

# Microstructure and mechanical properties of SiC whisker reinforced CoCrNi medium entropy alloys

Jiaying Wang<sup>a</sup>, Hailin Yang<sup>a,†</sup>, Hua Huang<sup>a</sup>, Jianming Ruan<sup>a</sup>, Shouxun Ji<sup>b</sup>

<sup>a</sup> State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China <sup>b</sup> Institute of Materials and Manufacturing, Brunel University London, Uxbridge, Middlesex UB8 3PH, United Kingdom

## Abstract

whisker (SiCw) composite was developed by a combination method of coating and spark plasma sintering (SPS). SiCw could be evenly distributed on the CoCrNi gas-atomized powder after coating and an obvious grain refinement could be observed in the microstructure of composite after sintering. Meanwhile, the CoCrNi/SiCw composite with a trace of in-situ M<sub>23</sub>C<sub>6</sub> phases showed superior mechanical properties: addition of 2 wt% SiCw led to an increase in the yield strength (YS) and hardness from 352 MPa and 159 HV to 595 MPa and 422 HV respectively, compared with the CoCrNi MEA. The improved strength is attributed to synergistic effects of Orowan strengthening, grain refinement and thermal mismatch mechanism.

## 1. Introduction

The entropy-based alloys shape an entirely new field of materials design and induce considerable excitement in the community of materials science and engineering [1]. Of which, medium entropy alloy (MEA) is becoming a focus of many scientific researches. Compared with conventional alloy materials, typical MEAs exhibit excellent structural stability and comprehensive properties because of the unique microstructure and alloy design [2,3]. For instance, the Fe<sub>80-x</sub>Mn<sub>x</sub>Cr<sub>10</sub>Co<sub>10</sub> and the CoCrNi MEAs could reach an excellent strength-ductility trade-off and showed superior mechanical properties in counterpart with metals, alloys and metallic glasses [3,4]. However, the yield strength of many FCC structured MEAs, such as the FeCoCrNi that synthesized by drop casting and powder metallurgy were only 165 and 395 MPa respectively [5,6]. Clearly, the MEAs with only FCC crystal structure may not strong enough for engineering applications. Therefore, the development in alloy design and/or materials synthesis approaches is necessary to increase the mechanical properties.

Taking the simple microstructure of MEAs into consideration, many MEAs have suitable matrices for metal matrix composites (MMCs) for improved mechanical properties. Meanwhile, the study on nano-scale reinforcements has become a very important field of research [7,8], from which, silicon carbide whiskers (SiCw) has been confirmed to provide excellent mechanical properties such as high strength, elastic modulus and superior elevated temperature stability in MMCs [9]. Therefore, we aim to synthesize a CoCrNi/SiCw composite using a combination method of coating and SPS in order to deliver homogeneous the CoCrNi/SiCw mixture through coating method and to obtain the composites with fine grain size and high density by SPS. The effects of SiCw on the mechanical properties of the CoCrNi MEA were investigated in association with the detail analysis of microstructure.

## 2. Experimental

The CoCrNi powder was synthesized using gas atomization method. The diameters and lengths of SiCw are non-uniform with a size distribution as specified by the supplier of 0.1–1 mm and 10–50 mm respectively. The CoCrNi/SiCw powder mixture was prepared by coating method. SiCw was dispersed into the normal hexane at 25 °C and the CoCrNi powder was then added into the solution to form the CoCrNi/SiCw suspension with constant stirring at 120 °C. Secondly, powder mixture was placed in vacuum at 60 °C for 24 h after the normal hexane has evaporated in suspension and mixture cannot be stirred further. Finally, powder mixture

was consolidated in a graphite die mould to experience SPS at a pressure/temperature of 40 MPa/1200 °C for a holding time of 15 min. Phase structures were characterized by X-ray diffractometer (XRD) with the Cu-K $\alpha$  radiation. Microstructural characterization was carried out by scanning electron microscope (SEM), electron backscattered diffraction (EBSD) and transmission electron microscope (TEM). Uniaxial tensile tests were performed using a material testing system (MTS Alliance RT30) tension machine with an engineering strain rate of  $1 \times 10^{-3} \text{ s}^{-1}$  and the hardness values were measured by an HVS-5 hardness tester.

### 3. Results and discussion

#### 3.1. Microstructure

Fig. 1 presents the SEM micrographs of the CoCrNi powder and the CoCrNi/SiCw mixture. A majority of the raw gas atomized powder displayed spherical shapes and satellite particles were observed in the microstructure of powder due to the collision of large and small particles during the flight process in the spray chamber. 1 wt% SiCw addition could homogeneously distribute among the matrix powder after coating, while a minority of SiCw were aggregated to form agglomerates in the microstructure of the CoCrNi/2 wt% SiCw mixture. In addition, the matrix powder particles in the mixture did not change obviously in the morphologies and still maintained spherical shapes. Clearly, coating method can produce the satisfied powder mixtures for this study.

Microstructures of the CoCrNi MEA without and with 2 wt% SiCw are shown in Fig. 2. An obvious grain refinement was observed in the CoCrNi/SiCw composite. The measurement showed that the average grain size of FCC grains in the MEA was 20.80  $\mu\text{m}$  and that was 6.38  $\mu\text{m}$  in the MEA with 2 wt% SiCw. In addition, the average size of the in-situ M23C6 phases shown in Fig. 2d was 0.25  $\mu\text{m}$ . The inverse pole figures (IPFs) of FCC phase shown as inserts in Fig. 2 confirmed that FCC grains have no obvious preferred orientation in the CoCrNi MEA and the CoCrNi/SiCw composite. XRD spectra of the CoCrNi MEAs with 0 and 2 wt% SiCw in Fig. 1d confirmed that the CoCrNi MEA only exhibited the peaks of FCC phase, implying that there are no other phases except CoCrNi matrix, in good agreement with previous studies [2,10]. However, the extra peaks (i.e. SiC and M23C6) were also identified in the CoCrNi/SiCw composite. These revealed the change in microstructure after adding the reinforcement phase and the phenomenon of in-situ M23C6 phases was also consistent with the results of EBSD and previous reports [11]. The details of the microstructure of the CoCrNi/SiCw composite were investigated by TEM as shown in Fig. 2g and f. The plenty of SiCw was found to evenly distribute in the microstructure of CoCrNi/SiCw composite. The crystal structures of the in-situ M23C6 and twinning phases are further verified by selected-area electron diffraction (SAED) as shown in Fig. 2L2 and L4. In addition, a trace of SiCw was also observed in the interface of matrix grains and matrix-M23C6.

#### 3.2. Mechanical properties

The stress-strain curves of the CoCrNi MEA with and without SiCw are shown in Fig. 3, the CoCrNi MEA exhibited outstanding elongation of 53.6% but moderate strength ( $Y_S = 352 \text{ MPa}$ ). The addition of SiCw into the MEA enhanced strength and decreased ductility, which showed high strength ( $Y_S = 595 \text{ MPa}$ ) with the moderate elongation of 18.6%. Moreover, the hardness was improved from 159 HV to 422 HV. In Fig. 3b, the yield strength phase maps of FCC and M23C6 in the microstructure of composite and the distribution of grain sizes; (g-h) TEM analysis of CoCrNi/SiCw composites and corresponding SADPs (L1-L4). and elongation of the pure MEA and the composite in this work are primary strengthening mechanisms include grain refinement, Orowan compared with those of the same MEA synthesized by other ways strengthening and thermal mismatch enhancement. As shown method [10], and with other typical HEAs/MEAs [3,12–15]. It is in Fig. 1c and 2g, coating method delivered more homogeneous seen that the CoCrNi MEA had superb ductility but moderate yield CoCrNi/SiCw mixture, and mixture with high quality is also the strength, while the CoCrNi/SiCw composite had high yield strength key to improvement of yield strength. Uniformly distributed ex-but

moderate elongation. Several strengthening mechanisms situ SiCw and in-situ M23C6 phases located at grain boundaries rationalized the improvement of strength of the composite. The can bring a drag force between two adjacent FCC grains. Then grain boundaries motion can be inhibited during sintering, achieving refine grains and improved mechanical properties. Meanwhile, evenly distributed SiCw at grain boundaries and in-situ nanoscale M23C6 phases interact with dislocation through the pinning effect and block the dislocations movement further (Orowan-type) during deformation, slip trace within a single grain can move forward when dislocation bypass SiCw and M23C6 phases. Also, the coefficient of thermal expansion of SiC, M23C6 and CoCrNi are

$4.7 \times 10^{-6} \text{K}^{-1}$ ,  $1.0\text{--}5.0 \times 10^{-6} \text{K}^{-1}$  [16] and  $17.4 \times 10^{-6} \text{K}^{-1}$  [10], respectively. The thermal mismatch dislocations could be generated at matrix-SiCw and matrix-M23C6 interfaces during deformation to relax thermal stresses. In summary, the improved strength of composite can be attributed to synergistic effects of various strengthening mechanisms.

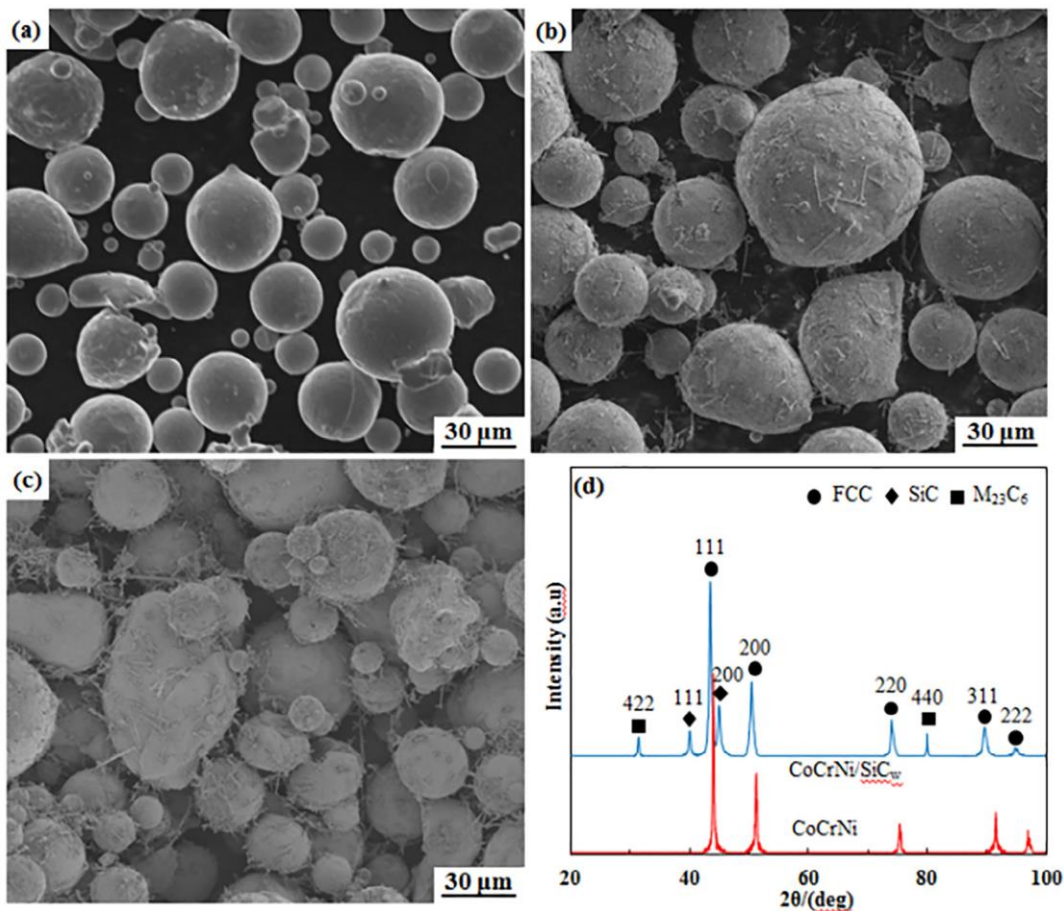


Fig. 1. SEM showing microstructure of (a) CoCrNi powder, (b) CoCrNi/1 wt% SiCw and (c) CoCrNi/2 wt% SiCw mixture; (d) XRD spectra of CoCrNi MEA and CoCrNi/SiCw composite.

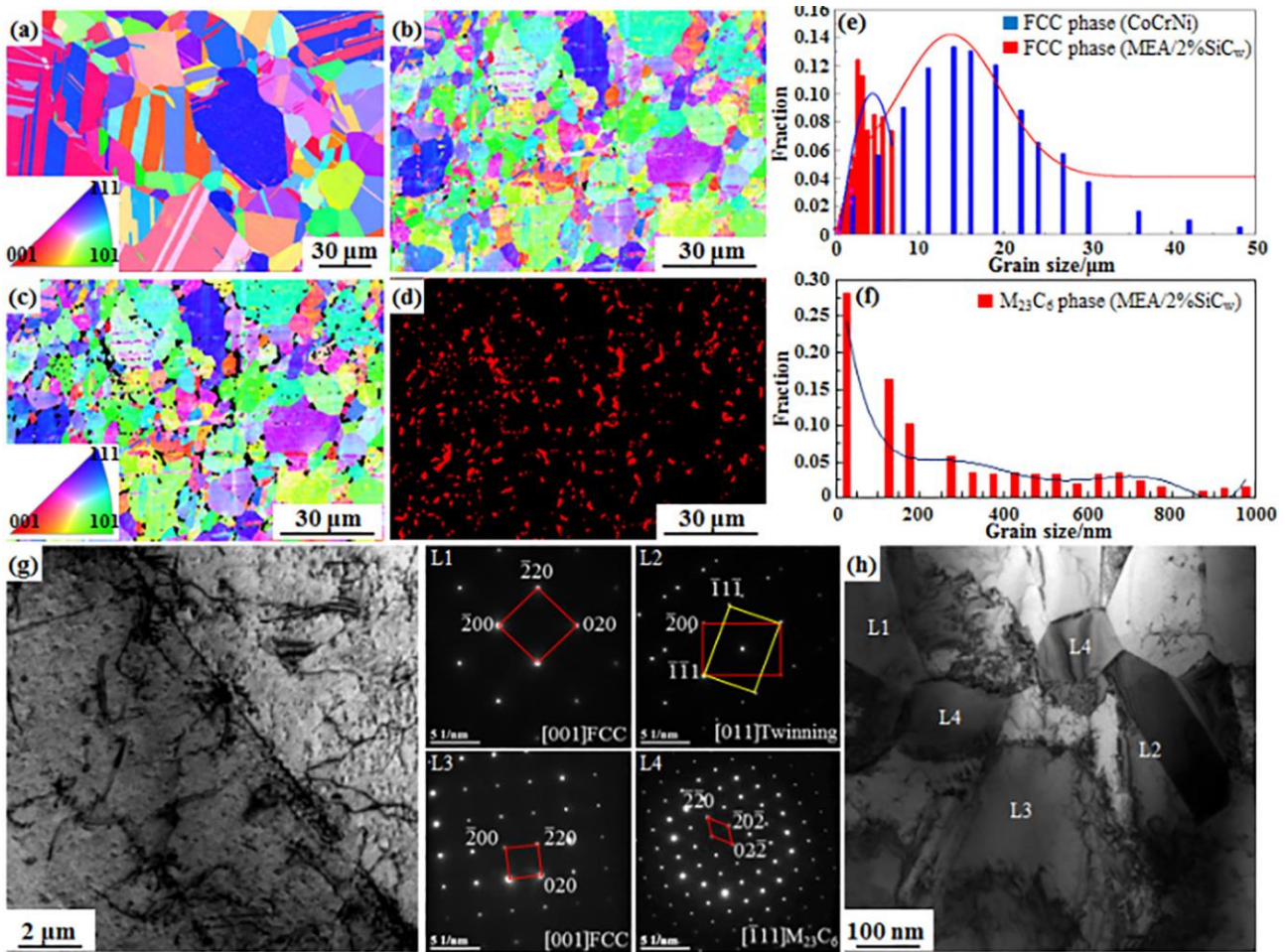


Fig. 2. EBSD maps showing the microstructure of (a) CoCrNi and (b) CoCrNi/SiCw composite; (c-f) EBSD

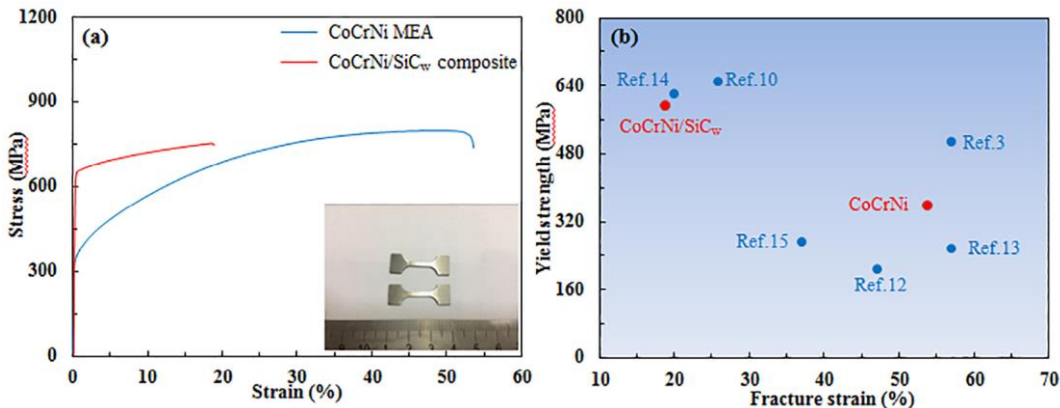


Fig. 3. (a) Tensile stress-strain curves of CoCrNi MEA and CoCrNi/SiCw composite, (b) Comparison of strength vs deformation of CoCrNi synthesized by other methods [10] and HEA/MEAs [3,12–15].

## 4. Conclusions

The CoCrNi/SiCw composite with grain refinement could be successfully synthesized by a combination method of coating and SPS. More homogeneous CoCrNi/SiCw mixture could be obtained after coating. Meanwhile, powder mixture with high quality was also the key to superior mechanical properties. Comparing with the CoCrNi MEA, the yield strength and the hardness of the CoCrNi/ SiCw composite with a trace of in-situ M23C6 phases were improved from 352 to 685 MPa (95.60%) and 159 to 422 HV (165.41%) respectively. The improved strength was attributed to various strengthening mechanisms including grain refinement, Orowan strengthening and thermal mismatch enhancement.

## Acknowledgement

This project was supported by National Natural Science Foundation of China with No. 51404302.

## References

- [1] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent, Microstructural development in equiatomic multicomponent alloys, *Mater. Sci. Eng. A* 375–377 (2004) 213–218.
- [2] Y.L. Zhao, T. Yang, Y. Tong, J. Wang, Heterogeneous precipitation behavior and stacking-fault-mediated deformation in a CoCrNi-based medium-entropy alloy, *Acta Mater.* 138 (2017) 72–82.
- [3] B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, E.P. George, A fracture-resistant high-entropy alloy for cryogenic applications, *Science* 345 (2014) 1153–1158.
- [4] Z.M. Li, K.G. Pradeep, Y. Deng, D. Raabe, C.C. Tasan, Metastable high-entropy dual-phase alloys overcome the strength-ductility trade-off, *Nature* 534 (2016) 227–230.
- [5] J.Y. He, H. Wang, H.L. Huang, X.D. Xu, M.W. Chen, A precipitation-hardened high-entropy alloy with outstanding tensile properties, *Acta Mater.* 102 (2016) 187–196.
- [6] B. Liu, J. Wang, Y. Liu, S. Chen, Microstructure and mechanical properties of equimolar FeCoCrNi high entropy alloy prepared via powder extrusion, *Intermetallics* 75 (2016) 25–30.
- [7] P. Nancy, J. James, S. Valluvadasan, R.A.V. Kumar, N. Kalarikkal, Laser-plasma driven green synthesis of size controlled silver nanoparticles in ambient liquid, *Nano-Struct. Nano-Objects* 16 (2018) 337–346.
- [8] V. Madhavan, P.K. Gangadharan, A. Ajayan, S. Chandran, Microwave-assisted solid-state synthesis of Au nanoparticles, size-selective speciation, and their self-assembly into 2D-superlattice, *Nano-Struct. Nano-Objects* 17 (2019) 218–222.
- [9] J.J. Petrovic, J.V. Milewski, D.L. Rohr, F.D. Gac, Tensile mechanical properties of SiC whiskers, *J. Mater. Sci.* 20 (1985) 1167–1177.
- [10] I. Moravcik, J. Cizek, Z. Kovacova, J. Nejezchlebova, M. Kitzmantel, Mechanical and microstructural characterization of powder metallurgy CoCrNi medium entropy alloy, *Mater. Sci. Eng. A* 701 (2017) 370–380.
- [11] Ł. Rogal, D. Kalita, A. Tarasek, P. Bobrowski, F. Czerwinski, Effect of SiC nanoparticles on microstructure and mechanical properties of the CoCrFeMnNi high entropy alloy, *J. Alloy. Compds.* 708 (2017) 344–352.
- [12] W. Huo, H. Zhou, F. Fang, X. Hu, Z. Xie, Strain-rate effect upon the tensile behavior of CoCrFeNi high-entropy alloys, *Mater. Sci. Eng. A* 689 (2017) 366–369.
- [13] Y. Deng, C.C. Tasan, K.G. Pradeep, H. Springer, A. Kostka, Design of a twinning-induced plasticity high entropy alloy, *Acta Mater.* 94 (2015) 124–133.

- [14] T. Bhattacharjee, R. Zheng, Y. Chong, S. Sheikh, S. Guo, Effect of low temperature on tensile properties of AlCoCrFeNi<sub>2.1</sub> eutectic high entropy alloy, *Mater. Chem. Phys.* 210 (2018) 207–212.
- [15] C.J. Tong, Y.L. Chen, J.W. Yeh, S.J. Lin, S.K. Chen, Microstructure characterization of Al<sub>x</sub>CoCrCuFeNi high-entropy alloy system with multiprincipal elements, *Metall. Mater. Trans. A* 36 (2005) 881–893.
- [16] X.Y. Chong, J.H. Jiang, J. Feng, Exploring the intrinsic ductile metastable Fe-C compounds: Complex chemical bonds, anisotropic elasticity and variable thermal expansion, *J. Alloys Comp.* 745 (2018) 196–211.