SEMESTER REPORT

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

Introduction

The main aims during the current semester were writing a manuscript on in-situ TEM annealing from RT to 700°C (in 50°C steps/5 minutes) of thin CrFeCuNiCo HEA film. The measurements conducted during annealing were the recording of selected area diffraction patterns as well as bright field images. The manuscript is practically written though not yet finished and is presented as part 1 of this report.

The results have shown that structural and morphological changes of HEA films can be divided into two different temperature ranges: RT-500 °C and 550-700°C. The basic conclusions are:

1/ the film is structurally and morphologically stable up to 450°C, while it shows a small grain (about 5-8 nm grain size) single phase fcc structure (a=0.36 nm).

2/ Above 450°C the appearance of a small quantity of bcc phase started to form which could be observed up to 650°C.

3/ the original fcc solid solution phase remains as the main constituent during annealing up to 700°C

4/ Measurable grain coarsening started at 600°C, simultaneously with segregation of copper and chromium rich phases. The Cr reach phase has a large unit cell and has grain size (about a few 100 nm) at 700 °C.

However, there remained a few open questions: the mechanism of the fcc-bcc transition is still unclear. This can be the part of a second manuscript. However, the description of the phase forming at high temperature we want to include in the present manuscript. Evaluation of high resolution images are in progress, some details are already contained in the manuscript under preparation. We would like to estimate the activation energies of grain growth/formation of new phase, though this needs additional experiments. Isothermal in-situ TEM annealing are in halfway and the HREM and STEM analysis of the observed changes are in progress. This will probably the part of the manuscript under preparation.

The second part of this report will include an overview about the lectures and exams have been studying during this semester

Part .1

The manuscript under praparation (without the introduction and references part for saving space in this report.

1.Introduction (left out)

2. Experimental

CrFeCoNiCu high entropy (HEA) films were co-deposited in a high vacuum system by direct current magnetron sputtering. Films with a thickness of 50 nm were grown at room temperature on NaCl single crystalline substrate as well as on 30 nm thick silicon oxide substrate, The SiOx film was deposited on cleaved NaCl substrate in 4×10^{-4} Pa. The equiatomic concentration CrFeCoNiCu target of 99.99%, purity was mounted 25° toward the vertical. The background pressure of the deposition system was 9×10^{-6} Pa. High purity Ar was used as sputtering gas at a pressure of 0.25 Pa. The target was pre-sputtered for 5 minutes before deposition with the shutter closed. The DC power and the deposition time were set to 50 W and 5 min respectively resulting is a 50 nm thick film.

The film grown directly on NaCl substrate was floated off and picked on Cu microgrid, then annealed in-situ in a Philips CM20 transmission electron microscope, operated at 200 keV. The temperature was raised in steps of 50 ^{o}C from room temperature to 700 ^{o}C, having the temperature constant at each step for 5 minutes. The vacuum in the microscope specimen area was maintained to stay at 4.5×10^{-5} Pa during the whole in-situ annealing process.

Two kinds of in-situ annealing were made. In one experiment the changes were followed by SAED, recording diffraction patterns from the same area of 5 µm in diameter at the end of each temperature step, for the evaluation of SAED pattern, the camera constant was calibrated using an Al etalon.

In the second kind of experiment bright field images were recorded at magnification of 50000x at each temperature. The experiments were performed in the way to ensure the observation of changes preferably in the same area of the film. Energy dispersive X-ray spectroscopy (EDS) analysis was performed to verify the composition of the samples before and after annealing. Further structural and EDS characterization was carried out by a FEI Titan-Themis transmission electron microscope (80-200keV, Cs corrected objective lens (point resolution ~0.09nm in image mode and 0.16 nm in STEM mode) operating at 200 keV.

3. Results and discussion

A. morphology and diffraction analysis of the HEA thin film during heating

As can be seen in Fig.1 the electron diffraction pattern indicates the presence of a single FCC solid solution phase and the TEM micrograph. The bright field (BF) TEM image shows that the film is composed of a fine-grained microstructure of about 5-8 nm average size. By averaging the lattice constants from all measurable FCC rings, the size of the unit cell of the FCC-phase is calculated to be 0.358 nm.

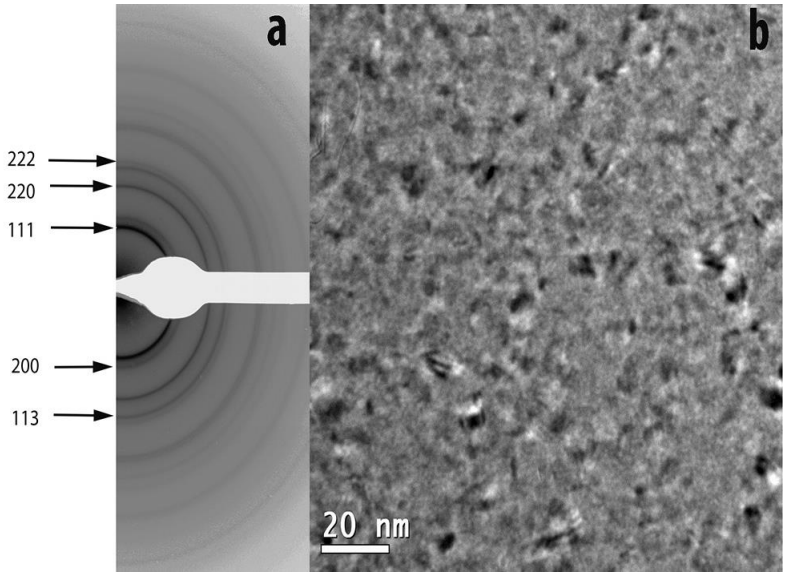

Fig. 1. Electron diffraction pattern (a) Bright field TEM image (b) of the HEA film before annealing. Electron diffraction indicates a single fcc phase.

To obtain microstructure and phase transition information of CrFeCoNiCu HEA film, the as-deposited film was subjected to in situ TEM heating from RT up 700° in 50°C steps, staying at each step for 5 minutes. Selected stations of the change as followed bright field and SEAD images are shown in Fig. 2.

From the analysis of SAED (Fig.2a) patterns we conclude that only the FCC phase is present up to 400°C, while at 450°C new reflections appear in the form of rings (continuous rings) which correspond to a BCC phase of lattice parameter a=0.296 nm. Thus we can say that the CrFeCoNiCu HEA film at 450°C has two-phase structure composed from the original fcc and the newly formed bcc phase. Analyzing of the BF images we notice that up to 400°C the same polycrystalline structure is preserved with an increase in grain size from 5-8 nm to about 10-11 nm (Fig. 2b).

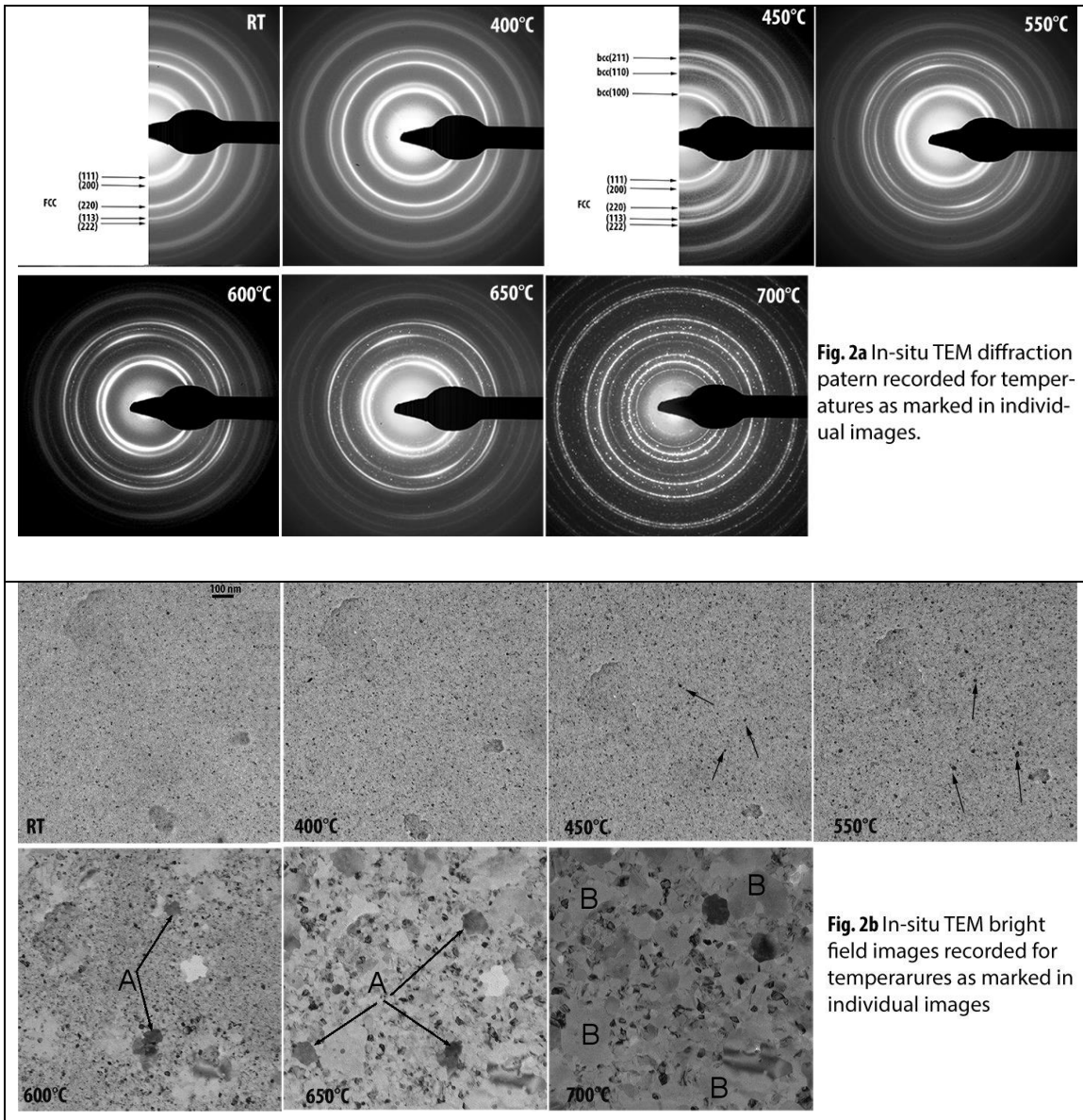

Fig. 2. SEAD patterns (a) and in-situ TEM bright field images (b) and) recorded for temperatures as marked in individual images.

Thus, it can be concluded that the single phase nanocrystalline HEA structure is stable up to 400°C. Heating to 450°C and further up to 550°C some grains having dark contrast and randomly distributed over all the film area appear as marked by arrows in fig 2b. At 600 °C a drastic change in the microstructure occurs. The diffraction rings belonging to the bcc phase become more discontinuous, corresponding to fewer spots on the rings and consequently larger bcc grains in the same selected area. However, individual spots on bcc rings in the diffraction pattern are preserved in all the SAED patterns above 600°C. On the other hand, new large grains, marked as A in Fig. 2b (600°C), appear and grow rapidly to a size of several 100 nm at the expense of the existing two phase matrix. Further up to 700°C new phase grows and occupies about 80 % of all of the available volume. Our first assumption is that the formation of the bcc phase is the precursor phase of the changes taking place above 600°C.

B. microstructure analysis after annealing at 700°C and cooling down to RT of the alloy

The HAADF image and elemental mapping of the annealed film is shown in Fig.3a, It shows that larger grains (about 500nm in diameter) with bright contrast.ie. higher atomic number (Z) are present. These grains correspond to grains marked B in Fig 2b (700 ^{o}C). Simultaneously, somewhat smaller grains with dark gray contrast have been observed, corresponding to lower Z in their composition as well as to grains marked A in Fig. 2b (600^{o}C). These two kinds of new grains formed in the temperature range between 600 ^{o}C and 700 ^{o}C are embedded in a light gray matrix of medium Z in comparison to the other two types of grains. This suggests that separation of the components in the single phase HEA film started during annealing. Elemental mapping indicates that the dark-gray and white grains are enriched in copper and chromium, respectively (Fig.3a (see table 1). Fe, Co and Ni are distributed rather evenly in the remaining matrix (Fig. 3c, d and f). The elemental maps also show that the Cu- and Cr- rich grains are depleted in Fe, Co and Ni.

Numerical calculations concerning the quantitative fractions of each component in different morphologies can be found in Table 1. The small grained areas are close in composition to the original HEA with some deficit of Cr and surplus of Cu in them (locations No.4 and No.5 in Table 1 and Fig. 4). The Cu rich white grains in Fig. 3a are really manly Cu (about 86 at.% with just a very few at.% of Cr, Fe, Co and Ni in them (location No.1 in Table 1 and Fig. 4). Locations No.2 and No.3 in Table 1 and Fig. 4 correspond to dark gray grains in Fig. 3a and contain mainly Cr (about 70 at.% and about twice as much Cu than all the remaining three elements (Fe, Co, Ni). These results show that separation of the components in the originally single phase solid solution HEA film occurred during the annealing

Table 1. Chemical composition (atomic percent) oh HEA annealed at 700°C in areas shown in Fig. 4 measured by EDS in STEM.

Area/at%	Cu	Cr	Co	Fe	Ni
No 1	86.39	1.30	2.82	2.65	6.76
No 2	13.65	71.89	3.99	9.10	1.37
No 3	14.66	68.84	7.76	6.89	1.85
No 4	33.30	10.21	19.25	19.22	18.30
No 5	29.04	13.58	19.45	18.36	19.57

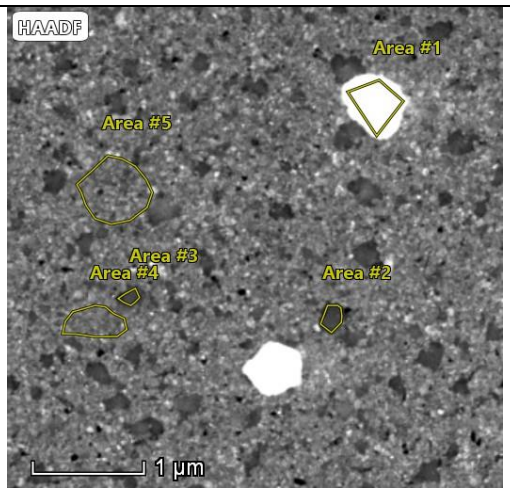

Fig. 4. Post annealing EDS analyses of individual grains in the annealed at 700 ^{o}C HEA film, measured at room temperature.

A general HREM view of the structure is shown in Fig.5a. In this figure the remaining fcc HEA metallic phase is seen having a grain size of about 50 nm, and larger grains of the new phase are present. Their internal structure displays a striped contrast, corresponding to a large period lattice spacing in them. The HRTEM image of these crystallites (grains) and the FFT diffraction pattern shown in the insert (Figure 5b) implies close structural relationship of the newly formed large grains with bcc Cr (a_{Cr}=0.291 nm). The indexed reflections (001 and 110) in 5b figure correspond to reflections of bcc Cr. This can explain the presence of bcc reflections at all temperatures above 600^{o}C as seen in fig. 2a.

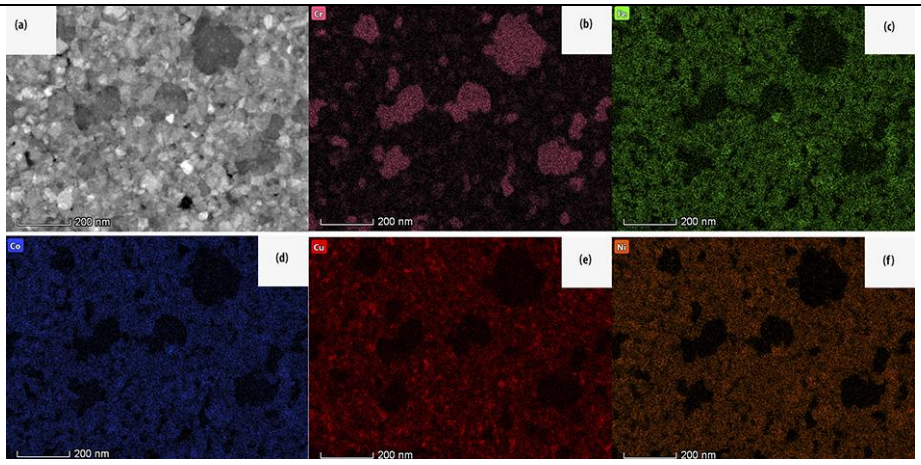

Fig. 5. Representative HAADF-STEM image of CoCuCrFeNi after annealed at 700℃(a), EDS elemental maps show the ddistribution of Cr (b), Fe (c), Co (d),Cu (e), and Ni (f).

Doubling the periodicity with respect to bcc Cr is evident in the Fourier transform; however, based on the appearance of the 1/(4×0.291) nm^{-1} periodicity in the reciprocal lattice, at least 2x2x4xa_{Cr} sized repeating units are deduced (Figure 5b) for the structure of the new phase. In addition, a continuous scattering of the ½½ l reflections is observed parallel to the $[001]_{Cr}$ direction indicating non-periodicity along the crystallographic c axis (Figure 5b). In figures 5c

and 5d Fourier filtered images of the same structure/area are shown. In Fig. 5c the periodic component of the structure is shown, and the aperiodic parts are removed from the image by filtering. The image visualizes the periods in two directions, corresponding to the **c** direction showing a period of 0.58 nm and at an angle of 85° to this period at a spacing of 0. 204 nm dominating the structure of the new phase in this projection. Fig. 5d shows an enlarged Fourier filtered image made with the ½½l diffuse scattering (continuous line) in the insert of Fig. 5b). The white arrows in the image indicate planes parallel to fringes seen in Fig. 5c, however, at a rather random spacing. Nevertheless, the 0.58 nm period still can be observed. This new phase can be considered a Cr-rich intermetallic phase (Fig. 3) with a large unit cell 2x2x4 times the unit cell of Cr.

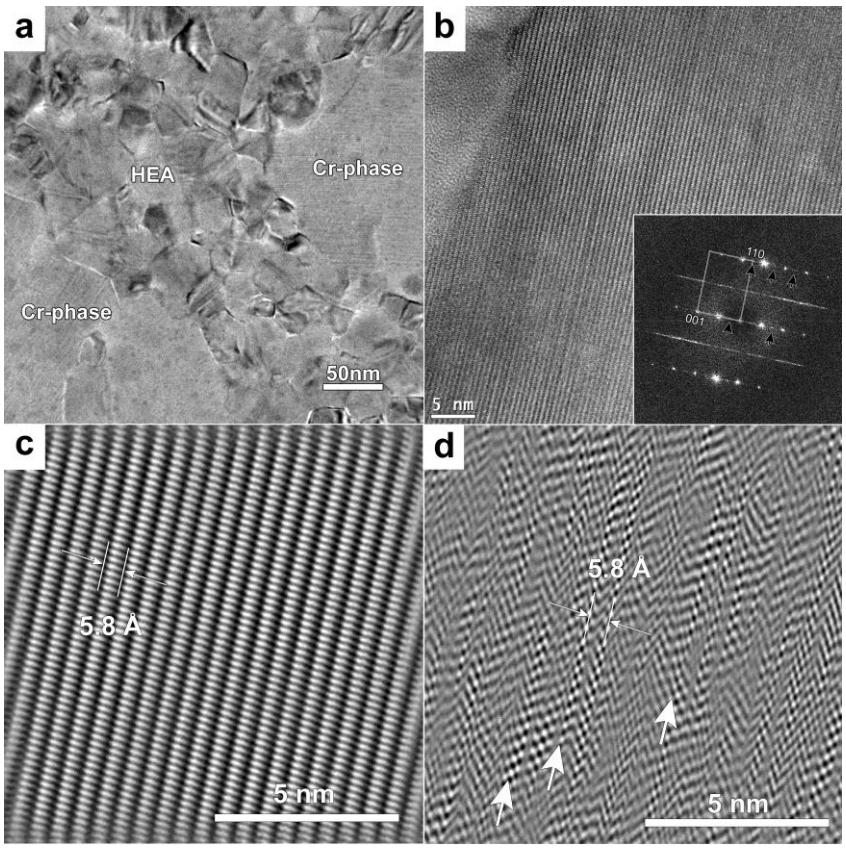

Figure 5. (a) Low magnification image showing spatial relationship of the Cr-rich intermetallic phase and the residual HEA phase formed during in-situ annealing up to 700ºC. (b) Atomic resolution image of the Cr-rich phase. On the Fourier transform (lower right corner) two reflections corresponding to the unit cell of bcc Cr (a_0=2.91Å) are indicated. Note the diffuse scattering parallel to [001]*. Black arrows indicate 11.6 Å periodicity, which is four times the lattice parameter of bcc Cr. (c) Enlarged Fourier filtered image made with the discrete Fourier components of (b). Sporadic reflections corresponding to 11.6 Å periodicity indicated by black arrows in (b) were not included in Fourier filtering. (d) Enlarged Fourier filtered image made with the ½½*l* diffuse scattering (continuous line) on (b). White arrows indicate non-periodic fringes parallel to (001). Note the presence of the 5.8 Å periodicity in (d) as well.

When we consider the chemical mixing enthalpy in a binary system composed of two elements also included in the current HEA, it may be possible to predict the priorities of separation for the components in the HEA film. Table 3 represents the chemical mixing enthalpy, ΔH_{mix} (kJ/mol) in

the binary system between Cu, Cr, Co, Fe, and Ni. Cu has positive values with the other elements. This implies that Cu atoms have repulsive interactions with other components and tend to form Cu-Cu bonding in terms of enthalpy. The composition of the white grain in Fig 4 corresponds practically to copper with a small amount of nickel as shown in Table 1 for the area No 1 (Fig. 4).

Table 2. Chemical mixing enthalpy $\Delta H_{mix}(KJ.mol^{-1})$ in binary systems composed of two elements included in the alloy

	Co	Cr	Cu	Fe	Ni
Co	-	-4	+6	-1	0
Cr	-	-	+12	-1	-7
Cu	-	-	-	+13	+4
Fe	-	-	-	-	-2
Ni	-	-	-	-	-

Part 2, Courses :

Amorphous alloys: Dr. Révész Adam, the exam has been done with oral presentation of the topic: BMG nanocomposites and phase separated BMGs

Analytical Electron Microscopy by Janos L. in this course we have been introduced to TEM SEM, STEM,SEAD, CBED,EELS, EDS. The exam have been done with EDS,EELS, and CBED topics

Conference: we have submitted an abstract for the 2019 EMRS Conference in Nice about the isothermal in-situ annealing of HEA films.