Synthesis of A2 and B2 Phases in the AlxCoCrFeNi Multi-Component System

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**Abstract**

A2 (Im3m, BCC) and B2 (Pm3m, primitive) phases are two of the phases which exist in the AlxCoCrFeNi multi-component system. These phases do not appear as single phases in the entire range studied so far (0<X<3). In order to measure thermochemical properties of alloys and improve prediction of thermodynamic models, single phases should to be synthesized and characterized. We studied first the mixture of A2 and B2 phases in the Al2.75CoCrFeNi multi-component alloy. The exact composition of each phase was determined followed by an attempt to synthesis individual phase. The “B2” alloy is Al-Ni-Co rich which exhibits a single primitive structure but a non-uniform composition. The “A2” alloy is a Cr-Fe rich alloy which is compositional uniform on the micro-scale but on the nanoscale still exhibits phase separation, into rich Al-Ni-Co nm B2 precipitates and a rich Cr-Fe, A2, matrix. This result exhibits the profound Al impact on the stabilization of the B2 phase in the AlxCoCrFeNi system.

While the B2 alloy is adequate for themochemical study, further efforts should be made to synthesis an A2 alloy. In this case, the Al content should be lower than 10 at.% and the Ni content about 1 at.%. These low contents of Al and Ni should prevent the formation of stable AlNi “like” B2 ordered intermetallics.

**Keywords** AlxCoCrFeNi, Multi-Component system, B2 ordered BCC, A2 disordered BCC

**Introduction**

High entropy alloys (HEA), also known as multicomponent alloys or multi-principal element alloys (MPEA), consist of five or more elements between 5 and 35 at % [1]. These systems usually possess two or more phases, with simple crystallographic structure (e.g., face-centered cubic (fcc), body-centered cubic (bcc), or hexagonal close-packed (hcp)). Among the HEA's The AlxCoCrFeNi system received the scientific and engineering communities' attention due to its superior mechanical properties and corrosion resistance compared to stainless steel [2-5]. Due to its' thermo-mechanical stability at elevated temperatures, it could offer improvements to the property and performance of TBC (Thermal Barrier Coating) systems [6].

In general the AlxCoCrFeNi series contains a mixture of simple structures, such as fcc and bcc, where the bcc phase has an important role in hardening the alloy [7]. With the increase of the Al content, the volume fraction of the bcc phase increases. In many cases, this bcc phase is a mixture of a disordered bcc(A2) which rich in Fe and Cr and ordered bcc (B2) that rich in Al and Ni [8], both phases have same lattice parameter ( 0.287 nm) [9]. Although this system consists only simple crystal structures large discrepancies concerning the calculated phase diagram that exist in the literature [10,11]. These discrepancies arise from the limited experimental data available at elevated temperatures. In order to determine the thermodynamic properties of the system, single phases must be synthesized and characterized using drop solution calorimetry, differential thermal analysis (DTA), dilatometry etc' (for example [12-14]). In this study, we present an attempt to synthesis single A2 and B2 phases, which was initiated by the determination of the composition of each phase in a binary mixture of the two in the Al2.75CoCrFeNi alloy. After synthesis, the alloys microstructure, crystallographic structure, and composition were characterized using X-Ray Diffraction (XRD), High-Resolution Scanning Electron Microscope (HR-SEM), and Transmission Electron Microscopy (TEM) analysis.

**Experimental**

In the first stage, in order to determine the compositions of the A2 and B2 phases, an Al2.75CoCrFeNi alloy was prepared (Table 2) by a non-consumable electrode arc melting using a Ti-getter and ultra-high purity argon atmosphere. The raw materials with purities higher than 99.9% were melted and turned-over five times for improved homogeneity, followed by last stage arc-melting of a 6 mm diameter rod. In order to coarsen the microstructure and reach compositional equilibrium, samples were cut from the casted rod, wrapped in tantalum foil and sealed in quartz capsules. The samples then were heat-treated and water quenched (Table 1). According to [11], for x>1.5, the AlxCoCrFeNi alloy contains a mixture of A2 and B2 phases in the temperature range of ~ 800oC-1300oC, which assist in determining heat treatment temperature.

**Table 1** Heat treatments of Al2.75CoCrFeNi alloy.

|  |  |
| --- | --- |
| Sample # | Heat treatment |
| 1 | 1200oC, 50 hours, 1000oC 25 hours and quenched |
| 2 | 1200oC, 50 hours, 1000oC 100 hours and quenched |

The structure and composition of the obtained phases were characterized using XRD, HR-SEM, and TEM. XRD analysis was performed using Empyrean Alpha 1 diffractometer (Malvern Panalytical Ltd, Royston, UK) with Cu-Kα radiation. XRD spectra were obtained with the following conditions**:** 40kV and 30mA in the 2θ range of 20o to 120o, with a step size of 0.02° and a scan step time of 1 sec. The XRD patterns were analyzed using a whole pattern fitting approach with MDI Jade 2010 software (MDI, Livermore, CA). Samples for SEM characterization were prepared using SiC paper form 320 grit up to 4000 grit and a final stage of polishing with 1µm diamond paste. SEM analysis was performed using Verios XHR 460L apparatus equipped with a Noran Energy Dispersive spectrometer at 15kV beam voltage. 200 kV TEM (JEOL JEM-2100F, Peabody, MA) was used to obtain structural information at the nanoscale, using selected area electron diffraction (SAED). The TEM sample was extracted from the SEMs' sample surface using focused ion beam (FIB, Helios G4 UC, Thermo-Fisher Scientific, MA, USA).

In the second stage, according to the chemical composition received from the SEM-Energy Dispersive Spectrometry (EDS) analysis and supplementary data from the literature, new alloys were prepared using the arc-melting procedure (Table 3). The same characterization procedures were implied to the synthesized alloys.

**Results and Discussion**

**Characterization of the heat-treated Al2.75CoCrFeNi alloys**

Measured compositions of heat-treated alloys are presented in Table 2 and the microstructure of the heat-treated samples in Fig.1. In both cases, the A2 phase (bright phase) precipitated from the B2 matrix in two ways; inside B2 grains with an equiaxed morphology and at grain boundaries with a high aspect ratio. The longer the heat treatment, the coarser the A2 phase gets at grain boundaries. The composition of the A2 and B2 phases in the heat-treated samples is presented in Table 3.

**Table 2** Composition of heat-treated samples determined by EDS.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Heat treatment (last isothermal temperature) | at.% Al | at.% Co | at.% Cr | at.% Fe | at.% Ni |
| #1  | 39.4±0.8 | 15.5±0.9 | 14.2±1.3 | 15.3±0.4 | 15.5±0.4 |
| #2  | 39.3±1.3 | 14.9±0.5 | 15.4±0.9 | 15.4±0.6 | 15.0±0.2 |

**Table 3** Composition of the A2 and B2 phases (EDS measurements) of the heat-treated samples.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Heat treatment  | at.% Al | at.% Co | at.% Cr | at.% Fe | at.% Ni |
| A2 phase |
| 1200oC\_50h, 1000oC\_ 100h\_q | 21.6±0.3 | 5.3±0.2 | 47.8±0.5 | 23.0±0.4 | 2.4±0.2 |
|  |  |  |  |  |  |
| B2 phase |
| 1200oC\_50h, 1000oC\_ 25h\_q | 44.2±0.1 | 17.9±0.4 | 5.8±0.2 | 12.8±0.4 | 19.3±0.1 |
| 1200oC\_50h, 1000oC\_ 100h\_q | 44.2±0.2 | 17.5±0.4 | 6.6±0.5 | 13.0±0.1 | 18.7±0.4 |

# Volume of interaction is too large for measurement of single A2 phase is the 1200oC\_50h, 1000oC\_ 25h\_q sample.

In a previous study, we show a temperature composition dependence of the B2 phase between 900oC to 1200oC [15]. Table 4 summarizes our data as well as data published in the literature concerning the composition of the A2 and B2 phases in the AlxCoCrFeNi system. According to Table 4, the composition of the new synthesized alloys was chosen.

**Table 4** Composition of the A2 and B2 phases in the literature.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Ref. | at.% Al | at.% Co | at.% Cr | at.% Fe | at.% Ni |
| A2 Phase |
| [5] (for x=1) | 3 | 19 | 43 | 30 | 6 |
| [11] (for x=1.5) | 5.0±1.0 | 8.8±0.6  | 52.9±4.0 | 31.8±4.8 | 1.1±0.8 |
| [10] (for x=2.75) | 16.6-30.9 | 5.3-8.5 | 34.2-47.8 | 19.8-27.5 | 2.4-6.6 |
| B2 Phase |
| [5] (for x=1) | 30 | 19 | 9 | 14 | 27 |
| [11] (for x=1.5) | 40.2±2.6 | 21.3±2.1 | 3.2±1.1 | 11.2±0.8 | 24±5.3 |
| [10] (for x=2.75) | 42.2-46.8 | 17.3-17.6 | 5.5-8.8 | 12.4-14 | 17.8-18.6 |

**Synthesis and characterization of Al-Ni rich and Cr-Fe rich alloys**

Table 5 summarizes the compositions of the different alloys synthesized. The Cr-Fe rich alloy was prepared twice since the B2 phase was found in the first alloy (as shown below).

According to the definition of high entropy alloys where each element content should be higher than 5 at.%, we chose not to synthesis alloys with minor elements.

**Table 5** Composition of synthesized alloys (area EDS measurements).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| alloy | at.% Al | at.% Co | at.% Cr | at.% Fe | at.% Ni |
| Al-Ni rich (n)  | 38 | 20 | 6 | 12 | 24 |
| Al-Ni rich (m) | 38.0±0.1 | 20.3±0.2 | 5.9±0.1 | 11.8±0.1 | 24±0.3 |
| Cr-Fe rich 1 (n) | 21 | 7 | 42 | 25 | 5 |
| Cr-Fe rich 1(m) | 19.6±0.3 | 7.5±0.1 | 42.4±0.6 | 25.6±0.4 | 4.9±0.4 |
| Cr-Fe rich 2 (n) | 15 | 8 | 45 | 27 | 5 |
| Cr-Fe rich 2 (m) | 14.7±0.2 | 8.6±0.4 | 44.3±0.3 | 27.3±0.2 | 5.1±0.3 |

n-nominal, m-measured

As was described in the introduction, in case the A2 and B2 phases have the same lattice parameter, the most significant difference between the two XRD patterns is an extra reflection (100) of the B2 phase (Fig. 2).

The experimental XRD patterns of the synthesized alloy are presented in Fig. 3. First, it could be seen that the Cr-Fe rich1 alloy contains the B2 (100) reflection while the Cr-Fe rich2 alloy contains lower contents of this phase. According to whole pattern fitting, the content of the B2 phase in the Cr-Fe rich1 and Cr-Fe rich2 alloys is 31±2 and 24±3 vol.% respectively. Second, the composition changes led to shift of reflections which are caused by differences in the lattice parameter (table 6).

**Table 6** The lattice parameter of the three synthesized alloys extracted by the whole pattern fitting analysis of the XRD data.

|  |  |  |
| --- | --- | --- |
| alloy | Structure (main phase) | Lattice parameter [nm] |
| Al-Ni rich | Ordered BCC | 0.2878±0.0001 |
| Cr-Fe rich1 | Disordered BCC | 0.2888±0.0003 |
| Cr-Fe rich2 | Disordered BCC | 0.2882±0.0001 |

Since XRD is an integral measurement, SEM and TEM analysis were perform. For the Al-Ni rich alloy, BSE-SEM image shows clear compositional variance on the micro-scale (Fig. 4). BSE image implies that there are compositional differences between the inner-grains (dendrites) and boundaries. Tables 7 and 8 summarize the SEM and TEM, EDS analysis.

**Table 7** EDS (SEM) analysis of Al-Ni rich alloy

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | at.% Al | at.% Co | at.% Cr | at.% Fe | at.% Ni |
|  Bright phase  | 32.0±1.0 | 20.8±0.2 | 10.3±1.0 | 17.7±1.0 | 19.2±0.9 |
| Dark phase | 41.1±0.9 | 19.7±0.3 | 3.8±0.5 | 9.5±1.0 | 25.9±0.5 |

**Table 8** EDS (TEM) analysis of Al-Ni rich alloy

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | at.% Al | at.% Co | at.% Cr | at.% Fe | at.% Ni |
|  Bright phase  | 31.4±0.2 | 21.3±0.6 | 9.1±0.6 | 16.3±0.7 | 21.9±0.4 |
| Dark phase | 42.1±0.6 | 19.2±0.6 | 4.1±0.4 | 9.3±0.2 | 25.3±0.3 |

These results are in good agreement with the reported results in the literature seen in Table 4 (except the value of Ni in the bright phase). The results imply a transformation similar to spinoidal decomposition transformation of the B2 phase.

TEM electron diffraction confirmed that the Al-Ni rich alloy contains a single primitive B2 structure. Fig. 5 shows a forbidden BCC reflection and allowed primitive reflection at $(11\overbar{1})$ when the zone axis is at [112]. This pattern exists in the core and boundaries of grains as well. The lattice parameters (a), extracted from the electron patterns as well as from the patterns with [111] zone axis are 0.2918±0.0006 nm and 0.2912±0.0005 nm for the core and boundaries respectively. The differences found by electron diffraction between the two regions are minor and these results are slightly higher than the lattice parameter extracted from XRD pattern (Table 6). Nevertheless, despite the significant differences in composition between the two regions, lattice parameters are practically the same (within the instrumental error).

 Concerning the Cr-Fe rich2 sample, BSE images (Fig. 6) show at low magnifications the grains structure and the relatively large grain size (~ 200-300 m), containing a finer periodic morphology inside grains. At higher magnifications, nano precipitates are observed.

TEM analysis of FIB prepared samples is shown in Figs. 7-8. These images prove that the alloy is a mixture of A2 (matrix) and B2 (precipitates). Again, it could be seen in the X-ray mapping that the primitive B2 phase is richer in Al, Co, and Ni while the A2 BCC phase is richer in Cr and Fe. EDS elemental analysis results, of the ~50 nm B2 precipitates are summarized in Table 9.

**Table 9** EDS (TEM) of A2 Matrix and B2 particles.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| alloy | at.% Al | at.% Co | at.% Cr | at.% Fe | at.% Ni |
| A2 matrix | 10.5±0.6 | 5.4±0.1 | 53.8±0.8 | 29.2±0.2 | 1.1±0.4 |
| B2 particles  | 33.3±2.5 | 13.5±1 | 21.4±3 | 16.3±1.5 | 15.5±1.8 |

Using these results and the nominal composition of the alloy, the volume fraction of each phase in the sample was calculated, giving 0.72±0.05 and 0.28±0.05 for the B2 and A2 phases respectively. These results are in in reasonable agreement with the XRD analysis. Furthermore, the data reported in Table 9 could assist in evaluating the order parameter () of the B2 phase. The B2 phase contains two sub-lattices; 1a (for =1, the sub-lattice is occupied by Co, Cr, Fe and Ni atoms) and 1b (for for =1, the sub-lattice is occupied by Al atom). If assuming that all Al atoms occupy the 1b sub-lattice and using equation (1) [16],

C1b=0.5(1+) (1)

Where C1 is the occupancy of sub-lattice 1b by Al atoms, ($C\_{1}=\frac{0.333}{0.5}$), then =0.33.

As for the A2 results, for the Cr, Fe, and Ni, it matches ref. [17] which means that single phase A2 could be stabilized if the content of Al is reduced to lower contents than 10 at.%. Therefore, in order to avoid the B2 presence, low content of Al and Ni (~ 1 at.%) should be used for synthesis. Al and Ni have high affinity to each other as seen in the high temperature stable AlNi (B2), ordered intermetallic [18].

**Summary and Conclusions**

The goal of this study was to synthesis single A2 and B2 phases which exist as a mixture in the AlxCoCrFeNi multi-component system. In order to determine the desired compositions, Al2.75CoCrFeNi alloy was heat-treated for long periods at elevated temperatures in order to coarsen the microstructure. The composition of each phase was determined by EDS (SEM) analysis and synthesized using the arc-melting technique. Characterization of the alloys showed that A2 alloy was homogeneous on the micro-scale but not on the nano-scale where nm precipitates of B2 phase formed. It also was shown that we obtained a single B2 alloy with compositional variance on the micro-scale. Despite the compositional changes in the B2 alloy, it could be used for further thermochemical research while the “A2” alloy should be refined in order to receive a single phase. The Al content should be reduce to values lower than 10 at.% and the Ni content to about 1 at.%. These low content of Al and Ni should prevent the formation of stable AlNi “like” ordered intermetallics.

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Figure Caption

Figure 1. BSE images of the heat treated Al2.75CoCrFeNi sample (a) 1200oC-50h, 1000oC-25h and quenched (b) 1200oC-50h, 1000oC-100h and quenched. (A2 - bright phase, B2-dark phase).

Figure 2. Theoretical XRD pattern of powder A2+50 vol.% B2 phases using a Cu cathode.

Figure 3. XRD patterns of synthesized alloys.

Figure 4. BSE-SEM image of the Al-Ni rich alloy, showing compositional differences between the core and the boundaries of the grains (dendrites).

Figure 5. Bright field TEM image of the Al-Ni rich alloy (a) electron diffraction proving the sample has a primitive structure in both grains core (b) and boundaries (c).

Figure 6. BSE image of the Cr-Fe rich2 sample after 30 sec etching using aqua regia solution at different magnifications (a) grain size is emphasized (b) nano-size precipitates inside grains.

Figure 7. DF image from (001) reflection, which is allowed for primitive structure and forbidden for BCC structure. Image shows ~50 nm B2 precipitates in A2 matrix.

Figure 8. STEM image (a) EDS X-ray mapping (b-f). B2 phase is rich in Al, Co and Ni compared to the A2 matrix.