Research Article

The effect of TiC addition on the microstructure and mechanical properties of $Al_{0.6}CrFe_2Ni_2$ high entropy alloys

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Abstract
To enhance the strength of single FCC phase high entropy alloys, TiC was selected as reinforced phase to improve the properties of high entropy alloys (HEAs). Therefore, a series of TiC/$Al_{0.6}CrFe_2Ni_2$ high entropy alloys with different TiC content which ranging from 0 to 5 vol% were prepared by vacuum arc melting furnace. The phase compositions, microstructures and mechanical properties of alloys were investigated detailedly. The results show that TiC has no effect on phase composition of the alloys, but the addition of ceramic phase TiC has an advantageous effect on the mechanical properties of alloys, the yield strength of TiC/$Al_{0.6}CrFe_2Ni_2$ HEAs increases due to the refined of grain size, when TiC content is 2.50 vol%, alloy has better properties, the yield strength and Vickers hardness are 576.93 MPa and 244 HV, respectively.

Keywords High entropy alloys · TiC · Microstructures · Mechanical properties · Nano-phase

1 Introduction

The concept of high entropy alloys (HEAs) was proposed by Yeh et al. [1] and Cantor et al. [2] respectively in 2004, and become a popular research direction in the metallic materials field promptly. The propose of HEAs breakthrough the limitations of traditional alloys because of their simple phase structure and excellent mechanical properties [3–16].

Composite material is a combination of two materials with different characters to obtain new materials with superior properties, ceramic phases were widely used due to their high melting point and high hardness in traditional alloys [17–23]. Due to the excellent properties of HEAs, some scholars investigated the effect of ceramic phases on high entropy alloys. Chen et al. [24] compound the WC/$Al_{0.5}$CoCrCuFeNi high entropy alloy, the hardness of WC/$Al_{0.5}$CoCrCuFeNi alloy is 200–300 HV higher than the traditional WC/Co alloys at room temperature. Zhao et al. [25] sintered the TiB_2/$CoCrFeNiMn_{0.5}Ti_{0.5}$ high entropy alloys, and found that when the content of TiB_2 was 10%, the Vickers hardness and flexural strength of alloys were 2174.64 HV and 427.69 MPa respectively. Fan et al. [26] studied the microstructure and mechanical properties of (FeCrNiCo)Al_xCu_y high-entropy alloys and their TiC reinforced composites, the results show that addition of TiC increased the comprehensive mechanical properties of the high-entropy alloy matrix tremendously, and when the TiC content was 10 vol%, the hardness, yield stress and fracture stress were as high as 621 HV, 1637 MPa and 2972 MPa, respectively. Fu et al. [27] prepared a series of TiB_2–TiNiFeCrCoAl high-entropy alloy composites, the addition of TiB_2 to HEA can enhance the densification significantly, when the TiB_2 was 20 wt%, the grain size, hardness and indentation fracture toughness of alloys were 0.74 ± 0.07 μm, 17.5 ± 1.2 GPa and 12.8 ± 0.6 MPa $m^{1/2}$, respectively. Liu et al. [28] developed TiC/$Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ composite and the results shows that the composite exhibits an ultra-fine microstructure,

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the TiC/HEA composite shows an ultra-high room-temperature compressive strength (> 3000 MPa). A refractory high-entropy alloy of $HfNbTiVSi_{0.5}$ was synthesized by Zhang et al. [29], the alloys were composed by BCC solid solution and a multi-component silicide ((Hf, Nb, Ti)–Si), the research results indicate that the generate of silicide is beneficial for the room temperature strength, ductility and the elevated temperature properties. Lin et al. [30] found that the addition of TiC in $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ HEAs can improve the hardness-toughness combination of the alloys. Wang et al. [31] investigated the anti-penetration performance of high entropy alloy, the results indicated that more uneven the ceramic distribution, the better the anti-penetration performance. Guo et al. [32] prepared the TiN-reinforced $CoCr_2FeNiTi_{0.5}$ high-entropy alloy composite, the results demonstrated that hardness and corrosion resistance of coating improve tremendously. Yim et al. investigated the microstructural evolution and mechanical properties of TiC-reinforced CoCrFeMnNi high-entropy alloy composite [33], the results show that the 5 wt% of TiC addition resulted in fine grain size; the yield strength, strain hardening of composite increased due to grain boundary strengthening, dislocation strengthening, and dispersion strengthening. The Y_2O_3-reinforced $Al_{0.3}CoCrFeMnNi$ high-entropy alloy composite was processed by Gwalani et al. [34], the paper find that the in-situ formation of complex oxide Al–Y_2O_3 enhancing the strength, the compressive yield strength of composite increased from 0.98 GPa (0 vol% Y_2O_3) to 1.76 GPa (3 vol% Y_2O_3). The significant increase in strength can be attributed to the nano-dispersoid strengthening coupled with grain refinement [35]. The addition of ceramic phases has positive impacts on the properties of HEAs, however the current researches focus on double-phases HEAs principally, the research on single-phase HEAs not been searched in available literatures.

In this paper, TiC was added to single-phase $Al_{0.6}CrFe_2Ni_2$ HEAs (FCC), and the phase compositions, microstructures and mechanical properties were investigated systematically.

2 Experimental

The TiC/$Al_{0.6}CrFe_2Ni_2$ high entropy alloys with different ceramic contents (0, 1.25, 2.50, 3.75, 5.00 vol%) were smelted by vacuum arc melting furnace in argon atmosphere, the alloys were remelting for five times to guarantee the homogeneity of the alloy. The purity of the metals was more than 99.9 wt% and the diameter of ceramic particles TiC was 50 nm. The samples were prepared by electrical discharge machining, after polishing and burnishing, electro-polished was carried out in 90% acetic acid and 10% perchloric acid mixture liquid. X-ray diffraction (XRD, Shimadzu XRD-7000) was used to measure the phase structure of alloy, the microstructure and elemental distribution were analyzed by Scanning Electron Microscope (SEM, Zeiss Gemini). The compression test was carried out by universal electronic laboratory machine (MTS-E45) with a strain rate of 5 mm min^{-1} and the size of compressed samples were φ4 × 6 mm, three samples were measured for every alloy to ensure the accuracy of the results, and the yield strength was measured using an extensometer. The Vickers hardness of the alloys were measured too.

3 Results and discussion

3.1 Phase analysis

Figure 1 shows the XRD patterns of TiC/$Al_{0.6}CrFe_2Ni_2$ HEAs with different content of ceramic phase (ranging from 0 to 5 vol%), and Fig. 1b is the partial enlarged drawing of 2.50 vol%TiC/$Al_{0.6}CrFe_2Ni_2$HEAs. As shown in Fig. 1a, only FCC diffraction peak can be observed in TiC-free alloy, and when the ceramic phase TiC is introduced into the alloy systems, TiC diffraction peaks appear in the XRD patterns, as shown in Fig. 1b, when the TiC content is 2.50 vol%, the diffraction peak of TiC can be observed near 36° and 43° clearly, and this indicating that TiC is added to alloys successfully; with the increase of TiC content, the quantities and peak increase accordingly. Therefore, the addition of TiC has no influence on the phase species of alloys, but the appearance of TiC diffraction peak will affect the microstructures and mechanical properties of the $Al_{0.6}CrFe_2Ni_2$ high entropy alloys.

3.2 Microstructures and elemental distribution

Figure 2a, b, c, e, f shows the microstructures of TiC/$Al_{0.6}CrFe_2Ni_2$ high entropy alloys with different TiC content, respectively, and Fig. 2d is the partial enlarged drawing of Fig. 2c. Table 1 shows the composition of $Al_{0.6}CrFe_2Ni_2$ high entropy alloy matrix.

As shown in Table 1, the composition of TiC-free high entropy alloy is $Al_{10.94}Cr_{18.39}Fe_{33.46}Ni_{35.20}$, after conversion, the composition of the alloy is $Al_{0.600}Cr_{1.009}Fe_{1.945}Ni_{1.931}$, the proportion of element content is basically in accordance with the theory. As shown in Fig. 2a, when ceramic phase TiC has not introduced to the alloy system yet, known by XRD diffraction pattern that there are only FCC structure grains in the matrix alloy, the grain boundaries of matrix are brightness and purity. There is some unanticipated oxides and inclusions structure can be observed in Fig. 2a, it is produced by the reaction of residual oxygen with metal during smelting;

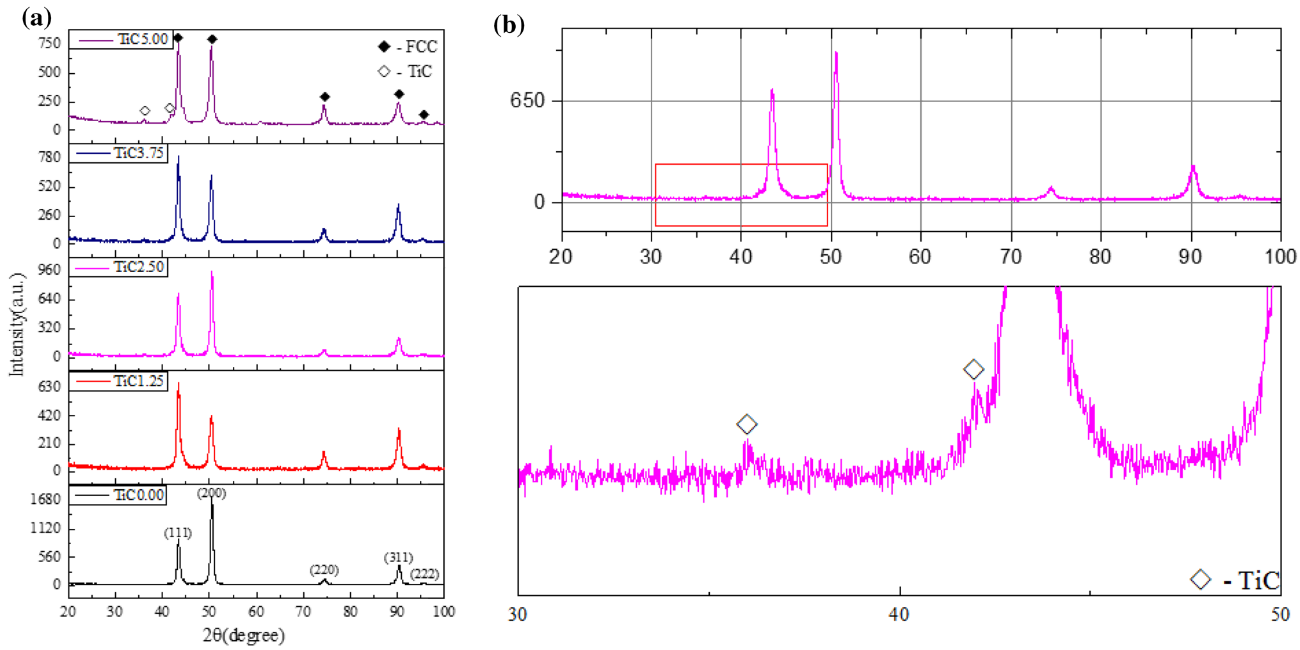

Fig. 1 **a** The XRD patterns of TiC/Al0.6CrFe2Ni2 high entropy alloys, **b** partial enlarged drawing of 2.50 vol%TiC/Al0.6CrFe2Ni2

When TiC is introduced to the alloy system, bright-white "skeletal" structures appear at the grain boundaries(as shown in Fig. 2b), according to the elements distribution of 1.25 vol%TiC/HEAs in Fig. 3f, g, the "skeletal" structures are composed by added TiC ceramics. With the increases of TiC content continually, as shown in Fig. 2c, d, granular nano-phase can be observed in the grain boundaries, which is wrapped by TiC. From Fig. 2a, b, c we can see that, the size of grains decreases with the addition of TiC. When the content of TiC increases to 3.75 vol% and 5.00 vol%, micropores can be observed in the alloys, this is due to excessive TiC agglomeration and separation from the alloy substrates, and this will have a negative effect on the properties of the alloys.

Figure 3 is the elemental distribution of 1.25 vol%TiC/HEAs and Fig. 4 shows the elemental distribution of Fig. 2d. As shown in Fig. 3b, c, d, e, matrix elements Al, Cr, Fe, Ni distribute within the grains uniformly. Although ceramic phase elements Ti and C exist in the grain interior, they mainly appear at the grain boundaries, this indicates that the bright-white structures at grain boundary in Fig. 2 are TiC ceramic reinforcing phase. From Fig. 4 we can see that, the main elements of nano-phase which exist in grain boundaries are Al and Ni element, e.g. Fig. 4a, d. The nano-phase is wrapped by TiC, and nano-phase plays the role of connecting the ceramic phase, so that the ceramic phase has higher performance, which improves the properties of the alloy. So it will enhance the properties of TiC/HEAs system inevitably.

3.3 Mechanical properties

The stress–strain curves and the Vickers hardness (HV)of TiC/$Al_{0.6}CrFe_2Ni_2$ HEAs are shown in Fig. 5a, b, the yield strength (δ_y) and the value of hardness are listed in Table 2. With the addition of TiC, the δ_y of alloys rising primarily and then falling. As shown in Table 2, the δ_y of TiC-free alloy is 113.03 MPa, with the addition of TiC phase, the δ_y increases and when the content of TiC reaches 2.50 vol%, the δ_y of alloy increases to maximum 576.93 MPa, this is due to that TiC is the core of heterogeneous nucleation, the addition of TiC reduces the grain size, this results in an advance in strength, meanwhile the TiC strengthened by nano-phase also plays a "supporting" role during compression tests, this also increases the strength of the alloy. With the increases of TiC ulteriorly, because of the appearance of microporous defect, as shown in Fig. 2e, f, the continuity of the alloys was broken, hence the strength of the alloys declines.

The strengthening of grain boundaries must lead to the reduction of plasticity, However, the TiC/$Al_{0.6}CrFe_2Ni_2$ HEAs don't fracture during compression tests (When the compression rate is 60%, compression test stop). So the plasticity of alloys have no change significantly with the addition of TiC phase, which is mainly caused by the precipitation of nano-phase, and this indicates that TiC can improve the strength of the alloy are greatly by adding appropriate TiC without affecting the plasticity of the alloy.

Since because that TiC phase has high hardness, the addition of TiC will increase the hardness of alloy

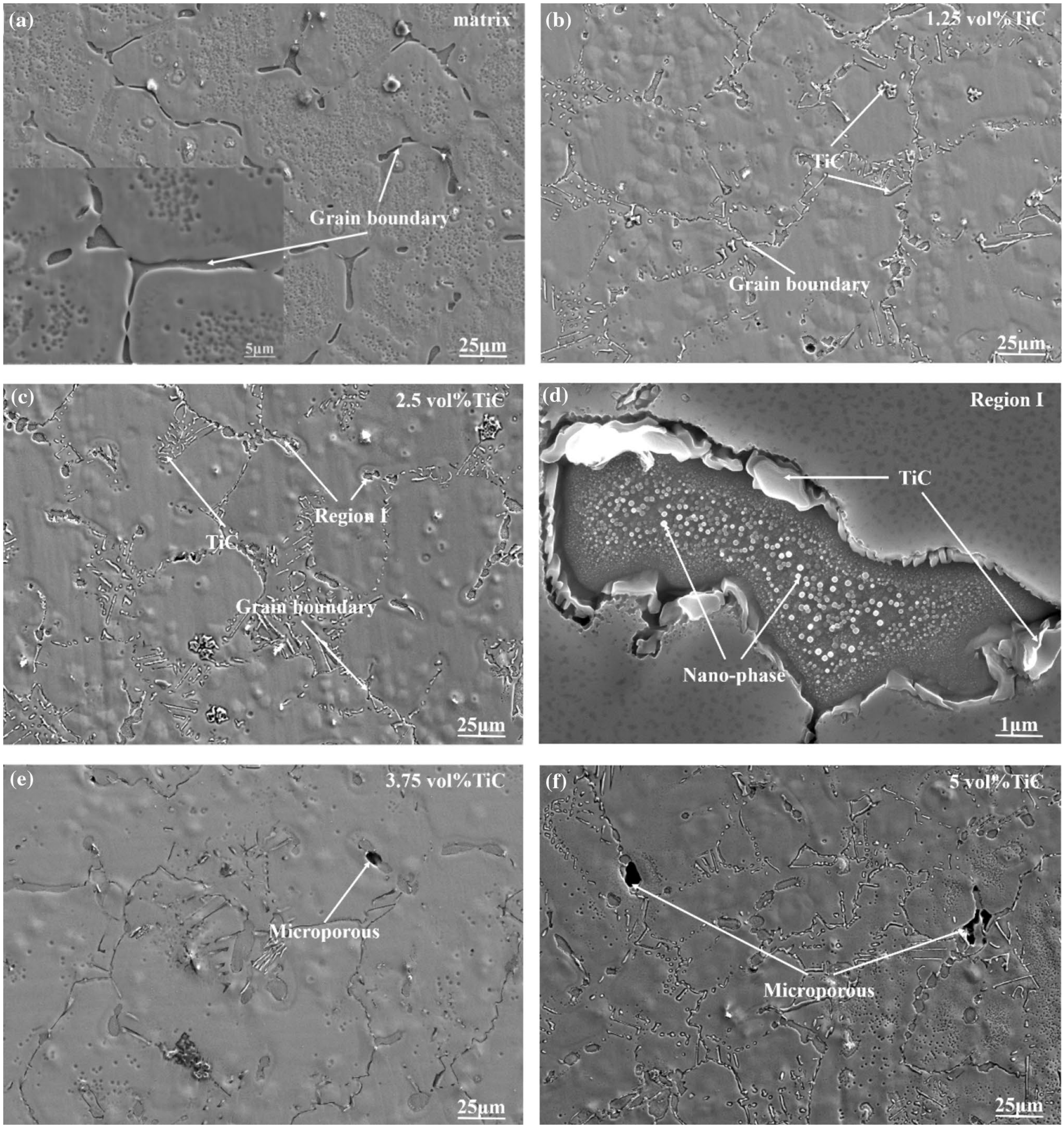

Fig. 2 Microstructures of TiC/$Al_{0.6}CrFe_2Ni_2$ high entropy alloys

Table 1 The composition of $Al_{0.6}CrFe_2Ni_2$ high entropy alloy matrix

Element	Atomic (%)
Al	10.94
Cr	18.39
Fe	35.46
Ni	35.20

inevitably, therefore, with the increase of TiC content, the hardness of TiC/$Al_{0.6}CrFe_2Ni_2$ HEAs increases from 152 to 264 HV, enhance 75% nearly. When the TiC content rises to 2.50 vol%, TiC agglomeration occurred, which led to a slowdown in the trend of hardness improvement. To conclude, the increase of TiC can improve the mechanical properties of the alloy immensely, and when TiC content is 2.50 vol%, the alloy has better properties, the δ_y of

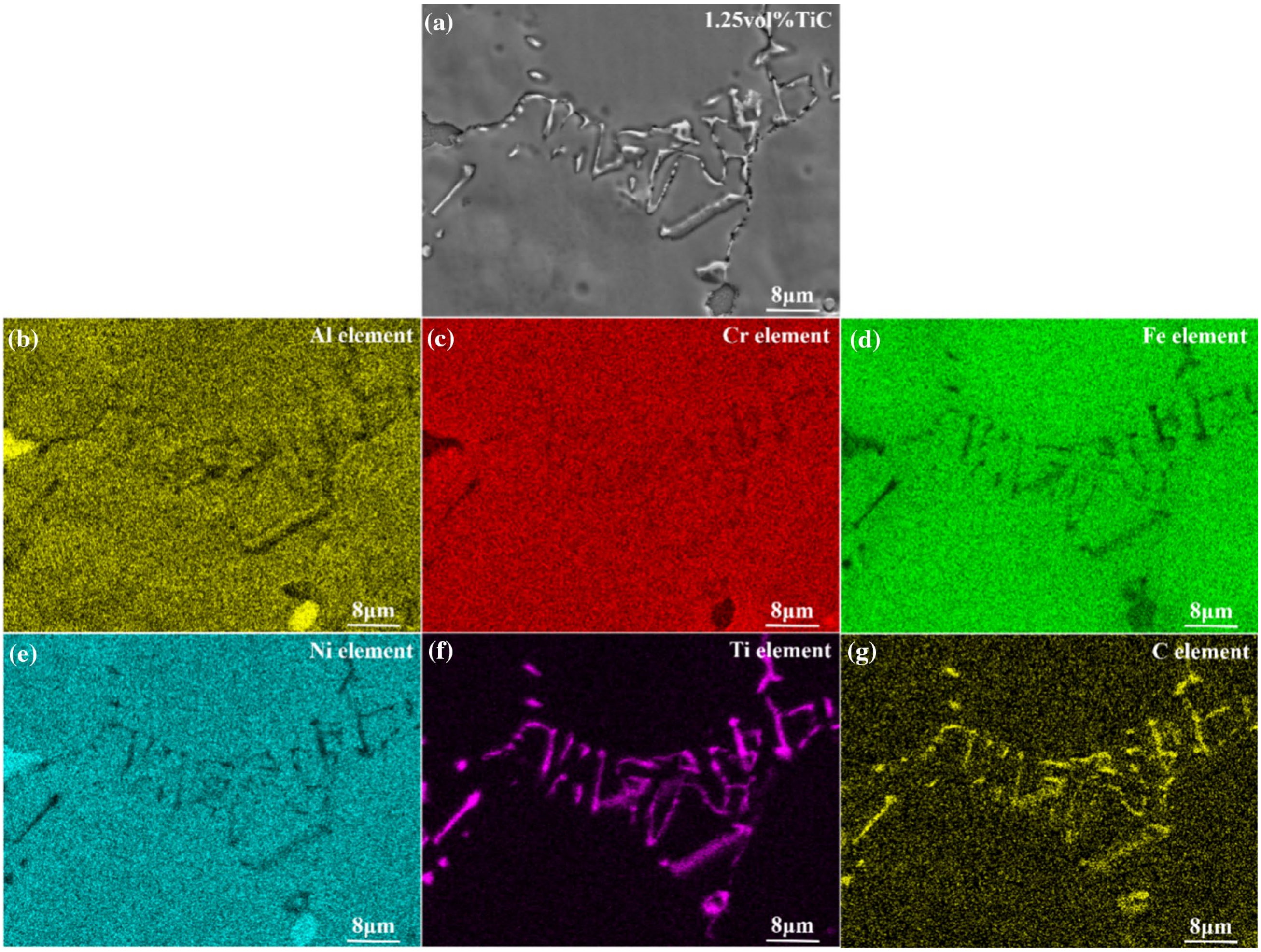

Fig. 3 The elements distribution of 1.25 vol%TiC/$Al_{0.6}CrFe_2Ni_2$ high entropy alloys

2.50 vol%/$Al_{0.6}CrFe_2Ni_2$ HEAs is 576.93 MPa, rising about 400% compared with the matrix, and the Vickers hardness is 244 HV, rising about 60%.

4 Conclusions

A series of TiC/$Al_{0.6}CrFe_2Ni_2$ high entropy alloys were prepared and the microstructure and mechanical properties were investigated minutely. Based on the above research, the introduce of ceramic phases have energetic effect on $Al_{0.6}CrFe_2Ni_2$ high entropy alloys, the conclusions are obtained as follows:

(1) The $Al_{0.6}CrFe_2Ni_2$ HEAs are composed by single FCC phase, the addition of ceramic phases TiC have no influence on the phase species of matrix alloys;
(2) Ceramic phases TiC addition decreases the grain size, and with the addition of TiC, nano-phases occur in the boundaries, when the TiC content up to 3.75 vol%, micropores occur in the alloys;
(3) The addition of TiC can improve the mechanical properties of the alloy, when the value of TiC is 2.50 vol%, alloys have better properties, the yield strength and Vickers hardness are 576.93 MPa and 244 HV, respectively.

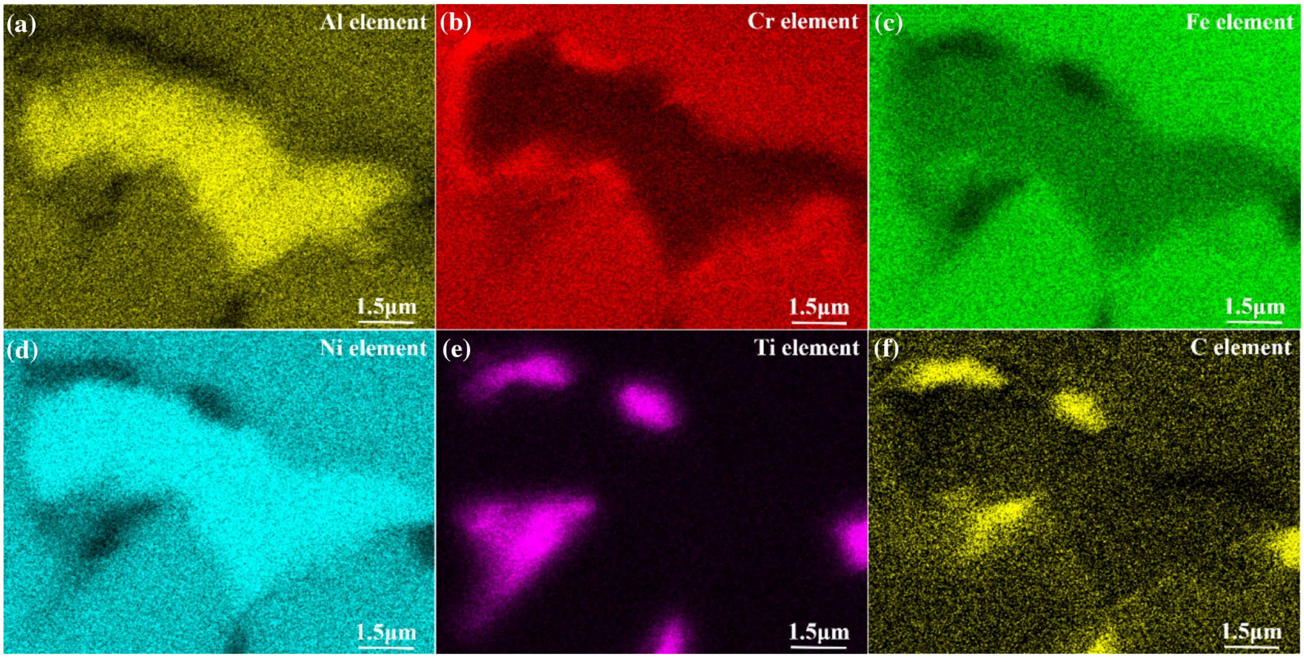

Fig. 4 The elements distribution of 2.50 vol%TiC/$Al_{0.6}CrFe_2Ni_2$ high entropy alloys

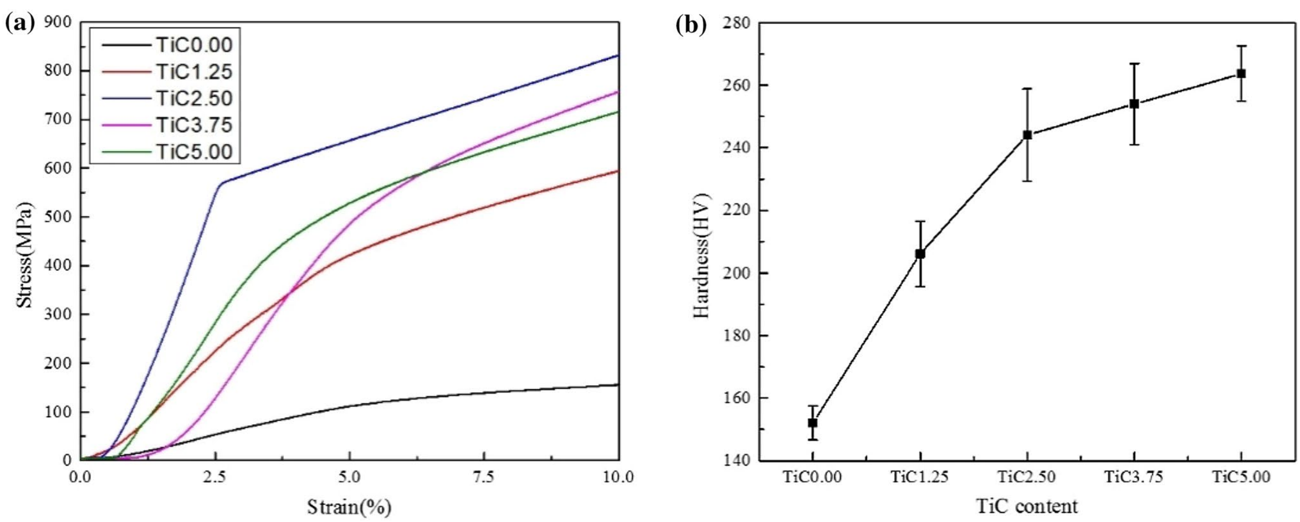

Fig. 5 The mechanical properties of $Al_{0.6}CrFe_2Ni_2$ high entropy alloys **a** the stress–strain curves of TiC/$Al_{0.6}CrFe_2Ni_2$ high entropy alloys and, **b** the Vickers hardness of TiC/$Al_{0.6}CrFe_2Ni_2$ high entropy alloys

Table 2 The yield strength and the hardness of $Al_{0.6}CrFe_2Ni_2$ high entropy alloys

TiC content (vol%)	δ_y (MPa)	Hardness (HV)
0	113.03	152
1.25	302.66	206
2.50	576.93	244
3.75	476.48	254
5.00	437.19	264

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Compliance with ethical standards

Conflict of interest The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or nonfinancial interest (such as personal or professional relationships, affiliations, knowledge, or beliefs) in the subject matter or materials discussed in this manuscript.

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