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Deposition of high entropy alloy sub-surface films on metal substrates via DC magnetron sputtering with a CoCrFeMnNi target ⊘

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ABSTRACT

High entropy alloys and high entropy alloy films (HEFs) are gaining increasing attention in the research community due to their superior mechanical properties. CoCrFeMnNi is one of the most investigated of these alloys in the literature; however, CoCrFeMnNi HEFs have not yet been extensively reported. To improve our understanding of the processes occurring during fabrication of CoCrFeMnNi HEFs, here, DC magnetron sputtering using a CoCrFeMnNi equimolar target is used to deposit HEFs on glass substrates, A5052 aluminum sheets, and S45C steel sheets. The resulting HEFs are observed to be embedded as sub-surface bands, less than a micrometer under the substrate surface. This is attributed to implantation of the HEF elements into the base material due to the high deposition energy of sputtering. Another possibility is that substrate elements migrate to the surface in an Ar plasma-assisted process. The HEF crystallite size on glass substrates was determined by x-ray diffraction to be several nanometers, meaning that high hardness is expected in HEFs produced by DC magnetron sputtering.

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High entropy alloys (HEAs) composed of five or more multicomponent elements in equimolar ratios are attracting increasing attention due to their exhibition of excellent mechanical properties over a range of different temperatures.^{1–3} HEAs are also characterized by the formation of single-phase alloys, despite the fact that the alloy design guidelines for HEAs are completely different from those for conventional alloys.² Typical isomorphic alloys that have been widely studied include $Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$ alloy with FCC structure (also called the Cantor alloy) and $Ti_{20}Zr_{20}Hf_{20}Nb_{20}Ta_{20}$ alloy with BCC structure. HEAs have been produced as a casting alloy, which often employs arc melting because of the relatively high melting temperature of the constituent elements. As a result, the crystal grain size is generally coarse, and attempts have been made to refine/control the grain size by subsequent thermomechanical processes.^{4–7}

HEAs are not only used in a bulk form, but have also been explored in thin films as coating materials.^{8–10} One downside of HEAs is the inclusion of relatively expensive elements. For example, Cantor alloy contains Cr, Mn, Co, and Ni, which are much more costly

compared with Fe. In such cases, thin films are one of the options to reduce the production costs, which could pave the way for practical application of HEAs. For instance, hot-dip plating is widely used to generate protective coatings for bulk/sheet steel. However, the hot-dip method cannot be used for, e.g., Cantor alloys due to their high melting temperature.

Sputtering is a physical vapor deposition (PVD) method, which is often used for thin film deposition, and is not restricted by melting temperature. Furthermore, HEA films (HEFs) reportedly generated by this technique include not only metallic films, ^{11–15} but also nitride, oxide, and oxynitride films.^{8–10,16} For instance, Cantor HEF has been deposited on Si substrates using DC magnetron sputtering with a Cantor alloy target. In this study, we attempt to deposit HEFs onto various substrates, including S45C steel sheets, A5052 aluminum alloy sheet, and glass substrates, using a $Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$ HEA target prepared by casting. This is undertaken to understand more about the relationship between the processing conditions and resulting Cantor HEF deposited by DC sputtering.

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Figures 1(a) and 1(b) show a schematic diagram and photograph of the DC magnetron sputtering apparatus used in this study, respectively. The sputtering apparatus consists of a vacuum chamber having a window, a rotary pump (RP, Osaka vacuum VRD-16), a turbo molecular pump (TMP, Osaka vacuum TG350FCAB), and a DC magnetron sputtering gun (MeiVac MAK3.0), which can mount a 3-in. target connected with a DC power supply (ALVAC DCS0052B). A substrate was placed on a rotating substrate holder, which is parallel to the sputtering target with a separation distance of 120 mm.

A cast Cantor alloy was used as a 3-in. target, and the chemical composition of the target was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) as shown in Table I. The vacuum chamber was pumped down to less than 1.0×10^{-4} Pa, which is the same order of the previously reported Cantor films deposited by DC magnetron sputtering.¹¹ An Ar gas with a purity of 99.999% was used as the sputter gas and introduced to the chamber with a flow rate of 10 standard cubic centimeters per minute (sccm). The gas pressure was controlled to 0.7 Pa using a manual gate valve. The target was first cleaned by Ar plasma with an input power of 300 W for 5 min, with the target shutter closed. The substrate holder was rotated at 300 rpm. The DC power supply was set to either 100, 200, and 300 W.

Three types of substrates were selected: S45C steel sheet; A5052 aluminum alloy sheet; and glass substrates. Glass slides of approximately $76 \times 26 \text{ mm}^2$ and 0.9 mm thick (Matsunami Glass Co. S1111) were used, and S45C and A5052 sheets was cut from blocks or sheets of approximately $12 \times 12 \text{ mm}^2$ size and 1 mm thickness using a wire



FIG. 1. (a) Schematic diagram and (b) photograph of the sputtering apparatus. (c) Glass substrate after creating a mask of patterned lines. (d) Glass substrate after depositing a film and removal of the mask. (e) Schematic illustration of the cross section of a HEF deposited on a glass substrate.

TABLE I. Chemical composition of the target as measured by ICP.

Chemical composition (at. %)	Cr	Mn	Fe	Со	Ni
Target (ICP)	20.0	19.9	20.1	19.9	20.1

electrical discharge machine (Brother HS-300). The target film thickness on S45C and A5052 substrates was set to $1 \,\mu$ m based on the growth rate evaluated using the films deposited on glass slides.

Steps were fabricated on the glass slides for film thickness measurement analogous to a liftoff process.¹⁷ First, straight lines were drawn using a permanent pen as a mask, as shown in Fig. 1(c). Next, sputtering was carried out. Then, the film deposited on the masked lines was removed by ultrasonication in acetone for 5 min. Consequently, steps were fabricated every 5 mm, as shown in Figs. 1(d) and 1(e). Finally, the film thickness was measured with a 3D surface roughness measuring machine (Zygo, NexviewTM NX2) otherwise known as a coherence scanning interferometer profiler.

The A5052 sheet was cut by EDM and then heat treated in ambient conditions in a furnace (Denken KDF 007EX) at a temperature of 673 K for 1 h. S45C was annealed at 1173 K for 1 h in a vacuumed quartz tube in the same furnace. The furnace was left to cool after annealing. The metal blocks and sheets were thermo-mechanically formed, which results in deformation microstructure. The abovementioned annealing was performed to cancel the deformation microstructure by recrystallization. After annealing, the sheets were mechanically polished using emery paper up to #4000 and then buffed with α -alumina with diameter down to 0.06 μ m.

Compositional analysis was performed on the surface of the deposited HEF on glass slides using energy dispersive x-ray spectroscopy (EDS) with a scanning electron microscope (SEM, JEOL JSM-6390A with EDS, JEOL JED-2300A). The acceleration voltage was 20 kV, and the working distance was 10 mm. A thin film sample with a thickness of 1 μ m on a glass substrate with an input power of 300 W was measured. Ten measurements were made near the center of the specimen, and the average value was taken as the composition of the film.

In addition to surface compositional analysis by SEM/EDS, crosssectional SEM/EDS measurements were also carried out by a fieldemission type SEM (JEOL JSM-7900F) with EDS detector (Oxford instrument, Ultim max) controlled by software (Oxford Instruments Aztec). The acceleration voltage was set to be 20 kV. To prepare specimens for cross-sectional SEM/EDS measurements, a cross-sectional Ar ion milling machine (Hitachi high-tech IM4000PLUS) was used with an acceleration voltage of 4 kV, a discharge voltage of 1.5 kV, a swing angle of $+-30^{\circ}$, and swing speed of 30 round trips/min up to several hours.

The crystal structure of the resulting films was performed using an x-ray diffractometer (X'Pert PRO MPD, PANalytical), with a Cu tube and a divergence slit width of 0.5° . The measurement conditions included a tube voltage of 45 kV, a tube current of 40 mA, and a step angle of $0.008\,356^{\circ}$. The Cu-k α line with a wavelength of $0.154\,18$ nm ($\sim 8.041.5$ keV) was used.

Table II shows the compositions of the Cantor alloy target and the resulting HEF deposited on a glass slide, as measured using SEM/EDS. These results indicate that the composition of the five metallic elements of HEF is within ± 3 at. % of that for target. Therefore, it is

TABLE II.	Chemical	composition	of the	Cantor	alloy	target	and	the	resulting	HEF
deposited	on a glass	slide, as mea	asured	by SEM	/EDS					

Chemical composition (at. %)	Cr	Mn	Fe	Со	Ni
(a) Target (EDS)	20.6	20.6	20.0	19.3	19.5
(b) Film (EDS)	22.9	21.3	19.8	18.8	17.1

evident that the compositions of the Cantor alloy target and the HEF can be regarded as almost identical.

Figure 2(a) shows the variation of HEF thickness (on glass) after deposition with an input power of 300 W, as measured using 3D surface roughness measuring equipment. From Fig. 2(a), the thickness of the films is confirmed to be uniform, and the coefficients of variation (C_V) for each deposition time were evaluated using Eq. (1) and are summarized in Table III,

$$C_{\rm V} = \frac{\sigma}{\bar{x}}.$$
 (1)

Here, σ is the standard deviation, and \bar{x} is the mean value. From Table III, it is evident that C_V is less than 0.02 in all cases, indicating that spatially homogeneous HEFs can be deposited by sputtering, regardless of the deposition time.

Figures 2(b) and 2(c) show the time dependence of film thickness with an input power of 300 W, as well as the dependance of film thickness on input power when the deposition time is fixed at 15 min, respectively. The red lines in Figs. 2(b) and 2(c) are the results of linear fitting. Both relationships are linear, so the deposition rate at 300 W could be evaluated to be 27.8 nm/min, and the dependance on power input was calculated to be 0.09 nm/W/min.

Figure 3 shows cross-sectional images of the HEF deposited on an A5052 substrate, obtained using SEM/EDS. Figures 3(a) and 3(b) show secondary electron images (SEI) and backscattered electron images (BEI), in which a band of darker contrast with a thickness of around 1 μ m is observed at a depth of around 0.3 μ m below the surface. In particular, the BEI image more clearly displays this band-like contrast, which is attributed to spatial differences in the constituent elements of the film throughout the cross section. To give further insight into this band, cross sections in this region were analyzed by two-dimensional (2D) EDS mapping, as shown in Figs. 3(c)-3(i). The white dashed lines indicate the position of the sample surface, and all the constituent elements of the Cantor alloy target were confirmed to be present in the layered band. From these results, it is confirmed that there is a sub-surface layer of around 1 μ m in thickness, containing Cr, Mn, Fe, Co, and Ni, located around 0.3 μ m below the substrate surface. From 2D EDS mapping, it can be concluded that the Cantor constituent elements are implanted and embedded inside the A5052 substrate by sputtering. It is also noted that the surface aluminum layer is oxidized.

Similarly, Fig. 4 shows the result of cross-sectional SEM/EDS observation of a HEF deposited on an S45C substrate. In this case, again a sub-surface band is observed, with a thickness of around 1.5 μ m, located around 0.3 μ m below the surface. However, in this case, there is very low contrast between the S45C substrate and this band, showing a distinct difference from the case of the A5052 sub-strate. This is as expected, since S45C is based on steel and therefore primarily made up of Fe, which is also one of the constituent elements



FIG. 2. (a) Spatial variation in HEF thickness for three different deposition durations (glass substrate, 300 W input power). (b) Time dependence of film thickness for an input power of 300 W. (c) Dependence of film thickness on input power for fixed deposition time of 15 min.

of the Cantor alloy target. In other words, a strong difference in contrast between the HEF formed from the Cantor alloy target and the S45C substrate is not expected. Despite the low contrast in SEI and BEI images, analysis of this band by 2D-EDS mapping confirms the **TABLE III.** Variation of HEF thickness for each deposition time (measured on a glass substrate).

Deposition time (min)	5	15	25
Coefficient of Variation	0.013	0.005	0.009

presence of the constituent elements of Cantor alloy in a sub-surface band, as shown in Figs. 4(c)-4(g). The thickness of the HEF band is around 1.5 μ m, located at around 0.3 μ m beneath the surface. It should be noted that the Fe located above the HEF band was oxidized.

From Figs. 3 and 4, it was confirmed that the HEFs consist of the Cantor alloy target constituent elements and that these elements exist in a sub-surface band several micrometers below the surface of the substrate. This is attributed to the high energy of sputtered elements from the target. It is well known that ion implantation into Si sub-strates is routinely performed to fabricate semiconductor devices,¹⁷ and it is proposed that a similar implantation phenomenon is observed in this study. It should also be noted that Prudencio *et al.* reported the formation of Al–Fe alloys at the surface of bulk Al by Fe ion implantation,¹⁸ and similar alloying process was observed. Meanwhile, oxygen atoms have relatively low atomic mass and cannot be implanted into the substrates, therefore forming the observed surface oxide layer.

Another possibility to explain the formation of the sub-surface band is that elements in the parent substrates (i.e., aluminum atoms in A5052 and iron atoms in S45C) may diffuse toward the surface due to the effect of the Ar plasma. For instance, while the synthesis of carbon nanofibers requires the presence of a catalyst and relatively high temperature, chemical vapor deposition can allow the plasma-assisted formation of carbon nanofibers at room temperature.¹⁹ Nevertheless, the main conclusion is that HEFs are confirmed to be formed near the surface of the different substrates by deposition via DC magnetron sputtering.

Figure 5 shows an x-ray diffraction (XRD) spectrum of the HEF deposited on a glass substrate, and the fitted pseudo-Voigt function²⁰ as described in Eq. (2) is also displayed as a red line,

$$f_p \nu(2\theta) = (1 - \eta) \frac{2a}{(\Delta 2\theta)} \left(\frac{\ln 2}{\pi} \right) \exp\left[-\frac{4\ln 2(2\theta)^2}{(\Delta 2\theta)^2} \right] + \eta \frac{2a(\Delta 2\theta)}{\pi \left\{ 4(2\theta)^2 + (\Delta 2\theta)^2 \right\}}.$$
 (2)

Here, *a* is the peak area, η is so-called mixing parameter, $\Delta 2\theta$ is the full-width at half maximum (FWHM), and 2θ is the diffraction angle of the peak. From the fitting, $\Delta 2\theta$ is determined to be 1.84° nm and the peak position is 43.9°. The normalized root mean square error is about 3.6%.

It is known that the average crystallite size can be estimated using Scherrer's formula²¹ as follows:

$$D = \frac{K\lambda}{\Delta 2\theta \cdot \cos\theta}.$$
 (3)

Here, *D* is the crystallite size (nm), *K* is the Scherrer constant, which is normally 0.9, λ is the x-ray wavelength (nm), $\Delta 2\theta$ is the diffraction linewidth spread (radians), and θ is the Bragg angle (radians). In order to determine the crystallite size, *D*, $\Delta 2\theta$ can be obtained by



FIG. 3. Cross-sectional SEM/EDS observations of a HEF deposited on an A5052 substrate: (a) SEI image; (b) BEI image; and (c)–(j) 2D elemental maps of Cr, Mn, Fe, Co, Ni, and O, respectively. The dotted lines indicate the approximate location of the surface of the substrate.

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FIG. 4. Cross-sectional SEM/EDS observations of a HEF on an S45C substrate: (a) SEI image, (b) BEI image, and (c)–(j) 2D elemental map of Cr, Mn, Fe, Co, Ni, and O, respectively. The dotted lines indicate the approximate location of the surface of the substrate.



fitting the experimental data (red line, Fig. 5). Using Eq. (3), the average crystallite size was evaluated to be 4.6 nm. This result indicates that the HEF fabricated by DC magnetron sputtering is nanocrystalline, and therefore, high hardness is expected due to the grain refinement strengthening via the Hall–Petch relationship.²²

In addition, HEAs have been reported to have other advantageous properties, including: corrosion resistance and tribological behavior (e.g., in CoCrFeMoNi) making then potentially useful as a vascular implant material;²³ uniform deformation behavior caused by mesoscopic-scale complexity (e.g., in AlCoCrFeNi);²⁴ and significant fatigue resistance (e.g., in AlCoCrFeNi).²⁵ As such, sub-surface HEFs of CoCrFeMoNi and AlCoCrFeMoNi may also have potential applications as protective layers in terms of corrosion resistance, tribology, and fatigue resistance for, e.g., bulk Al alloys.

In conclusion, CoCrFeMnNi HEF was fabricated by DC magnetron sputtering using a CoCrFeMnNi equimolar HEA target. The resulting HEF existed in a sub-surface band just below the substrate surface, attributed to the implantation of transition elements into bulk substrate due to their high energy, or plasma-assisted migration of Al (for A5052) or Fe (for S45C). The HEF films produced by DC magnetron sputtering on glass substrates were confirmed to be nanocrystalline, indicating that high hardness can be expected. Sub-surface HEA films fabricated in this way have potential applications in corrosion resistance, tribological coatings, and fatigue resistance.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Daisuke Tanada: Data curation (equal); Formal analysis (equal); Investigation (equal); Writing – original draft (equal). Stephen M. Lyth: Writing – review & editing (equal). Kazuhiro Ishikawa: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – review & editing (equal). Yoji Miyajima: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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