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ARTICLE

Design of High Entropy Alloys Based on Phase Formation Criteria and Big Data System

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Abstract: The development and phase formation criteria of high entropy alloys (HEAs) were described briefly. A new alloy design form was proposed in view of the big data system of high entropy alloy, and a new high entropy alloy was designed and studied. The result shows that the design form, $A_xB_yC_{(100-a-b-x-y)}D_aE_b$, is more in line with the requirements of the big data system compared with the previous alloy forms such as A_xBCDE. The proposed design method can rapidly and visually screen out the expected alloy composition from the big data system of high entropy alloy. The designed high entropy alloy, $AlCoCrFeMo_{0.05}Ni_2$, agrees with the target alloy, and has a great application prospect below 700 ºC.

Key words: high entropy alloys; criteria; big data; design; application

The research of multi-principal alloys can be traced back to the 70s, last century[1]. But the study of high entropy alloy was initiated by Yeh Jien-Wei, a Taiwan scholar, in 1995[2], and was put forward in 2004 formally. Yeh defined HEAs as alloys containing five or more elements in equimolar or near-equimolar ratios, and no element is more than 50%[3]. Originally, the research of high entropy alloy was concentrated in the equiatomic alloy system, such as AlCoCrFeNi[4]. With the in-depth understanding of the high entropy alloy, it is believed that alloys which have the mixing entropy greater than 1.5 R and can form a simple solid solution can be called HEAs. Then, high entropy alloys in non-equimolar ratio and high entropy alloy matrix composites, such as high entropy alloy steel, appeared[5]. Because HEAs show remarkable characteristics compared with the conventional alloy and its unique alloying way breaks the traditional metallurgical theory, it has become a new research hotspot after bulk amorphous materials[6,7].

In order to study the influence of the main elements on the microstructure and properties of HEAs, the trial-error method and A_xBCDE or $A_x(BCDE)_{100-x}$ pseudo two element system were often used before[8-16]. However, the high entropy alloy is usually composed of 5~13 alloying elements, and the kinds of metal elements in the periodic table which can be alloyed are more than 80. Besides, the alloy composition is also converted from equal atomic ratio to non-equal atomic ratio. Therefore, using conventional trial-error method to study high entropy alloy will waste a lot of manpower and material resources. And the A_xBCDE or $A_x(BCDE)_{100-x}$ form is not conducive to the improvement of performance. If the content of A element increases while others decrease, that is, the role of A element is enhanced and the other elements are weakened. Thus, both of the previous research method and alloy forms have a great limitation.

In order to break the limitations and follow the big data system of high entropy alloys, this work proposed a new design form, $A_xB_yC_{(100-a-b-x-y)}D_aE_b$, and a design method. Then, a new high entropy alloy was designed and studied to illustrate their advancement.

1 Alloy Design

Table 1 gives the summary of the phase formation criteria, in which the criterion range is derived from the statistical analysis of a large number of experimental results[17-23]. In addition,

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Table 1 Theoretical criterions of high entropy alloys

Criterion	Single phase	Single/ multiphase	Multi-phase	Amorphous
ΔS_{mix}[3]	>1.5 R	>1.5 R	>1.5 R	>1.5 R
ΔH_{mix}[17]	(–3,7)	(–15,–3)	(–22,–15)	(–∞,–22)
δ[18]	(0,4.5)	(4.5,6)	(6,9)	(9,+∞)
Ω[18]	Ω>1.1	Ω>1.1	Ω>1.1	Ω>1.1
X_{Allen}[19]	(0,6)	(6,10)	(6,10)	(10,+∞)
Φ[23]	(20,+∞)	(16,20)	(4,16)	(–∞,4)

according to the traditional theory of metallurgy, the valence electron concentration (VEC) can be used to determine the structure of phases. If VEC>8, the fcc structure will form. For VEC<6.87, the bcc structure will form. When 6.87<VEC<8, hybrid structure will appear. This rule has also been proved to be applicable to the high entropy alloys [24].

According to Ref.[25], $AlCoCr_2FeMo_{0.5}Ni$ alloy has high hardness and excellent thermal stability. However, we observed a large number of brittle intermetallic compounds and cracks in its ingot, which was smelted by the 10 kg vacuum induction furnace in our laboratory; thus it is difficult to process and has no practical value. In order to get a high entropy alloy with good high temperature performance and processability, it is feasible to design a new high entropy alloy containing Al, Co, Cr, Fe, Mo and Ni.

The form of $A_x B_y C_{(100-a-b-x-y)} D_a E_b$ was used, in which A, B and C were set to Mo, Ni and Cr, respectively, in the range of 0%~35%, and the rest elements were set at 16.5% (because the mixing entropy of alloy with an equimolar ratio is the largest, and thus the near-average content was set in this work), and they can also be set according to the requirements of performance. Therefore, the final alloy form is $Al_{16.5}Co_{16.5}Cr_{50.5-x-y}Fe_{16.5}Mo_xNi_y$. Compared with the pseudo-binary systems of A_xBCDE or $A_x(BCDE)_{100-x}$, there are two variables in this form (x and y), so it can be regarded as a surface in space, and it has a wider range of ingredients. Moreover, the elements of Mo, Ni and Cr can work together to meet the requirements of the phase formation criteria and to obtain the expected high entropy alloy organization. Therefore, the current form is more in line with the requirements of the big data system of high entropy alloys.

Fig.1 shows the surface graphs of the different criteria of $Al_{16.5}Co_{16.5}Cr_{50.5-x-y}Fe_{16.5}Mo_xNi_y$ high entropy alloy system (undefined range). It can be seen from the color bar that the overall mixing entropy of the alloy system is between 1.5 R

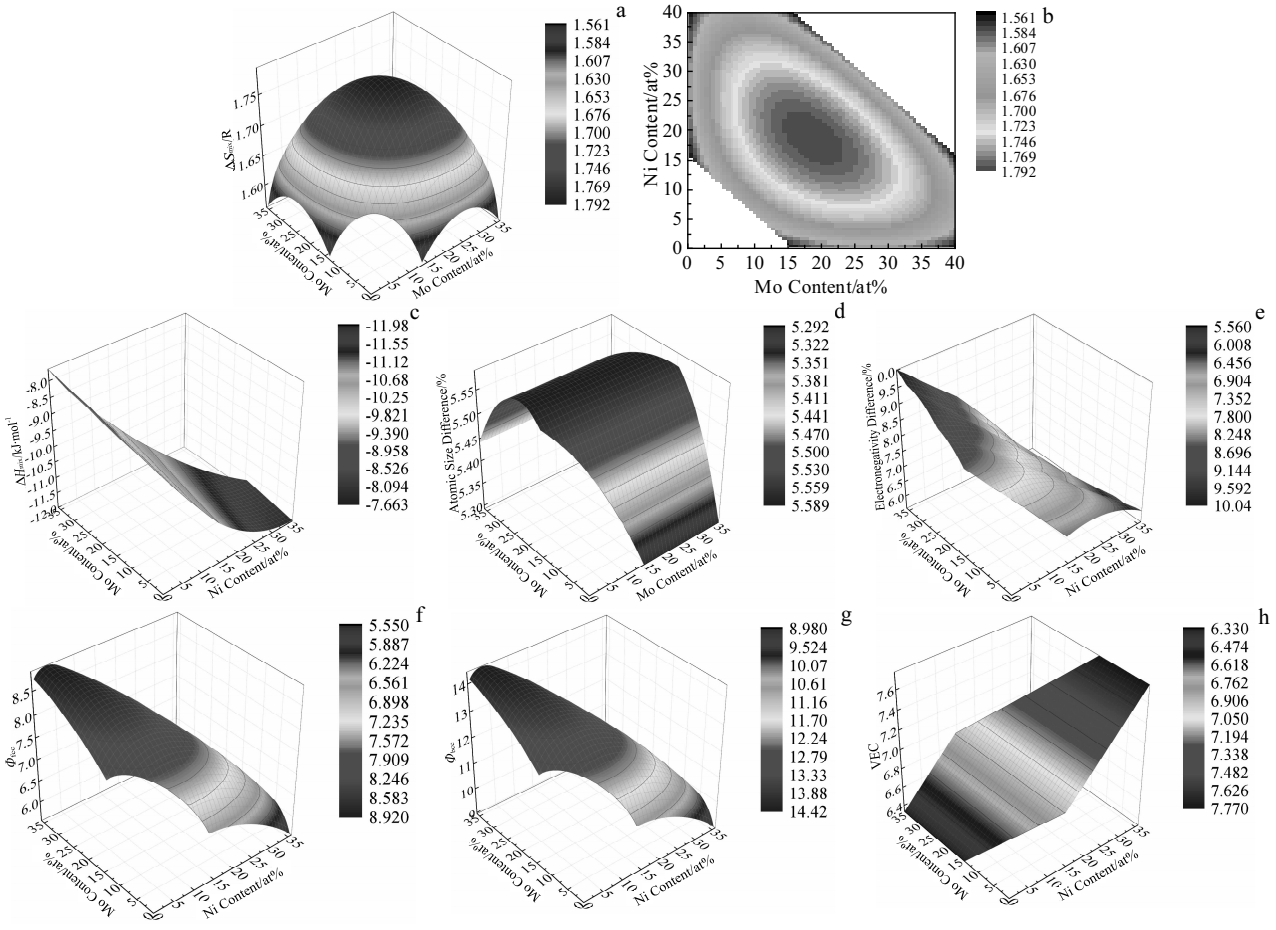

Fig.1 Surface graphs of different criteria: (a, b) ΔS_{mix}, (c) ΔH_{mix}, (d) δ, (e) X_{Allen}, (f) Φ_{fcc} (ξ=0.74), (g) Φ_{bcc} (ξ=0.68), and (h) VEC

and 1.8 R. The enthalpy of mixing is between −12 kJ/mol and −7.5 kJ/mol. The atomic size difference is between 5.3% and 5.6%. The elector-negativity difference is between 5.5% and 10%. The values of Φ are between 5.5 and 14.5. The valence electron concentration is between 6.3 and 7.8. And the influence of Mo and Ni on the values of criteria can be seen visually from the X (Mo)-Y (Ni) view. For instance, as shown in Fig.1b, it can be seen that the entropy of mixing decreases gradually from the center of the curved surface to the surrounding area.

Except for the elector-negativity difference (from 5.5% to 10%), others are in the range of multi-phase according to the range of criteria in Table 1, so the alloy system is difficult to form single phase structure. And because of $AlCoCr_2FeMo_{0.5}Ni$ alloy, a large number of intermetallic compounds and cracks are formed, which has been mentioned above. Therefore, it is necessary to reduce the elector-negativity difference and the atomic size difference to enhance the solid solubility of the alloy. The overall atomic size difference of $Al_{16.5}Co_{16.5}Cr_{50.5-x-y}Fe_{16.5}Mo_xNi_y$ high entropy alloy system is between 5.3% and 5.6%, whose range is small and does not need to be limited. Thus the elector-negativity difference can be controlled between 6% and 6.5%. In addition, the VEC is controlled greater than 7.5 to ensure that the alloy is dominated by the fcc structure and has better plasticity. The calculation results are shown in Fig.2.

Considering that the low content of Cr will decrease the oxidation resistance of the alloy, it is limited greater than 16.5% (this value can also be set according to the conventional high temperature oxidation resistant alloy). The results are shown in Fig.3.

Fig.4 shows the superposition of the two criteria. And the alloy composition in the superposition region conforms to all criteria except for the criterion Ω. In order to obtain an alloy composition with an integer atomic ratio, y (Ni content) is chosen to be 33 (two times of 16.5) and x (Mo content) is 1, resulting in a composition of $AlCoCrFeMo_{0.05}Ni_2$. Its criteria are shown in Table 2. It can be seen that the criterion Ω is also satisfied.

2 Experimental Research and Verification

2.1 Microstructure

Fig.5 shows the as-cast microstructure of the $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy which was smelted by 10 kg vacuum induction furnace in our laboratory. It is a typical dendritic structure composed of dendrite region A and interdendritic region B, as shown in Fig.5a. In Fig.5b, it is found that the region B is composed of irregular eutectic structures of C and D. The EDS results of the as-cast microstructure in Table 3 show that there is a significant difference in the component between A and C. A is rich in Fe, Co, Cr and Mo, while C is rich in Al and Ni. And the XRD analysis in Fig.6 shows that the alloy consists of fcc and bcc structures. Because the interdendritic C is so small that the bcc diffraction intensity is too weak to be captured by X-ray, the electron diffraction was used to confirm it, as shown in Fig.7. The interdendritic C was determined as a NiAl intermetallic

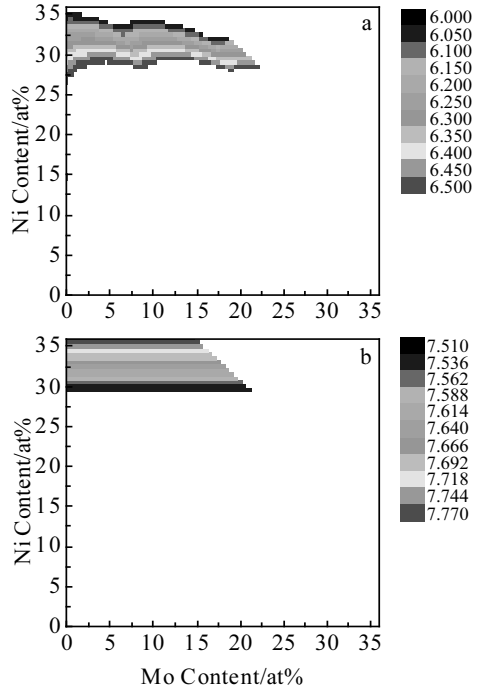

Fig.2 Criterion surface graphs after primary screening: (a) X_{Allen} and (b) VEC

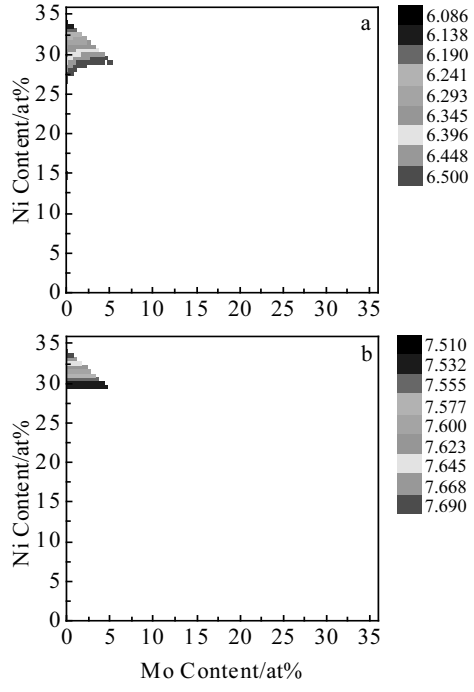

Fig.3 Criterion surface graphs: (a) X_{Allen} and (b) VEC

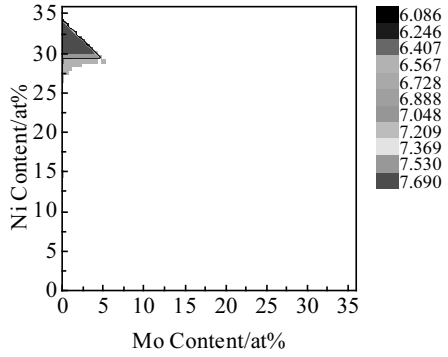

Fig.4 Overlay surface graph of the two criteria in Fig.3

Table 2 Criteria of $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy

ΔS_{mix}	ΔH_{mix}/kJ·mol^{-1}	σ	x	Ω	Φ	VEC
1.6 R	–11.94	5.32	6.16	1.89	9.5	7.6

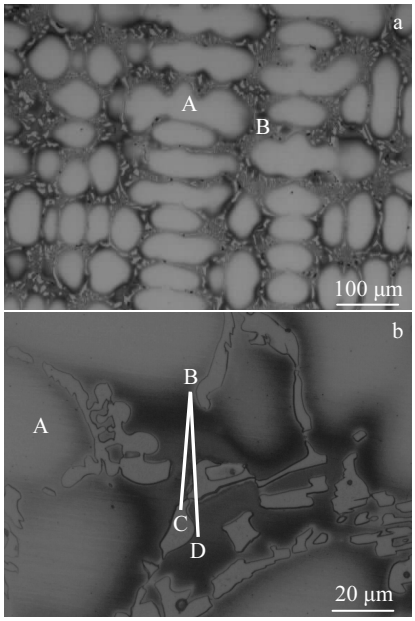

Fig.5 As-cast structure of $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy: (a) dendrite region A and interdendritic region B; (b) region B is composed of irregular eutectic structures of C and D

compound, and the space group is Pm-3m (221), a simple cubic system. In fact, it is an ordered bcc structure, B2, which can be seen as two simple cubic lattice units passing through each other.

Fig.8 shows the as-forged structure of $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy, which was forged from an ingot (about Φ130 mm) into a bar (Φ16 mm). It can be seen that the as-forged structure of the alloy is a typical dual phase structure with uniform distribution. And the EDS results in Table 4 show

Table 3 EDS results of the as-cast structure of $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy in Fig.5 (at%)

Region	Al	Co	Cr	Fe	Mo	Ni
A (matrix)	7.06	19.24	17.08	21.73	0.98	33.50
C	18.43	14.21	8.97	12.44	0.37	45.57
D	7.11	18.12	18.46	20.23	1.52	34.17

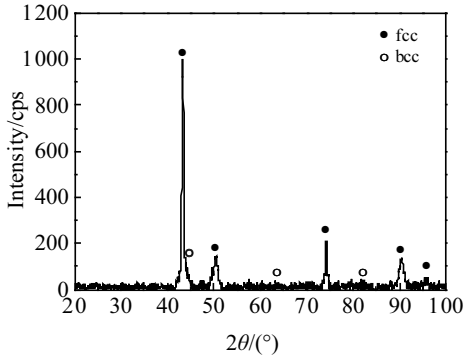

Fig.6 XRD pattern of the as-cast microstructure of $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy

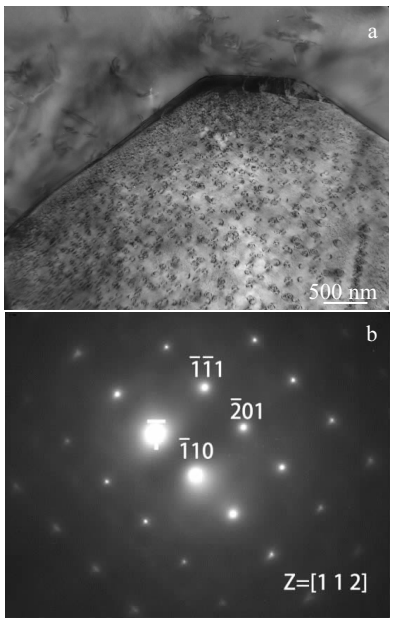

Fig.7 TEM bright-field image (a) and SAED pattern (b) of interdendritic precipitate

that the composition of region B in Fig.8 is similar to that of region C in Fig.5. Therefore, the microstructure of the alloy meets the design requirements, and the alloy has good forging performance.

2.2 Mechanical properties

Fig.9 shows the tensile curve of the as-cast alloy of $AlCoCrFeMo_{0.05}Ni_2$ at room temperature. The yield strength, tensile strength and elongation are measured as 640 MPa, 927

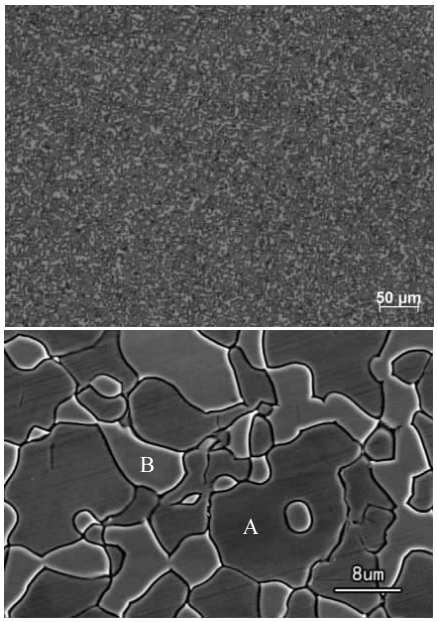

Fig.8 Structure of as-forged $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy

Table 4 EDS results of the structure of as-forged $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy in Fig.8 (at%)

Region	Al	Co	Cr	Fe	Mo	Ni
A (matrix)	6.11	19.27	20.35	20.33	0.90	33.05
B	18.01	14.23	8.95	12.63	0.37	45.81

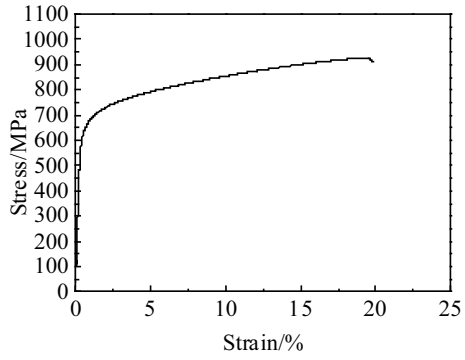

Fig.9 Tensile curve of the as-cast alloy $AlCoCrFeMo_{0.05}Ni_2$ at room temperature

MPa and 19%, respectively. It has been reported that the $AlCoCrFeNi_{2.1}$ high entropy alloy, which is a lamellar eutectic microstructure, has a similar composition to the current alloy. And it shows the most excellent tensile properties in the AlCoCrFeNi high entropy alloys system with a yield strength of 545 MPa, a tensile strength of 950 MPa, and an elongation of 17%[26]. $AlCoCrFeNi_{2.1}$ has excellent high temperature performance, and is expected to be a new generation of high temperature materials. At 700 ºC, its yield strength is 108 MPa (exhibiting discontinuous yielding), the tensile strength is 538

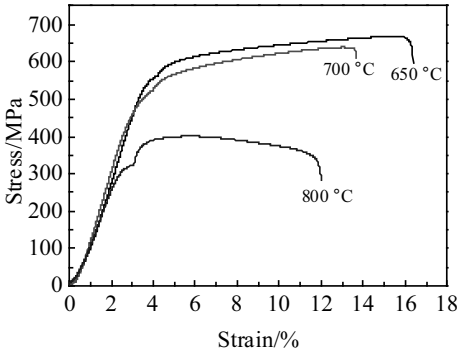

Fig.10 High temperature tensile stress-strain curve of the as-cast $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy

MPa[27], while the yield strength and tensile strength of the designed $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy are 540 and 630 MPa, respectively, as shown in Fig.10. It shows that Mo elements can effectively enhance the high temperature properties of high entropy alloys, and $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy has great research value in the field of superalloys.

3 Conclusions

1) The design form of $A_xB_yC_{(100-a-b-x-y)}D_aE_b$ makes the previous high entropy alloy system has a wide range of composition, which is favorable for the design of high-performance alloy.

2) Based on the big data system, the reverse design method according to the phase formation criteria makes the study of high entropy alloy convenient, quick and intuitive.

3) The designed $AlCoCrFeMo_{0.05}Ni_2$ high entropy alloy agrees with the target alloy, and has excellent room temperature and high temperature performance. Thus it has great research value in the high temperature field.

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基于相形成判据和大数据系统的高熵合金设计

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摘 要：简要介绍高熵合金的发展和其相形成判据。针对高熵合金的大数据体系提出一种新的合金设计形式，涉及并研究了一种新型的高熵合金。结果表明：$A_xB_yC_{(100-a-b-x-y)}D_aE_b$ 的涉及形式比起以往的伪二元系合金形式，如 A_xBDE，更加符合大数据体系的要求。提出的设计方法能够直观快捷的从高熵合金大数据体系中筛选出预期的合金成分。本研究设计的高熵合金 $AlCoCrFeMo_{0.05}Ni_2$ 与目标合金相符，且在 700 ℃下有很好的应用前景。

关键词：高熵合金；判据；大数据；设计；应用

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