Microstructure and property of AlTiCrFeNiCu high-entropy alloy

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ABSTRACT

In this study, an AlTiCrFeNiCu high entropy alloy (HEA) was synthesized by vacuum arc furnace in high-purity argon atmosphere. The heat resistance of this HEA was investigated by using a differential scanning calorimeter (DSC) and a chamber type electric resistance furnace. The results showed that the microstructure of the as cast HEA treated at 500 °C was almost unchanged, which consisted of two kinds of BCC solid solution phases and small amount Fe_2Ti. The hardness of AlTiCrFeNiCu HEA increased with treating temperature to a maximum value at 950 °C. It is found that, the content of Cu, Ni and Al decreased badly in the surface of as cast AlTiCrFeNiCu after immersed in the water solution of 5% HCl for 7 days. The compressive fracture strength of as cast AlTiCrFeNiCu HEA was 1219 MPa. The high compressive strength may owe to the solid solution strengthening from multi elements.

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1. Introduction

The conventional design concept of new alloy systems has one element as their principal constituent and other minor elements as their constituents for the enhancement of properties and performances. This design concept has a limit of the number of alloys that can be developed. To avoid this limitation, a new alloy system which is called "high-entropy alloy (HEA)" is firstly proposed by professor Ye et al. [1–3]. A HEA was originally defined as an alloy composed of at least five principal elements in equimolar or near equimolar ratios. The content of each major constituent is greater than 5 at% and less than 35 at%. Due to the high entropy mixing effect, HEAs likely consist of random solid solutions, nano-structure even amorphous during solidification instead of inter-metallic compounds or complex phases [4–9]. The HEAs usually have high hardness and strength, good thermal stability and good corrosion resistance [10].

A new HEA, AlTiCrFeNiCu was prepared to investigate the microstructure and properties.

2. Materials and methods

To provide reference data for further research in the field of HEAs and possible application of these alloys, a HEA with a nominal chemical composition of AlTiCrFeNiCu was prepared by vacuum arc melting with electromagnetic stir from a mixture of pure bulk metals (purity better than 99 wt%) in high-purity argon atmosphere and solidified in a water-cooled copper mould. The alloy was then reversed and re-melted 4 times to assure chemical homogeneity. The solidified ingots were about 30 mm in diameter and 10 mm in thickness. The samples cut from the ingot

were heated to 500–1070 °C for 4 h, and then cooled slowly in furnace. Hardness measurements, phase identification, compression test, corrosion observation and microstructure analyses were then carried out on the as cast and heat treated specimens. The crystal structure was identified by X-ray diffraction (XRD, D/Max2500 V) using Cu Kα radiation. The microstructure examination and composition analyses of elements were carried out by scanning electron microscope (SEM, JEOL JSM-6360LV) equipped with energy dispersive spectrometry (EDS, GENESIS2000XMS60). Room-temperature compressive properties of samples were carried on materials testing machine (Instron MTS569). The heating behavior of the alloy was measured in a Netzsch 404 DSC with an alumina container under flowing purified argon at a heating rate of $10\,K\,s^{-1}$.

3. Results and discussion

3.1. Microstructure characterization

Fig. 1 shows the XRD patterns of the as cast AlTiCrFeNiCu. From Fig. 1, two BCC phases and one order phase Fe_2Ti were observed in this alloy. Fig. 2 shows the microstructure characteristic of the as cast AlTiCrFeNiCu. Only three phases were observed in Fig. 2, which is consistent with the result of Fig. 1.

According to the Gibbs phase rule, the maximum number of equilibrium phases in a C component system at constant pressure is $P = C + 1$ (here, C is the number of components, and P is the number of phase). When the alloy is solidified under non-equilibrium condition, $P > C + 1$. Hence, in the non-equilibrium solidified AlTiCrFeNiCu alloy, the maximum equilibrium number allowed by the Gibbs phase rule could be 7. While the total number of phases in this research is 3, it is far less than 7. As we know, Gibbs free energy difference (ΔG_{l-s}) between liquid and solidified phase means the driving force of solidification. In a supercooled alloying liquid, the less ΔG_{l-s} means the more stable. ΔG can be calculated

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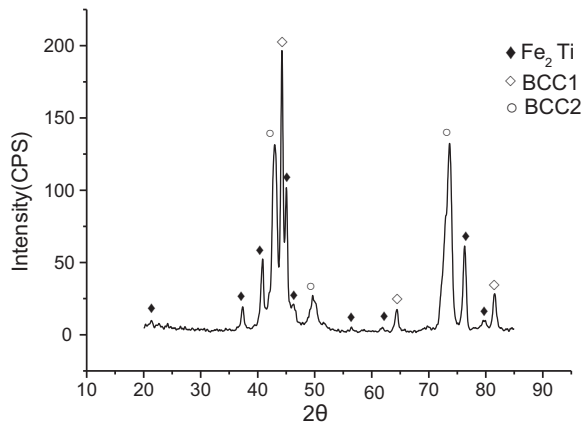**Fig. 1.** XRD patterns of as cast AlTiCrFeNiCu high-entropy alloy.

by (1) $\Delta G = \Delta H - T\Delta S$ where T is the temperature value, ΔH is the forming enthalpy, and ΔS is mixing entropy. And in this paper, the values for the ΔG, ΔH and ΔS are actual value, not absolute value. Since the value of ΔS is positive, and the value of ΔH is usually negative, the value of $\Delta H * \Delta S$ can be used to evaluate the driving force of solidification. The more negative value of $\Delta H * \Delta S$ means the more huge driving force. For six principal element solid solution alloy, ΔS can be calculated by

$$\Delta S_{l-\text{solid solution}} = -R\sum_{i=1}^{n} c_i \ln c_i \qquad (2)$$

Here, $\Delta S_{l-\text{solid solution}}$ is the entropy of mixing change from the liquid to the solid solution. R is the ideal gas constant, $R = 8.314\,\text{J/(mol K)}$, c_i is the atomic fraction of the ith component. By Eq. (2), $\Delta S_{l-\text{solid solution}} = 1.72R$. Considering the effect of atomic

size, $\Delta S_{l-\text{solid solution}}$ can be also represented by:

$$\Delta S_{l-\text{solid solution}} = -R\sum_{n=1}^{n} c_i \left(\ln c_i r_i^3 - \ln \sum_{i=1}^{n} c_i r_i^3 \right) \qquad (3)$$

where r_i is the radius for the ith atom. By Eq. (3), the value of $\Delta S_{l-\text{solid solution}}$ for AlTiCrFeNiCu HEA is $1.81R$. It is close to the value calculated by Eq. (2). For convenience, the value of $\Delta S_{l-\text{solid solution}}$ can be calculated by Eq. (2) approximately. The large value of $\Delta S_{l-\text{solid solution}}$, the more negative value of $\Delta H * \Delta S$ might be, the less ΔG_{l-s} accordingly.

The mixing entropy change is so small in the course of inter-metallic compound formation that $\Delta S_{l-\text{intermetallic compound}}$ can be considered to be 0 [11]. The value of $\Delta H * \Delta S$ for inter-metallic compounds is close to 0 consequently. Accordingly, the Gibbs free energy of mixing of the solid solution AlTiCrFeNiCu alloy is much smaller than that of inter-metallic compounds. That is why the main composing phases are two BCC crystals.

Since the contribution from mixing entropy is very small in the course of inter-metallic compound formation, the mixing entropy contribution to the free energy term can be neglected, and the mixing enthalpy (ΔH^{mix}, actual value) become the main factor affecting the forming tendency and stability of inter-metallic compounds. The less value of ΔH^{mix}, the more stable it is. ΔH^{mix} can be calculated as follow [12]:

$$\Delta H^{\text{mix}} = \sum_{i=1,i\neq j}^{n} \Omega_{ij}c_ic_j = 4\sum_{i=1,i\neq j}^{n} \Delta H_{i-j}^{\text{mix}}c_ic_j \qquad (4)$$

where $\Delta H_{i-j}^{\text{mix}}$ is the mixing enthalpy of atomic pairs between the ith and jth elements. c_i and c_j are the atomic fraction of the ith and jth component, respectively. The values of ΔH_{i-j}^{mix} can be obtained from reference [13].

Additionally, the factors affecting the formation of solid solutions and compounds also involve chemical bond, difference of electro negativity, electron concentration, dimension of atom, and
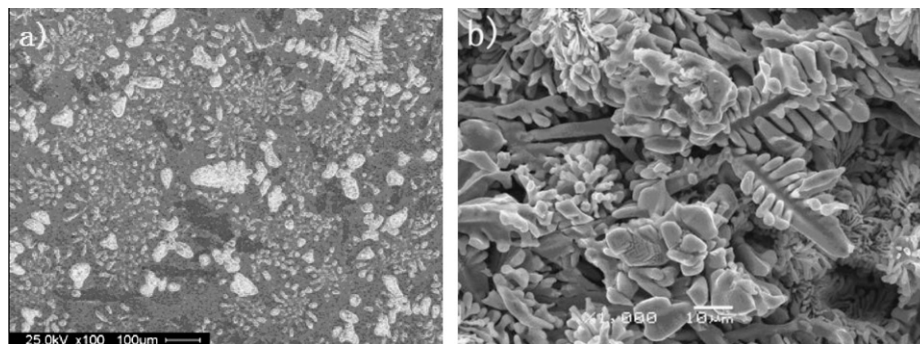

Fig. 2. Microstructure characteristic of the as cast AlTiCrFeNiCu high-entropy alloy: (a) ×100; (b) ×1000.

Table 1
Calculated value of ΔH_{mix}, and ΔH_h for intermetallic compounds.

Intermetallic compounds	ΔH^{mix}	ΔH_h	Intermetallic compounds	ΔH^{mix}	ΔH_h	Intermetallic compounds	ΔH^{mix}	ΔH_h
CuAl	−1.00	3.24	Cr2Al	−8.89	3.03	NiAl	−22.00	3.66
CuAl2	−0.89	3.88	Cr5Al8	−9.47	5.13	NiAl3	−16.50	5.13
Cu12Al9	−0.98	2.98	Cr4Al9	−8.52	5.75	Ni3Fe	−1.50	5.97
Cu3Al2	−0.96	2.89	CrAl4	−6.40	6.49	NiFe3	−1.50	6.02
Cu9Al4	−0.85	2.66	Cr2Al11	−5.21	6.76	Ti3Al	−22.50	3.55
Al3Fe	−8.25	8.24	CrAl7	−4.38	6.91	TiAl	−30.00	4.22
Al5Fe2	−8.98	8.23	CrFe	−1.00	6.69	Al2Ti	−26.70	6.24
Al2Fe	−9.78	8.18	Ni2Cr	−6.22	6.84	Al3Ti	−22.50	6.35
AlFe	−11.00	7.54	Ni3Al	−16.50	2.52	Fe2Ti	−15.10	5.04
Al2Fe9	−6.55	4.66	Ni2Al3	−21.10	4.29			
Al6Fe	−5.39	8.21	Ni5Al3	−20.60	2.95			

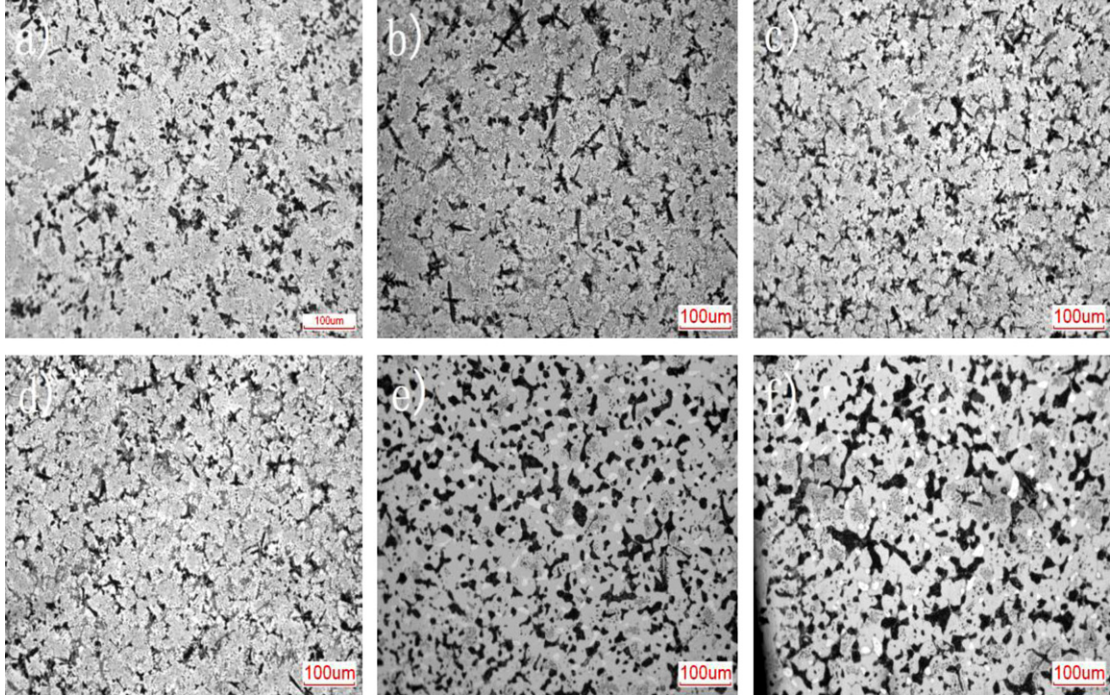**Fig. 3.** Microstructures of heat-treated AlTiCrFeNiCu high-entropy alloy: (a) 500 °C; (b) 720 °C; (c) 800 °C; (d) 950 °C; (e) 1030 °C; (f) 1070 °C.
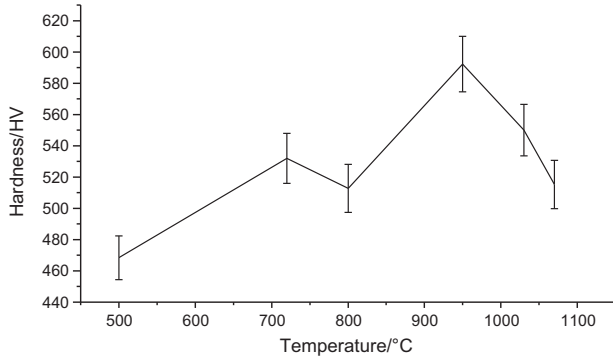

Fig. 4. Hardness of heat-treated AlTiCrFeNiCu HEA.

so on. Among these factors, vacancy forming enthalpy (ΔH_h, actual value) is an important one. Compound is more inclined to form with
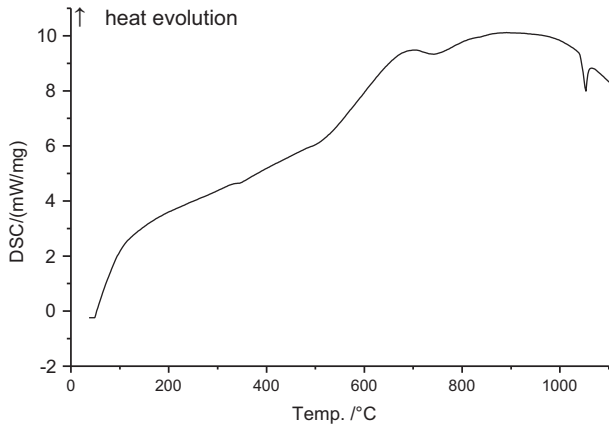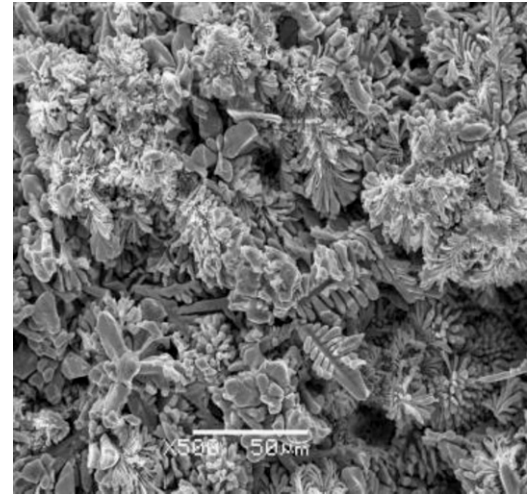

Fig. 6. Morphological characteristic of the eroded AlTiCrFeNiCu alloy.

less ΔH_h value [12]. ΔH_h can be calculated as follow:

$$\Delta H_h^{i-j} = (1 - f_j^i)\Delta H_{IV}^{f-i} + f_j^i \left(\frac{V_i}{V_j}\right)^{5/6} \Delta H_{IV}^{f-j} \tag{5}$$

$$\text{where} f_j^i = (1 - C_j^S)[1 + 8(C_i^S)^2(1 - C_i^S)^2] = C_i^S[1 + 8(C_i^S)^2(C_j^S)^2] \tag{6}$$

$$C_i^S = \frac{x_i V_i^{2/3}}{x_i V_i^{2/3} + x_j V_j^{2/3}} \tag{7}$$

$$C_j^S = \frac{x_j V_j^{2/3}}{x_i V_i^{2/3} + x_j V_j^{2/3}} \tag{8}$$

Here ΔH_{IV}^{f-i} and ΔH_{IV}^{f-j} are the vacancy forming enthalpy for the ith and jth pure element, respectively. V_i and V_j are the molar volumes of element i and j, respectively. x_i and x_j are the atomic fraction of

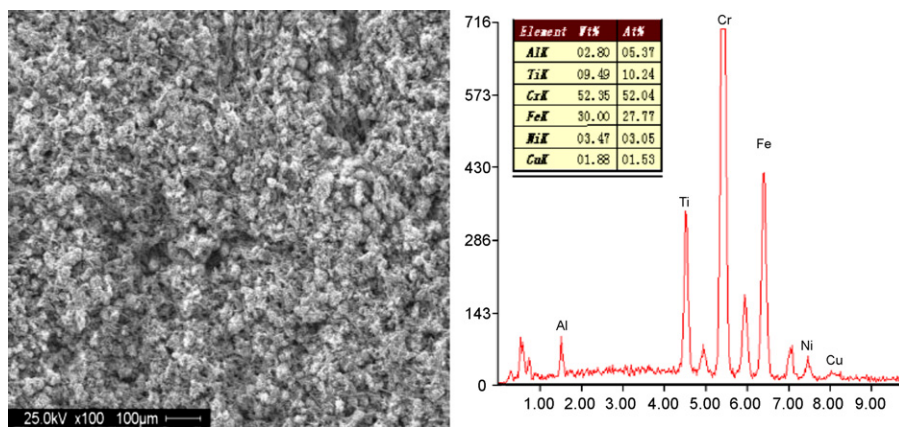**Fig. 5.** DSC curves of the as cast AlTiCrFeNiCu HEA.

Fig. 7. The surface chemical compositions of the erode AlTiCrFeNiCu alloy.
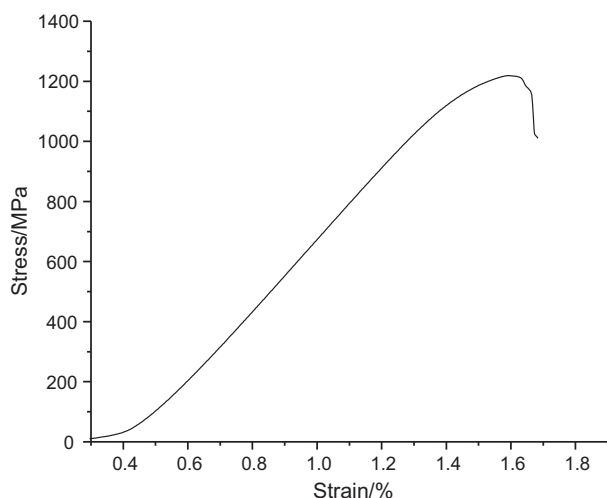

Fig. 8. Stress-strain curve of the as cast AlTiCrFeNiCu high-entropy alloy.

the ith component, respectively. All needed parameters for calculating ΔH_h can be obtained from reference [12].

The calculated values of ΔH^{mix}, and ΔH_h for inter-metallic compounds are shown in Table 1.

From Table 1, inter-metallic compounds with small value of both ΔH^{mix} and ΔH_h at the same time are compounds of Ni–Al systems, Ti–Al systems and Fe–Ti systems. Ti and Al are relatively large in atomic size, which reduces the ability to diffuse, reducing the forming chance of Ti–Al inter-metallic compounds. The difference of radius between Ti and Fe is larger than that of Al and Ni,

resulting larger interstice for atoms diffuse. Hence, the Ti–Fe system inter-metallic compounds form prior to the Ti–Al and Al–Ni system inter-metallic compounds. That is why only small amount Fe_2Ti was detected, no any other inter-metallic compounds was found in as cast AlTiCrFeNiCu HEA.

3.2. Thermal stability

Fig. 3 shows the variation in microstructure of AlTiCrFeNiCu HEA after heat treated at different temperature for four hours. The hardness of AlTiCrFeNiCu HEA after heat treated was indicated in Fig. 4 shows the corresponding variation in hardness. The result of DSC test is show in Fig. 5.

From Figs. 2 and 3, AlTiCrFeNiCu HEA shows good thermal resistance due to stable microstructure under 500 °C. The stability of AlTiCrFeNiCu HEA can be explained by Fig. 5. It is known that exothermic peaks or endothermic peaks emerge in the DSC curve when new phase precipitates or phase transformation occurs. There is no obvious peak in this DSC curve below 500 °C. The unique good thermal stability may contribute to the very small value of $\Delta H^* \Delta S$. Additionally, the existence of multi-principal elements can restrict the diffusion of atoms.

The hardness of AlTiCrFeNiCu HEA increased with treating temperature to a maximum value at 950 °C. It may contribute to the increased amount of the white phase in microstructures. Subsequent hardness drop may contribute to the coarser microstructures.

As we known, most internal stresses can be relived after treated at high to 950 °C for four hours. So, AlTiCrFeNiCu HEA heat-treated at 950 °C for four hours has the highest hardness and less internal stresses, leading it suitable for high temperature applications.
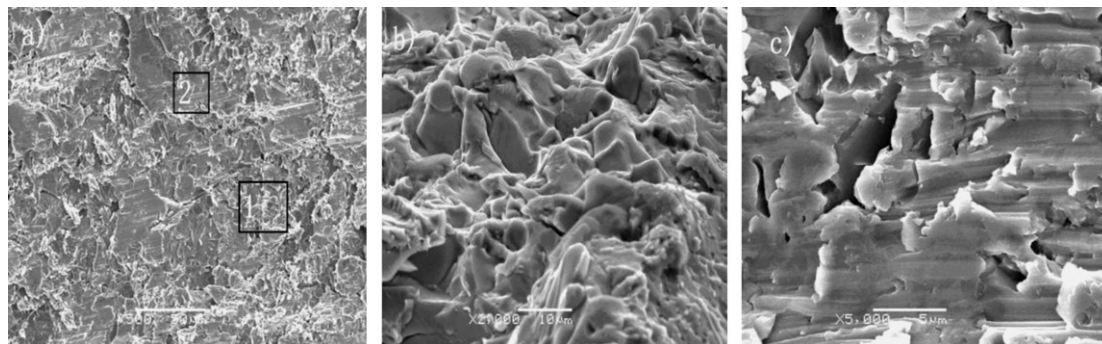

Fig. 9. Fractographic feature of the as cast AlTiCrFeNiCu high-entropy alloy: (a) ×500; (b) magnification of zone 1 in figure a; (c) magnification of zone 2 in figure a.

3.3. Chemical stability

Fig. 6 shows the morphological characteristic of AlTiCrFeNiCu HEA after immersed in the water solution of 5% HCl for 7 days. As observed in Fig. 7, the main loss element from AlTiCrFeNiCu HEA is Cu, Ni and Al.

3.4. Compressive experiment

Fig. 8 depicts the compressive curves of as cast AlTiCrFeNiCu alloy at room temperature. And Fig. 9 shows the corresponding fractographic feature of the alloy.

It can be seen that the as cast AlTiCrFeNiCu HEA shows very high compressive fracture strength, which is high to 1219 MPa. High compressive strength may owe to the solid solution strengthening from multi elements.

Cleavage steps and small deformation areas were observed on the fracture surface. The rough facets in the fracture surface indicate its poor ductility.

4. Conclusions

In this study, an AlTiCrFeNiCu HEA was prepared by vacuum arc furnace, which consisted of two BCC solid solution phases and a small amount of Fe_2Ti. This alloy has the stable microstructure under 500 °C, and has the maximum value of hardness at 950 °C. For this alloy, Cu, Ni and Al may lose badly when immersed in the water solution of 5% HCl for 7 days. It was also found that the compressive fracture strength of as cast AlTiCrFeNiCu HEA is 1219 MPa due to the solid solution strengthening from multi elements.

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