cu [62]). One of the simple interpretations is that the electrical resistivity induced from spin fluctuation becomes saturated above the Curie temperature, leading to a sudden slow-down in the increase of electrical resistivity as a function of temperature which, according to the

Wiedemann-Franz relationship, causes the increase of thermal conductivity above Curie temperature [66]. However, it should be noted that such critical point anomalies in thermal conductivity might also be somewhat attributed to the contribution from the lattice component through spin-lattice coupling [63]. While non-trivial this possibility will not be discussed in the present work.

For the paramagnetic and non-magnetic Cr-containing alloys the thermal diffusivity and thermal conductivity increase with increasing temperature over the entire temperature range. This is mainly because these alloys have large residual resistivity (the resistivity at 0 K), and very low temperature dependence of the resistivity. Such invariant electrical resistivity as a function of temperature makes their electronic thermal conductivity increase almost linearly with temperature [19].

4. Summary and conclusions

In summary, the temperature dependence of specific heat, lattice parameter, and thermal diffusivity has been measured in a family of Ni-containing single phase concentrated solid solution alloys at elevated temperature. The thermal conductivity and thermal expansion coefficient of these alloys have been derived, and their Curie temperatures have been determined. All these alloys have similar specific heat at room temperature, but their temperature dependence varies a great deal depending on the magnetic state and possible short-range order-disorder transitions. The lattice contribution of the specific heat has been calculated from first-principles, and the electronic and magnetic contributions have been derived accordingly. The neutron-diffraction-determined lattice parameters, in order from small to large at room temperature are: Ni, NiCo, Ni-20Cr, NiCoCr, NiCoFeCr, NiCoFe, NiFe, NiCoFeCrMn, and NiCoFeCrPd (the latter being determined by X-ray diffraction). The QHA-based calculations provide a good estimate of the lattice parameters of NiCo and NiFe, within 0.2% error, but underestimate that of Ni-20Cr by ~1%. All these alloys have similar thermal expansion coefficients, except that NiFe and NiCoFe show strong magnetostriction effects at their

ferromagnetic state, and NiCoFeCrMn shows slightly higher CTE than that of the others. The thermal transport properties can be grouped whether or not they contain the element Cr. Nickel and alloys without Cr show larger thermal diffusivity and conductivity, have negative temperature coefficients below their Curie points, and have positive temperature coefficients at higher temperatures. All the alloys containing Cr have very similar thermal diffusivity and thermal conductivity, which increase with increasing temperature from room temperature to at least 1000 K.

Acknowledgment

This work was supported as part of the Energy Dissipation to Defect Evolution (EDDE), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. A portion of this research used resources at Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

References

- [1] J.D. James, J.A. Spittle, S.G.R. Brown, R.W. Evans. A review of measurement techniques for the thermal expansion coefficient of metals and alloys at elevated temperatures, *Meas. Sci. Technol.* 12 (2001) R1-R15.
- [2] M. van Schilfgaarde, I.A. Abrikosov, B. Johansson. Origin of the Invar effect in iron–nickel alloys, *Nature* 400 (1999) 46-49.
- [3] D.M. Kroeger, C.C. Koch, J.O. Scarbrough, C.G. McKamey. Effects of short-range order on electronic properties of Zr-Ni glasses as seen from low-temperature specific heat, *Phys. Rev. B* 29 (1984) 1199-1208.
- [4] S. Kim, I.H. Kuk, J.S. Kim. Order–disorder reaction in Alloy 600, *Mater. Sci. Eng. A* 279 (2000) 142-148.
- [5] R.E. Pawel, E.E. Stansbury. Specific heat contributions of the ferromagnetic transition in nickel and nickel-copper alloys, *J. Phys. Chem. Solid.* 26 (1965) 757-765.
- [6] M. Caro, L.K. Béland, G.D. Samolyuk, R.E. Stoller, A. Caro. Lattice thermal conductivity of multi-component alloys, *J. Alloy. Comp.* 648 (2015) 408-413.
- [7] M. Toulemonde, W. Assmann, C. Dufour, A. Meftah, F. Studer, C. Trautmann. Experimental phenomena and thermal spike model description of ion tracks in amorphisable inorganic insulators, *Mat. Fys. Medd. K. Dan. Vidensk. Selsk.* 52 (2006) 263-292.
- [8] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent. Microstructural development in equiatomic multicomponent alloys, *Mater. Sci. Eng. A* 375-377 (2004) 213-218.
- [9] O.N. Senkov, G.B. Wilks, J.M. Scott, D.B. Miracle. Mechanical properties of Nb₂₅Mo₂₅Ta₂₅W₂₅ and V₂₀Nb₂₀Mo₂₀Ta₂₀W₂₀ refractory high entropy alloys, *Intermetallics* 19 (2011) 698-706.
- [10] M.S. Lucas, G.B. Wilks, L. Mauger, J.A. Muñoz, O.N. Senkov, E. Michel, J. Horwath, S.L. Semiatin, M.B. Stone, D.L. Abernathy, E. Karapetrova. Absence of long-range chemical ordering in equimolar FeCoCrNi, *Appl. Phys. Lett.* 100 (2012) 251907.
- [11] F. Tancet, I. Toda-Caraballo, E. Menou, P.E.J. Rivera Díaz-Del-Castillo. Designing high entropy alloys employing thermodynamics and Gaussian process statistical analysis, *Mater. Des.* 115 (2017) 486-497.
- [12] Y. Zhang, T. Zuo, Z. Tang, M.C. Gao, K.A. Dahmen, P.K. Liaw, Z. Lu. Microstructures and properties of high-entropy alloys, *Prog. Mater. Sci.* 61 (2014) 1-93.
- [13] Z. Zhang, E. Axinte, W. Ge, C. Shang, Y. Wang. Microstructure, mechanical properties and corrosion resistance of CuZrY/Al, Ti, Hf series high-entropy alloys, *Mater. & Des.* 108 (2016) 106-113.
- [14] Z. Wu, S.A. David, Z. Feng, H. Bei. Weldability of a high entropy CrMnFeCoNi alloy, *Scripta Mater.* 124 (2016) 81-85.
- [15] B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, E.P. George, R.O. Ritchie. A fracture-resistant high-entropy alloy for cryogenic applications, *Science* 345 (2014) 1153-1158.
- [16] B. Gludovatz, A. Hohenwarter, K.V. Thurston, H. Bei, Z. Wu, E.P. George, R.O. Ritchie. Exceptional damage-tolerance of a medium-entropy alloy CrCoNi at cryogenic temperatures, *Nat. Commun.* 7 (2016) 10602.
- [17] Y.D. Wu, Y.H. Cai, X.H. Chen, T. Wang, J.J. Si, L. Wang, Y.D. Wang, X.D. Hui. Phase composition and solid solution strengthening effect in TiZrNbMoV high-entropy alloys, *Mater. & Des.* 83 (2015) 651-660.
- [18] K. Jin, C. Lu, L.M. Wang, J. Qu, W.J. Weber, Y. Zhang, H. Bei. Effects of compositional complexity on the ion-irradiation induced swelling and hardening in Ni-containing equiatomic alloys, *Scripta Mater.* 119 (2016) 65-70.
- [19] K. Jin, B.C. Sales, G.M. Stocks, G.D. Samolyuk, M. Daene, W.J. Weber, Y. Zhang, H. Bei. Tailoring the physical properties of Ni-based single-phase equiatomic alloys by modifying the chemical complexity, *Sci. Rep.* 6

(2016) 20159.

- [20] Y. Zhang, G.M. Stocks, K. Jin, C. Lu, H. Bei, B.C. Sales, L. Wang, L.K. Beland, R.E. Stoller, G.D. Samolyuk, M. Caro, A. Caro, W.J. Weber. Influence of chemical disorder on energy dissipation and defect evolution in concentrated solid solution alloys, *Nat. Commun.* 6 (2015) 8736.
- [21] B.C. Sales, K. Jin, H. Bei, G.M. Stocks, G.D. Samolyuk, A.F. May, M.A. McGuire. Quantum Critical Behavior in a Concentrated Ternary Solid Solution, *Sci. Rep.* 6 (2016) 26179.
- [22] K.Y. Tsai, M.H. Tsai, J.W. Yeh. Sluggish diffusion in Co–Cr–Fe–Mn–Ni high-entropy alloys, *Acta Mater.* 61 (2013) 4887-4897.
- [23] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chang. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes, *Adv. Eng. Mater.* 6 (2004) 299-303.
- [24] G. Laplanche, P. Gadaud, O. Horst, F. Otto, G. Eggeler, E.P. George. Temperature dependencies of the elastic moduli and thermal expansion coefficient of an equiatomic, single-phase CoCrFeMnNi high-entropy alloy, *J. Alloy. Compound.* 623 (2015) 348-353.
- [25] H. Chou, Y. Chang, S. Chen, J. Yeh. Microstructure, thermophysical and electrical properties in $Al_xCoCrFeNi$ ($0 \leq x \leq 2$) high-entropy alloys, *Mater. Sci. Eng. B* 163 (2009) 184-189.
- [26] Z. Wu, H. Bei, F. Otto, G.M. Pharr, E.P. George. Recovery, recrystallization, grain growth and phase stability of a family of FCC-structured multi-component equiatomic solid solution alloys, *Intermetallics* 46 (2014) 131-140.
- [27] F. Otto, A. Dlouhý, C. Somsen, H. Bei, G. Eggeler, E.P. George. The influences of temperature and microstructure on the tensile properties of a CoCrFeMnNi high-entropy alloy, *Acta Mater.* 61 (2013) 5743-5755.
- [28] M. Hirabayashi, M. Koiwa, K. Tanaka, T. Tadaki, T. Saburi, S. Nenno, H. Nishiyama. An experimental study on the ordered alloy Ni_2Cr , *Trans. JPN. I. Met.* 10 (1969) 365.
- [29] K. An, H.D. Skorpenske, A.D. Stoica, D. Ma, X. Wang, E. Cakmak. First In Situ Lattice Strains Measurements Under Load at VULCAN, *Metall. Mater. Trans. A* 42 (2010) 95-99.
- [30] P.E. Blöchl. Projector augmented-wave method, *Phys. Rev. B* 50 (1994) 17953-17979.
- [31] G. Kresse, J. Hafner. Ab initio molecular dynamics for open-shell transition metals, *Phys. Rev. B* 48 (1993) 13115-13118.
- [32] G. Kresse, J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* 54 (1996) 11169-11186.
- [33] J.P. Perdew, K. Burke, M. Ernzerhof. Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (1996) 3865-3868.
- [34] A. Zunger, S. Wei, L.G. Ferreira, J.E. Bernard. Special quasirandom structures, *Phys. Rev. Lett.* 65 (1990) 353-356.
- [35] M.J. Besnus, Y. Gottehrer, G. Munschy. Magnetic properties of Ni-Cr alloys, *Phys. Status Solidi b* 49 (1972) 597-607.
- [36] B.L. Gyorffyt, A.J. Pindors, J. Staunton, G.M. Stocks, H. Winter. A first-principles theory of ferromagnetic phase transitions in metals, *J. Phys. F: Met. Phys.* 15 (1985) 1337.
- [37] J. Orehotzky, K. Schröder. Specific Heat of Nickel-Iron and Nickel-Cobalt Alloys between 600°K and 1500°K, *Phys. Cond. Matter* 17 (1973) 37-53.
- [38] P. Handler, D.E. Mapother, M. Rayl. AC Measurement of the Heat Capacity of Nickel Near its Critical Point, *Phys. Rev. Lett.* 19 (1967) 356-358.

- [39] D.L. Connelly, J.S. Loomis, D.E. Mapother. Specific Heat of Nickel near the Curie Temperature, *Phys. Rev. B* 3 (1971) 924-934.
- [40] T.C. Pilkington, J.L. Artley, F.T. Wooten. Prediction of Curie Temperatures in Ternary Fe-Co-Ni Alloys. II, *J. Appl. Phys.* 35 (1964) 3493.
- [41] B.H. Rabin, W.D. Swank, R.N. Wright. Thermophysical properties of Alloy 617 from 25°C to 1000°C, *Nucl. Eng. Des.* 262 (2013) 72-80.
- [42] B. Wilthan, H. Reschab, R. Tanzer, W. Schützenhöfer, G. Pottlacher. Thermophysical Properties of a Chromium–Nickel–Molybdenum Steel in the Solid and Liquid Phases, *Int. J. Thermophys* 29 (2007) 434-444.
- [43] K.G. Binnatov, A.A. Katsnel'son, Y.L. Rodionov. Atomic ordering in Ni-Fe-Cr solid solutions, *Soviet Phys. J.* 18 (1975) 397-398.
- [44] A. Marucco, B. Nath. Effects of Ordering on the Properties of Ni-Cr Alloys, *J. Mater. Sci.* 23 (1988) 2107-2114.
- [45] E.E. Stansbury, C.R. Brooks, T.L. Arledge. Specific-Heat Anomalies in Solid Solutions of Chromium and Molybdenum in Nickel - Evidence for Short-Range Order, *J. Inst. Metal.* 94 (1966) 136-138.
- [46] H. Thomas. Über Widerstandslegierungen, *Z. F Physik* 129 (1951) 219-232.
- [47] P. Nash. The Cr-Ni (chromium-nickel) system, *Bull. Alloy Phase Diagn.* 7 (1986) 466-476.
- [48] B. Schonfeld, F. Klaiber, G. Kostorz, U. Zaune, G. McIntyre. Diffuse Neutron-Scattering and Short-Range Order in Ni-19.4 at Percent Cr, *Scripta Metal.* 20 (1986) 385-387.
- [49] B. Schönfeld, L. Reinhard, G. Kostorz, W. Bührer. Short-Range Order and Atomic Displacements in Ni–20 at% Cr Single Crystals, *Phys. Status Solidi B* 148 (1988) 457-471.
- [50] B. Schönfeld, G.E. Ice, C.J. Sparks, H.G. Haubold, W. Schweika, L.B. Shaffer. X-ray study of diffuse scattering in Ni–20 at% Cr, *Phys. Status Solidi B* 183 (1994) 79-95.
- [51] M. Rahaman, B. Johansson, A.V. Ruban. First-principles study of atomic ordering in fcc Ni-Cr alloys, *Phys. Rev. B* 89 (2014) 064103.
- [52] S. Kim. Order-disorder reaction in Ni₂Cr alloy, *Transactions of the Korean Nuclear Society Autumn Meeting Gyeongju, Korea, October 29-30 (2009)* 313.
- [53] W. Bendick, H.H. Ettwig, W. Pepperhoff. Anomalies in Specific-Heat and Thermal-Expansion of Fcc Iron-Alloys, *J. Phys. F Metal Phys.* 8 (1978) 2525-2534.
- [54] Y. Tanji, H. Asano, H. Moriya. Specific Heats of Fe-Ni (fcc) Alloys at High Temperature, *Sci. Rep. Res. Inst., Tohoku University. Ser. A, Phys., Chem. Metall.* 24 (1972) 205-217.
- [55] G. Hausch. High-Temperature Specific-Heat of Feni and Fept Invar-Alloys, *J Magn Magn Mater* 92 (1990) 87-91.
- [56] Y. Tanji. Thermal Expansion Coefficient and Spontaneous Volume Magnetostriction of Fe-Ni (fcc) Alloys, *J. Phys. Soc. Japan* 31 (1971) 1366-1373.
- [57] S.M.C. van Bohemen. The nonlinear lattice expansion of iron alloys in the range 100–1600K, *Scripta Mater.* 69 (2013) 315-318.
- [58] Z. Wu. Temperature and alloying effects on the mechanical properties of equiatomic FCC solid solution alloys., *Ph. D Dissertation in Materials Science and Engineering, Knoxville* (2014).
- [59] D. Hobbs, J. Hafner, D. Spišák. Understanding the complex metallic element Mn. I. Crystalline and noncollinear magnetic structure of α -Mn, *Phys. Rev. B* 68 (2003) 014407.
- [60] T.G. Kollie. Measurement of the thermal-expansion coefficient of nickel from 300 to 1000 K and determination

of the power-law constants near the Curie temperature, *Phys. Rev. B* 16 (1977) 4872-4881.

[61] D. Yu, K. An, X. Chen, H. Bei. Phase-specific deformation behavior of a NiAl–Cr(Mo) lamellar composite under thermal and mechanical loads, *J. Alloy Comp.* 656 (2016) 481-490.

[62] C.Y. Ho, M.W. Ackerman, K.Y. Wu, S.G. Oh, T.N. Havill. Thermal conductivity of ten selected binary alloy systems, *J. Phys. Chem. Ref. Data* 7 (1978) 959-1177.

[63] R.W. Powell, R.P. Tye, M.J. Hickman. The thermal conductivity of nickel, *Int. J. Heat .Mass Tran.* 8 (1965) 679-688.

[64] M.D. Lanchbury, N.H. Saunders. Critical behaviour in the transport properties of pure iron, *J. Phys. F Metal Phys.* 6 (1976) 1967-1977.

[65] C. Glorieux, J. Thoen, G. Bednarz, M.A. White, D.J.W. Geldart. Photoacoustic investigation of the temperature and magnetic-field dependence of the specific-heat capacity and thermal conductivity near the Curie point of gadolinium, *Phys. Rev. B* 52 (1995) 12770-12778.

[66] H. Ebert, S. Mankovsky, K. Chadova, S. Polesya, J. Minár, D. Ködderitzsch. Calculating linear-response functions for finite temperatures on the basis of the alloy analogy model, *Phys. Rev. B* 91 (2015) 165132.

Figures

Fig. 1. (a) Backscattered electron images of the microstructures of NiCoFeCrPd after homogenized at 1473 K for 24 h. The square inset indicates the region where the EDX scan was performed (shown in b). (c) X-ray diffraction pattern of NiCoFeCrPd, in which only FCC peaks appear.

Fig. 2. Temperature dependent constant pressure specific heat of (a) Ni, NiCo, NiFe, and NiCoFe, which do not contain Cr, and (b) Ni-20Cr, NiCoCr, NiCoFeCr, NiCoFeCrMn and NiCoFeCrPd. The inset of (b) is the enlarged plot for NiCoFeCrPd showing a small peak at 374 K.

Fig. 3. Neutron diffraction pattern of (a) Ni-20Cr and (b) NiCoFeCrMn at room temperature (RT) and high temperature (HT). The patterns have been indexed, and the low-index peaks are labeled in (a). Only FCC peaks appear.

Fig. 4. The measured and calculated (lattice) specific heat of (a) NiCo and NiFe, and (b) Ni-20Cr and NiCoFeCr. The electronic and magnetic contributions are also separated for each alloy.

Fig. 5. (a) Neutron diffraction measured lattice parameter as a function of temperature of Ni and the alloys. (b) Comparison between the calculated lattice parameter (lines) and the experimental data (symbols) of NiCo, NiFe, and Ni-20Cr. The legends apply for both figures.

Fig. 6. The coefficient of thermal expansion of the alloys derived from the data shown in Fig. 5a.

Fig. 7. (a) Thermal diffusivity and (b) the calculated thermal conductivity of Ni and Ni-containing single phase concentrated solid solution alloys. *Room temperature density of NiCoFeCrPd was used since the temperature dependent data are not available, which may lead to as much as 3% error in the high temperature region. Legends apply to both figures.