Microstructure and properties of CoCrNi medium entropy alloy produced by gas atomization and spark plasma sintering

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A homogeneous structured CoCrNi MEA was synthesized by gas atomization and spark plasma sintering (SPS). The mechanical properties, corrosion resistance, and magnetic properties were reported in this study. The as-atomized CoCrNi MEA powder, with a spherical morphology in shape and mean particle diameter of 61 μm, consisted of a single face centered cubic (FCC) phase with homogeneous distributions of Co, Cr, and Ni elements. Also, the cross-section of microstructure of powder particles gradually transformed from fully cellular structure into equiaxed-type structure with increased particle size. After being sintered by SPS, the CoCrNi MEA consisted of a single FCC phase with a mean grain size of 20.8 μm. Meanwhile, the CoCrNi MEA could offer the ultimate tensile strength of 799 MPa, the yield strength of 352 MPa, the elongation of 53.6%, and the hardness of 195.3 HV. In addition, the MEA showed a superior corrosion resistance in comparison with that of 304 stainless steel in both 0.5 mol/L HCl and 1 mol/L NaOH solutions. The magnetization loop indicated that this MEA has good soft-magnetic properties.

I. INTRODUCTION

High entropy alloys (HEAs), consisting of at least five equiatomic or near-equiatomic elements crystalized as simple solid solution structures, have attracted significant interest owing to their unique phase structures and superior properties.[1-6] For example, the typical simple FCC CoCrFeNiMn HEA generally exhibited excellent tensile strength (above 1 GPa) and fracture toughness (exceeding 200 MPa·m$^{1/2}$).[7] The Al$_x$CoCrFeNi HEAs exhibit superior corrosion resistance, compared to those of conventional corrosion-resistant alloys, such as stainless steels and Al, Ni, Ti, and Cu alloys.[6] Nevertheless, the origin of the formation of simple solid solution structures and answer on whether more elements improve the mechanical properties of HEAs are still controversial. The explanation of development of simple solid solution structures rather than intermetallic phases by increasing the number of elements to obtain a higher entropy might be wrong, as demonstrated by related experimental and CALPHAD simulation results.[2,8] On the other hand, Gali et al. reported that the introduction of Mn to the CoCrFeNi medium entropy alloy (MEA) had a negligible effect on the degree of solid solution strengthening, as evidenced by their similar yield strength and ultimate tensile strength.[9] Therefore, there was no systematic correlation between the mechanical properties and the number of alloying elements.

Considering the above controversial results, MEAs, a similar design approach of HEAs and consisting of two to four elements in equiatomic or near-equiatomic elements, have been presented by recent studies.[9-11] Particularly, the three component CoCrNi MEA exhibits a high work hardenability and excellent toughness.[12-17]

Laplancche et al. fabricated a CoCrNi MEA by arc melting and reported that the strength and fracture toughness of the CoCrNi MEA were improved, compared with those of CoCrFeMnNi HEAs.[18] The results indicated that the superior mechanical properties were attributed to twinning activation at higher stress and strain levels. However, the current investigations are seldom focused on the synthesis of the CoCrNi MEA with powder metallurgy (P/M). Generally, the preparation methods of HEAs/MEAs by smelting ingots, conventional sintering, and mechanical alloying have distinct disadvantages. For example, HEAs/MEAs synthesized by arc and induction melting have restrictions in processing, associated to the high temperature melting of the ingots and repeated melting to obtain homogeneous compositions.[19–21] Similarly, HEAs/MEAs produced by mechanical alloying can be easily contaminated by the material milling owing to the longer time of high energy milling. Igor et al. prepared CoCrNi powder by mechanical alloying and reported that a number of oxide phases were formed in the microstructure of CoCrNi MEA owing to the contact of the powder with air during the milling process.[17]

Among several existing manufacturing processes, gas atomization process is a widely used powder making route that provides good homogeneity, high processing efficiency and potential for mass production. The unique spherical natures of gas atomized powder are also preferred for additive manufacturing. In addition, the combination of gas atomization and spark plasma sintering (SPS) could be used to overcome the above fabrication drawbacks owing to the smaller risk of contamination, grain refinement, reduced segregation, etc. To the best of our knowledge, no studies

have been reported on the investigation of CoCrNi MEA using gas atomization and SPS. Therefore, CoCrNi MEA was produced by combination of gas atomization and SPS in this study. The microstructure and composition of the as-atomized powder and sintered alloy were carefully characterized. Meanwhile, the mechanical properties, corrosion resistance, and magnetic properties of the MEA were systematically investigated and discussed.

II. EXPERIMENTAL PROCEDURE

A. Powder and alloy manufacturing

The composition of the investigated alloy was ternary Co–Cr–Ni, with equal atomic contents of the elements. Element ingots of cobalt, chromium, and nickel were provided by the Beijing Jiaming platinum industry (cobalt > 99.98 wt%, chromium > 99.2 wt%, and nickel > 99.97 wt%). The powder of the same composition was then prepared using the high-pressure nitrogen gas atomization method. The ingots were heated up to the operating temperature ($T_m = 1943$ K); subsequently, the molten alloy was ejected through a nozzle with a N_2 pressure of 1.8 MPa. This resultant CoCrNi MEA powder was subsequently consolidated by SPS in a graphite die of an inner diameter of 40 mm at 1473 K for 15 min with a uni-axial pressure of 40 MPa. To limit the exposure to air, as-sintered CoCrNi powder was stored in sealed containers and inserted into the SPS dies under protective Ar atmosphere.

B. Microstructure characterization

The particle size distribution of CoCrNi powder was analyzed by a laser particle size

analyzer (Malvern-Mastersizer V3.60). X-ray diffraction (XRD, Rigaku X-2000) was utilized to characterize the phase constituents of CoCrNi powder and SPSed CoCrNi MEA at 40 Kv and 30 mA with K_α radiation (λ_{ka} = 1.54 Å). A scanning electron microscope (SEM, FEI nano 230 field emission) equipped with an energy-dispersive spectrometer (EDS) was used to evaluate the surface, cross-sectional microstructure of as-atomized powder and SPSed CoCrNi MEA. CoCrNi powder was embedded and then the sample was mechanically polish and etched using 170 mL H_3PO_4 + 10 mL H_2SO_4 + 10 g Cr_2O_3. Furthermore, the grain size and preferred lattice orientation of SPSed CoCrNi MEA were investigated by electron backscattered diffraction (EBSD) using a FEI Quanta FEG 250 field-emission-gun scanning electron microscope (FEG-SEM) and analyzed by the TSL OIM Analysis software. Detailed microstructure characterizations were performed using a Tecnai G2 F20 transmission electron microscope (TEM). In order to prepare thin foils for the TEM analysis, slices cut from SPSed MEA were mechanically ground and cut into discs with a diameter of 3 mm. These discs were then ground to 50 μm in thicknesses and finally ion-beam-thinned using a Gatan precision ion polishing system (PIPS) at a voltage of 5 kV and incident angle in the range of 3~7°.

C. Evaluation of mechanical properties

Dog-bone-shaped specimens with a gauge length of 10 mm and cross-section of 2.2 × 1.5 mm^2 were fabricated by electrical discharge machining for tensile test. Both sides of the specimens were carefully ground to a 2000 grit finish using SiC paper. The uniaxial tensile tests were performed using a material testing system (MTS Alliance

RT30) tension machine at room temperature with an engineering strain rate of 1×10^{-3} s^{-1}. Vickers hardness was measured on the polished surfaces of CoCrNi MEA samples using an HVS-5 hardness tester at 5 kgf for 10 s. All of the reported data are average values of at least 5 specimens.

D. Electrochemical performance and magnetic tests

Potentiodynamic polarization curves in 0.5 mol/L H_2SO_4 and 1 mol/L NaOH solutions were recorded using a CHI604D electrochemical working station. All of the electrochemical analyses were carried out using a conventional three-electrode cell with a saturated calomel electrode (SCE) as the reference electrode, platinum plate as the auxiliary electrode, and specimen as the working electrode. The electrochemical measurements were performed at room temperature (300 K). Samples with a dimension of 10 mm $\times$ 10 mm $\times$ 2 mm were ground from 400 to 2000 grit SiC paper, sequentially polished with 0.1 μm diamond powder. Subsequently, they were cleaned with deionizer water, alcohol, and then dried in cool air. The electrodes used for the electrochemical tests were connected by a wire welded to the back side of the samples, and sealed with a curing epoxy resin, leaving only one face with a size of $1\,cm^2$ exposed to the solution.

The magnetic properties were characterized by a vibrating-sample magnetometer (VSM) (Lakeshore 7100) at 300 K with a maximum applied field of 2 T, after calibration with a standard sample.

III. RESULTS AND DISCUSSION

A. Microstructure and chemical composition analysis of as-atomized CoCrNi MEA powder

SEM micrographs and the particle size distribution of gas-atomized CoCrNi MEA powder are shown in Fig. 1. The majority of raw gas-atomized powder had a spherical structure in shape. Satellite particles were observed on the surface of a few powder particles emerged by collisions of large and small powder particles during the flight process in the spray chamber. Additionally, very few powder particles were relatively flat with rounded edges, marked by the yellow circles in Fig. 1(a). This is because the spheroidization time of liquid droplets was longer than the solidification time, so that CoCrNi MEA powder were solidified before they were globalized. As shown in Fig. 1(b), the median particle size D_{50} synthesized by gas atomized in this study was approximately 61 μm. In addition, CoCrNi gas atomization powder fabricated by this study with high purity, superior sphericity and fine particle size can be potentially used for additive manufacturing.

EDS mappings of an as-atomized CoCrNi powder particle are shown in Figs. 1(c)–(f). The results indicated that the Co, Cr, and Ni elements were uniformly distributed in the single-phase solid solution without any composition segregation.

The surface morphologies and cross-section microstructure of CoCrNi MEA powder particles with different sizes are shown in Figs. 2(a)–(f). As shown in Figs. 2(a)–(c), the surface of as-atomized CoCrNi powder particles became gradually smooth as the diameter decreasing. The cross-section morphologies exhibited that an approximately

full cellular structure appeared as the particle diameter was approximately 8.0 μm owing to the higher cooling rate. However, the grains gradually transformed from fully cellular structures into equiaxed-type structures with increasing the particle size, as shown in Figs. 2(e)–(f). This could be attributed to the promoted eutectic process brought by decreasing cooling rate.

B. Microstructure and chemical composition analysis of as-sintered CoCrNi MEA

Figs. 3(a)–(b) show SEM-BSE micrographs of CoCrNi MEA. SPSed CoCrNi MEA exhibited a homogenous single phase with a few small pores, as marked by arrows in Fig. 3(a). In addition, annealing twins were observed in the microstructure of CoCrNi MEA after electrolytic polishing (Fig. 3(b)). The EBSD map with an inverse pole figure (IPF) of CoCrNi MEA is shown in Fig. 3(c). The annealing twins are also clearly visible in the microstructure. The average grain size of the FCC phase was 20.8 μm, which was significantly smaller than the mean particle size of raw as-atomized CoCrNi MEA powder, as shown in Fig. 1(b). This could be attributed to two factors: (1) the larger surface of the powder particles have more than one nucleation particle in the solidification process, as shown in Figs. 2(e) and 2(f); and (2) the SPS process can inhibit grain growth in the sintering process owing to the fast heating and cooling rate. The IPFs of the FCC phase, shown as insets in Fig. 3(c), confirm that the FCC grains have no obvious preferred orientation in SPSed CoCrNi MEA.

XRD spectra of as-atomized CoCrNi MEA powder and SPSed CoCrNi MEA are

shown in Fig. 3(d). The results indicated that as-atomized powder has a single-phase FCC structure. After being sintered at a high temperature, CoCrNi MEA also has the single-phase FCC structure with no visible change in the phase composition, which is in good agreement with previous studies.[12-14] This also demonstrated that no impurities, such as O and C, were introduced.

Further insights into the microstructure are obtained by bright-field (BF) TEM image, high-resolution TEM (HRTEM), and fast Fourier transform (FFT). Fig. 4(a) shows the BF image with a selected-area diffraction pattern (SADP) from SPSed CoCrNi MEA. The diffraction spot from the L_1 position in the inset of Fig. 4(a) verified that the phase has an FCC structure. The annealing twin phase is also observed in Fig. 4(b). The formation of annealing twins revealed that this CoCrNi MEA has a low stacking fault energy (γ_{SFE}) in the range of 18 to 45 MJ·m^{-2}.[19] Corresponding HRTEM image and FFT pattern of twin phase are shown in Fig. 4(c). The results are consistent with the SEM results in Fig. 3. It is also noted that there are no new phases (oxide or carbide) generated, which is in accord with the result of XRD spectrum in Fig.3(d).

C. Mechanical properties of SPSed CoCrNi MEA

Fig. 5 shows the stress–strain curve of SPSed CoCrNi MEA tensile-deformed to fracture at room temperature. CoCrNi MEA exhibited yield strength (σ_{YS}) of 352 MPa, ultimate tensile strength (σ_{UTS}) of 799 MPa, total elongation of 53.6%, and Vickers hardness of 195 HV. The fracture surfaces of the tensile test specimens were shown in Figs. 5(b) and (d). A number of dimples with features of typical ductile fractures were

observed. In Fig. 5(c), the ultimate tensile strength and elongation of CoCrNi MEA alloy analyzed in this study are compared with those of the same MEAs synthesized by other methods,[16,17] other typical HEAs/MEAs,[7,22–25] and conventional alloys.[26,27] CoCrNi MEA produced by this combination method of gas atomization and SPS in this study exhibited superb ductility but moderate yield strength.

TEM micrographs of SPSed CoCrNi MEA after the tensile deformation are shown in Fig. 4(d)–4(f). A high density of dislocations can be observed in CoCrNi MEA, as indicated in Fig. 4(a). Furthermore, some narrow deformation twins in Fig. 4(b) with a width of tens of nanometers are observed. Therefore, the plastic deformation of CoCrNi MEA was dominantly accommodated by dislocation motion and deformation-induced twinning. Thus, this superior ductility can be attributed to two reasons: one is the combination of gas atomization and SPS methods can deliver fabrication advantages such as the smaller risk of contamination and grain refinement; the other is that twins boundaries resulted from nanotwinning provide a steady source of strain hardening by blocking the motion of dislocations.

D. Magnetic properties of SPSed CoCrNi MEA

Fig. 6(a) presents the magnetic hysteresis loop of SPSed CoCrNi MEA measured by the VSM at room temperature. The saturated magnetization (M_s) and coercivity (H_c) of CoCrNi MEA are approximately 1.70 emu/g and 45.24 Oe under a magnetic field of 20000 Oe, which indicated that the prepared CoCrNi MEA can be capable of a soft magnetic characteristic. It has been reported that the single-FCC-phase FeCoCrNi

MEA exhibits a paramagnetic curve with an M_s of 3 emu/g.[28] Ji et al. investigated the magnetic properties of a CoCrFeNiMn HEA prepared by SPS.[29] It is well known that the M_s highly depends on the composition and grain size of the alloy.[30,31] SPSed CoCrNi MEA has a lower M_s than those of the FeCoCrNi MEA and CoCrFeNiMn HEA, which can be attributed to the higher atomic ratio of Cr (antiferromagnetic element) and larger grain size (20.8 μm).

E. Corrosion properties of SPSed CoCrNi MEA

Fig. 6(b)–(c) shows the representative potentiodynamic polarization curves of SPSed CoCrNi MEA, compared with those of a 304 SS in the 0.5 mol/L H_2SO_4 and 1 mol/L NaOH solutions at room temperature. The relevant parameters are summarized in Table I. Based on the electrochemical theory, the more-positive free corrosion potential (E_{corr}) and smaller free corrosion current density (I_{corr}) indicate an improved corrosion resistance.[32,33] It is worth noting that compared with the 304 SS, CoCrNi MEA exhibited a higher E_{corr} and lower I_{corr} in both 0.5 mol/L H_2SO_4 and 1 mol/L NaOH solutions. The results indicate that CoCrNi MEA exhibits a superior corrosion resistance than that of the 304 SS in the two different solutions.

Electrochemical impedance spectra (EIS) of CoCrNi MEA and 304 SS in the 0.5 mol/L H_2SO_4 and 1 mol/L NaOH solutions were measured at the open-circuit potential (OCP). The Nyquist and Bode spectra are shown in Fig. 7. The Nyquist spectra show that both specimens exhibit similar features. The capacitive semicircle covers the high-, mid-, and low-frequency regions; the arc radius of CoCrNi MEA is

larger than that of the 304 SS. From the Bode spectra of the two kind of materials in Figs. 7(c)–(d), only one time constant is obtained in the two different solutions. In addition, the value of $|Z|$ at a fixed frequency of 0.1 HZ in the Bode spectra usually corresponds to the polarization resistance, which reflects the corrosion resistance of the alloy in the solution.[34] As shown in Figs. 7(c)–(d), the values of $|Z|$ at 0.1 HZ for CoCrNi MEA ($\sim 2.293 \times 10^3 \ \Omega \cdot cm^2$ and $1.206 \times 10^3 \ \Omega \cdot cm^2$) are higher than those of 304 SS ($\sim 4.61 \times 10^2 \ \Omega \cdot cm^2$ and $5.75 \times 10^2 \ \Omega \cdot cm^2$) in the 0.5 mol/L H_2SO_4 and 1 mol/L NaOH solutions, respectively. Both Nyquist and Bode spectra indicate that the corrosion-resistant of CoCrNi MEA is superior to that of the 304 SS. Table II shows the equivalent-circuit parameters of CoCrNi MEA and 304 SS. The R_f of CoCrNi MEA are higher than those of 304 SS under the same conditions. This suggests that the applied potential (in the passive region) leads to the formation of stable and protective passive films in the two alloys. The passive films on the surface of CoCrNi MEA are more stable with higher protective abilities, compared to the passive films on the surface of 304 SS. These findings are consistent with the above EIS results obtained under OCP conditions.

Surface morphologies of CoCrNi MEA and 304 SS after immersions in the 0.5 mol/L H_2SO_4 and 1 mol/L NaOH solutions are shown in Fig. 8. It can be found that the surfaces were not significantly corroded, which indicates that the two kind of materials have good corrosion resistances. Figs. 8(a) and (c) show surface morphologies of CoCrNi MEA after immersions in the 0.5 mol/L H_2SO_4 and 1 mol/L NaOH solutions, respectively. Only a small number of corrosion pits were observed

on the surfaces, which suggests that CoCrNi MEA suffered only from localized corrosion. Similarly, Figs. 8(b) and (d) show surface morphologies of 304 SS after immersions in the 0.5 mol/L H_2SO_4 and 1 mol/L NaOH solutions, respectively. After the immersion in the 0.5 mol/L H_2SO_4 solution, some corrosion pits were invisible and localized corrosion also occurred at the surface. Fig. 8(d) shows that the localized and intergranular corrosions are the major corrosion types of the 304 SS after the immersion in the 1 mol/L NaOH solution.

IV. CONCLUSIONS

In this paper, CoCrNi MEA was fabricated by gas atomization and SPS. Microstructures, mechanical and magnetic properties, and corrosion resistances were characterized. The main results can be summarized as follows.

(1) As-atomized CoCrNi MEA powder (~61 μm) shows a spherical morphology and homogeneous distributions of Co, Cr and Ni. Both as-atomized CoCrNi powder and SPSed CoCrNi MEA consists of a single FCC phase.

(2) The surface of the CoCrNi powder becomes smoother as the diameter decreases. With increasing the particle size, the equiaxed-type structures are dominant, which can be attributed to the promoted eutectic process induced by decreasing the cooling rate.

(3) CoCrNi MEA exhibits a high tensile yield strength of 352 MPa, ultimate tensile strength of 799 MPa, tensile elongation to fracture of 53.6%, and hardness of 195 HV. The improved mechanical properties can be attributed to the fabrication methods and

the formation of deformation twinning.

(4) CoCrNi MEA shows a higher M_s (1.70 emu/g) and lower H_c (45.24 Oe), promising for its application as a soft magnet. Lower M_s of CoCrNi can be attributed to the higher atomic ratio of Cr (antiferromagnetic element) and larger grain size (20.8 μm).

(5) CoCrNi MEA exhibits the superior corrosion resistances to that of the 304 stainless steel in both 0.5 mol/L HCl and 1 mol/L NaOH solutions.

References

1. J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, and S.Y. Chang: Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. *Adv. Eng. Mater*. **6**, 299 (2004).

2. B. Cantor, I.T.H, Chang, P. Knight, and A.J.B. Vincent: Microstructural development in equiatomic multicomponent alloys. *Mater. Sci. Eng. A*. **375**, 213 (2004).

3. Z.G. Wu, W. Guo, K. Jin, J.D. Poplawsky: Enhanced strength and ductility of a tungsten-doped CoCrNi medium-entropy alloy. *J. Mater. Res*. **33**, 3301 (2018).

4. T. Yang, Y.L. Zhao, W.H. Liu, J.J. Kai, C. Liu: $L1_2$-strengthened high-entropy alloys for advanced structural applications. *J. Mater. Res*. **33**, 2983 (2018).

5. R.D. Li, P.D. Niu, T.C. Yuan, P. Cao, C. Chen: Selective laser melting of an equiatomic CoCrFeMnNi high-entropy alloy: Processability, non-equilibrium microstructure and mechanical property. *J. Alloys. Compd.* **746**, 125 (2018).

6. Y. Shi, L. Collins, R. Feng, C. Zhang, and N. Balke: Homogenization of Al_xCoCrFeNi high-entropy alloys with improved corrosion resistance. *Corros. Sci.* **133**, 120 (2018).

7. B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, and E.P. George: A fracture-resistant high-entropy alloy for cryogenic applications. *Science.* **345**, 1153 (2014).

8. F. Zhang, C. Zhang, S.L. Chen, J. Zhu, and W.S. Cao: An understanding of high entropy alloys from phase diagram calculations. *Calphad.* **45**, 1 (2014).

9. A. Gail and E.P. George: Tensile properties of high- and medium-entropy alloys. *Intermetallics.* **39**, 74 (2013).

10. Z.G. Wu, W. Guo, K. Jin, J.D. Poplawsky: Enhanced strength and ductility of a tungsten-doped CoCrNi medium-entropy alloy. *J. Mater. Res.* **33**, 3301 (2018).

11. J.Y. Wang, H.L. Yang, Z.L. Liu, S.X. Ji, R.D. Li, J.M. Ruan: A novel $Fe_{40}Mn_{40}Cr_{10}Co_{10}$/SiC medium-entropy nanocomposite reinforced by the nanoparticles-woven architectural structures. *J. Alloys. Compd.* **772**, 272 (2019).

12. B. Gludovatz, A. Hohenwarter, K.V.S. Thurston, H. Bei, and Z. Wu: Exceptional damage-tolerance of a medium-entropy alloy CrCoNi at cryogenic temperatures. *Nat. commun.* **7**, 10602 (2016).

13. Y.L. Zhao, T. Yang, Y. Tong, J. Wang, and J.H. Luan: Heterogeneous precipitation

behavior and stacking-fault-mediated deformation in a CoCrNi-based medium-entropy alloy. *Acta Mater.* **138**, 72 (2017).

14. Y. Ma, F. Yuan, M. Yang, P. Jiang, and E. Ma: Dynamic shear deformation of a CrCoNi medium-entropy alloy with heterogeneous grain structures. *Acta Mater.* **148**, 407 (2018).

15. J. Miao, C.E. Slone, T.M. Smith, C. Niu, and H. Bei: The evolution of the deformation substructure in a Ni-Co-Cr equiatomic solid solution alloy. *Acta Mater.* **132**, 35 (2017).

16. S. Yoshida, T. Bhattacharjee, B. Yu, and N. Tsuji: Friction stress and Hall-Petch relationship in CoCrNi equi-atomic medium entropy alloy processed by severe plastic deformation and subsequent annealing. *Scr. Mater.* **134**, 33 (2017).

17. I. Moravcik, J. Cizek, Z. Kovacova, J. Nejezchlebova, and M. Kitzmantel: Mechanical and microstructural characterization of powder metallurgy CoCrNi medium entropy alloy. *Mater. Sci. Eng. A.* **701**, 370 (2017).

18. G. Laplanche, A. Kostka, C. Reinhart, and J. Hunfeld: Reasons for the superior mechanical properties of medium-entropy CrCoNi compared to high-entropy CrMnFeCoNi. *Acta Mater.* **128**, 292 (2017).

19. Z. Li, K.G. Pradeep, Deng. Y, D. Raabe, and C.C. Tasan: Metastable high-entropy dual-phase alloys overcome the strength-ductility trade-off. *Nature.* **534**, 227 (2016).

20. J. Wang, T. Guo, J. Li, W. Jia, and H. Kou: Microstructure and mechanical properties of non-equilibrium solidified CoCrFeNi high entropy alloy. *Mater. Chem. Phys.* **210**, 192 (2018).

21. J.B. Seol, J.W. Bae, Z. Li, J.C. Han, and J.G. Kim: Boron doped ultrastrong and ductile high-entropy alloys. *Acta Mater.* **151**, 366 (2018).

22. W. Hao, H. Zhou, F. Fang, X. Hu, and Z. Xie: Strain-rate effect upon the tensile behavior of CoCrFeNi high-entropy alloys. *Mater. Sci. Eng. A.* **689**, 366 (2017).

23. Y. Deng, C.C Tasan, K.G. Pradeep, H. Springer, and A. Kostka: Design of a twinning-induced plasticity high entropy alloy. *Acta Mater.* **94**, 124 (2015).

24. T. Bhattachajee, R. Zheng, Y. Chong, S. Sheikh, and S. Guo: Effect of low temperature on tensile properties of AlCoCrFeNi$_{2.1}$ eutectic high entropy alloy. *Mater. Chem. Phys.* **210**, 207 (2018).

25. D. Li, C. Li, T. Feng, Y. Zhang, and G. Sha: High-entropy Al$_{0.3}$CoCrFeNi alloy fibers with high tensile strength and ductility at ambient and cryogenic temperatures. *Acta Mater.* **123**, 285 (2017).

26. C. Herrera, D. Ponge, and D. Raabe: Design of a novel Mn-based 1 GPa duplex stainless TRIP steel with 60% ductility by a reduction of austenite stability. *Acta Mater.* **59**, 4653 (2011).

27. Z. Wang and I. Baker: Interstitial strengthening of a f.c.c. FeNiMnAlCr high entropy alloy. *Mater. Lett.* **180**, 153 (2016).

28. M.S. Lucas, L. Mauger, J.A. Munoz, and Y. Xiao: Magnetic and vibrational properties of high-entropy alloys. *J. Appl. Phys.* **109**, 299 (2011).

29. W. Ji, W. Wang, H. Wang, J. Zhang, and Y. Wang: Alloying behavior and novel properties of CoCrFeNiMn high-entropy alloy fabricated by mechanical alloying and spark plasma sintering. *Intermetalllics.* **56**, 24 (2015).

30. Y. Zhang, T.T. Zuo, Y.Q. Cheng, and P.K. Liaw: High-entropy alloys with high saturation magnetization, electrical resistivity, and malleability. *Sci. Rep.* **3**, 1455 (2013).

31. A.Z. Arsad and N.B. Ibrahim: Temperature-dependent magnetic properties of YIG thin films with grain size less 12 nm prepared by a sol-gel method. *J. Magn. Magn. Mater.* **15**, 70 (2018).

32. X.W. Qiu, Y.P. Zhang, and C.G. Liu: Effect of Ti content on structure and properties of $Al_2CrFeNiCoCuTi_x$ high-entropy alloy coatings. *J. Alloys. Compd.* **585**, 282 (2014).

33. X.W. Qiu, Y.P. Zhang, L. He, and C.G. Liu: Microstructure and corrosion resistance of AlCrFeCuCo high entropy alloy. *J. Alloys. Compd.* **549**, 195 (2013).

34. C.A.D. Rovere, J.H. Alano, R. Silva, P.A.P. Nascente, and J. Otubo: Characterization of passive films on shape memory stainless steels. *Corros. Sci.* **57**, 154 (2012).