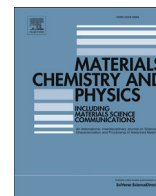




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Abnormal temperature dependence of impact toughness in $\text{Al}_x\text{CoCrFeNi}$ system high entropy alloys

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H I G H L I G H T S

- Impact toughness of $\text{Al}_x\text{CoCrFeNi}$ ($x = 0, 0.1$) increase with decreasing temperature.
- The impact toughness (397.87 J) of CoCrFeNi is the highest among all known metals.
- Increasing nano-twinning activities enhances the impact toughness below 298 K.
- The $\text{Al}_x\text{CoCrFeNi}$ ($x = 0.75, 1.5$) HEAs are very brittle with very low impact toughness.
- High Al contents induce the formation of brittle BCC phase and B2 compound.

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In this work, the effect of Al contents and the associated phase transformations on the impact toughness of $\text{Al}_x\text{CoCrFeNi}$ high-entropy alloys (HEAs) (x denotes Al molar ratio; $x = 0, 0.1, 0.75$, and 1.5) in the as-cast state were investigated at $T = 77$ K, 200 K, and 298 K. For the alloys with $x = 0$ and 0.1 , the alloys have the FCC structure, and an inverse temperature dependence of impact toughness between 298 K and 77 K was observed. The enhanced impact toughness (397.87 J) at 77 K is attributed to the capability of extensive nano-twinning as well as ductile dimple fracture. Increasing Al contents to $x = 0.75$ and 1.5 induces the formation of brittle BCC phase and ordered B2 compound and accordingly embrittlement, leading to tremendously reduced Charpy-impact energies. The present study demonstrates that FCC $\text{Al}_x\text{CoCrFeNi}$ system HEAs with low Al contents ($x < 0.5$) may be well suitable for cryogenic applications.

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1. Introduction

The development of structural materials suitable for cryogenic applications is a persistent quest in materials science and technology. The challenge is that most materials usually lose most of their toughness when the temperature falls below a particular level [1,2]. For example, dual-phase 590 (DP590) steels have a well-defined ductile-to-brittle transition temperature (DBTT) at about 178 K, below which the steels become very brittle [3]. The ductile-to-brittle transition is also well known in certain austenite steels with the face-centered cubic (FCC) structure [4], ferritic steels with the body-centered cubic (BCC) structure [5], and metals and alloys with the hexagonal close-packed (HCP) structure [6]. Although the

ductile-to-brittle transition in certain FCC steels (e.g., TWIP steel [7]) is not sharp, the Charpy-impact energy drops to less than 100 J at 77 K. Generally speaking, below the DBTT, materials can fail in a catastrophic fashion, often leading to serious accidents. The sinking of the Royal Mail Ship Titanic [8] and Liberty Ships in the 1940s [9] was attributed to the ductile-to-brittle transition of the steels used at cryogenic temperature. In fact, any brittle failure will not only be catastrophic but also unpredictable. Therefore, it has been endless effort for material scientists and engineers to design new alloys and novel processing routes to improve the impact toughness of existing materials to a level appropriate for cryogenic applications.

Representing a radical departure from conventional alloy design [10], high entropy alloys (HEAs) [11–13] provide a novel alloying concept and greatly expand the number of applicable alloy systems. For recent comprehensive reviews on the formation mechanisms and properties of HEAs, readers are referred to Ref. [14]. One

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definition for HEAs by Yeh [11] is based on the chemical composition, and HEAs are defined to preferentially contain at least five principal elements, each with an atomic percentage between 5% and 35%, regardless whether they are single-phase or multi-phases at room temperature.

As a new family of compositionally complex but structurally simple alloys, the HEAs provide very exceptional mechanical properties compared with conventional alloys. For example, the prior studies on the temperature dependence of tension [15,16] and fracture toughness [17] of FCC CoCrFeMnNi family HEAs show that higher strength and greater ductility are obtained at 77 K than 293 K. The mechanism for simultaneous increase in strength and ductility is due to the additional deformation mechanism of nano-twinning at cryogenic temperature. Recently Wu et al. [18] reported that the twinning activity in $\text{Al}_{0.1}\text{CoCrFeNi}$ HEA is strongly inhibited by grain refinement resulting from recrystallization compared to the as-casts state, which degrades the promotion of twinning on the strain-hardening ability and the tensile ductility.

However, the CoCrFeNi and CoCrFeMnNi FCC HEAs have relatively weak yield strength and thus are insufficiently strong for engineering applications. One alloying strategy to enhance their strength is to dope with Al due to strong interatomic interaction between Al and 3d transition metals [19]. Another method can be grain refinement by thermomechanical processing. In fact, the microstructure and compression behavior of $\text{Al}_x\text{CoCrFeNi}$ have been studied at room or higher temperatures [20–22]. With increasing the Al contents, the crystal structure of the stable phases

in the microstructure evolve from FCC, to FCC + BCC, and BCC structures. However, a systematic investigation on the effects of Al contents and temperature on the impact toughness of $\text{Al}_x\text{CoCrFeNi}$ is still absent. The main objective of this study is to investigate the effect of Al contents and the associated phase transformations on the impact toughness of $\text{Al}_x\text{CoCrFeNi}$ ($x = 0, 0.1, 0.75, \text{ and } 1.5$) in as-cast state with three representative structures at 77 K, 200 K, and 298 K, not limited to only the FCC-structured HEAs.

2. Experimental procedures

The four $\text{Al}_x\text{CoCrFeNi}$ alloys with Al molar ratios of 0, 0.1, 0.75, and 1.5, denoted by Al0, Al0.1, Al0.75, and Al1.5 in this report, respectively, were synthesized by the vacuum levitation melting (VLM) method, and the purity of the raw elemental metals was above 99.9 wt.%. The ingots were remelted at least four times to improve the chemical homogeneity, and the dimension of solidified ingots was about $\phi 80 \times 50$ mm. The Charpy-impact specimens were obtained from the transverse cross section of the ingots. The impact tests were performed following the ASTM standard E-23 [23] (size: $10 \text{ mm} \times 10 \text{ mm} \times 55 \text{ mm}$; with a 2 mm deep, V-notch at the center of the specimen) at $T = 298 \text{ K}$, 200 K, and 77 K by a Tinius Olsen impact tester of 500 J capacity. To increase the accuracy of this procedure, the hammer was released only if the entire process occurred within 5 s. For each composition, three specimens were tested, and the average value was used and the each data's repeatability is high.

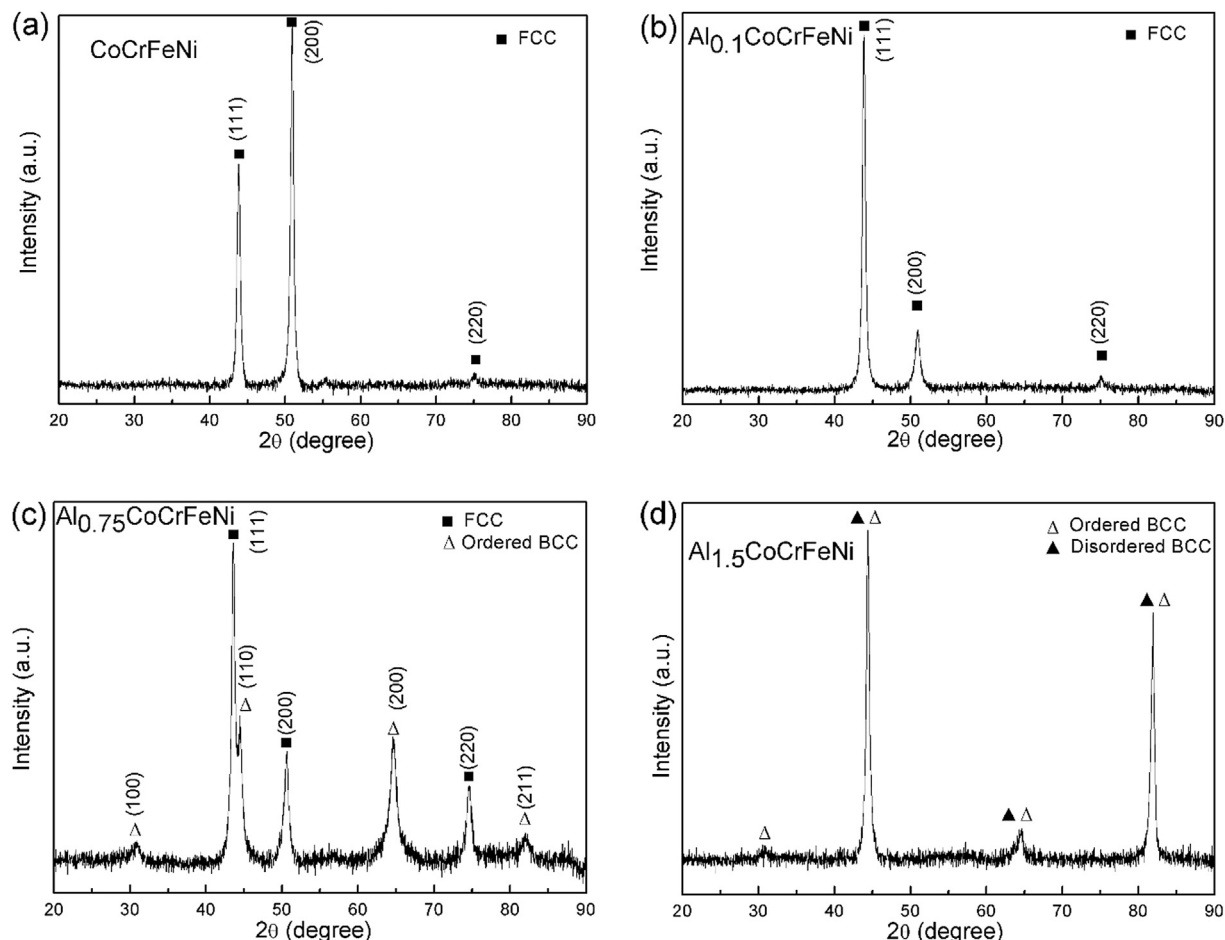


Fig. 1. XRD patterns of (a) Al0, (b) Al0.1, (c) Al0.75, and (d) Al1.5 HEAs in the as-cast state.

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