



# Microstructures and mechanical properties of multiprincipal component CoCrFeNiTi<sub>x</sub> alloys

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## ABSTRACT

The purpose of this study is to investigate the effects of Ti addition on the microstructures and mechanical properties of multiprincipal component CoCrFeNiTi<sub>x</sub> ( $x$  values in molar ratio,  $x=0, 0.3$ , and  $0.5$ ) alloys. The CoCrFeNi quaternary alloy displayed a crystalline structure constructed by a simple face-centered cubic solid solution, whereas a plate-like structure consisting of a mixture of (Ni, Ti)-rich R phase and (Cr, Fe)-rich  $\sigma$  phase was observed within the face-centered cubic matrix of a CoCrFeNiTi<sub>0.3</sub> alloy. In a CoCrFeNiTi<sub>0.5</sub> alloy, an face-centered cubic matrix, a (Ti, Co)-rich Laves phase, and R +  $\sigma$  mixed phases were discovered. The compressive strength of the alloys rose by approximately 75% after the addition of Ti. Alloys with high levels of Ti content had high yield stress values and low ductility values. The solid-solution strengthening of the face-centered cubic matrix and the secondary-phase hardening were the two main factors that strengthened the alloy. The CoCrFeNiTi<sub>0.3</sub> alloy exhibited a compressive strength of 1529 MPa and a fracture strain of 0.60; this indicates that this material shows potential for the development of a ductile, high-strength alloy.

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## 1. Introduction

Traditional alloys include one or two principal elements, but high-entropy alloys composed of multi-principal elements have attracted much attention since 2004 [1]. A typical high-entropy alloy contains at least five principal elements, each with concentrations between 5 at% and 35 at%. Due to the highly entropic effects of mixing on solidification, these multi-principal elements facilitated the formation of simple solid solutions rather than complex phases [1–5]. Al<sub>x</sub>CoCrCuFeNi alloys were the first to be widely studied in terms of their microstructures and mechanical properties [6–10]. Despite the segregation of Cu-rich phases, the crystal structures of these alloys displayed simple face-centered cubic (FCC) solid solutions with Al content below 0.5 and FCC+body-centered cubic (BCC) duplex solid solutions with Al content in the range from 0.8 to 2.5. These results indicated that Al was a strong BCC former. Analyses of these alloys' mechanical properties usually showed high values of hardness, strength, and wear resistance, but poor ductility at room temperature, especially for alloys with high Al content. To expand and enrich the field of high-entropy alloys, some researchers added Ti into the above alloys and studied the microstructures and compressive properties of alloys such as Al<sub>x</sub>CoCrFeNiTi, AlCoCrFeNiTi<sub>x</sub>, and AlCoCrCuFeNiTi [11–13]. Those studies revealed that the alloys

generally showed a microstructure of BCC or BCC+Laves phase at room temperature. The alloys, especially those with high Al or Ti content, exhibited high compressive strengths but inferior fracture strains. We attribute the poor fracture strains of these alloys to the presence of the hard and brittle BCC solid solution. Wang et al. [14] presented an FCC CoCrCuFeNiTi<sub>0.5</sub> high-entropy alloy which exhibited a compressive strength of 1650 MPa and a fracture strain of 0.22. In addition to the FCC matrix, the microstructure of this alloy also disclosed some secondary phases which were not clarified further.

The purpose of this study is to develop high-strength and ductile high-entropy alloys with FCC matrices. Since addition of Al tended to form BCC matrices, we excluded Al and prepared a CoCrFeNi quaternary alloy and two high-entropy alloys: CoCrFeNiTi<sub>0.3</sub> and CoCrFeNiTi<sub>0.5</sub>. We investigated the effects of variations in Ti content on the microstructures and mechanical properties of the alloys.

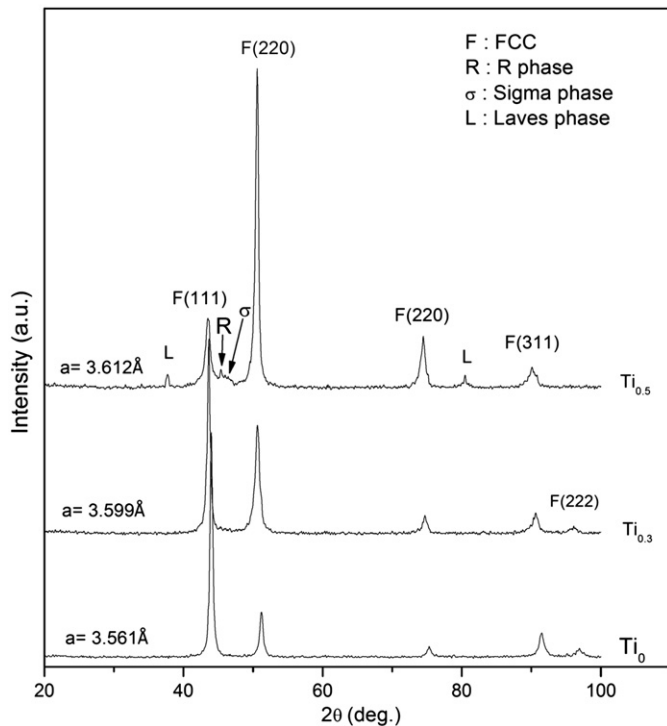
## 2. Material and methods

Three levels of Ti were set for three alloys; the  $x$  values in their molar ratios,  $x=0, 0.3$ , or  $0.5$ , were denoted as Ti<sub>0</sub>, Ti<sub>0.3</sub>, and Ti<sub>0.5</sub>, respectively. Three CoCrFeNiTi<sub>x</sub> alloys were synthesized by arc melting under a Ti-gettered high-purity argon atmosphere in a water-cooled copper crucible. Elemental Co, Cr, Fe, Ni, and Ti of 99 wt% purity were used as raw materials. To ensure the homogeneity of the alloys, the ingot was melted 5 times. The size of the

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**Table 1**  
Chemical compositions (at%) of the CoCrFeNiTi<sub>x</sub> alloys.

Alloy	Co	Cr	Fe	Ni	Ti
Ti <sub>0</sub>	25.7	24.8	25.2	24.3	0
Ti <sub>0.3</sub>	22.8	23.7	23.2	23.5	6.8
Ti <sub>0.5</sub>	22.8	21.4	21.1	22.8	11.9



**Fig. 1.** XRD patterns for the CoCrFeNiTi<sub>x</sub> alloys.

ingot was approximately 60 mm × 40 mm × 10 mm. Table 1 lists the chemical compositions of the alloys. The crystal structure was identified by an X-ray diffractometer (XRD, Bruker D8 SSS) using Cu K<sub>α</sub> radiation scanning from 20 to 100 degrees in 2θ at a scanning rate of 4 degrees/min. The microstructures and chemical compositions of the alloys were examined using scanning electron microscopy (SEM, HITACHI-S3000), transmission electron microscopy (TEM, FEI E.O Tecani 20 G2 FE-TEM), and energy dispersive spectrometer (EDS). Aqua regia was employed as an etching solution for the SEM sample after polishing. A thin foil TEM sample was prepared by a twin-jet electron polishing machine using a 95% C<sub>2</sub>H<sub>5</sub>OH + 5% HClO<sub>4</sub> solution. Macrohardness and microhardness values were measured using a Vickers hardness tester (FUTURE-TECH FR-300e) under loads of 1 kg and 5 g, respectively, with a duration of 15 s. Compressive tests were carried out on φ5 × 10 mm samples using a materials testing machine (CHUN-YEN CY6040A4) with a strain rate of 1.6 × 10<sup>-3</sup> s<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Crystal structure

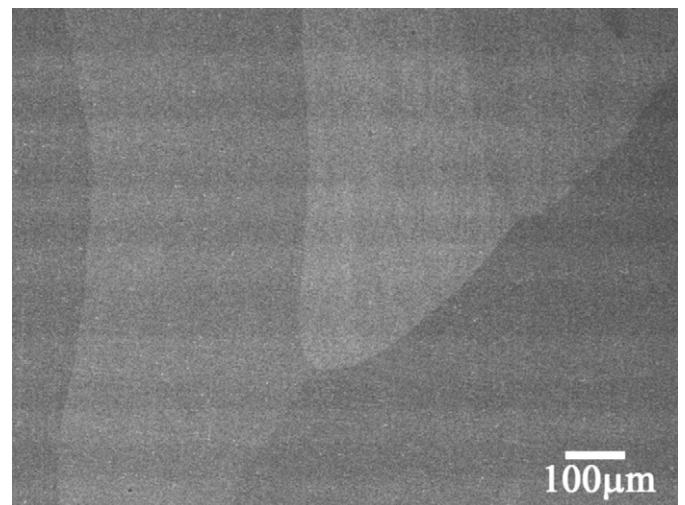
The XRD patterns for the CoCrFeNiTi<sub>x</sub> alloys are shown in Fig. 1. The Ti<sub>0</sub> and Ti<sub>0.3</sub> alloys displayed a simple FCC solid solution. For Ti<sub>0.5</sub> alloy, apart from the strong FCC diffraction peaks, several other diffraction peaks were detected. This

indicates that other phases had formed in the FCC matrix. According to the JCPDS cards, these diffraction peaks resulted from three different kinds of phases which were identified as (1) R phase (Pearson Symbol hR7, *a* = 2.579 Å, *c* = 44.162 Å, *c/a* = 17.12) with a structure similar to a rhombohedral Ni<sub>2.67</sub>Ti<sub>1.33</sub> phase; (2) σ phase (Pearson Symbol tP30, *a* = 8.845 Å, *c* = 4.567 Å, *c/a* = 0.52) with a structure similar to a tetragonal FeCr phase; and (3) Laves phase (Pearson Symbol hP24, *a* = 4.768 Å, *c* = 15.545 Å, *c/a* = 3.26) with a structure similar to a hexagonal close-packed Co<sub>2</sub>Ti phase. The lattice parameter of the FCC phase increased gradually from 3.561 Å to 3.612 Å. This change resulted from the addition of solid-solution Ti atoms. The fact that the atomic radius of Ti (1.47 Å) is larger than the atomic radii of the other constitutional elements (Co (1.25 Å), Cr (1.28 Å), Fe (1.26 Å) and Ni (1.24 Å)) explains this lattice expansion.

#### 3.2. Microstructure

Fig. 2 shows an SEM image of the Ti<sub>0</sub> alloy. Its crystalline structure had a grain size of 300–500 μm; no compositional segregation occurred. It is suggested that the formation of a simple FCC solid solution in the Ti<sub>0</sub> alloy was caused by the high mixing entropy from multi-principal elements, the approximate atomic size of each constitutional element, and the lack of any significantly negative or positive mixing enthalpy of atom pairs between each element (that is, the elements had similar electro-negativities). The mixing enthalpy Δ*H*<sub>mix</sub> of atom pairs [15] and the electronegativity of each element [16] are reported in Table 2.

The SEM microstructures of Ti<sub>0.3</sub> alloy are shown in Fig. 3. The low-magnification image in Fig. 3(a) shows that the alloy displayed a typical dendritic structure. The dendrite (DR) was an FCC solid solution containing approximately similar amounts of Co, Cr, Fe, and Ni, but a smaller amounts of Ti. The interdendrite



**Fig. 2.** SEM image of the Ti<sub>0</sub> alloy.

**Table 2**

The mixing enthalpy Δ*H*<sub>mix</sub> (kJ/mole) of atom pairs and electronegativity (data in bracket) of each element.

	Co (1.88)	Cr (1.66)	Fe (1.83)	Ni (1.91)	Ti (1.54)
Co	0	-4	-1	0	-28
Cr	-	0	-1	-7	-7
Fe	-	-	0	-2	-17
Ni	-	-	-	0	-35
Ti	-	-	-	-	0

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