SEMESTER REPORT 2

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Co-supervisor: Dr. Viktoria Kovács-Kis,

Ph.D thesis title: Structural characterization of multicomponent alloys and compounds in bulk and thin film form
Place of research: Centre for Energy Research, Thin Film physics Laboratry

I/ Experimental part

Reaserch plan:

High entropy alloys (HEAs), containing five to thirteen metallic elements, with a concentration in the range of 5 to 35 % for each element, exhibit very interesting properties (mechanical, tribological, formability, magnetism...). Their high mixing entropy promotes the formation of simple solid solutions with amorphous or nanocrystallized structure. These alloys are known to be stable at relatively high temperature (until 800°C) for that purpose, during the second semester we studied the thermal stability of CoCrCuFeNi high entropy alloy thin films at temperatures in the range of30-700 °C .The first task was to synthesize nm thick films of HEAs. HEAs thin films have been synthesized by DC magnetron sputtering by using high entropy alloy target of CoCrCuFeNi compositionwith 20 at% from each element on three different substrates at the same deposition conditions. In fact this technique allows us to deposit equiatomic HEAs. Furthermore the thickness could be controlled either by varying the magnetron power or by the deposition time. The annealing of CoCrCuFeNi thin films was to be performed in-situ in the electron microscope and by recording the images and selected area electron diffraction (SAED) patterns. Morphology, composition and grain size measurements were planned by High Resolution Transmission Electron Microscopy (HREM) before and after annealing to different temperatures. For the present study we have chosen samples exhibiting single phase FCC structure.

Experimental Procedures

To synthesize HEA thin film; DC magnetron sputtering technique was used with CoCrCuFeNi target of pure equiatomic concentration of elements (99.9%) at room temperature. The deposition conditions are detailed in table 1. For the present study we have chosen to work on sample Nr 2. To determine the morphology and the structure of the HEA thin film before annealing; two microscopes, the HREM (JOEL 3010 at 300 kV) and a TEM (Philips CM20 at 200 kV) were used. SAED and bright field images were recorded with the CM20electron microscope at 200 kV. This microscope was fitted with a heating stage, giving

the possibility to in-situ record SAED patterns and microscopic images between room temperature and 700°C.Recordings were made after each 50 °C annealing step lasting 5 minutes. The sample was kept under a residual pressure of 4.5 10^{-7} mbar during the whole in-situ annealing process. The SAED patterns were recorded at 0.5m camera length; and lens currents: C1=664 mA; C2=1848 mA, OB=5596 mA, spot2, HV=200kV. Two experiments were made, in one experiment the changes were followed by SAED, recording diffraction patterns from the same area of 50 □m in diameter, in the other experiment bright field images were recorded at magnification of 50 kx. The experiments were performed in this way to ensure the observation of changes in the same area of the film.

Table1 Sputtering deposition parameters

HEA	CuNiCOCrFe (Nb.1)	CuNiCOCrFe (Nb.2)	CuNiCOCrFe (Nb.3)
Substrate	Si; C/Cu	SiO2	Cleaved Nacl
Target power	50W	50W	50W
Deposition time	5 munites	5 munites	5 munites
Argon pressure	2.510^{-3}	2.510^{-3}	2.510^{-3}
Base pressure	9.10^{-8}	9.10^{-8}	9.10^{-8}
Temperature	Room temperature	Room temperature	Room temperature

1/ Characteristics of CuNiCoCrFe thin film befor annealing

Fig.1 shows the TEM Bright field image(B)and selected-area diffraction pattern (A) of an unannealed film, deposited at room temperaure.The average grain size of this film was measured to be around 5 to 7 nm. The structureof as-deposited thin film has been identified as single phase FCC with latice paramere a=3.60Å based on the measurement of the diffraction pattern (Fig. 1A and Table A). The TEM image confirms the polycrystalline and the fine crystallite size, the SAED pattern shows the formation of continuous rings, in the diffraction pattern and random orientation of crystallites (no texture). The HREM image (Fig. 1C)is confirming the presence of the matrix FCC phase with an interplanar spacing of 210pm with 1% error corresponding to the distance of the {111} planes of the HEA phase.

A/ Indexing of the CoCrCuFeNi HEA thin film

Indice Miler hkl	Lattice Spacing d(Å)	Lattice constant (Å)
111	2.11	3.68
200	1.8	3.60
220	1.26	3.56
311	1.07	3.59
222	1.03	3.56

Average unit cell from last five last lines…….3.60

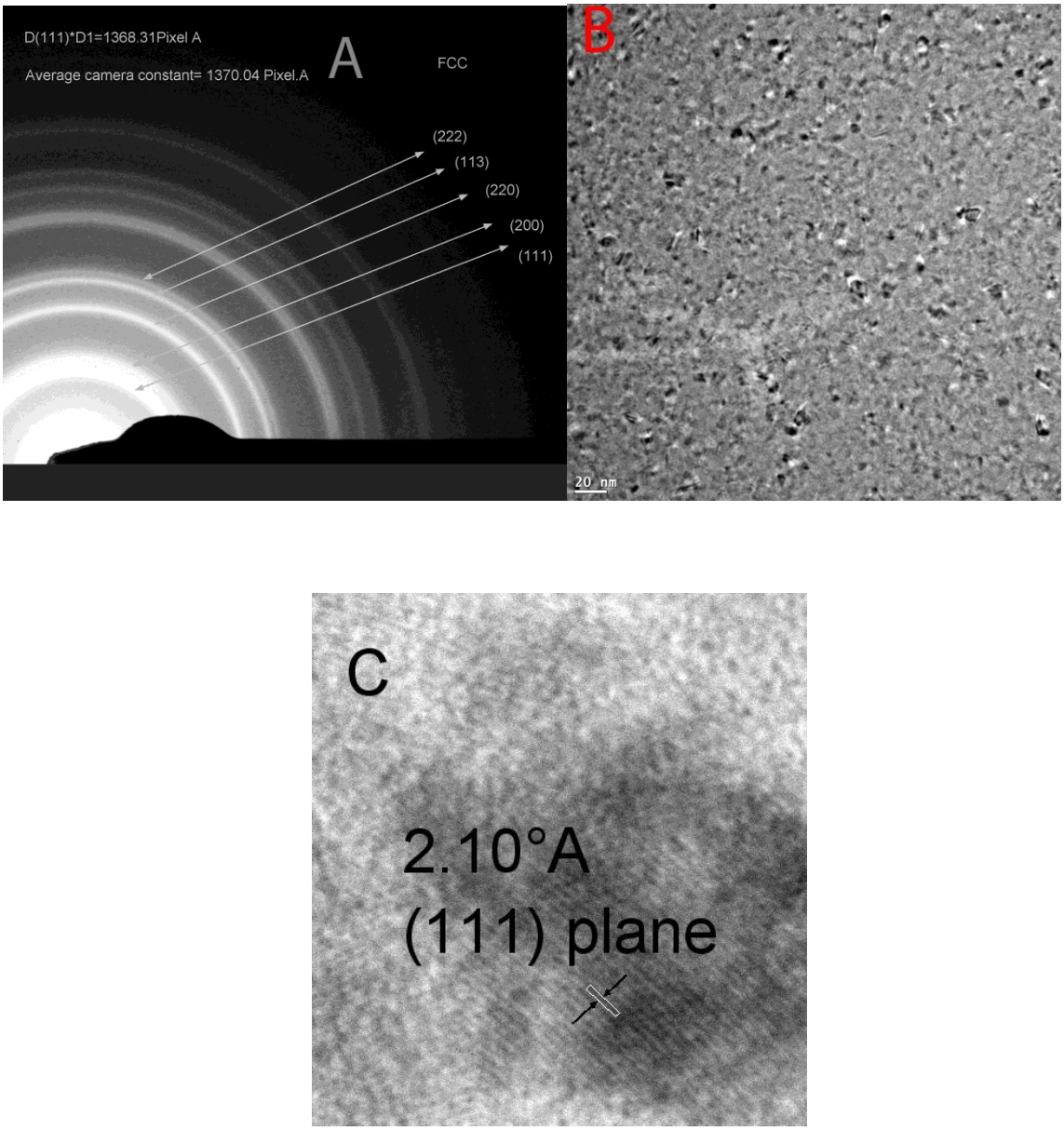


Fig. 1. (A) SAED pattern showing the diffraction rings of the FCC phase of the as deposited sample; (B) Bright field TEM image of the unannealed CoCrCuFeNi HEA film; (C) HREM image of a region showing atomic planes corresponding to the FCC phase with an interplanar spacing of 210 pm

2/ Morphology and structure during annealing

A/ development of grain size during in-situ annealing.

The grain size measurement was performed after each annealing step. Fig. 2 and 3 show the grain size and bright field images of the HEA films during annealing. As we see there is no much change in the grain size, only a few nanometer additions were observed from 50 to 550^{o}C. So, it can be concluded, that the film is morphologically stable up to 550 ^{o}C. At 600°C some fast growing new grains appear. From this moment two types of crystalline grains were

observed belonging to two different phases; small grains of average size around 40 nanometers belonging to the original HEA FCC phase and larger size grainsof about 100 nm diameter. The graph below (Fig. 2) shows the evolution of grain size as a function of temperature.

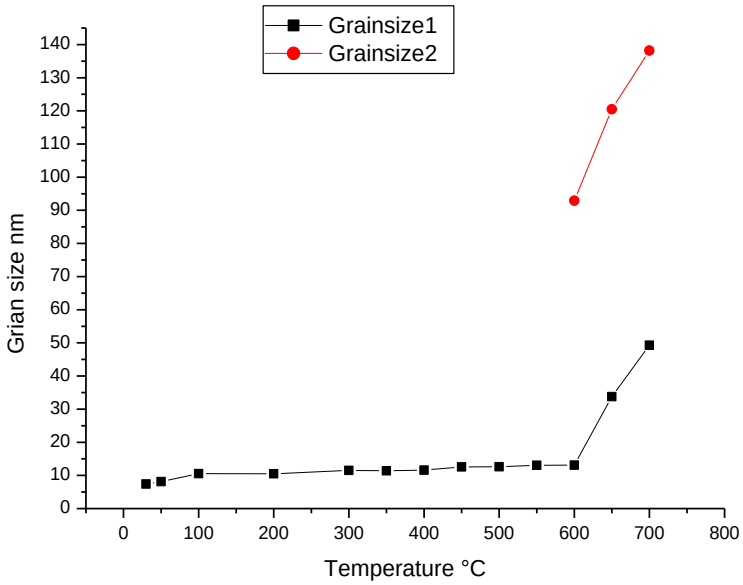
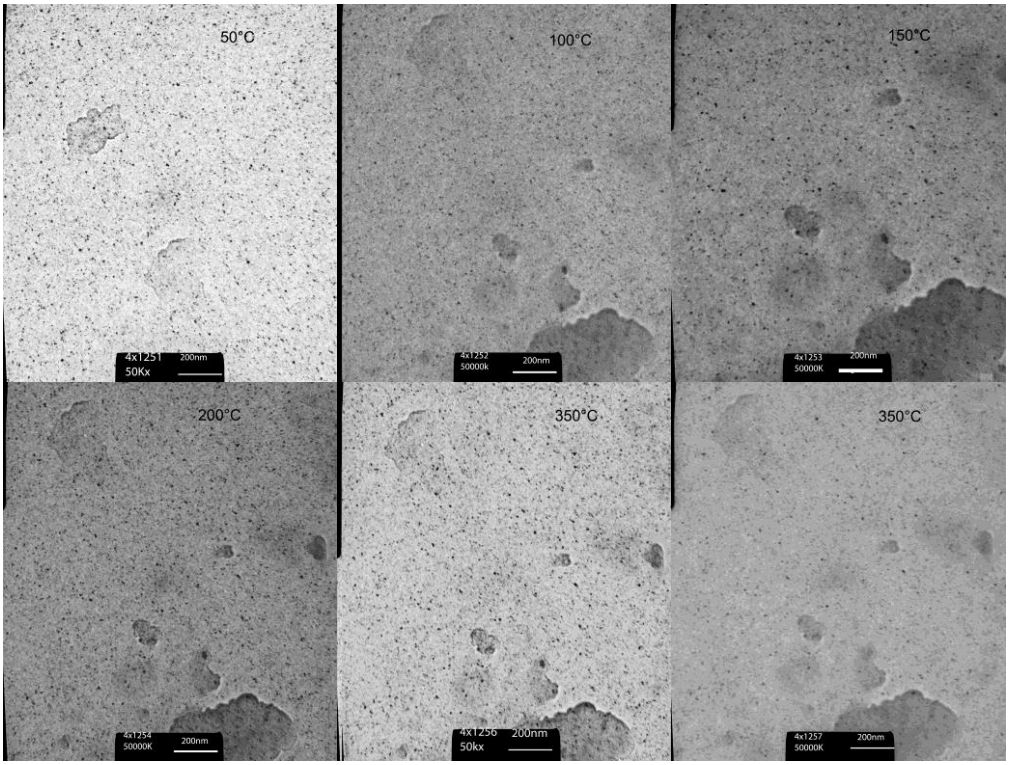
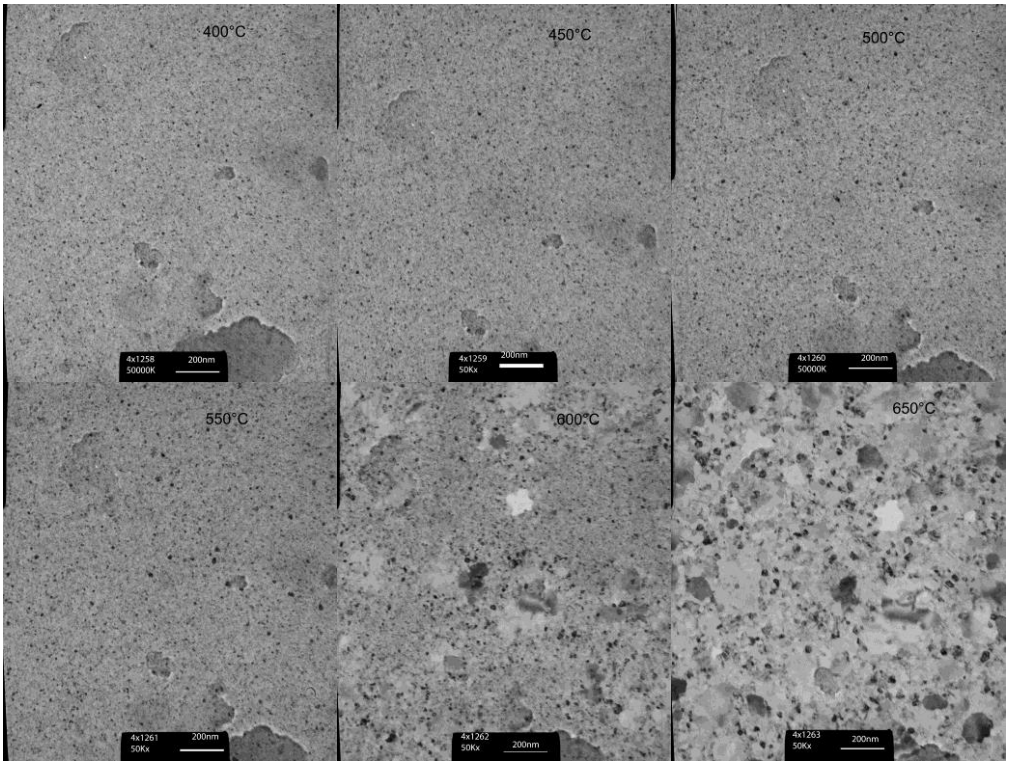
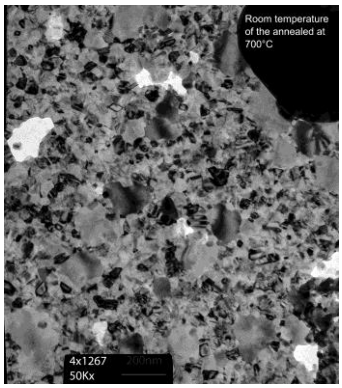


Fig. 2.Evolution of grain size as a function of temperature

Fig.3 TEM bright field images from 50°C to 700




400°C
4x1258
50000K
200nm
450°C
4x1259
50Kx
200nm
500°C
4x1260
50000K
200nm
550°C
4x1261
50Kx
200nm
600°C
4x1262
50Kx
200nm
650°C
4x1263
50Kx
200nm


Room temperature
of the annealed at
700°C
4x1267
50Kx
200nm

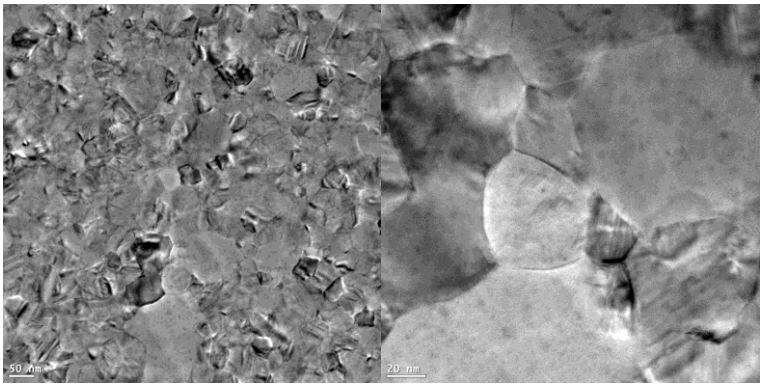


Fig 4. HRTEM images of the CuCOCRFENi thin film after annealing (700°C) at room temperature, proved the higher increase of the grain in different shape and size

B/ In-situ electron diffraction analyses

Figures 5; 6; 7 illustrate the phase evolution of CrCoCuFeNi HEA thin film during annealing. Fig 5 shows that from room temperature to 300°C there no change in the structure, only FCC phase is present. After annealing at 400 a new bcc phase is observed with lattice parameter a=2.97Å. the BCC fraction reach constant intensity after annealing at 450°C, the structure evolution followed by SAED of the HEA thin film during annealing up to 600 °C were attributed as fcc-bcc dual phase as shown fig 5, and 6 . Since the Cr and Fe are the only components that have BCC phase and due a higher melting point of Cr (1907°C) in comparison to Fe (1530°c). It can lead that Fe dissolve into Cr rather than vise versa. Thus, the BCC phase must be phase formed by dissolution of Fe in Cr and since Cr is a BCC stabilizer and because of its higher melting point comparing to other elements therefore the minor bcc phase can be explained in such a way that the dissolution of the bcc phase could not be to much in the FCC phase. The analytical confirmation of this consideration, we plan to do by local EDS measurement in the future. However from 700°C a big change happened to the structure where first a three forbidden reflections (100);(110);(211) from fcc phase have appeared and the rings of (211) reflection of the bcc rings has disappeared and replace it by discontinuous ring which show a small amorphous state is appearance in the CrCoCufeNI thin film whereas an increase of the grain size rise to 150nm. The individual spots can be belonging to oxidation phase. The rest of the analysis will be studied later.

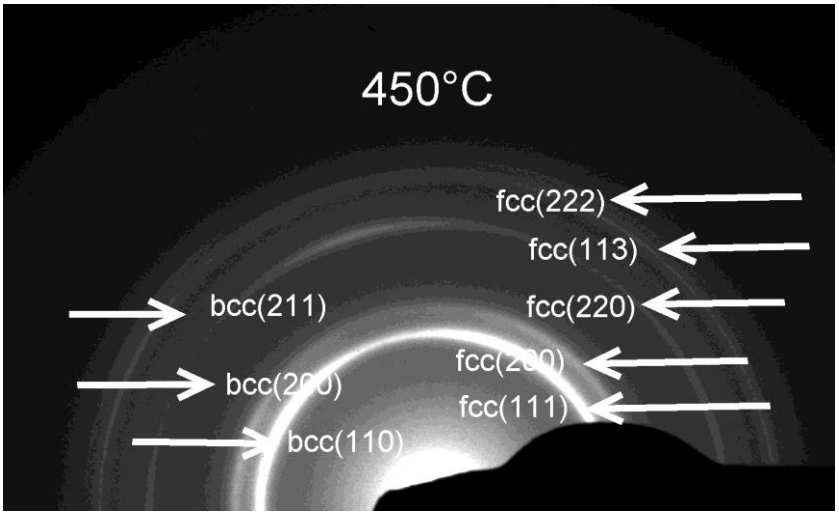


Fig. 5 Electron diffraction pattern of CrCuCoFeNi at 450°C

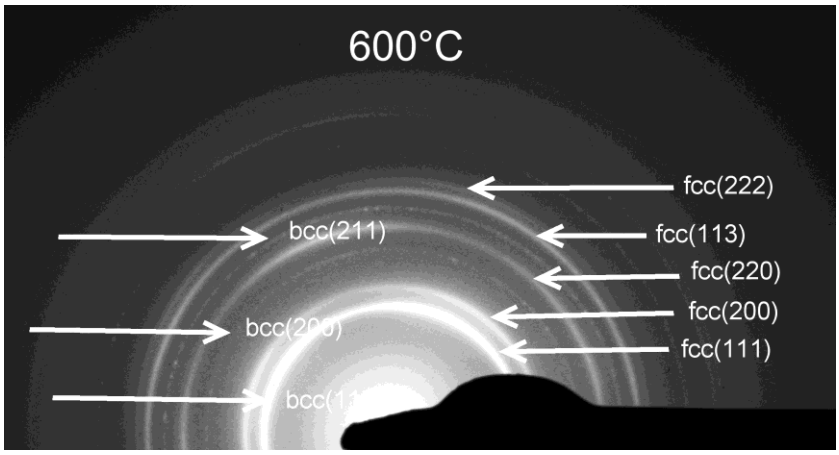


Fig. 6 Electron diffraction pattern of CrCuCoFeNi at 600°C

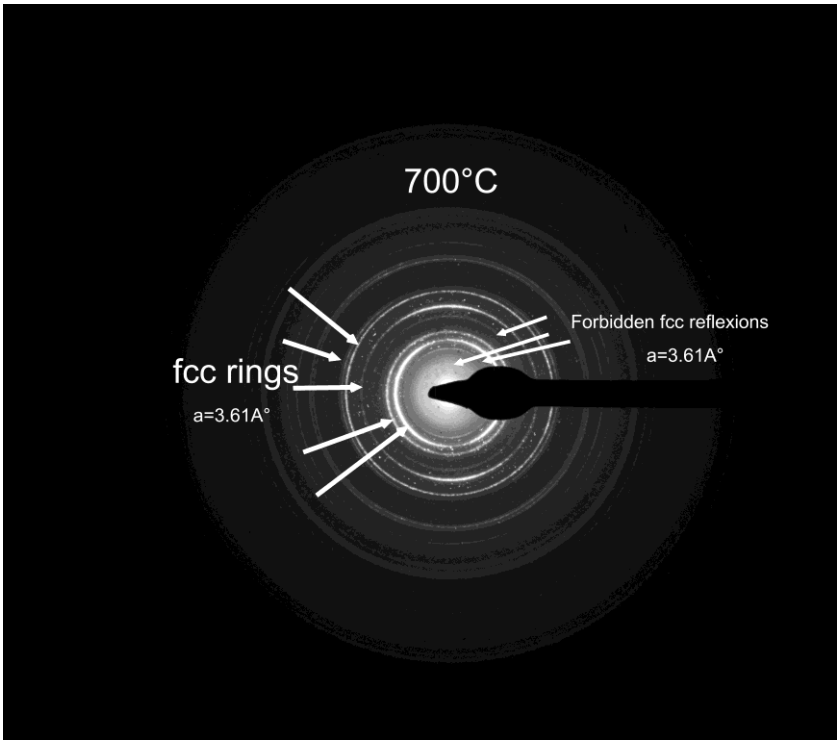


Fig. 7 Electron diffraction pattern of CrCuCoFeNi at 700°C

II/ lectures and exams

Transmission electron microscopy: Prof. György Radnóczi

Technology of materials: Prof. Frantisek Chemelik;

Exams have done successfully