Experimental report

28/03/2017

Proposal:	**5-23-670**	**Council:**	10/2014
Title:	Investigation of structrural properties of the B2 phase in Al_xFeNiCrCo High Entropy Alloys.		
Research area:	Physics		

This proposal is a new proposal

Main proposer:	**Jakub CIESLAK**
Experimental team:	Jakub CIESLAK
Local contacts:	Emmanuelle SUARD

Samples: FeCrNiCoAl

Instrument	Requested days	Allocated days	From	To
D2B	2	2	21/09/2015	23/09/2015

Abstract:

AlxCoCrFeNi system is known, that fcc/bcc structures are observed dependent on x and thermal history of the sample. For experiments the samples were synthesized witch two different techniques, arc melting and a new method based on sintering of pure elements. As determined from an XRD, some amount of ordered B2 structure has been also found. This phase has already been reported and identified as AlNi-B2, but the identification was done by comparing formation energies of pure binary phases, possibly existing in the system. On the other hand the only certain information that can be obtained from XRD is that the Al atoms occupy one position of the B2 since the other components of the alloy are indistinguishable. Electronic structure calculations were performed in order to verify the most energetically favorable sublattice occupancy. Structures were analyzed using semi-ordered super cells with various atomic arrangements. Preliminary results indicate that (Al,Cr)-(Co,Ni) B2 phase tends to form (Fe-atoms are distributed randomly). It should be stressed here, that neutron diffraction is the only method, which allows for verification of the theoretically obtained results in this case

In order to complete and classify the results obtained so far, a systematic study of a series of $\mathrm{Al_xFeNiCrCo}$ alloys were performed, as obtained with the frequently used method of arc-melting as well as a method of powder sintering being uncommon in the context of HEA synthesis. Since the grains representing different phases detected in our sintered samples are large and both chemically and crystallographically homogeneous, such HEA samples appear to be relevant objects to study various physical properties of each phase, separately. On this basis, the phase stability in the $\mathrm{Al_xFeNiCrCo}$ system is presented and discussed in detail for $x \leq 1.5$.

Several series of samples were prepared by the two aforementioned synthesis methods. Each series consisted of six samples of $\mathrm{Al}_x\mathrm{FeCrCoNi}$, with variable Al content ($x = 0$, 0.25, 0.5, 0.75, 1 and 1.5) and equimolar concentrations of the other elements (Fe, Cr, Co, Ni).

Series 1 (SM1) was a control set of samples, prepared with a traditional method by melting of pure elements in the arc-furnace and under argon atmosphere. Each sample was re-melted four times, flipping ingots to improve their homogeneity. Since the mass of each sample was only ~ 5 g, cooling of droplets of this alloy, from the melting temperature (~1400°C) to room temperature (RT), was quite fast (no longer than one minute). In a consequence, it can be assumed that the elements distibution in such prepared samples corresponds to equilibrium state near the melting temperature. No additional heat treatment was applied to the series SM1.

Series 2 (SM2) was prepared in the same way, but all samples were additionally annealed at 1000°C in vacuum of $6 \cdot 10^{-6}$mbar for 72 hours.

Series 3 (SS3) constituted of samples prepared by sintering of a mixture of pure metal powders, with an average grain size larger than 10 μm. The powders were mixed in appropriate amounts and then compressed. The obtained pellets were pre-annealed at 500°C for one day and next annealed at 1000°C for 2 weeks in vacuum of $6 \cdot 10^{-6}$mbar. Finally, they were quenched on a massive piece of brass (still in the same vacuum). Cooling of samples was also quite fast, similiarly as for the samples of SM1. This two-step procedure of annealing and cooling was carried out in order to avoid Al loss from the sample. It is worth noting that the maximum temperature at which the samples were processed is much lower than melting temperature corresponding to HEAs (above 1400°C) as well as the melting points of transition metal constituents, since Al melts at $\sim$ 660°C.

Series 4 (SS4) was prepared according to the same procedure as the SS3 one, but using powders with finer grains, below 7 μm. And for series 5 and 6 (SS5 and SS6) preparation procedures were identical to that of the SS4 one, except for the annealing temperatures, being 850°C and 700°C, respectively.

All prepared samples were next the subject of diffraction analysis using X-ray (XRD) and neutrons (ND) as well as microscopic analysis using scanning electron microscope (SEM) equiped with the energy dispersive X-ray spectrometer (EDX). Besides, for some selected samples phases and compounds identification by electron backscatter diffraction (EBSD) technique was also performed.

The XRD patterns were collected from 10° to 130° in 2θ. For measurements flat surfaces of solid samples were used. In the case of the samples of SM1 and SM2 series, the ingots were sectioned using low-speed diamond saw and cut surface was then polished. Generally, such procedure induces some strain in the surface layers, visible as characteristic small shifts of diffraction peaks, which in principle do not affect the interpretation of the obtained results. The more so the XRD amplitudes of diffraction peaks are strongly influenced by the undesirable texture already present in the droplets of alloys, caused by the solidifying and cooling processes during its preparation. The surface of the samples of the remaining SS3-SS6 series did not require any additional treatment for XRD measurements and they were also found to be texture-free (with randomly oriented grains).

Data were analyzed by the Rietveld method as implemented in the FULLPROF program. It was assumed, that each diffractogram corresponds to one, two or three phases, namely *fcc*, *bcc* or *B2*, depending on the Al concentration. The phases were then analysed with separate lattice parameters and common line widths. It was also assumed, that each crystallographic position was occupied by all constituent elements, with probabilities corresponding to nominal composition of the sample. The only exception was *B2*, where the unit cell was analysed as a simple cubic structure, with two crystallographic positions $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and Al atoms occupying selectively only one of them.

On the basis of the measured diffraction pattern, one can determine the percentage of each phase in the sample. As can be seen, nearly all samples of the control series SM1 are single-phase (*fcc* or *bcc*). Exceptionally, in the sample SM1:x=0.75 the coexistence of *fcc* and *bcc* phases has been observed. The range of such phase coexistence expands when the samples are additionaly annealed (the case of the SM2 series), however the texture present in the melted samples hinders proper analysis of the diffraction peak amplitudes, and hence precise estimation of the abundance of particular phases. On the whole, the results obtained for both series (SM1 and SM2) agree well with the reported data and provide a good reference for samples made by sintering method.

In a series of sintered samples SS3, the coexistence of phases was observed for all samples containing Al. Unfortunately, as confirmed by EDX analysis, the signal from *bcc* phase originates not only from HEAs (resulting from the increase in the amount of Al), but also from not completely dissolved starting chromium grains. The lattice parameters of these two components are so similar that distinguishing these phases is impossible using this technique. It is also worth noting that the melting point of Cr (1907°C) is the highest of all the alloy constituents, so probably annealing time was too short for complete diffusion of this element in the samples.

The phase compositions of SS4, SS5 and SS6 are quite similar to that of SS3, but it can be seen that with increasing annealing temperature the region of phase coexistence narrows for the lower Al concentrations. In any case, the samples analyzed for the border contents of Al are single-phase: *fcc* for $x = 0.0$ and *bcc* for $x = 1.5$. Since the samples corresponding to these series are texture-free, the obtained results on the phase contribution seems to be reasonable.

The $B2$ phase is accompanying the *bcc* one, in the samples with higher Al concentrations. Since the $B2$ phase is easily detectible in the diffractograms it must contain Al, which is in contrast to other transition metal elements (very poorly distinguishable each other by the XRD technique). At this stage, it can not be resolved whether the $B2$ phase forms separate areas with well defined superstructure, or one observes arrangement of Al atoms in the framework of the whole *bcc* phase. To face this problem one needs to apply experimental method, which is more sensitive to different elements occupying two different lattice sites.

Neutron diffraction brings information from the volume of the sample, in contrast to the XRD technique where the signal comes from the surface layers only. Furthermore, as the neutron diffraction occurs on the nuclei (not on the electrons as in the case of XRD) and different elements exbibit different scattering factors, it is often possible to distinguish all used elements, also with close atomic numbers. The purpose of using neutron diffraction technique for the samples containing *B2* phase was to shed some light on the character of atomic ordering in this structure. One would like to understand whether neutron diffraction peaks corresponding to the *B2* phase arise from separate areas of the samples, or they rather result from ordering of any element on one sublattice and random distribution of other elements on the second site. And consequently, the open question is which elements (besides Al atoms) might be ordered?

The experiment was carried out at ILL, Grenoble (D2B), using wavelength λ =1.594Å. Diffractograms were collected at RT from 10° to 160° in steps of 0.05° in 2θ. They were analysed in the same way as described above for XRD. As one can easily notice, the diffractograms are quite similiar to those obtained using XRD and no additional type of ordering (except for the above-mentioned *B2* phase) can be detected. There are also no additional new phases visible with respect to all phases already detected using XRD. The amounts of the fcc, *bcc* and $B2$ phases determined using ND are very similar to those obtained using XRD. The fact that results arisen from two complementary diffraction techniques (ND and XRD)are so similiar, in spite of different possibilities to distinguish different atoms, points to the conclusion that only Al atoms are responsible for the formation of the *B2* phase. Unfortunatelly, on the basis of measured diffractograms it is not possible to characterise the ordering type in the unique way, without any additional information. Such complementary data enabling a better description of ordering may be derived from electronic structure calculations (considering different structural models of HEAs) which are in progress.

At the first glance, the performed ND investigations have confirmed the results obtained from the XRD experiments. However, more careful analysis leads to the conclusion that the amounts of the *bcc* phase determined using ND are systematically higher than that one obtained using XRD for the samples with $x=$ 0.5, 0.75 and 1.0 for all series. There are two plausible explanations of this finding: (i) the phase composition on the surface differs from that in the bulk, which seems unlikely or (ii) the concentrations of elements in the coexisting phases are not identical (as it was assumed when analyzing XRD and ND diffractogramms).

Detailed results regarding microscopic measurements (EDX, EBSD), containing also pictures and references can be found in the full paper, sended to *Acta Materialia* journal for publication. On this stage the results of experimental investigations of $\mathrm{Al_xFeNiCrCo}$ HEAs using XRD, ND, EDX and EBSD techniques can be sumarized and conclusions can be drawn:

—Annealing of the pressed mixture of pure metal powders at temperatures not exceeding 1000°C leads to successful synthesis of HEAs. Upon reduction of the annealing temperature or with the increase of powder granulation, a part of Cr grains were not solved in the matrix after annealing of 14 days.

—Sintering at temperatures above 700°C leads to the formation of regular grains with well-defined borders and a homogeneous chemical composition (also when the undissolved part of Cr is present).

—With increasing of the Al content, decreasing of the *fcc* phase amount occurs, in favor of one or two *bcc* phases. Stoichiometries of these phases only slightly change upon varying the amount of Al, whereas the changes of the phase proportions are apparently visible.

—Small amount of the σ-phase was detected in the sample with equimolar composition, annealed at 1000°C. Its presence in the samples annealed at lower temperatures is likely, but needs more, careful investigations.

—The phases with close chemical composition and having the same crystallographic structure were detected both in the samples prepared by arc-melting as well as in those prepared by sintering. Also the proportions between the quantities of *fcc* and *bcc* phases in the samples obtained by various methods are similar.

—The overall results obtained for sintered and melted samples indicate that the phase compositions of $\mathrm{Al_xFeNiCrCo}$ alloys are very similiar for all investigated HEA, but the corresponding microstructures are quite different. Arc-melting and sintering lead to either dendritic structure or large regular grains with wel-defined borders, respectively.

This work was supported by the Ministry of Science and Higher Education as well as the National Science Centre in Poland (Grant UMO-2015/17/B/ST3/01204). We also thank to Dr. Emmanuelle Suard the Institut Laue-Langevin in Grenoble) for helpful support during data collection.