



Solid-Solution CrCoCuFeNi High-Entropy Alloy Thin Films Synthesized by Sputter Deposition

Zhinan An, Haoling Jia, Yueying Wu, Philip D. Rack, Allan D. Patchen, Yuzi Liu, Yang Ren, Nan Li & Peter K. Liaw

To cite this article: Zhinan An, Haoling Jia, Yueying Wu, Philip D. Rack, Allan D. Patchen, Yuzi Liu, Yang Ren, Nan Li & Peter K. Liaw (2015) Solid-Solution CrCoCuFeNi High-Entropy Alloy Thin Films Synthesized by Sputter Deposition, Materials Research Letters, 3:4, 203-209, DOI: [10.1080/21663831.2015.1048904](https://doi.org/10.1080/21663831.2015.1048904)

To link to this article: <https://doi.org/10.1080/21663831.2015.1048904>



© 2015 The Author(s). Published by Taylor & Francis.



View supplementary material [↗](#)



Published online: 01 Jun 2015.



Submit your article to this journal [↗](#)



Article views: 8436



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 51 View citing articles [↗](#)

Solid-Solution CrCoCuFeNi High-Entropy Alloy Thin Films Synthesized by Sputter Deposition

Zhinan An^{a†}, Haoling Jia^a , Yueying Wu^a, Philip D. Rack^{a,b}, Allan D. Patchen^c, Yuzi Liu^d, Yang Ren^e, Nan Li^{a,f} and Peter K. Liaw^{a*}

^aDepartment of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA;

^bCenter for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA;

^cDepartment of Earth and Planetary Science, The University of Tennessee, Knoxville, TN 37996, USA; ^dCenter for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439, USA; ^eAdvanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA; ^fSchool of Materials Science and Engineering, Beijing Institute of Science and Technology, Beijing 100081, People's Republic of China

(Received 26 February 2015; final form 4 May 2015)

Supplementary Material Available Online

The concept of high configurational entropy requires that the high-entropy alloys (HEAs) yield single-phase solid solutions. However, phase separations are quite common in bulk HEAs. A five-element alloy, CrCoCuFeNi, was deposited via radio frequency magnetron sputtering and confirmed to be a single-phase solid solution through the high-energy synchrotron X-ray diffraction, energy-dispersive spectroscopy, wavelength-dispersive spectroscopy, and transmission electron microscopy. The formation of the solid-solution phase is presumed to be due to the high cooling rate of the sputter-deposition process.

Keywords: Microstructure, Sputtering, Thin films, Solid solution

The concept of high-entropy alloys (HEAs) is a novel alloy design method that combines multi-principal metallic elements with an equal or near-equal atomic ratio to form a single-phase solid solution. This method results in high configurational entropy, which may yield better thermal stability than conventional alloys. Recent studies in this area have demonstrated many exciting properties, such as the high hardness retention up to 800°C,[1–3] high yield strengths at elevated temperatures,[4] high corrosion resistance to acids,[5,6] high fatigue and fracture resistance,[7,8] desirable balance of magnetic and mechanical properties,[8–12] etc. However, to date, elemental segregation and phase decomposition are quite common in many ‘claimed’ bulk HEAs, such as Cu segregation,[1] Cr segregation,[13,14] Ni–Al precipitation,[15] Ti–Al precipitation,[16,17] and spinodal decomposition of ordered and disordered phases [2,18] due to the negative mixing enthalpy of these elements.[19]

It has been widely reported that thin films can be applied to improve the properties of many types of materials, including amorphous and crystalline films, especially the mechanical performance of substrate materials.[20–22] Due to the unique properties of HEAs, it would be very promising to employ HEAs as a thin-film material. Amongst the reported HEA thin-film work,[23–27] Huang et al. [24] reported the sputter deposition of an amorphous phase of an AlCrCoCu_{0.5}FeNi film. Dolique et al. [25] deposited crystalline films and determined that the microstructure of the film was dependent on the operating power of the sputtering target. The simple face-centered cubic (FCC) crystalline Al_{0.5}CrCoCuFeNi film solid solution was first reported in 2004 by Chen et al. [23] based on the lab X-ray diffraction (XRD) results. However, a recent paper reported Cr-phase separation in an HEA, whereas the XRD showed only a single FCC structure.[13] The observation of a single-crystal structure via XRD does

*Corresponding author. Email: pliaw@utk.edu

†Deceased.

not necessarily imply that the HEA is a single phase, primarily because XRD is not necessarily sensitive to second phases that have extremely small amounts [28] and/or that have some degree of lattice coherency with the matrix, for example, the possibility of Cu precipitates in the CrCoCuFeNi HEA alloys used in the present study. Another reason that the typical XRD data may miss the existence of a possible ordered phase is the similarity of the scatter factors of elements from the ordered phase and the matrix. In the case of the CrCoCuFeNi alloy, all five elements have quite similar scatter factors to any photon energy that is away from their absorption edges. Therefore, some ordered phases, such as FeNi₃ ordered structure,[29] will be invisible to the XRD. In order to identify the presence of a second phase, especially when present in small concentrations, not only does the structure have to be investigated via the high-quality XRD experimentation, but also quantified compositional changes over different length scales have to be performed.

Despite the conclusions of the earlier work, sputter deposition has the advantage of fabricating structure-controllable high-entropy films. The present study focuses on comparing the microstructure and composition distributions of an as-deposited sputtered thin film and an as-cast bulk CrCoCuFeNi alloy. The microstructures of the as-cast alloy and radio-frequency (RF) magnetron sputter-deposited CrCoCuFeNi high-entropy film are studied, using high-energy synchrotron X-ray with transmission diffraction for the bulk materials and grazing incident X-ray scattering (GIXS) for thin films. Additionally, the chemical-composition distributions were characterized on different length scales employing: scanning electron microscopy (SEM) equipped with the energy-dispersive spectroscopy (EDS) and wavelength-dispersive spectroscopy (WDS) capabilities, as well as nanoscaled elemental analyses under transmission electron microscopy (TEM).

Chromium, cobalt, copper, iron, and nickel pure metals (> 99.99%, weight percent) were used to fabricate the target. An RF magnetron sputtering system was used to deposit the films in a vacuum chamber at room temperature (RT) with the base pressure of 4×10^{-7} Pa. The Ar gas flow was 25 sccm, and the chamber pressure was maintained at 0.67 Pa (5 mTorr) during sputtering. The RF power was set to 200 W. The film thickness was controlled to be ~ 800 nm based on the measured sputter rate of ~ 4 nm/min. The surface morphology and the chemical composition were examined on a field-emission LEO 1512 SEM equipped with EDS and WDS on a Cameca SX-100 electron microprobe. For the EDS characterization, the operating conditions were 20 keV and 100 s count time. For elements with extremely small concentrations, the EDS results may not be reliable, since its sensitivity is of the order of 1%. In such cases,

a more precise technique, WDS, was applied to measure the chemical composition for dilute elements. For WDS, pure metals were used as standards, and the Pouchou and Pichoir (PAP) model [30] was applied for corrections. The operating conditions were 15 keV, 20 nA electron beam, and 30 s count collection time on the peaks and background. High-energy synchrotron XRD studies were performed at the Advanced Photon Source (APS) of the Argonne National Laboratory (ANL). Transmission XRD was conducted on the bulk alloy with the 115 keV incident beam energy at the beam line of 11-ID-C at APS. For the film sample, GIXS was performed with the 20 keV incident beam energy and 0.5° grazing angle at the beam line of 33-BM [31] at APS. The cross-sectional TEM specimen was prepared by the lift-out in dual-beam scanning electron microscope/focused ion beam (DB-SEM/FIB) systems.[32] It should be noted that a ~ 200 nm thick layer of Pt was deposited across the entire lift-out bar from the *in situ* FIB gas injection system to avoid the ion-beam damage on the lamella. The lamella was showered by the 5 kV ion beam to remove the damage layer on the surface of the TEM specimen. The sample was characterized on a JEOL 2100F working under 200 keV and equipped with the Gatan GIF Quantum[®] system. The three-window background subtraction method for the energy-filtered TEM [33] was applied to obtain the elemental distributions of Cr, Co, Fe, Ni, and Cu.

Synchrotron XRD results indicate that two FCC structure phases exist in the as-cast bulk CrCoCuFeNi alloy, as shown in Figure 1. The small peak separation in the inset in Figure 1(a) indicates a slight difference in the lattice constants between the two FCC phases. By averaging the calculated lattice constants from all measurable FCC peaks, one FCC-phase lattice constant is calculated to be 3.61 Å, whilst the other one is calculated to be 3.58 Å. The thin film shows crystalline diffraction features with just one FCC structure, also shown in Figure 1(b).

The film has a strong (111)_{FCC} preferential orientation along the film growth direction, which is due to the surface-energy-controlled grain growth. An increase of the planar-packing density reduces the number of unsatisfied atomic bonds, resulting in a lower surface energy.[34] For materials with the FCC crystalline structures, the lowest surface energy planes are the 111 family of planes, which have been numerically calculated, using the embedded atom model.[35] It is worth noting that the final thickness of the film also has a strong effect on the extent of the preferential orientation for FCC materials,[36,37] which may be due to the increasing influence of the strain-energy minimization with increasing film thickness. The present experimental results show that the film strain is not sufficient to compete with the surface-energy factor. A possible explanation for this trend may be that the film was deposited at RT

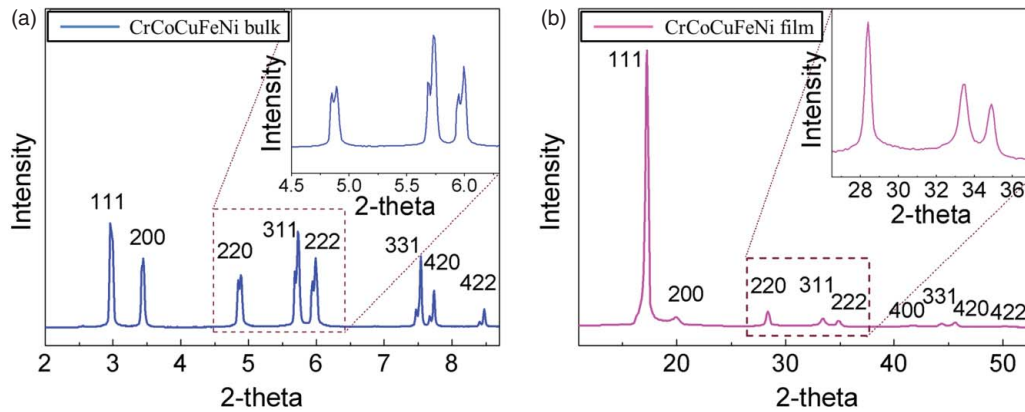


Figure 1. High-energy synchrotron XRD of as-deposit CrCoCuFeNi films and as-cast CrCoCuFeNi alloys serving as the target material for film deposition.

without an additional substrate bias, which can reduce the effect of thermal strains significantly. A surface-energy-dominated film growth at RT in vapor deposition [38] is widely observed in such deposition experiments, which has been demonstrated by Lee's [39] and Carel et al.'s [40] models.

The two phases in the as-cast bulk alloy are evident on the EDS maps acquired in SEM, as shown in Figure 2(a). These phases contain a Cu-poor phase

with a dendritic morphology that formed during casting, and a Cu-rich interdendritic phase. The average size of dendritic arms is of the order of 10 μm . The mechanisms of phase segregation in the HEA and amorphous alloys have been investigated, using the approach of density-functional-theory modeling by Middleburgh et al. [41,42]. Their results indicate that, for the CrCoFeNi HEA alloy, the vacancy-formation energies of Co, Fe, and Ni are positive, which is expected as a stable solid.

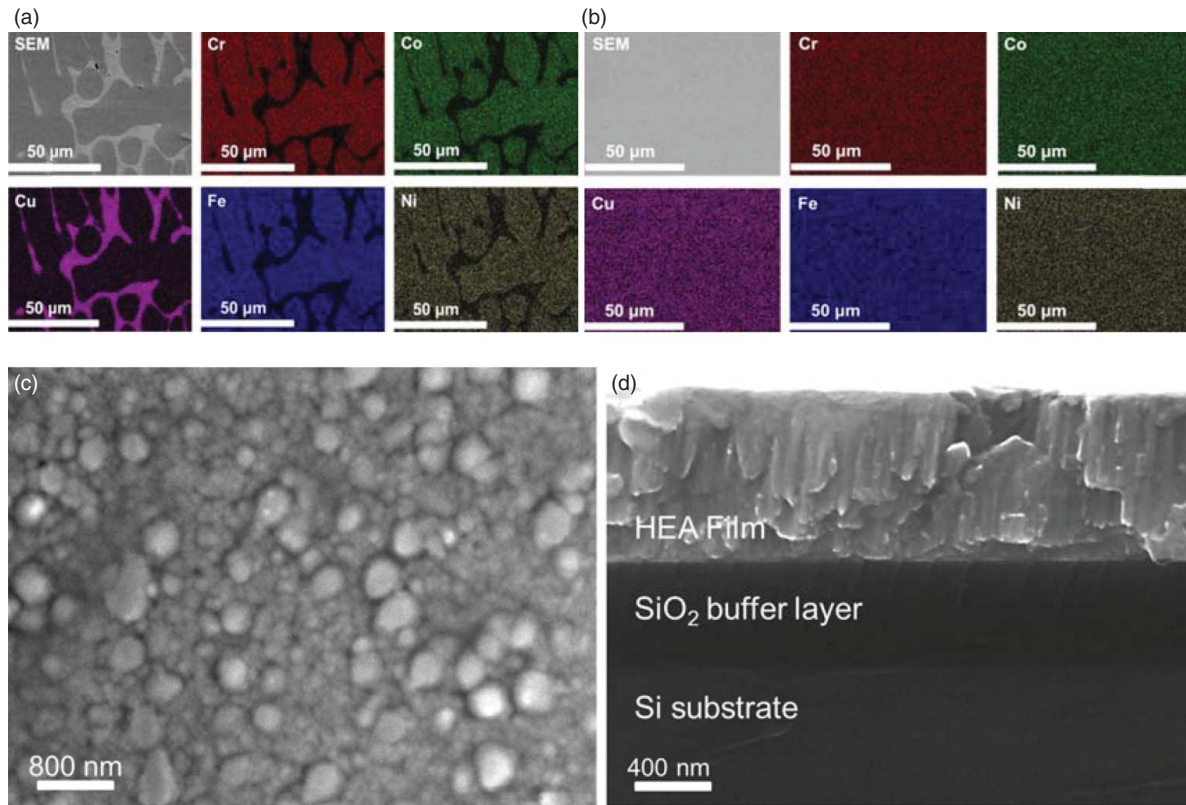


Figure 2. SEM microstructure images and elemental distributions determined by EDS: (a) as-cast bulk CrCoCuFeNi alloys; (b) as-deposited CrCoCuFeNi alloy films; (c) grain structures on the top surface of the as-deposited film; and (d) grain structures on the cross-sectional surface of the as-deposited film.

Table 1. Chemical compositions of the CrCoCuFeNi bulk target (average, dendrites, and interdendrites), and the as-deposited film measured with different methods.

Sample	Method	Cu	Cr	Co	Fe	Ni
Bulk average	EDS	19.5	20.4	20.0	20.2	19.9
Bulk dendrites	WDS	10.1	22.9	23	23.6	20.4
Bulk interdendrites	WDS	83.2	2.4	3	3.2	8.2
Film average	EDS	23.3	18.9	18.9	18.9	20.0
Film average	WDS	23.7	19.1	18.8	18.8	19.6

Note: Values are given in atomic ratio (%).

However, the vacancy-formation energy of Cr is negative, which indicates a thermodynamic drive for Cr to segregate. This segregation mechanism can also be applied to explain the phenomenon observed in the present work. The differences of the elemental compositions of the two phases in the bulk alloy are given in Table 1. It can be noticed that the Cr element has the lowest composition percentage in the interdendrites region of the bulk HEA specimens compared to the other compositions, which indicates that most of the Cr serve as the stabilizer, and result in the segregation of the current HEA alloys.

In contrast to the strong Cu elemental separation observed in the bulk alloy, the thin-film sample exhibited a relatively-uniform distribution of all elements at the micrometer scale on the surface (Figure 2(b)), which indicates that the sputtering technique improves the uniformity of the composition. Sputtering is effective in depositing alloy films from a single target even though individual elements have different sputter yields, because the surface composition of the target equilibrates after a pre-sputter step. The sputter-deposited materials have the same stoichiometry as the original target alloy. Additionally, the energetic atoms/molecules can quench condensate rapidly ($\sim 10^9$ K/s) for thin films, thereby minimizing concentration fluctuations in the films, which is consistent with the work of Singh et al.[18] They found that only one body-centered cubic (BCC) phase appeared in the quenched alloy (a cooling rate of 10^6 – 10^7 K/s), whereas multi-phases, including one BCC and two FCC phases, were detected in the cast alloy (a cooling rate of 10–20 K/s). Although the surface diffusion from species that arrive off-normal to the substrate, and substrate heating at high sputter rates, can influence the as-deposited composition, it appears that under the conditions used in the present work, the concentration fluctuations observed in the film materials have been greatly minimized.

Although the sputtering technique can minimize the concentration fluctuation, a slight difference in the Cu concentration between the bulk and the as-deposited film samples can also be found (Table 1). The slight enrichment of Cu observed in the as-deposited film may be due to an insufficient pre-sputter (as described in the

experimental section). During the pre-sputter process, elements with higher sputtering yields sputter faster, leaving a smaller volume fraction of these elements on the target surface. Since the total sputtering rate of an element is the production of its sputter yield and its surface–volume fraction, the ultimate result of the pre-sputter process attains a sputter rate ratio for all the elements that is the same as the elemental volume fraction in the target. If the pre-sputter is insufficient, the element with a higher sputtering yield is likely to have a higher sputtering rate. Consequently, an insufficient pre-sputter for this alloy target will result in a higher Cu concentration in the film, because Cu has the highest sputtering yield amongst all the target elements. In this case, the growth of the CrCoCuFeNi film will start with a slightly higher Cu concentration and terminate with equal atomic ratios at the final steady state.

The morphology of the as-deposited CrCoCuFeNi film was characterized with the use of SEM for both the top surface (Figure 2(c)) and the cross section (Figure 2(d)), which exhibits the columnar grains in the thin film with an average grain width about several tens of nanometers. The columnar grains can also be observed in TEM with a better resolution, which is shown in Figure 3(a). A magnified area on the column structure is displayed in Figure 3(b), which is marked with a red square in Figure 3(a). Extensive stacking faults can be observed all over the film in this column-grain region. Note that the total film thickness is ~ 800 nm, as observed in Figure 2(d). However, in the cross-sectional TEM results (Figure 3(a)), the film thickness is ~ 200 nm, which is due to the fact that the film is over milled during the TEM-sample preparation process. It means that part of the thin film is removed in the TEM images (Figure 3).

Due to the limited resolution of the EDS mapping image (~ 500 nm), any phase separation at the nanometer scale could not be positively determined. With the use of TEM, any compositional partitioning within the thin film is possible to be observed on a finer scale. For an arbitrary small volume, roughly $600 \times 200 \times 50$ nm³ (thickness), all the elements are almost uniformly distributed, as shown in Figure 3(c). All five-element distributions are shown in Figure 3(d). A second Cu-element mapping under TEM (in supporting materials) on a different as-deposited CrCoCuFeNi HEA film sample also indicates a similar uniform distribution as in Figure 3(c). Hence, the elemental analysis on fine scales suggests that the five elements are distributed in a near-perfect uniform solid solution in the as-deposited CrCoCuFeNi film.

Combining the TEM result with the single FCC structure obtained from XRD, it was determined that the as-deposited CrCoCuFeNi film is predominantly a single-phase solid solution. Although the Cu element may have a slight concentration gradient along the

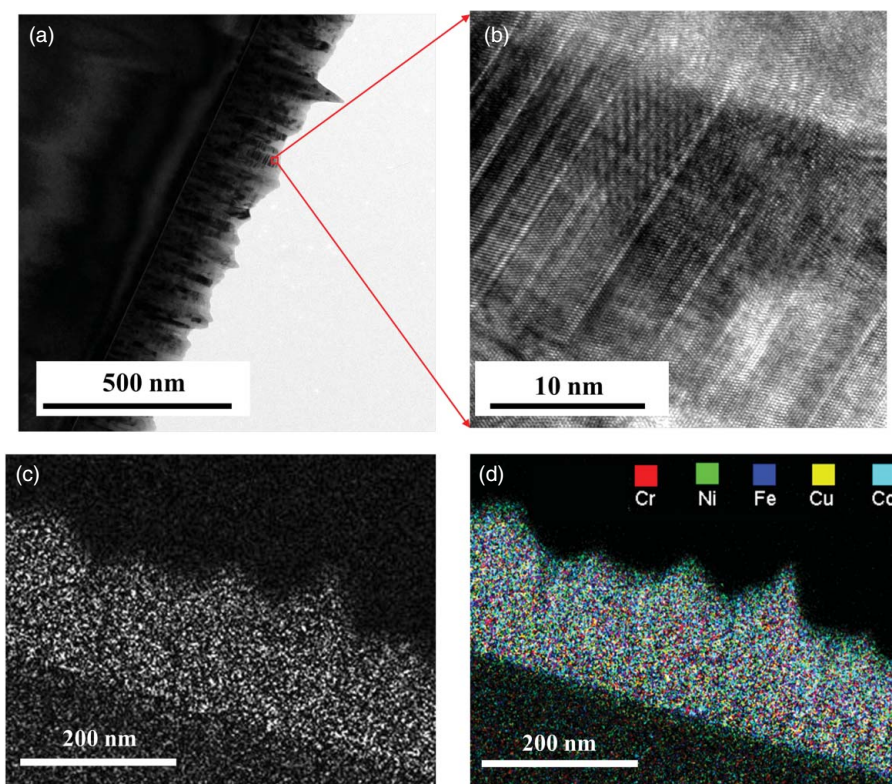


Figure 3. (a) TEM micrograph of the as-deposited films. (b) An enlarged region of (a), as marked in the red square box. Energy-filtered TEM results under TEM representing the Cu elemental distribution (c), and Cr, Co, Cu, Fe, and Ni elemental distribution (d) in an as-deposited film.

film-thickness direction, which will be explained in our future study, the Cu element still forms a solid solution in the matrix. Note that a single phase does not have to be exactly the same composition throughout the whole sample; fluctuation within a limited range should be acceptable, as long as the fluctuation does not result in a second phase. In the studied CrCoCuFeNi film, no obvious Cu segregations at either nanometer scale or micrometer scale could be observed. Therefore, the sputtering technique has great potential for fabricating solid-solution films.

In summary, the RF-sputtering technique is capable of depositing CrCoCuFeNi single-phase solid-solution films from a two-phase bulk target. The single-phase solid solution was confirmed by different techniques, including high-energy synchrotron XRD for the lattice structure determination as well as SEM/EDS, WDS, and TEM for the chemical-composition analysis. The sputtered film favors a much more uniform elemental distribution due to fast quenching in the sputter procedure, compared to the as-cast target. The Cu segregation in this system is dynamically limited due to the high quenching rate and low diffusivity, indicating that the sputter technique is a good way of fabricating multi-principal-element solid-solution films.

Acknowledgements We very much appreciate the financial support from the US National Science Foundation (DMR-0909037, CMMI-0900271, and CMMI-1100080), the Department of Energy (DOE), Office of the Nuclear Energy's Nuclear Energy University Program (NEUP) 00119262, the DOE, Office of Fossil Energy, National Energy Technology Laboratory (DE-FE-0008855, DE-FE-0011194, and DE-FE-0024054), and the Army Research Office (W911NF-13-1-0438) with C. Huber, C.V. Cooper, A. Ardell, E. Taleff, V. Cedro, R. Dunst, R.O. Jensen, L. Tan, S. Lesica, J. Mullen, and D. Sterr as contract monitors. PDR acknowledges support from NSF grant No. CBET-1235651. The use of the 33-BM and 11-ID-C at the Advanced Photon Source and Center for Nanoscale Materials at the Argonne National Lab was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The authors also appreciate the enlightening discussion with E.A. Karapetrova.

Disclosure statement No potential conflict of interest was reported by the authors.

Supplementary online material. A more detailed information on experiments is available at <http://dx.doi.org/10.1080/21663831.2015.1048904>.

ORCID

Haoling Jia  <http://orcid.org/0000-0002-4287-2929>

References

- [1] Tong CJ, Chen MR, Chen SK, Yeh JW, Shun TT, Lin SJ, Chang SY. Mechanical performance of the Al_xCoCrCuFeNi high-entropy alloy system with multiprincipal elements. *Metall Mater Trans A*. 2005;36A:1263–1271.
- [2] Yeh JW, Chen SK, Lin SJ, Gan JY, Chin TS, Shun TT, Tsau CH, Chang SY. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. *Adv Eng Mater*. 2004;6:299–303.
- [3] Zhang Y, Zhou YJ, Lin JP, Chen GL, Liaw PK. Solid-solution phase formation rules for multi-component alloys. *Adv Eng Mater*. 2008;10:534–538.
- [4] Senkov ON, Wilks GB, Miracle DB, Chuang CP, Liaw PK. Refractory high-entropy alloys. *Intermetallics*. 2010;18:1758–1765.
- [5] Chen YY, Duval T, Hung UD, Yeh JW, Shih HC. Microstructure and electrochemical properties of high entropy alloys—a comparison with type-304 stainless steel. *Corros Sci*. 2005;47:2257–2279.
- [6] Chen YY, Hong UT, Shih HC, Yeh JW, Duval T. Electrochemical kinetics of the high entropy alloys in aqueous environments—a comparison with type 304 stainless steel. *Corros Sci*. 2005;47:2679–2699.
- [7] Hemphill MA, Yuan T, Wang GY, Yeh JW, Tsai CW, Chuang A, Liaw PK. Fatigue behavior of Al_{0.5}CoCrCuFeNi high entropy alloys. *Acta Mater*. 2012;60:5723–5734.
- [8] Zhang Y, Zuo TT, Tang Z, Gao MC, Dahmen KA, Liaw PK, Lu ZP. Microstructures and properties of high-entropy alloys. *Prog Mater Sci*. 2014;61:1–93.
- [9] Zhang Y, Zuo TT, Cheng YQ, Liaw PK. High-entropy alloys with high saturation magnetization, electrical resistivity, and malleability. *Sci Rep*. 2013;3:1455-1–1455-7.
- [10] Gludovatz B, Hohenwarter A, Catoor D, Chang EH, George EP, Ritchie RO. A fracture-resistant high-entropy alloy for cryogenic applications. *Science*. 2014;345:1153–1158.
- [11] Antonaglia J, Xie X, Tang Z, Tsai CW, Qiao JW, Zhang Y, Laktionova MO, Tabachnikova ED, Yeh JW, Senkov ON, Gao MC, Uhl JT, Liaw PK, Dahmen KA. Temperature effects on deformation and serration behavior of high-entropy alloys (HEAs). *JOM*. 2014;66:2002–2008.
- [12] Tang Z, Gao MC, Diao H, Yang T, Liu J, Zuo T, Zhang Y, Lu Z, Cheng Y, Zhang Y, Dahmen KA, Liaw PK, Egami T. Aluminum alloying effects on lattice types, microstructures, and mechanical behavior of high-entropy alloys systems. *JOM*. 2013;65:1848–1858.
- [13] Chen ST, Tang WY, Kuo YF, Chen SY, Tsau CH, Shun TT, Yeh JW. Microstructure and properties of age-hardenable Al_xCrFe_{1.5}MnNi_{0.5} alloys. *Mat Sci Eng A*. 2010;527:5818–5825.
- [14] Cantor B. Multicomponent and high entropy alloys. *Entropy*. 2014;16:4749–4768.
- [15] Santodonato LJ, Zhang Y, Feyngenson M, Parish CM, Gao MC, Weber RJ, Neufeld JC, Tang Z, Liaw PK. Deviation from high-entropy configurations in the atomic distributions of a multi-principal-element alloy. *Nat Commun*. 2015;6:5964-1–5964-14.
- [16] Chuang MH, Tsai MH, Wang WR, Lin SJ, Yeh JW. Microstructure and wear behavior of Al_xCo_{1.5}CrFeNi_{1.5}Ti high-entropy alloys. *Acta Mater*. 2011;59:6308–6317.
- [17] Chen SY, Yang X, Dahmen KA, Liaw PK, Zhang Y. Microstructures and crackling noise of Al_xNbTiMoV high entropy alloys. *Entropy*. 2014;16:870–884.
- [18] Singh S, Wanderka N, Murty BS, Glatzel U, Banhart J. Decomposition in multi-component AlCoCrCuFeNi high-entropy alloy. *Acta Mater*. 2011;59:182–190.
- [19] Takeuchi A, Inoue A. Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element. *Mater Trans*. 2005;46:2817–2829.
- [20] Jia HL, Liu FX, An ZN, Li WD, Wang GY, Chu JP, Jang JSC, Gao YF, Liaw PK. Thin-film metallic glasses for substrate fatigue-property improvements. *Thin Solid Films*. 2014;561:2–27.
- [21] Chu JP, Greene JE, Jang JSC, Huang JC, Shen YL, Liaw PK, Yokoyama Y, Inoue A, Nieh TG. Bendable bulk metallic glass: effects of a thin, adhesive, strong, and ductile coating. *Acta Mater*. 2012;60:3226–3238.
- [22] Chu JP, Liu T-Y, Li C-L, Wang C-H, Jang JSC, Chen M-J, Chang S-H, Huang W-C. Fabrication and characterizations of thin film metallic glasses: antibacterial property and durability study for medical application. *Thin Solid Films*. 2014;561:102–107.
- [23] Chen TK, Shun TT, Yeh JW, Wong MS. Nanostructured nitride films of multi-element high-entropy alloys by reactive DC sputtering. *Surf Coat Technol*. 2004;188:193–200.
- [24] Huang YS, Chen L, Lui HW, Cai MH, Yeh JW. Microstructure, hardness, resistivity and thermal stability of sputtered oxide films of AlCoCrCu_{0.5}NiFe high-entropy alloy. *Mat Sci Eng A*. 2007;457:77–83.
- [25] Dolique V, Thomann AL, Brault P, Tessier Y, Gillon P. Complex structure/composition relationship in thin films of AlCoCrCuFeNi high entropy alloy. *Mater Chem Phys*. 2009;117:142–147.
- [26] Dolique V, Thomann AL, Brault P, Tessier Y, Gillon P. Thermal stability of AlCoCrCuFeNi high entropy alloy thin films studied by in-situ XRD analysis. *Surf Coat Technol*. 2010;204:1989–1992.
- [27] Wu ZF, Wang XD, Cao QP, Zhao GH, Li JX, Zhang DX, Zhu J-J, Jiang JZ. Microstructure characterization of Al_xCo₁Cr₁Cu₁Fe₁Ni₁ ($x = 0$ and 2.5) high-entropy alloy films. *J Alloys Compd*. 2014;609:137–142.
- [28] Fu XL, Li Y, Schuh CA. Mechanical properties of metallic glass matrix composites: effects of reinforcement character and connectivity. *Scr Mater*. 2007;56:617–620.
- [29] Lucas MS, Wilks GB, Mauger L, Munoz JA, Senkov ON, Michel E, Horwath J, Semiatin SL, Stone MB, Abernathy DL, Karapetrova E. Absence of long-range chemical ordering in equimolar FeCoCrNi. *Appl Phys Lett*. 2012;100:251907-1–251907-4.
- [30] Pouchou JL, Pichoir F. Quantitative microanalytic possibilities using a new formulation of matrix effects. *J Phys*. 1984;45:17–20.
- [31] Karapetrova E, Ice G, Tischler J, Hong HW, Zschack P. Design and performance of the 33-BM beamline at the advanced photon source. *Nucl Instrum Methods Phys Res, Sect A*. 2011;649:52–54.
- [32] Mihajlovic G, Schreiber DK, Liu YZ, Pearson JE, Bader SD, Petford-Long AK, Hoffmann A. Enhanced spin signals due to native oxide formation in Ni₈₀Fe₂₀/Ag lateral spin valves. *Appl Phys Lett*. 2010;97:112502-1–112502-3.
- [33] Hofer F, Warbichler P, Grogger W. Imaging of nanometer-sized precipitates in solids by electron spectroscopic imaging. *Ultramicroscopy*. 1995;59:15–31.

- [34] Penn RL, Banfield JF. Imperfect oriented attachment: dislocation generation in defect-free nanocrystals. *Science*. 1998;281:969–971.
- [35] Daw MS, Baskes MI. Embedded-atom method—derivation and application to impurities, surfaces, and other defects in metals. *Phys Rev B*. 1984;29:6443–6453.
- [36] Hasmy A, Medina E. Thickness induced structural transition in suspended fcc metal nanofilms. *Phys Rev Lett*. 2002;88:096103-1–096103-4.
- [37] Diao JK, Gall K, Dunn ML. Surface-stress-induced phase transformation in metal nanowires. *Nat Mater*. 2003;2:656–660.
- [38] Zhang JM, Xu KW, Ji V. Competition between surface and strain energy during grain growth in free-standing and attached Ag and Cu films on Si substrates. *Appl Surf Sci*. 2002;187:60–67.
- [39] Lee DN. A model for development of orientation of vapor deposits. *J Mater Sci*. 1989;24:4375–4378.
- [40] Carel R, Thompson CV, Frost HJ. Computer simulation of strain energy effects vs. surface and interface energy effects on grain growth in thin films. *Acta Mater*. 1996;44:2479–2494.
- [41] King DJM, Middleburgh SC, Liu ACY, Tahini HA, Lumpkin GR, Cortie MB. Formation and structure of V–Zr amorphous alloy thin films. *Acta Mater*. 2015;83:269–275.
- [42] Middleburgh SC, King DM, Lumpkin GR, Cortie M, Edwards L. Segregation and migration of species in the CrCoFeNi high entropy alloy. *J Alloys Compd*. 2014;599:179–182.