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An Experimental Study of Thermophysical Properties for Quinary High-Entropy NiFeCoCrCu/Al Alloys *

Wei-Li Wang(王伟丽), Li-Jun Meng(孟利军), Liu-Hui Li(李留辉), Liang Hu(胡亮), Kai Zhou(周凯), Zhang-Huan Kong(孔章环), Bing-Bo Wei(魏炳波)**

Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072

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Two quinary high-entropy alloys (HEAs) with equiatomic concentrations formed by doping either Cu or Al elements into the quaternary NiFeCoCr alloy are produced by arc melting and spray casting techniques. Their entropy of fusion, thermal expansion coefficient and thermal diffusivity are experimentally investigated with differential scanning calorimetry, dilatometry and laser flash methods. The NiFeCoCrCu HEAs contain a face-centered cubic high-entropy phase plus a minor interdendritic (Cu) phase and display a lower entropy of fusion and the Vickers hardness. The NiFeCoCrAl HEAs consist of two body-centered cubic high-entropy phases with coarse dendritic structures and show higher entropy of fusion and the Vickers hardness. Both the thermal expansion coefficient and the thermal diffusivity of the former Cu-doped alloy are significantly larger than those of the latter Al-doped alloy. Although the temperature dependence of thermal diffusivity is similar for both HEAs, it is peculiar that the thermal expansion curve of the NiFeCoCrAl alloy exhibits an inflexion at temperatures of 860–912 K.

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High-entropy alloys (HEAs) have developed into a new category of advanced materials owing to their high strength, good ductility and strong corrosion resistance.[1–7] These HEAs are usually characterized by equiatomic compositions and thus tend to form simple face-centered cubic, body-centered cubic or hexagonal closely packed solid-solution phase structures.[8–11] So far, most of the extensive investigations have been focused upon alloy design, structure control and application performance.

The thermophysical properties such as the entropy of fusion, the thermal expansion and the thermal diffusivity are also essential for the fundamental research and practical applications of high-entropy alloys.[12–18] Nevertheless, there have been only a few relevant works in the recent years.[7,19,20] The objective of this work is to develop two quinary high-entropy alloys by doping either Cu or Al elements into the quaternary NiFeCoCr matrix alloy. Special attention is directed toward a detailed experimental study of the thermal expansion and thermal diffusion of these two HEAs.

The preparation of NiFeCoCrCu and NiFeCoCrAl HEAs was accomplished inside a high vacuum chamber with arc melting and spray casting methods in an argon atmosphere. The raw materials were component metals of high purity better than 99.95%. The melting procedure was repeated for at least 4 times to improve the chemical homogeneity of the alloys. Each sample had the mass of 8 g and was placed in a 13 mm ID × 15 mm OD × 160 mm quartz tube, which had a small orifice about 0.3 mm in diameter at the bottom and was installed on the top of the spray casting device. The spray casting device was then evacuated to 2×10^{-4} Pa and backfilled with a gas mixture of He (99.995%) and Ar (99.999%) to 1×10^{5} Pa. The superheatings to 100–150 K above the liquidus temperatures of HEAs alloys were achieved by induction heating. After that, the bulk sample was sprayed into a copper mould by high-pressure Ar jetting gas. The liquidus temperatures and the enthalpy of fusion for these two HEAs were determined by an NETZSCH STA-449C differential scanning calorimetry (DSC). Their crystal structures were analyzed by a Rigaku D/max 2500 x-ray diffractometer (XRD), whereas their solidification structures were investigated with an FEI Sirion electron microscope (SEM). The Vickers hardness was measured by a Struers Dura-min A300 testing machine with a load of 2.94 N. The densities of these two alloys were measured with the Archimedes method. The thermal expansion of specimen length was explored by a DIL-402C dilatometer, while their thermal diffusivity was studied by an LFA1000 laser flash conductance instrument.

The microstructures of the as-solidified high-entropy NiFeCoCrCu and NiFeCoCrAl HEAs display the different characteristics, as shown in Figs. 1(a) and 1(b). The morphology of the NiFeCoCrCu alloy shows the homogeneous feature, whereas the coarse dendritic structure is present in the NiFeCoCrAl alloy. The x-ray diffraction patterns of these two HEAs are shown in Fig. 1(c). The crystal structure of the as-solidified NiFeCoCrCu alloy consists of two FCC phases: the major high-entropy phase and the minor solid solution (Cu) phase. Meanwhile, the phase constitution of the high-entropy NiFeCoCrAl alloy exhibits two high-entropy BCC phases. To distinguish the microstructural characteristics of these two alloys, their chem-

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**Corresponding author. Email: bbwei@nwpu.edu.cn
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ical compositions are detected by EDS analysis and the results are presented in Fig. 1(d). For the NiFeCoCrCu HEA, the matrix phase with gray feature in Fig. 1(a) shows that the chemical compositions of Co, Cr, Fe and Ni elements exceed the original component of 20 at%, while the Cu element content reduces to only 11.08 at%, which is much less than the original component. The black phase contains as high as 66.98 at% Cu, while the other elements are far below the original compositions of this HEA. Apparently, the matrix phase is the high-entropy phase which is formed mainly by Co, Cr, Fe and Ni elements plus a reduced amount of Cu, and the black phase is the (Cu) solid solution phase. According to the XRD analysis, the crystal structure of high-entropy phase is characterized by face-centered cubic (FCC), therefore this FCC phase is defined as the HEF phase in this work. Similarly, for the NiFeCoCrAl HEA, the white dendritic structure shows that the Ni, Co and Al contents are higher than the original composition of 20 at%, the Fe and Cr are lower than the original components in this alloy. Here the black phase displays that its Ni, Fe, Co and Cr contents are slightly larger than the original compositions, while the Al content is lower than the original composition. Combined with the XRD patterns in Fig. 1(c), it is found that this alloy exhibits two body-centered cubic (BCC) phases: these are the high-entropy 1 phase that shows the white dendrite structure mainly composed of Ni, Co and Al constituents, and the high-entropy 2 phase which displays the black structure composed of Ni, Fe, Co and Cr elements. Hereafter, these two high-entropy BCC phases are defined as the HEB 1 and HEB 2, respectively, in this work.

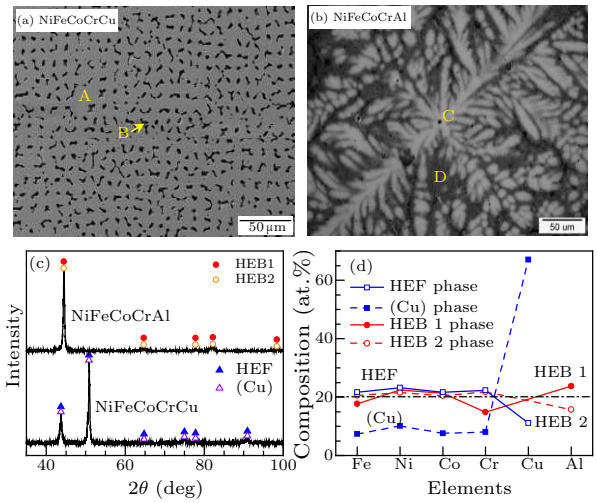

Fig. 1. As-solidified microstructure and phase constitution of two high-entropy alloys: (a) structure of the NiFeCoCrCu alloy, (b) structure of the NiFeCoCrAl alloy, (c) XRD patterns, and (d) phase compositions.

The liquidus temperatures of these two HEAs were detected by the DSC method with 10 K/min, the samples are about 35 mg, and the results are illustrated in Table 1. The liquidus temperature of the high-entropy NiFeCoCrCu alloy is 1655 K, and that of the NiFeCoCrAl HEA is 1681 K. Obviously, the liquidus temperature of adding Al element into quaternary NiFeCoCr alloy is 26 K higher than that of adding Cu element, although the melting temperature of Al is lower than Cu. As designated in Fig. 1, the HEF phase of the A region is a high-temperature phase in the NiFeCoCrCu HEA, which grows firstly as the primary phase from the liquid during solidification, then the (Cu) solid solution phase solidifies as the low-temperature phase and shows the interdendritic structure. In contrast, the dendritic characteristic of the HEB 1 phase labeled as C region in the NiFeCoCrAl HEA is the high-temperature phase and grows firstly as the primary phase from the liquid, the low-temperature HEB 2 phase labeled as D region solidifies as the interdendritic structure.

Table 1. Measured thermophysical properties of two high-entropy alloys.

Alloy	T_L (K)	ΔH_m (J/g)	ΔS_m (J/g·K)	ρ (g/cm^3)	H_v (MPa)
NiFeCoCrCu	1655	159.0	0.096	8.295	178.2
NiFeCoCrAl	1681	175.9	0.105	7.525	489.1

The enthalpy of fusion for the NiFeCoCrCu and NiFeCoCrAl HEAs are determined by the solid–liquid transformation peaks during the melting process with DSC analysis. The results are listed in Table 1. The fusion enthalpies (ΔH_m) of primary high-entropy phases are 159.0 J/g for the NiFeCoCrCu alloy and 175.9 J/g for the NiFeCoCrAl alloy, respectively. These are apparently lower than the corresponding values of the component elements. The entropies (ΔS_m) of fusion for these two HEAs can be subsequently calculated by the measured enthalpy and liquidus temperature, which is expressed as

$$\Delta S_f = \Delta H_m / T_L. \tag{1}$$

The calculated fusion entropies are also listed in Table 1. Similarly, the fusion entropies of the primary high-entropy phase are lower than that of any component element in these two HEAs. Their values are 0.096 J/g·K for the NiFeCoCrCu alloy and 0.105 J/g·K for the NiFeCoCrAl alloy, respectively.

The alloy density has a significant influence on the applied performances of new materials. The theoretical density of a solid-solution alloy by ignoring the volume change is estimated by[21]

$$\rho_{mix} = \frac{\sum C_i A_i}{\sum C_i A_i / \rho_i}, \tag{2}$$

where C_i and A_i are the atomic fraction and atomic weight of the element i, respectively, and ρ_i is the density of the element i. The theoretical density of the NiFeCoCrCu alloy is 8.324 g/cm^3, which is close to the experimental value of 8.295 g/cm^3, because the crystal structure of the NiFeCoCrCu HEA is FCC and identical to the Cu element. However, the theoretical density of the NiFeCoCrAl alloy is 6.716 g/cm^3, which is

lower than the experimental result, $\rho = 7.525\,\mathrm{g/cm^3}$. The crystal structure of the NiFeCoCrAl HEA is BCC and different from the Al FCC structure, thus the addition of Al element will influence on the density of HEA significantly.

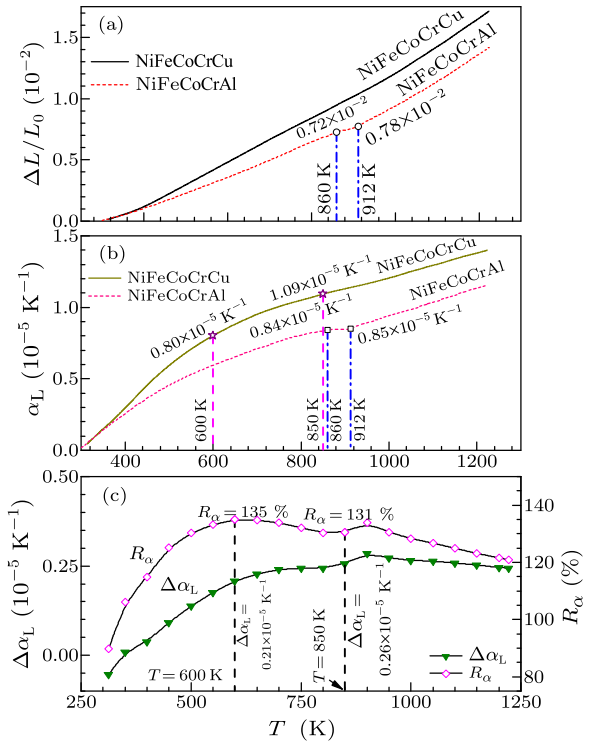

Fig. 2. Thermal expansion characteristics of the high-entropy NiFeCoCrCu/Al alloys (a) expansion of specimen length, (b) thermal expansion coefficients, and (c) comparison of thermal expansion.

The measured Vickers hardness of the NiFeCoCrCu alloy is 178.2 MPa, which is slightly lower than that of the pure Cu metal, and of the NiFeCoCrAl alloy is 489.11 MPa to be about 2.92 times higher than the pure Al metal. Obviously, the Vickers hardness of adding the Al element in the NiFeCoCr alloy is 2.74 times larger than adding the Cu element. Therefore, the BCC phase formed in the NiFeCoCrAl HEA has the better Vickers hardness than the FCC phase obtained in the NiFeCoCrCu HEA.

The thermal expansion coefficients play an important role in the application performance of metallic alloys. The relative change in specimen length due to thermal expansion was described by

$$\Delta L/L_0 = (L - L_0)/L_0, \tag{3}$$

where L is the sample length with the temperature T, and L_0 is the sample length at the ambient temperature T_0, which can be fitted in the temperature range of 314–1223 K.[22,23] Figure 2(a) clearly shows that the specimen length change of thermal expansion displays the nonlinear growth feature with the increase of temperature. The maximum value of the NiFeCoCrCu HEA attains 1.71×10^{-2} at $T = 1223\,\mathrm{K}$, where the NiFeCoCrAl HEA is only 1.42×10^{-2}. However, the specimen length of the NiFeCoCrAl HEA demonstrates the expansion different characteristics, that is, a sluggish growth range appears between the temperature of 860 K and 912 K. Here it increases only from 7.2×10^{-3} to 7.8×10^{-3}, and then it increases rapidly with the temperature. Furthermore, the thermal expansion coefficient of α_L is defined as

$$\alpha_L = \frac{1}{L_0}\frac{d\Delta L}{dT}. \tag{4}$$

The measured results are shown in Fig. 2(b). The thermal expansion coefficients of both HEAs display the rapid and slow growth ranges with the increase of temperature, while they have the different transition temperatures. For example, the thermal expansion coefficient of the NiFeCoCrCu HEA increases quickly when the temperature is less than 600 K where its value is $8.0 \times 10^{-6}\,\mathrm{K^{-1}}$, then it increases slowly with the temperature. However, the value of the NiFeCoCrAl HEA displays three characteristic zones, that is, the rapid, sluggish and slow increase zones, respectively. The thermal expansion coefficient rises rapidly when the temperature is less than 860 K, then the sluggish feature appears at the temperatures between 860 K and 912 K. Subsequently, it increases slowly with temperature and the value of the NiFeCoCrCu HEA is larger than that of the NiFeCoCrAl HEA.

The difference $\Delta\alpha_L$ and ratio R_α of the thermal expansion coefficients for those two HEAs are illustrated in Fig. 2(c). When the temperature is below 375 K, the thermal expansion coefficient displays the coincident feature for these two HEAs. Once the temperature exceeds 375 K, the value for the NiFeCoCrCu HEA is larger than that of the NiFeCoCrAl HEA, and they exhibit the rapid increase characteristics when the temperature is less than 600 K. Then $\Delta\alpha_L$ rises slowly and R_α reduces with temperature from 600 K to 850 K. However, $\Delta\alpha_L$ increases rapidly when the temperature rises to 900 K, afterwards the difference and the ratio reduce slightly.

The specimen length and thermal expansion coefficient are related to the properties of the constituent elements, the crystal structure and the lattice vibration of the alloy. From experiments, the Cu and Al elements have different thermal expansions and the crystal structures of the HEAs are unalike. Furthermore, the phase transition of the NiFeCoCrAl HEA is more complex. Consequently, the two HEAs exhibit different thermal expansion behavior as mentioned above.

The thermal diffusion coefficient displays the different characteristics in comparison with the thermal expansion coefficient,[24] as illustrated in Fig. 3. As the temperature is less than a certain value, such as 981 K for the NiFeCoCrCu HEA and 882 K for the NiFeCoCrAl HEA, respectively, the thermal diffusion coefficient shows the increase feature with temperature. Once the temperature exceeds these values, the thermal diffusion coefficient shows the decrease tendency

with the increase of the temperature. In addition, the thermal diffusion coefficient of the solid Cu element is about $1.12 \times 10^{-1}\,\mathrm{cm}^2/\mathrm{s}$, which is higher than that of the solid Al element of $8.56 \times 10^{-2}\,\mathrm{cm}^2/\mathrm{s}$, thus the thermal diffusion coefficient of adding Cu component in the NiFeCoCr alloy is significantly larger than that of adding Al component in the NiFeCoCr alloy. For example, the highest value of the NiFeCoCrCu HEA attains $7.43 \times 10^{-2}\,\mathrm{cm}^2/\mathrm{s}$ at $T = 981\,\mathrm{K}$, whereas that of the NiFeCoCrAl HEA is only $4.6 \times 10^{-2}\,\mathrm{cm}^2/\mathrm{s}$ at $T = 882\,\mathrm{K}$. Similar to the case of thermal expansion, the intrinsic properties of the constituent elements and the crystal structure of the alloy may account for the difference of the thermal diffusion.

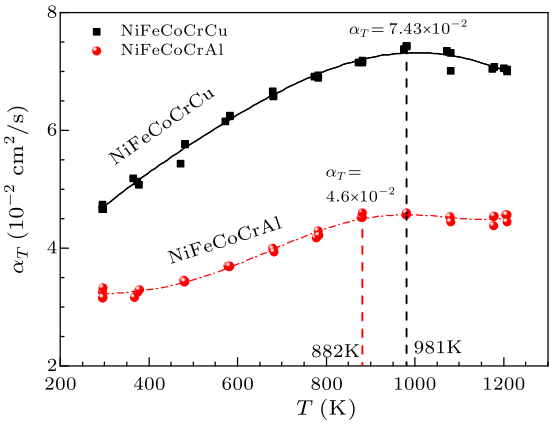

Fig. 3. Thermal diffusion coefficients of the high-entropy NiFeCoCrCu/Al alloys.

In summary, the quinary high-entropy NiFeCoCrCu and NiFeCoCrAl alloys have been produced by doping either Cu or Al element into the quaternary NiFeCoCr alloy. The solidification microstructures of the NiFeCoCrCu alloy are characterized by a major FCC high-entropy phase together with a minor interdendritic (Cu) phase. In contrast, the NiFeCoCrAl alloy involves two BCC high-entropy phases with coarse dendritic structures. The doping with the Cu element results in lower entropy of fusion and the Vickers hardness, whereas the doping with the Al element leads to higher entropy of fusion and the Vickers hardness. Both the thermal expansion coefficient and the thermal diffusivity of these two HEAs displays nonlinear temperature dependence. The doping of the Cu element brings about significantly larger thermal expansion and thermal diffusivity as compared with the introduction of the Al element. An inflexion point appears on the thermal expansion curve of the NiFeCoCrAl alloy at 860–912 K temperatures, which remains to be further elucidated.

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