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The microstructure and high-temperature properties of novel nano precipitation-hardened face centered cubic high-entropy superalloys

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ABSTRACT

The present work reports two novel γ′(Ni_3Al type)-enhanced high-entropy superalloys $Ni_{45-x}(FeCoCr)_{40}(AlTi)_{15}Hf_x$ (x = 0, 0.2 at.%) with high-entropy fcc (face centered cubic) matrix and γ′ particles microstructure at cast condition. A large number of γ′ particles, with an average diameter size of 52 nm (dendritic regions) and 90 nm (inter-dendritic regions), are homogeneously distributed in a high-entropy fcc matrix and are coherent with the matrix. Attributable to the γ′ particles, the alloys show prominent mechanical properties at both room temperature and high temperatures. Coherent strength and atomic ordering strength are the primary strengthening mechanisms.

High-entropy alloys(HEAs) were proposed in 2004, requiring multiple constituents (≧5) with an equimolar ratio, near equimolar ratio or a high configurational entropy (≧1.5R). HEAs have some unique characteristics: sluggish diffusion, heavy lattice distortion, strong formation ability of nanophase, as well as many others. HEAs are endowed with excellent mechanical properties and phase stability attributed to the microstructure characteristics [1–4]. Therefore, HEAs have great potential for the application of structural materials, especially at elevated temperature. For example, bcc (body centered cubic) HEAs exhibited excellent hot strength and phase stability. Recently, refractory bcc HEAs, such as TaNbHfZrTi [5], NbMoTaW and VNbMoTaW alloys [6], were reported having superior yield strength compared to traditional superalloys. However, Nb, Ta, W, and V are extremely expensive raw elements, the cost is too high to be commonly utilized. By comparison, Fe, Cr, Al, Ni and Mn are much more affordable. Consequently, a B2 nanoprecipitation-enhanced bcc $Al_{0.7}CoCrFe_2Ni$ alloy was designed. The strength of the alloy at elevated temperatures is lower than that of Inconel 706, but runs close to Income 690 [7]. However, the alloy becomes brittle when the temperature exceeds 600 °C. Furthermore, the oxidation performance of bcc alloys need to improve. As far as fcc HEAs are concerned, high-temperature studies mainly focus on the FeCoNiCrMn alloy, which presents outstanding ductility, fracture toughness properties and good microstructure and phase stability at 1223 K after one month [8–10]. Nevertheless, the yield strength of the alloy in as-cast state is only approximately 200 MPa [9,11]. In summary, it is impossible to apply fcc HEAs to high-temperature structural materials by means of solution strengthening.

Second phase strengthening has been applied to fcc CoCrFeNi and CoCrFeNiMn HEAs with minor additions of Al, Ti and Nb. Unfortunately, bcc and topologically close-packed (TCP) phases always formed, threatening the high temperature mechanical properties. In the $Al_xCoCrFeNi$ HEAs system, σ phase appeared when the alloys were treated at 500 °C [12], and BCC phase could even be found even at room temperature [13,14]. Nb-enriched Laves phase was observed in $CoCrFeNiNb_x$ HEAs [15].As we know, γ′ (Ni_3Al type phase) is the significant strengthening phase in Ni-based superalloys. The high volume fraction and uniform distribution of γ′ play an important role in preventing dislocation motion, which are the key factors for high temperature strength. In order to obtain better mechanical properties, γ′ phase was introduced into HEAs.

After solution and aging heat treatment, the γ′ phase (less than 100 nm) was formed in $Al_xCo_{1.5}FeCrNi_{1.5}Ti_y$ (x + y = 0.5) HEAs after solution and aging heat treatment. The high hardness of some alloys at elevated temperatures was mainly due to γ′ precipitations [16]. J.Y. et al. obtained γ′ and Ni_2AlTi nanopaticles in fcc $(FeCoNiCr)_{94}Ti_2Al_4$ high entropy alloy after thermal mechanical treatment. However, they just reported the mechanical property at room temperature [17]. Compared with the Ni-based superalloy, it is difficult for traditional high entropy

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alloys to form a large amount of dispersed γ′ phase at the as-cast state or even heat treatment state. Accordingly, the design, preparation, and study on the microstructure and properties of γ′-enhanced HEAs have great significance.

In the present paper, we break through the definition of traditional HEAs. Ni is increased to 45% (at.%). The configurational entropy of the alloy is 1.56 R, which is still larger than the defined value (1.5 R). New $Ni_{45-x}(FeCoCr)_{40}(AlTi)_{15}Hf_x$ high-entropy superalloys with excellent γ′/γ structure are designed, and these alloys exhibit outstanding mechanical properties. The alloys have the potential to be applied to in the field of engine blades, turbines and other high temperature parts, similar to that of cast Ni-based superalloys.

The $Ni_{45-x}(FeCoCr)_{40}(AlTi)_{15}Hf_x$ ($x = 0$, 0.2 at.%) alloys were prepared by arc melting process in a high-purity argon atmosphere. The purity of all elements is higher than 99.95% (wt, %). The alloys were melted for four times to obtain homogeneous element distribution. The phase constitution and crystal structure were identified using D/max-rB X-ray diffractometer with Cu Ka. The microstructure was analyzed by scanning electron microscope (SEM, Quanta 200FEG) and transmission electron microscopy (TEM, Talos F200x). The average diameter size of particles was measured by the software called Nano Measurer. To ensure accuracy, over 500 particles were measured in different fields. After grinding to 2000-grit SiC paper, the SEM specimens were etched in a solution of 5 g $CuSO_4$ + 20 ml HCl + 25 ml H_2O. TEM samples have the size of Φ3 mm × 60 μm, followed by twin-jet electro-polishing using a mixed solution of 10% perchloric acid solution and 90% ethanol. The cylindrical compressive samples have a height of 6 mm and a diameter of 4 mm. Sheet dog bone-shaped tensile specimens (10 mm × 2 mm × 1 mm) were cut from the middle of the cast ingot. The compressive and tensile properties were evaluated at room temperature and elevated temperatures using AG-X Plus 250 KN/50 KN testing machine.

Due to the fact that the microstructures of the two alloys are almost the same, $Ni_{45}(FeCoCr)_{40}(AlTi)_{15}$ alloy is taken as the example to discuss. The XRD result in Fig.1(a) shows that the as-cast $Ni_{45}(FeCoCr)_{40}(AlTi)_{15}$ alloy is primarily composed of fcc phase. Moreover, a weak (100) diffraction peak identified as an ordered fcc phase ($L1_2$) is detected. Fig. 1(b) shows that spherical and ellipsoidal nanoparticles with a volume fraction of 53% and an average diameter size of 52 nm are uniformly precipitated in matrix in dendritic region. Nanoparticles with a volume fraction of 54% and an average diameter of 90 nm are observed in inter-dendritic region, as shown in Fig. 1(c). Precipitated phase has radiating structure with the size of several microns, as Fig. 1(d) shows. Moreover, α-Ni_2AlTi phase (less than 2%) with ordered BCC structure is also found in inter-dendritic regions.

The view of nanoparticles is given in a bright field (BF) TEM image derived from the dendritic region is presented in Fig. 2(a). The selected area electron diffraction (SAED) pattern result taken from matrix and particles is shown in Fig. 2 (b). The diffraction spots indicate that the structure of the alloy is FCC, while the superlattice L12 structure is proven to exist according to the spots marked with a red circle. The interface between a particle and the matrix is shown in the high resolution TEM picture, as the Fig. 2 (c) shows. It can be confirmed that the matrix and precipitate phases are completely coherent. Matrix and particle regions are selected to determine the structure. The Fourier transformation (FFT) images reveal that the matrix has fcc structure and the particle has a superlattice L12 structure. According to the compositions of matrix and particles shown in Table 1, the element composition of particles is rather closed to $(Ni,Co)_3(Al,Ti)$ and the (Ni, Cr, Fe)-enriched fcc matrix is itself a high-entropy phase ($\Delta S_{matrix} = 1.56R$). Combined with the lattice constant (0.35872 nm) of particles measured from the XRD result, particles can be identified as $(Ni,Co)_3(Al,Ti)$ type γ′ phase. High-entropy fcc matrix + fine γ′ particles microstructure is obtained in this high-entropy superalloy.

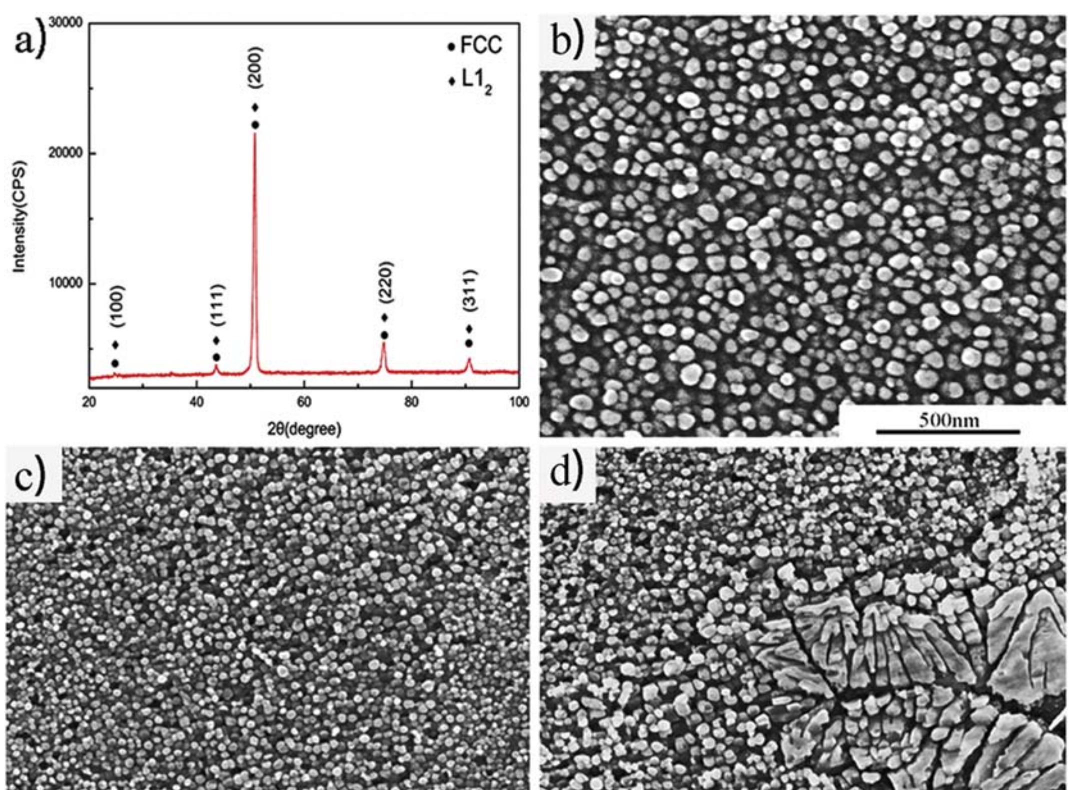

Fig. 1. a) XRD pattern of the as-cast $Ni_{45}(FeCoCr)_{40}(AlTi)_{15}$ alloy, b)–d) SEM micrographs of precipitated phase in different regions.