

Combinatorial Exploration of the High Entropy Alloy System Co-Cr-Fe-Mn-Ni

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Abstract

In high entropy alloys, the number of base alloying elements is increased to at least five and their individual concentrations are rather high in comparison to conventional metallic alloys. This strategy aims at maximization of the configurational part of entropy and stabilization of disordered, single-phase solid solutions with simple crystal structure. In the present contribution, a first attempt is presented for the exploration of the phase field of the face centered cubic solid solution in the vicinity of the well-known equimolar composition of CoCrFeMnNi (Cantor alloy) on the basis of combinatorial thin film deposition from sectioned, circular targets by magnetron sputtering. A variation of the chemical composition of the thin films from almost binary systems for substrates (placed on circular positions at the rim of the coated area) towards thin films with an almost equimolar composition (i.e. obtained for samples coated at the center region of the target) was achieved. Crystal structures of the binary thin films were studied and the according lattice parameters of body centered cubic, face centered cubic, hexagonally closed packed and complex cubic (α -Mn prototype) crystal structures are in good accordance with expectations for solid solutions from literature data. The microstructure of the face centered solid solution thin films deposited at the center region of the target was investigated in detail by transmission electron microscopy and atom probe tomography. An ultra-

26 fine grained, columnar microstructure was found exhibiting disorder down to atomic length scale.
27 Thus, a suitable platform for future investigations of the entire face centered cubic phase field is
28 provided and the strength of the combinatorial thin film approach for the investigation of complex
29 microstructure development in high entropy alloy systems is revealed.

30 **Introduction**

31 The concept of high entropy alloys (HEA) differs from conventional alloy design strategies by
32 increasing the number of base elements as well as their concentrations. Rather than being composed of
33 a single principal element and minor additions for obtaining desired microstructures and materials
34 properties, this new class of materials is chemically complex. It is composed of multiple principal
35 elements, usually in almost equiatomic ratios [1,2]. Here, the basic intention is to increase the
36 configurational part of entropy $\Delta S_{\text{config}} = -k_B \cdot \sum_{i=1}^n \ln x_i$ (with k_B as Boltzmann constant, x_i as the
37 molar concentration of species i and n as the number of elements) towards its maximum value of
38 $\Delta S_{\text{config}}^{\text{max}} = k_B \cdot \ln n$ (with equimolar composition $x_i = 1/n$). This procedure should stabilize
39 disordered, single-phase materials with simple crystal structure such as face-centered cubic (FCC),
40 body-centered cubic (BCC) and hexagonally closed packed (HCP). Examples found so far which
41 follow this assumption are CoCrFeMnNi (FCC) [1], AuCuNiPdPt (FCC) [3], MoNbTaVW (BCC) [4],
42 HfNbTaTiZr (BCC) [5] and DyGdHoTbY (HCP) [6]. Accordingly, ordered intermetallic phases are
43 suppressed in this kind of alloys. Nevertheless, the configurational entropy is not the sole decisive
44 factor for the thermodynamic stability of particular phases, as the vast majority of multi-phase
45 compositionally complex alloys reveals – most alloys do not exclusively exhibit simple solid solutions
46 [7-13]. Motivated by fundamental investigations for future materials development, compositions
47 different from equimolar concentrations are of central interest, for example for the development of
48 high temperature materials or wear resistant alloys. This might for example be driven by controlled
49 precipitation of intermetallic phases from supersaturated solid solution [14-16] or by small additions
50 of supplemental elements for subtle property adjustment [17,18] as well as by studying composition-
51 depending effects like stacking fault energy or solid solution hardening [19]. Hence, efficient
52 theoretical and experimental methods have to be conducted in order to screen the appearance of phase

53 fields in the center of five or more component systems. Beside from diffusion multiples as a common
54 tool which are already employed in the case of HEAs [20], combinatorial thin film deposition
55 techniques provide innovative high-throughput platforms which fit these requirements at best [21].
56 Here, a first substantial study of HEAs was performed by Marshal et al. [22] revealing that the BCC
57 solid solution in AlCoCrFeMn is formed for an Al content of ± 6 at% around the equiatomic
58 composition. In contrast to the aforementioned diffusion multiples, thin film deposition methods
59 provide the possibility to explore and investigate samples prepared under highly non-equilibrium
60 growth conditions. Hence, variable film deposition parameters as well as further heat-treatments of as-
61 deposited thin films offer additional degrees of freedom.

62 In the present contribution we are focusing on CoCrFeMnNi – the so-called Cantor alloy, which
63 crystallizes with FCC structure [1]. It is one of the few examples of HEAs which can be tailored by
64 means of classical metallurgical processes [23-25]. Thus, CoCrFeMnNi and its derivatives have
65 attracted most interest by the scientific community among the class of HEAs so far [26-31]. Its
66 outstanding mechanical properties result from a complex interplay of the impact of lattice distortion,
67 deformation twinning and dislocation slip. The stacking fault energy is strongly depending on the Fe,
68 Mn and Ni content whereas lattice distortion significantly altered by changing Cr and Mn content. In
69 order to experimentally separate these fundamental parameters, HEA samples with deviations from the
70 almost equimolar composition need to be investigated. We hence provide experimental results on
71 chemistry and crystal structure of as-deposited thin films within the Co-Cr-Fe-Mn-Ni system
72 deposited from sectioned targets onto Si substrates by means of magnetron sputtering. The thin films
73 are crystallographically analyzed towards the almost binary border systems. The disorder of the thin
74 film with quinary, (nearly) equimolar composition deposited at the center multi-element target is
75 verified down to atomic length scale and compared to bulk CoCrFeMnNi as well.

76 **Experimental**

77 Co-Cr-Fe-Mn-Ni thin films were deposited by non-reactive r.f. magnetron sputtering in a Leybold Z
78 550 PVD coater. For this purpose, a specifically designed segmented sputter target of 152.4 mm
79 diameter was prepared as shown in Figure 1a. It consists of five segments of same geometry of

80 individual pure metal plates that were bound onto a target holder made of copper which provides water
81 cooling and electrical power connection. The individual metallic segments were prepared from 6 mm
82 thick, 152.4 mm diameter circular metal plates (Fe, Mn, Cr, Co and Ni by MaTeck GmbH, Germany;
83 each with a purity of 99.98 % and better) by electro discharge machining (EDM). Subsequent to the
84 cutting process, the metal plates were grinded to remove potential contamination resulting from EDM.
85 This segmented sputter target allows for high-throughput preparation of multi-element systems by thin
86 film growth as well as screening of locally resolved phase formation. The vacuum chamber was
87 pumped to a base pressure of $2 \cdot 10^{-4}$ Pa. Substrates used were $10 \cdot 10$ mm² Si wafers (Si wafer with 1
88 μ m thermal oxide layer, CrysTec GmbH, Germany); these were placed after ultrasonic bath cleaning
89 in acetone in the vacuum chamber at various defined positions in relation to the segmented sputter
90 target (according to Figure 1b). They correspond to the center position (Pos. 0), an inner circle of
91 small diameter (Pos. 1 to 5) and an outer circle of larger diameter (Pos. 6 to 10) right within the binary
92 systems. Thus, a set of sputtered Co-Cr-Fe-Mn-Ni thin films of various compositions was
93 systematically created in one deposition process, offering the advantage, that all thin films experienced
94 the same plasma conditions and pre-treatment. Prior to the deposition process, the substrates were
95 plasma etched for 5 min in a 500 W r.f. plasma of 0.5 Pa Ar. To enhance adhesion of the Co-Cr-Fe-
96 Mn-Ni films, a 100 nm thin pure Cr thin film was deposited first; for that, a pure Cr target (152.4 mm
97 diameter, 6 mm thick, supply of Cr by FHR Anlagenbau GmbH, Germany) was operated in d.c. mode
98 at 0.5 Pa Ar, 500 W and 0 V substrate bias for 20 s. The Cr and the segmented target were placed in
99 the vacuum chamber opposite to each other, and the sequential depositions of individual layers were
100 done by using an appropriate shutter system. The Co-Cr-Fe-Mn-Ni thin film deposition was carried
101 out at 0.1 Pa Ar, 500 W and 0 V substrate bias for 960 min to achieve thin films of approximately 5
102 μ m in thickness. Bulk CoCrFeMnNi samples in near equilibrium-like condition were prepared from
103 elemental materials mixed in equiatomic concentration by means of arc-melting (AM/0.5 provided by
104 Edmund Bühler GmbH). The Ar base pressure for arc-melting was 60 kPa following several
105 alternating iterations of pumping and Ar flooding. Re-melting a Zr lump in the vacuum chamber was
106 used in order to reduce residual oxygen by liquefying prior to every melting step. The prepared button
107 was flipped and re-melted for at least five times for homogenization. After the final melting step, the

108 alloy was cast into a rod-shaped Cu mold. The diameter and the length of the cast rod were 12 mm and
109 60 mm, respectively. For homogenization, the sample was encapsulated into a quartz glass tube under
110 vacuum and annealed at 1200 °C for 72 h. The chemical composition was analyzed using inductively
111 coupled plasma optical emission spectrometry (ICP-OES). Elemental powders with purities of 99.95
112 % and higher were used for validation of the performed X-ray diffraction experiments.

113 X-ray diffraction (XRD) analyzes in Bragg-Brentano geometry were carried out on a D2 Phaser
114 system by Bruker equipped with a LynxEye line detector. The Cu tube was operated at 30 kV and 10
115 mA, and the according radiation was filtered by means of a Ni foil. In order to suppress fluorescence
116 radiation of Fe, Co and Ni a suitable discrimination interval of the LynxEye detector was used.

117 Precise lattice parameters were determined using extrapolation of the peak positions by means of a
118 Nelson-Riley approach [32]. For HCP crystal structure, an adopted least square fitting according to
119 Ref. [33] was used. The digits provided for lattice parameters indicate the error of the measurement
120 which is mainly altered by texture (number of peaks) and peak width. Scanning electron microscopy
121 (SEM) investigations were performed on a Zeiss EVO50 system operated at 25 kV (for complete
122 stimulation of the necessary L-lines of Co, Cr, Fe, Mn and Ni for standard-less quantification)
123 equipped with a Thermo Scientific energy-dispersive X-ray spectroscopy (EDX) system. For
124 determination of local chemical composition, five measurements on approx. 200 · 200 μm² areas were
125 performed for each wafer position. Characteristic Si lines resulting from the substrate were analyzed
126 for deconvolution of the spectra but omitted during standard-free quantification of the composition.

127 For transmission electron microscopy (TEM), an aberration- corrected (image) FEI Titan 80-300 (FEI,
128 Eindhoven) operated at 300 kV and equipped with field emission gun, Gatan Ultrascan CCD camera
129 (Gatan Inc., Pleasanton, CA), and EDAX S-UTW EDX detector was used. Dark field images (DF) and
130 selected area diffraction (SAD) pattern were acquired to study the local crystallography and
131 microstructure. Scanning-TEM studies were carried out to investigate local concentration changes.

132 Atom probe tomography (APT) was performed in laser mode using a LEAP4000X HR by Cameca.
133 The pulse efficiency (fraction of pulses leading to detection event) was 1 %. The pulse rate and energy
134 was 200 kHz and 50 pJ, respectively. The tips were cooled down to 50 K. The mass spectra generally
135 contain numerous small peaks besides the expected peaks of Fe, Co, Cr, Mn and Ni. For both purposes

136 TEM and APT, target preparation by in-situ lift-out was performed using a FEI Strata 400 S (FEI,
137 Eindhoven) dual electron and focused ion beam (FIB) system (30 kV for ions). Subsequent to Pt
138 deposition for protection of the target, specimen preparation was performed with consecutively
139 decreasing FIB probe currents in order to avoid beam damage. APT specimens were transferred to a
140 pre-sharpened micro-tip coupon (provided by Cameca) and annular milling with decreasing inner radii
141 to achieve tip shaped specimens with an initial tip radius below 100 nm. Finally, a milling step with a
142 closed circle was performed at 5 kV to remove the severely Ga-damaged surface of the tips.
143 Thermodynamic calculations presented in this study were carried out using the thermochemical
144 software FactSage (V6.4) in conjunction with the commercial database FRAN which includes the
145 following elements: Ni, Cr, Mn, Fe, Co, Si, Mo, W, Al, N, O, C.

146 **Results and Discussion**

147 **Chemical composition**

148 By means of EDX, the chemical composition of thin films was determined at the center of their
149 sample surfaces (the placement of the substrates was according to Figure 1b). The compositions of the
150 thin films are summarized in Table 1. At “Pos. 0” according to Figure 1b, Fe, Mn and Co are equally
151 distributed in the thin film while an enlarged Ni content (28.0 at%) and a reduced Cr content
152 (14.2 at%) in comparison to the nominal Cantor alloy were observed. For the sake of simplicity, this
153 thin film composition is called almost equimolar composition in the following. Figure 2 visualizes the
154 chemical compositions of the thin films deposited on off-centered substrates (Pos. 1 to 5 and 6 to 10,
155 respectively). While significant contributions of third elements up to 12.5 at% (Ni in the case of
156 CrMn) are observed in pseudo-binary thin films at the inner circle, these contributions are significantly
157 reduced to values lower than 5 at% for thin films deposited at the outer rim. In general, contributions
158 of opposite placed elements are in the range of 1 at% only. An almost equimolar, binary composition
159 is exclusively obtained for CrMn. This indicates a similar sputter yield for these two elements whereas
160 in all other cases deviations from this ideal situation up to 75 at% of one contributing element were

161 observed. Ni exhibits a significantly higher sputter yield in comparison to the other elements which is
162 in good accordance with the enlarged Ni content at the center of the film.

163 **Crystal structure**

164 XRD patterns of the thin films are presented in Figure 3. At the center position (Pos. 0), a FCC solid
165 solution can clearly be revealed for the as-deposited CoCrFeMnNi thin film. A comparison to bulk
166 CoCrFeMnNi in Figure 3a reveals significantly broadened reflections in the case of the film indicating
167 microstructural defects or chemical inhomogeneity across the investigated area. Microstructure
168 analyses in the last paragraph of the present article reveal a nanocrystalline, aligned microstructure as
169 a possible origin of the broadened reflections. Moreover, the absence of the {220} reflection indicates
170 slight texturing of the film. Evidence for super lattice formation (B2 or L2₁ crystal structure) or
171 additional intermetallic phases cannot be found at this stage. The lattice parameter of 0.3597 nm
172 obtained for bulk CoCrFeMnNi can be reproduced in the thin film exhibiting a value about 0.361 nm
173 (please see Table 2).

174 Since chemical compositions of films deposited on substrates which are placed on the inner and outer
175 circle are similar (Table 1), similar crystal structure data was obtained for these films as shown in
176 Figures 3b and 3c as well as in Table 2. For the almost binary Ni-rich Ni-Cr films, a FCC crystal
177 structure is obtained. In equilibrium, up to 50 at% Cr can be solved in FCC solid solution at about
178 1350 °C [34]. At lower temperatures, CrNi₂ occurs. This phase cannot be identified in the films grown
179 at Pos. 1 and 6. Thus, Ni is either supersaturated in the solid solution or remains segregated with a
180 volume fraction below the resolution limit of XRD. Lattice parameters of Ni-rich Ni-Cr FCC solid
181 solutions approach almost 0.36 nm at maximum solubility [34]. This is in good accordance with the
182 experimentally determined lattice parameter of 0.357 nm and 0.358 nm for the films summarized in
183 Table 2.

184 The Cr-Mn binary system exhibits a rather complicated phase diagram incorporating numerous
185 intermetallic phases. Nevertheless, the BCC solid solution can solve up to about 70 at% of Mn at
186 roughly 1300 °C [35]. In this case, lattice parameter increases from 0.2885 nm with 0.00036
187 nm/10 at% [35]. The obtained lattice parameter of 0.289 nm in the case of the BCC structured thin

188 film at Pos. 2 is in good agreement with the according expectation of 0.2894 nm. The thin film at
189 Pos. 7 was not further processed since partial delamination occurred. This might be attributed to
190 residual stresses resulting from film growth.

191 The Mn-rich Mn-Fe thin films exhibit the complex cubic (CC) crystal structure of α -Mn. α -Mn can
192 solve up to 30 at% of Fe in equilibrium condition almost independent of temperature below the α/β -
193 transition temperature at about 730 °C [36]. In this case, the lattice parameter of the CC crystal
194 structure decreases with increasing Fe content from 0.89125 nm to 0.88875 nm at 30 at% Fe [36]. The
195 determined values of 0.8868 (inner circle, Pos. 3, supersaturated at 35.5 at%) and 0.8883 nm (outer
196 circle, Pos. 8, at 20.1 at%) agree well with the above mentioned expectation of 0.8869 (extrapolated)
197 and 0.8888 nm [36], respectively.

198 Due to the high content of Co in the case of the Co-Fe thin films, both BCC and HCP crystal structure
199 are obtained. An obvious texture in the BCC phase does not allow a verification or falsification of the
200 appearance of a B2 super lattice in the case of the cubic phase. Lattice parameters found for the BCC
201 solid solution (0.285 nm) are in accordance with the expectations from the chemical composition
202 (0.2839 nm [37]) whereas the HCP crystal structure exhibits strong similarity with pure Co [39]
203 indicating that Fe is mostly dissolved within the BCC solid solution.

204 For the Ni-rich Ni-Co thin films, a FCC crystal structure was found which is expected for equilibrium
205 conditions. For the determined thin film compositions, a lattice parameter of 0.3537 nm is expected
206 [38] and is in good agreement with the experimentally found values of 0.355 and 0.354 nm,
207 respectively.

208 **Local investigations of the thin film deposited at the center position**

209 A detailed microstructure investigation of the as-deposited films was done in case of the CoCrFeMnNi
210 thin film at the center position (Pos. 0 in Figure 1b) since it macroscopically compares well to the
211 Cantor alloy. Figure 4a shows a DF image of the thin film microstructure. Columnar grains aligned
212 parallel to the surface normal of the deposited films are clearly visible. The 10 μm objective aperture
213 for DF imaging was placed on the {400} ring of the FCC structure revealed in Figure 4b in the

214 direction of the film normal. TEM-DF investigations in thin parts of the lamella lead to about 7 to
215 12 nm crystallite size in the respective direction. Line broadening $\Delta 2\theta$ of the diffraction peaks at the
216 angles θ as shown in Figure 3a is used for a rough estimate of the crystallite size D in a greater
217 volume of the thin film. The application of the Scherrer equation $D \approx \frac{K \cdot \lambda}{\Delta 2\theta \cdot \cos \theta}$ [42] for the applied
218 wavelength λ yields about 10 nm perpendicular to the growth direction. Hence, a reasonable
219 agreement of XRD and TEM-DF is obtained. Additional defects, namely stacking faults and twin
220 boundaries appearing during film growth, as they are expected for this kind of medium stacking fault
221 energy alloy [43], might contribute to line broadening as well. Slight texturing of the columnar grains
222 with $\langle 100 \rangle$ direction parallel to film normal is observed. Potential candidates for secondary phases can
223 be either derived from thermodynamic calculations as shown in Figure 5 or by the decomposition
224 studies performed in Refs. [14-16]. Figure 5 suggests a decomposition of the FCC solid solution into
225 numerous phases at low temperature in equilibrium condition. There are a potential Cr-rich σ -phase
226 (Ref. [15] and Figure 5), a $L1_0$ -NiMn phase (Ref. [16] and Figure 5, possible chemical congruence
227 with Ref. [14]), a B2-FeCo (Refs. [14,16]) as well as a Cr-rich BCC phase (Ref. [16] and Figure 5).
228 None of these suggested phases were found in the as-deposited thin film. While the identified FCC
229 structure matches perfectly with the macroscopic lattice parameter for the film parallel to the film
230 normal (due to the geometry used in the XRD experiment) presented in Table 2, there is a significant
231 deviation within the film plane. The lattice parameter is increased by approx. 4 % (clearly visible at
232 high angle reflections) indicating residual in-plane tensile stress within the film. Since in the prepared
233 TEM lamella the HEA thin film remains attached to the Cr buffer, thermal oxide layer and parts of the
234 substrate, the residual stress can be taken as representative for this film architecture. In order to reveal
235 if the contrast changes in Figure 4a are attributed to chemical inhomogeneity or diffraction by varying
236 orientations, STEM-EDX line scan was performed and is shown in Figure 6. Despite the high-angle
237 annular dark-field (HAADF) signal is slightly varying, no indications of phase separation on the
238 nanoscale are found. Thus, the DF intensity variations arise from different diffraction conditions for
239 different grain orientations. Further prove of complete disorder and absence of phase separation is
240 provided by means of atom probe tomography and displayed in Figure 7. Both, 3D elemental
241 (Figure 7a) as well as spatial distributions of the elements along a cylinder cut from the reconstructed

242 APT tip (Figure 7b) are completely homogeneous. Chemical inhomogeneity on local scale – although
243 present on macroscopic length scale when using the presented deposition technique – does not seem to
244 contribute to the line broadening observed in Figure 3a.

245 **Conclusions**

246 For the first time, an attempt is presented for the exploration of the phase field of the face centered
247 cubic solid solution in the vicinity of the important equimolar composition of CoCrFeMnNi (Cantor
248 alloy) on the basis of combinatorial thin film deposition from sectioned targets by magnetron
249 sputtering. A variation of the chemical composition from pseudo-binary thin films on substrates placed
250 at the rim of the coated area towards an almost equimolar composition at the center region was
251 achieved. The following conclusions can be drawn:

- 252 • Crystal structures of the binary border systems are BCC (Cr-Mn, Fe-Co), FCC (Ni-Cr, Co-Ni,
253 Ni-Cr), HCP (Fe-Co) and CC (α -Mn prototype; Mn-Fe).
- 254 • The lattice parameters of all analyzed thin films are in good agreement with expectations from
255 literature data either for solid solutions or for extrapolations in case of supersaturated solid
256 solutions.
- 257 • The microstructure of thin films with the almost equimolar face centered cubic solid solution
258 at the center region is ultra-fine grained and columnar. Disorder is revealed down to atomic
259 length scale and the absence of phase separation suggested by thermodynamic calculation as
260 well as former decomposition experiments is verified.
- 261 • Despite significantly different grain size, a remarkable similarity in terms of crystal structure
262 of the as-deposited CoCrFeMnNi thin film and the according bulk material can be achieved.

263 Hence, a suitable platform for future investigations of the entire face centered cubic phase field is
264 provided. The specific arrangement of pure metal plates from the present contribution will allow fast,
265 efficient investigation of subsystems in the vicinity of minimum and maximum mechanical strength on
266 the one hand – for the equimolar subsystems these are Ni-Co and Co-Cr-Ni, respectively [19]. On the
267 other hand, placing Fe-Mn next to each other and opposite to Co-Ni-Cr provides the possibility to

268 access high Fe and high Mn alloys which exhibit intense twinning and transformation induced
269 plasticity [41].

270 The combinatorial approach presented in this contribution might be used as a basis for more advanced
271 investigations by for example using asymmetric target segmentation, variation of deposition
272 parameters for active microstructure determination or heat-treatments of thin films. This can contribute
273 to a more systematic investigation of the composition- microstructure -property correlation and a
274 facilitated development of thermodynamic databases for materials development.

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Table 1: Chemical composition of the thin films in at% (substrates were placed according to the scheme in Figure 1b). Bold numbers indicate major elements.

#	sample	Cr	Mn	Fe	Co	Ni
0	CoCrFeMnNi	14.2	19.4	19.0	19.4	28.0
1	NiCr	27.8	5.4	0.7	1.2	64.9
2	CrMn	59.3	25.8	1.4	1.0	12.5
3	MnFe	3.5	59.4	35.5	0.8	0.9
4	FeCo	1.7	7.7	17.0	67.9	5.7
5	CoNi	2.8	7.4	1.2	26.4	62.3
6	NiCr	22.9	4.1	0.3	0.5	72.2
7	CrMn	48.5	50.2	0.7	0.1	0.5
8	MnFe	1.6	77.2	20.1	0.8	0.3
9	FeCo	1.2	4.9	17.6	74.4	1.9
10	CoNi	1.3	2.8	0.6	33.9	61.4
-	CoCrFeMnNi (bulk sample, ICP-OES)	19.7	19.2	20.3	20.4	20.4

Table 2: Crystallographic data obtained from the XRD patterns presented in Figure 3. In addition, precise lattice parameters from elemental powders are included for comparison. Number of provided digits provide information about the error of the measurement.

#	sample	condition	prototype	lattice parameter(s) / nm	reference latt. parameter(s) / nm
	CoCrFeMnNi	bulk material	Cu (FCC)	0.3597	0.359 [9]
0	CoCrFeMnNi	film	Cu (FCC)	0.361	
1	NiCr	film	Cu (FCC)	0.358	0.3557 [34]
2	CrMn	film	W (BCC)	0.289	0.2894 [35]
3	MnFe	film	α -Mn (CC)	0.8868	0.8869 [36]
4	FeCo	film	W (BCC) Mg (HCP)	0.285 0.251/0.409	0.2839 [37]
5	CoNi	film	Cu (FCC)	0.355	0.3537 [38]
6	NiCr	film	Cu (FCC)	0.357	0.3549 [34]
7	CrMn	film	W (BCC)	partially delaminated	0.2903 [35]
8	MnFe	film	α -Mn (CC)	0.8883	0.8888 [36]
9	FeCo	film	W (BCC) Mg (HCP)	0.285 0.251/0.409	0.2839 [37]
10	CoNi	film	Cu (FCC)	0.354	0.3537 [38]
	Co	powder	Mg (HCP)	0.25074/0.40699	0.25074/0.4070 [39]
	Cr	powder	W (BCC)	0.28850	0.28840 [39]
	Fe	powder	W (BCC)	0.28665	0.286645 [39]
	Mn	powder	α -Mn (CC)	0.89125	0.891250 [40]
	Ni	powder	Cu (FCC)	0.35241	0.35238 [39]

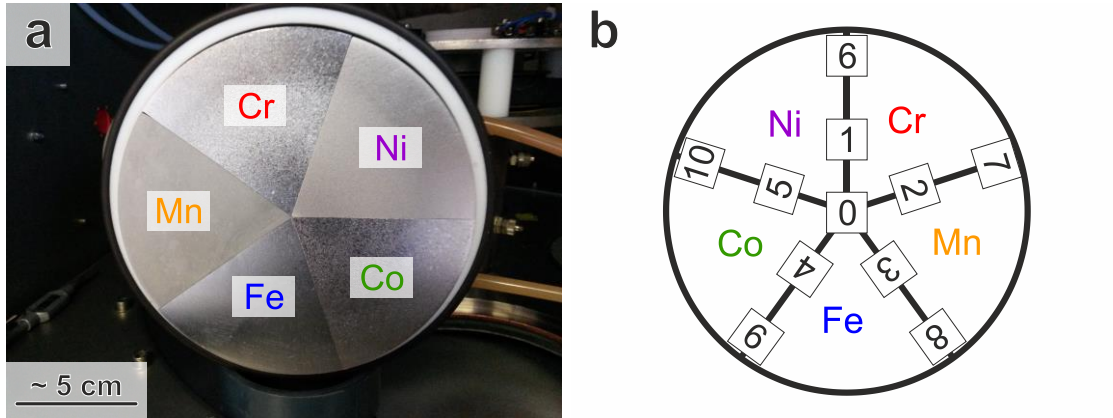


Figure 1: Magnetron sputter target used in this work: a) photograph of mounted target sections and b) scheme of the placement of the eleven Si substrates (no. 0 to 10) underneath the target sections and numbering used throughout this article.

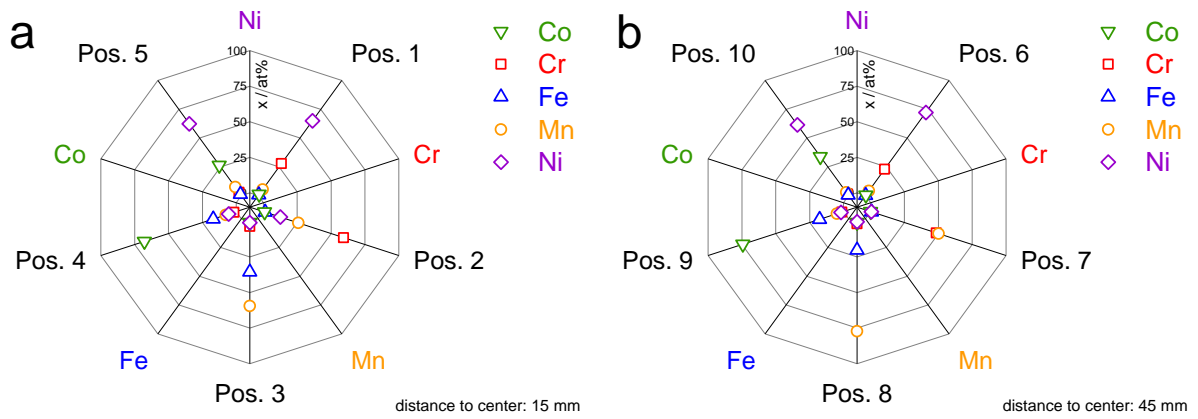


Figure 2: Visualization of chemical compositions of the thin films on substrates placed on the: a) inner, and b) outer circle according to the scheme in Figure 1b.

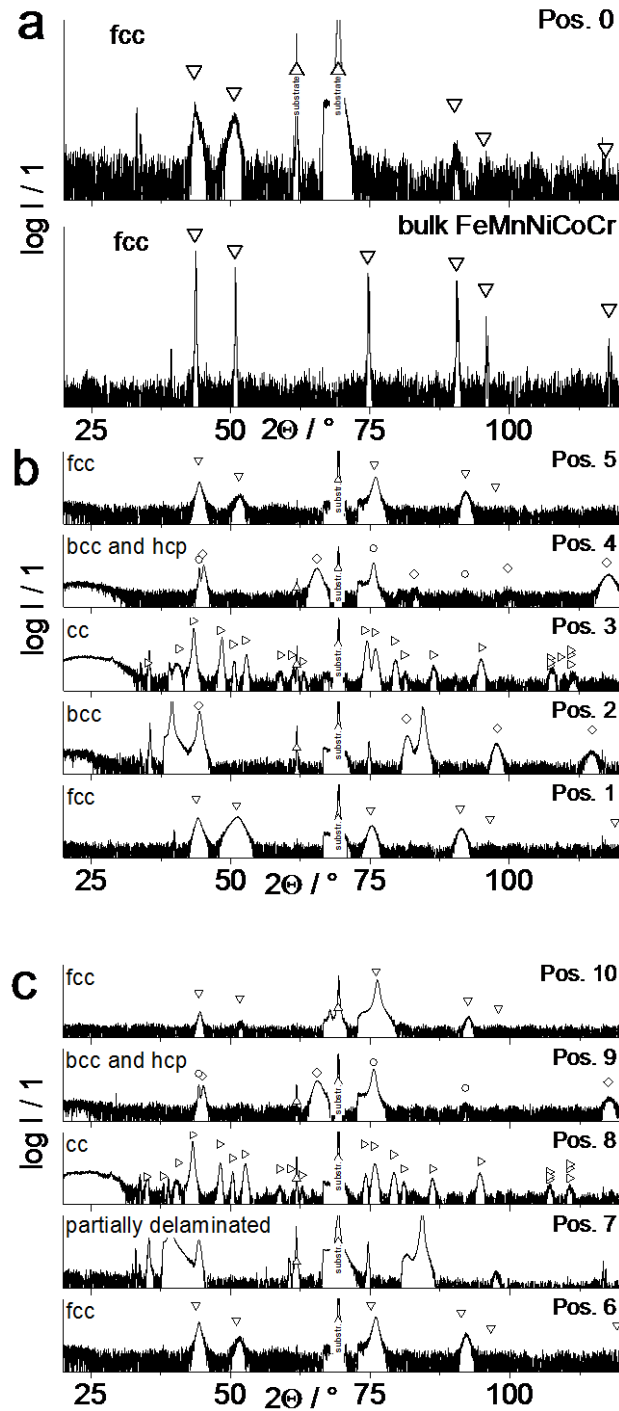


Figure 3: Diffraction patterns (logarithmic intensity scale for the sake of clarity) of: a) CoCrFeMnNi thin film deposited at Pos. 0 in comparison to bulk CoCrFeMnNi, b) thin films on substrates placed on the inner circle (Pos. 1 to 5) and c) on the outer circle (Pos. 6 to 10). Phases are indicated by: ∇ Cu prototype (face-centered cubic, fcc), \diamond W prototype (body-centered cubic, bcc), \circ Mg prototype (hexagonally closed packed, hcp), \triangleright α -Mn prototype (complex cubic, cc) and Δ substrate (Si).

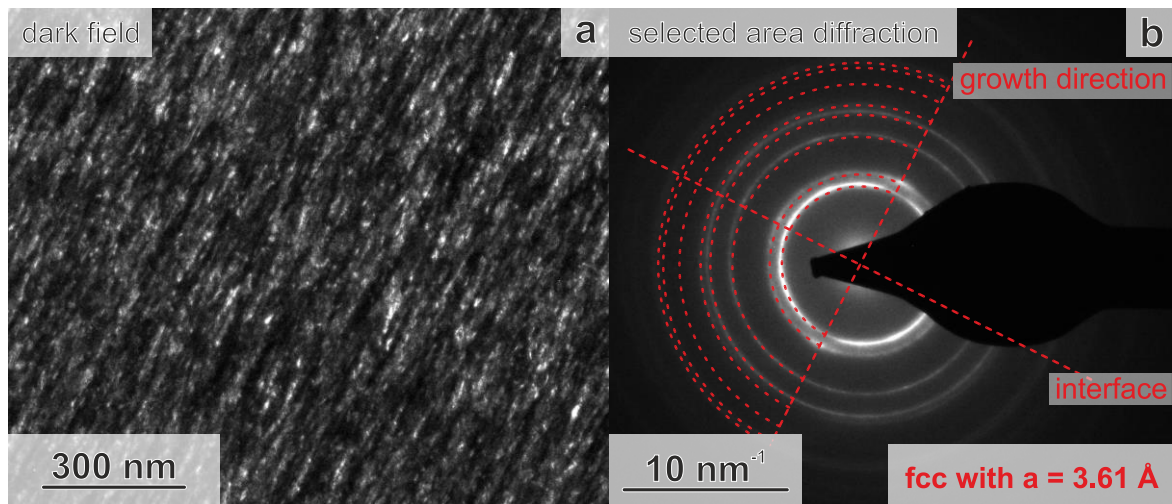


Figure 4: TEM investigations on an in-situ FIB lift-out specimen of the CoCrFeMnNi thin film deposited at Pos. 0 according to Figure 1b: a) DF image using the (400)-ring in approximately the direction of the growth direction and b) SAD pattern with the corresponding FCC rings according to the lattice parameter determined by XRD (please see Table 3).

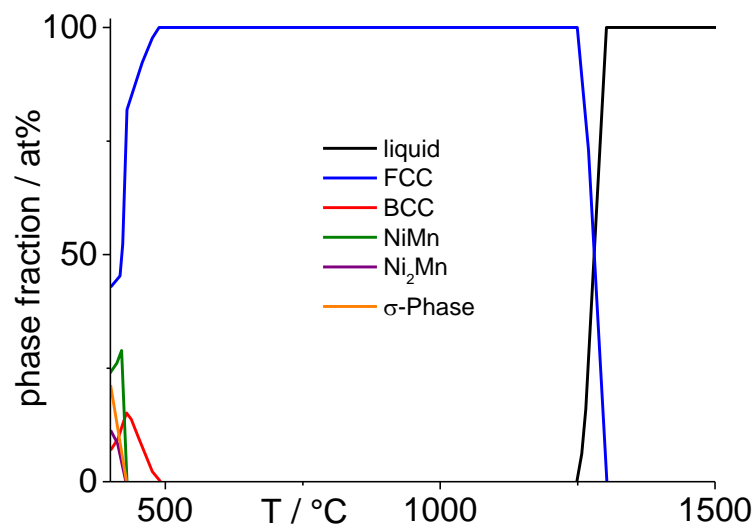


Figure 5: Thermodynamic calculation (utilizing FactSage) of the molar phase fraction as a function of temperature for the composition determined for the CoCrFeMnNi thin film deposited at Pos. 0.

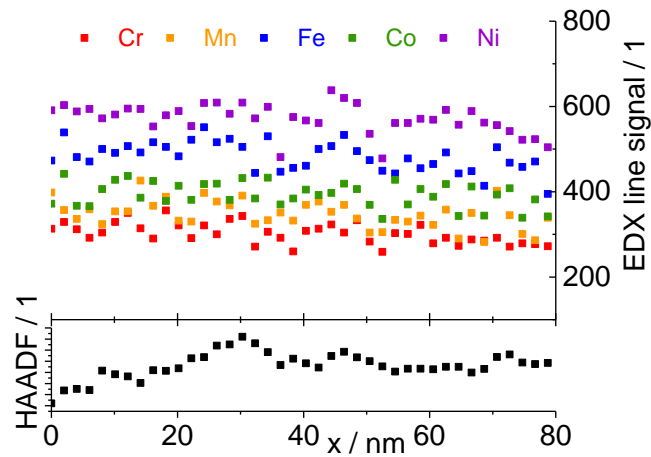


Figure 6: STEM-EDX line scan performed on the in-situ lift-out specimen of the CoCrFeMnNi thin film deposited at Pos. 0. The signal of the EDX lines is uncorrected. The HAADF signal is plotted as reference as well.

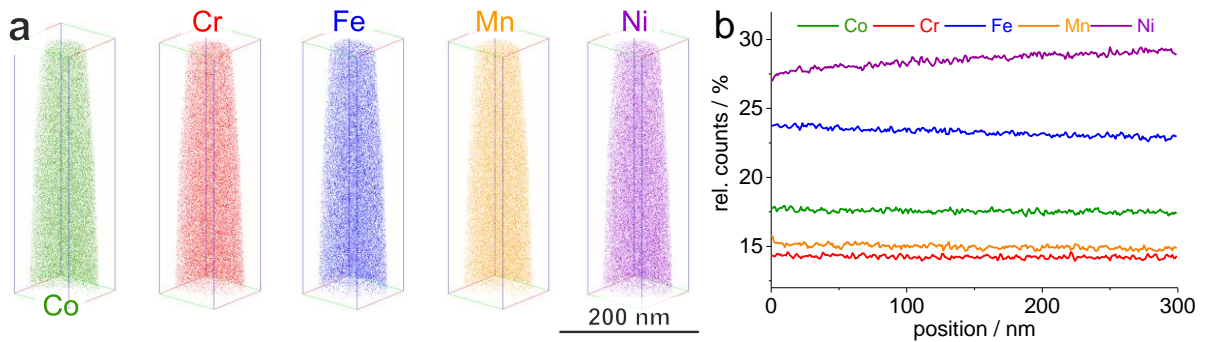


Figure 7: Exemplary APT results on a CoCrFeMnNi thin film specimen taken a film deposited at Pos. 0: a) 3D element distribution and b) spatial element distribution along a cylinder of 50 nm in diameter (uncorrected rel. counts). The total concentration after deconvolution supports the standard-free EDX including the enlarged Ni content and the Cr deficite presented in Table 1.