Influence of W, Mo and Ti trace elements on the phase separation in Al$_8$Co$_{17}$Cr$_{17}$Cu$_8$Fe$_{17}$Ni$_{33}$ based high entropy alloy

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ABSTRACT

Compositionally complex alloys, also called high entropy alloys, have been investigated for over a decade in view of different applications, but so far only a small number of alloys can be considered as presenting good enough properties for industrial application. The most common family of elements is Al–Co–Cr–Cu–Fe–Ni. The equiatomic alloy having 5 phases and being too brittle, the composition has been modified in order to improve the mechanical properties. Different compositions have been tested and as a first result ductile Al$_4$Co$_{17}$Cr$_{17}$Cu$_8$Fe$_{17}$Ni$_{33}$ has been chosen for deeper investigation. It shows a dendritic segregation into Co–Cr–Fe rich cores and Al–Cu–Ni rich interdendritic sites. The as-cast state is characterized mainly by two phases, namely Al–Cu–Ni rich precipitates of L1$_2$ structure inside a solid solution matrix. After homogenization both alloys consists of a single solid solution phase. Results are compared to calculations by ThermoCalc. In order to further improve the properties of the alloy the Cr content has been decreased and replaced by trace elements W, Mo and Ti, which, according to ThermoCalc, increase the melting point and the phase transition temperature which leads to the formation of the L1$_2$ phase. As-cast and heat treated samples of the base and the modified alloy have been investigated by transmission electron microscopy and three dimensional atom probe. Results of the investigations will be discussed in terms of microstructure, hardness and coherence with ThermoCalc predictions.

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1. Introduction

Since their discovery in the beginning of this century [1–4] high entropy alloys, or compositionally complex alloys, have been subject to intensive investigation. However, the initial assumption [1,4], that a mix of five or more elements would lead to a solid solution of all elements because of the high configurational entropy, has been found to be true for only a very small number of alloys. The best known example is the equiatomic CoCrFeMnNi, for which the fcc solid solution can be obtained even in the as-cast state and with a pronounced dendritic morphology [2,5,6]. Another example is the equiatomic MoNbTaVW of bcc structure [7]. Several attempts have been made to find other single phased solid solutions, but there are two main problems: on the one hand there is no universal prediction criterion [8] and on the other hand single phase alloys do not show the best mechanical properties. Thus, a new alloy design concept has been established.

Former works on alloys of the Al–Co–Cr–Cu–Fe–Ni family [9–11] have shown promising results, but the mechanical properties of this family should be optimized by a choice of the best composition and an adequate heat treatment which lead to a microstructure with good mechanical properties. Equiatomic AlCoCrCuFeNi is a bcc based alloy with five main phases and too brittle for application [10]. Equiatomic AlCoCrFeNi is also bcc based and too brittle, even though it shows only two phases [12]. An improved Al$_{23}$Co$_{15}$Cr$_{23}$Cu$_8$Fe$_{15}$Ni$_{16}$ alloy shows three phases, two bcc and one fcc, but it remains too brittle for applications [11]. Finally, after several tests to find a ductile alloy with fcc phases, the Al$_4$Co$_{17}$Cr$_{17}$Cu$_8$Fe$_{17}$Ni$_{33}$ alloy has been chosen for further investigation because according to ThermoCalc simulations [13,14] it is supposed to be single phased after homogenization at high temperatures and grow a γ phase inside a solid solution matrix when annealed at an intermediate temperature. The formation of γ particles inside a solid solution matrix is known to imply good mechanical properties in Ni-based alloys and this idea is adapted in case of the present high entropy alloys development. The γ morphology has been observed in the as-cast Al$_4$Co$_{17}$Cr$_{17}$Cu$_8$Fe$_{17}$Ni$_{33}$ alloy [13] but the aspect of the γ precipitates should be improved e.g. by increasing their current size of about 10 nm. This attempt is made by the addition of γ and γ' stabilizers known from Ni-based alloys, namely Mo, Ti and W [15].
microstructure formation needs to be clarified. The partitioning of W to either the γ or the γ′ phase in a multicomponent alloy such as Alloy B is hard to predict [17], even though it partitions to γ in basic Ni- superalloys [18]. Mo is expected to partition to the γ phase [18]. Ti is known to partition to the γ′ phase and to stabilize its domain of existence. The chemical composition of the phases has often been determined by energy dispersive X-ray (EDX) analysis. However, the partitioning of small amount of elements is difficult to quantify by EDX. One of the methods that allow a quantitative analysis of phases is atom probe tomography (APT).

Thus, in the present study the influence of the small addition of W, Mo and Ti on the microstructure and the phase formation of Alloy B in the as-cast state and after different heat treatments have been investigated by transmission electron microscopy (TEM); the chemical information on the phases has been obtained by atom probe tomography. The results are compared with those of the base Alloy A. The investigation of the microstructure is accompanied by microhardness measurements in order to understand the influence of the morphological changes on one mechanical property.

### 2. Experimental

Alloy A was prepared in a vacuum induction furnace of elements with ≥ 99.95% purity. Alloy B was prepared of elements with ≥ 99.999% purity in an induction levitation furnace under argon atmosphere. The alloy was re-melted at least three times in order to ensure homogeneity. At this point the melting temperature of the alloys has been recorded with a pyrometer, which gives only an approximate value of the melting temperature because of its possible error of 50 °C. The ingots solidified in a water cooled Cu crucible into the as-cast state. After different heat treatments the alloys were quenched in water to room temperature. The heat treatments are summarized in Table 1.

Specimens for investigation with optical microscope and scanning electron microscope (Zeiss Ultra) were ground and polished down to a grain size of 50 nm with a final polishing OP-U colloidal silica suspension. Some specimens were etched for 5 s with an etching solution consisting of Mo-acid, HNO₃, HCl and H₂O.

TEM specimens were electropolished with a solution of 83% ethanol, 10% perchloric acid and 7% glycerine at −20 °C and a voltage of 30 V. TEM observations were carried out in a Philips CM30 microscope, operated at 300 kV and equipped with an EDX detector.

Specimens for atom probe investigations were first cut to a size of 0.25 × 0.25 × 10 mm³ and then electropolished in two steps. Final polishing was achieved with a solution of 98 vol% butoxyethanol and 2 vol% perchloric acid at room temperature and a final voltage of 3 V. The tomographic atom probe (CAMECA) used for investigations is operated with a standing DC voltage and 20% pulse fraction, with a pulse repetition rate of 1000 Hz. Investigations are performed at 70 K and in a vacuum better than 10⁻⁷ Pa.

Vickers microhardness measurements were performed with a load of ~0.5 N on a Reichert-Jung MHT-10 microhardness tester.

### Table 1

Summary of the heat treatments of Alloy A and Alloy B.

<table>
<thead>
<tr>
<th>State/alloy</th>
<th>Alloy A</th>
<th>Alloy B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>as-cast</td>
<td>as-cast</td>
</tr>
<tr>
<td>Homogenized</td>
<td>1250 °C/1 h</td>
<td>1250 °C/1 h</td>
</tr>
<tr>
<td>Homogenized &amp; annealed</td>
<td>1250 °C/1 h + 700 °C/24 h</td>
<td>1250 °C/1 h + 700 °C/24 h</td>
</tr>
<tr>
<td>Heat treatments for TAP investigation</td>
<td>700 °C/5 h</td>
<td>1250 °C/80 min + 875 °C/100 h</td>
</tr>
</tbody>
</table>

In addition, trace elements Ti (1 at%), W and Mo (0.1 at% each), have been added with the aim to enlarge the domain of existence of the γ phase and to increase the melting temperature of the Al₈Co₁₇Cr₁₇Cu₈Fe₁₇Ni₃₃ alloy, which will be called Alloy A. A new alloy with a composition close to Al₈Co₁₇Cr₁₄Cu₈Fe₁₇Ni₃₄.₈W₀.₁Mo₀.₁Ti₁ was finally made. In the manuscript it will be called Alloy B. ThermoCalc simulations were used for the microstructure development of the alloys in this study. However, the ThermoCalc diagrams show the phase formation in the equilibrium state, and it needs to be checked whether the prediction for the present alloy is valid.

The influence of the addition of W, Mo and Ti to Alloy A on the microstructure formation needs to be clarified. In Ni-based superalloys W and Mo promote the solid solution strengthening of the γ matrix [16]. The partitioning of W to either the γ or the γ′ phase in a multicomponent alloy such as Alloy B is hard to predict [17], even though it partitions to γ in basic Ni- superalloys [18]. Mo is expected to partition to the γ phase [18]. Ti is known to partition to the γ′ phase and to stabilize its domain of existence. The chemical composition of the phases has often been determined by energy dispersive X-ray (EDX) analysis. However, the partitioning of small amount of elements is difficult to quantify by EDX. One of the methods that allow a quantitative analysis of phases is atom probe tomography (APT).

Thus, in the present study the influence of the small addition of W, Mo and Ti on the microstructure and the phase formation of Alloy B in the as-cast state and after different heat treatments have been investigated by transmission electron microscopy (TEM); the chemical information on the phases has been obtained by atom probe tomography. The results are compared with those of the base Alloy A. The investigation of the microstructure is accompanied by microhardness measurements in order to understand the influence of the morphological changes on one mechanical property.
Phase diagrams have been simulated with the CALPHAD-based software ThermoCalc, using the NiTT7 database [13,19].

Differential scanning calorimetry (DSC) measurements were carried out in a DSC 404 C Pegasus Thermal analyzer by the Netzsch company and in a DSC by Linseis.

3. Results and discussion

Fig. 1 shows the phase diagrams of both alloys as calculated by ThermoCalc. The already published phase diagram of Alloy A shown in Fig. 1a [11,14] indicates a large number of phases below 600 °C which could not be found experimentally. Former studies [11,14] proved the presence of the disordered fcc solid solution matrix marked in red, which is supposed to form above 400 °C, and the \( \gamma \) phase marked in brown, which is supposed to transform above \( \sim 750 \) °C. At 700 °C, a \( \gamma \) volume fraction of about 20% is expected. Additionally, Cr carbides have been found in specimens heat treated at 700 °C. The last phase is due to material impurities and could not be predicted by ThermoCalc because impurities have not been taken into account. More details are given in Ref. [14].

The phase diagram in Fig. 1b shows the phases in Alloy B. The evolution of the fcc phase is almost unchanged compared to the

![Fig. 2. Optical micrographs of the Al\(_{80}\)Co\(_{17}\)Cr\(_{7}\)Cu\(_{7}\)Fe\(_{17}\)Ni\(_{33}\) alloy (Alloy A): (a) as-cast, (b) homogenized at 1250 °C/1 h; and of the Al\(_{80}\)Co\(_{17}\)Cr\(_{7}\)Cu\(_{7}\)Fe\(_{17}\)Ni\(_{34.8}\)W\(_{0.1}\)Mo\(_{0.1}\)Ti\(_{1}\) alloy (Alloy B): (c) as-cast and (d) homogenized at 1250 °C/80 min. Dendrites are clearly visible in both non-homogenized samples.]

![Fig. 3. DSC curves of (a) Al\(_{80}\)Co\(_{17}\)Cr\(_{7}\)Cu\(_{7}\)Fe\(_{17}\)Ni\(_{33}\) (Alloy A) and (b) Al\(_{80}\)Co\(_{17}\)Cr\(_{7}\)Cu\(_{7}\)Fe\(_{17}\)Ni\(_{34.8}\)W\(_{0.1}\)Mo\(_{0.1}\)Ti\(_{1}\) (Alloy B). An exothermic peak can be seen in the heating curve at about 840 °C in the case of Alloy A and at about 920 °C in the case of Alloy B. These peaks correspond to the \( \gamma \) formation temperature.]

The curve of the γ phase has been shifted upwards and to the right and the phase thus has a higher volume fraction and exists at higher temperatures, as has been expected by the addition of Ti. The NiAl phase predicted in Alloy A has disappeared and thus there is a range of temperature between 730 °C and 920 °C where the desirable morphology (γ' precipitates in solid solution fcc matrix) would exist. At 700 °C the volume fraction of γ' is expected to be around 35%. The melting temperature according to Fig. 1b has not changed compared to the base alloy (see Fig. 1a). The melting range predicted by ThermoCalc for both alloys lies between 1286 and 1330 °C. The small addition of 1 at% Ti and 0.1 at% of Mo and W does not considerably influence the melting point.

The experimental verification of the ThermoCalc prediction proves difficult for room temperature observations because the cooling of the cast alloys is of course faster that the assumed equilibrium and therefore the formation of phases below 600 °C is less probable. Thus, the experimental observations of the as-cast alloys are not expected to correspond to the predictions.

The microstructure of the as-cast Alloy A and Alloy B is shown in Fig. 4 using optical microscopy. Two states are being investigated for each alloy, namely the etched as-cast state in (a) and (c) and the one homogenized at 1250 °C for 1 h in (b) and (d). The bright imaged Al–Cu–Ni rich precipitates with an L12 structure are embedded in the fcc matrix. The corresponding electron diffraction patterns of the [001] zone axis in the insets in (a), (c), (d), (e) and (f) display superlattice reflections corresponding to the L12 structure.

![DF TEM micrographs of the Al8Co17Cr17Cu17Fe17Ni31 alloy (Alloy A): (a) as-cast, (b) homogenised at 1250 °C/1 h, (c) annealed at 1250 °C/1 h + 700 °C/24 h; and of the Al8Co17Cr17Cu17Fe17Ni31Mo0.1Ti1 alloy (Alloy B): (d) as-cast, (e) homogenised at 1250 °C/80 min and (f) annealed at 1250 °C/80 min + 700 °C/24 h. The bright imaged Al–Cu–Ni rich precipitates with an L12 structure are embedded in the fcc matrix. The corresponding electron diffraction patterns of the [001] zone axis in the insets in (a), (c), (d), (e) and (f) display superlattice reflections corresponding to the L12 structure.](image)
both alloys is present at this temperature.

The microstructure of the as-cast samples illustrated in Fig. 2 (a) and (c) show a dendritic morphology. Observations with SEM/EDX (not shown here) visualize an enrichment of the high-melting elements Co, Cr and Fe in the dendrite cores and a more (Cu) or less (Al and Ni) pronounced segregation into the interdendritic regions of the low-melting elements Al, Cu and Ni. After the homogenization at 1250 °C dendrites are not visible any more in either alloy. The thermal stability of the investigated alloys was characterized by about 5 nm sized precipitates with L12 structure formed and their heat releases interfere with each other. Thus, the difference in temperature between the one calculated (770 °C) by ThermoCalc and the one obtained from DSC (840 °C) is much larger. From these results the temperature of 700 °C was chosen for heat treatment of both alloys to form the γ’ phase.

The microstructure is observed after three stages: as-cast, homogenized at 1250 °C and heat treated at 700 °C; and it has been compiled in Fig. 4. Dark field TEM images of Alloy A and Alloy B give a closer view of the inside of the grains (Fig. 4). Fig. 4a shows bright imaged, about 10 nm sized precipitates embedded in a matrix in the as-cast Alloy A. The corresponding SAD confirms that the matrix is a disordered fcc solid solution and the precipitates have an ordered L12 structure which is coherent with the matrix. The homogenized Alloy A at 1250 °C/1 h sample in Fig. 4b shows a homogeneous fcc solid solution. No superlattice reflexes can be seen in the corresponding SAD. The same type of precipitates as in the as-cast alloy, though slightly bigger (~20 nm) can be found in the alloy homogenized at 1250 °C/1 h and aged at 700 °C/24 h (Fig. 4c).

Fig. 4d shows the microstructure of the as-cast Alloy B, which is characterized by about 5 nm sized precipitates with L12 structure.

### Table 2

Concentration (in at%) of the phases in Alloy A and Alloy B measured by APT. The error bar corresponds to the standard deviation 2σ. The average cluster size in the homogenized Alloy B is 160 atoms.

<table>
<thead>
<tr>
<th></th>
<th>AlCo2Cr1Cu6Fe11Ni15 (Alloy A)</th>
<th>AlCo2Cr1Cu6Fe11W1Mo1Ti1 (Alloy B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-cast 700 °C/5 h</td>
<td>As-cast 1250 °C/80 min + 875 °C/100 h</td>
</tr>
<tr>
<td>Matrix</td>
<td>Matrix γ' Phase</td>
<td>Matrix γ' Phase</td>
</tr>
<tr>
<td>Al</td>
<td>6.3 ± 0.3</td>
<td>8.0 ± 0.2</td>
</tr>
<tr>
<td>Co</td>
<td>18.7 ± 0.7</td>
<td>16.9 ± 0.2</td>
</tr>
<tr>
<td>Cr</td>
<td>18.3 ± 0.8</td>
<td>14.3 ± 0.3</td>
</tr>
<tr>
<td>Cu</td>
<td>4.5 ± 0.6</td>
<td>3.3 ± 0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>19.0 ± 0.3</td>
<td>18.0 ± 0.2</td>
</tr>
<tr>
<td>Ni</td>
<td>33.2 ± 1.8</td>
<td>36.3 ± 0.5</td>
</tr>
<tr>
<td>W</td>
<td>–</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>Mo</td>
<td>–</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>Ti</td>
<td>–</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Vol%</td>
<td>83</td>
<td>85</td>
</tr>
<tr>
<td>70%</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>80%</td>
<td>20</td>
<td>93</td>
</tr>
</tbody>
</table>
the addition of W, Mo and Ti leads to an enhanced growth of the microstructure, the microhardness has been measured on samples of different heat treatments.

Fig. 6 shows the Vickers microhardness measurements of both alloys at three different states. The addition of W, Mo and Ti softens the alloy in the as-cast state. This can be explained by the smaller size of the Al–Cu–Ni rich γ' precipitates, as can be seen in Fig. 6. APT measurements also show that the volume fraction of the γ' precipitates is lower in the Alloy B alloy (~15%) than in the Alloy A (~20%). In both alloys the precipitates heat treated at 1250 °C are the softest. However, in the homogenized state the Alloy B is slightly harder because of the presence of some γ' precipitates that have not been removed by the homogenization treatment (see Fig. 5). The heat treatment at 1250 °C/1 h + 700 °C/24 h induces the highest hardness in both alloys. This subsequent annealing at 700 °C/24 h makes the Alloy B harder than the Alloy A because the average size of the γ' precipitates in the former is bigger than in the latter. The tendency in the microhardness is in accordance with observations in Ni base alloys, in which the best mechanical properties are obtained for precipitates of about 500 nm in size [22]. In our study the size of the γ' precipitates is far away from this optimum. To find the right heat treatment in order to produce large γ' precipitates is the next step of our investigations. In addition, the mechanical properties of Ni-based alloys are derived from the volume fraction of γ' precipitates which nowadays reaches 70–80% [15]. To reach the maximum volume fraction of γ' precipitates in the alloy with additions of W, Mo and Ti is another aim for the future investigations.

It can thus be concluded that the controlled formation of ordered precipitates enhances the hardness and the initial concept of high entropy alloys concerning the benefits of a solid solution does not apply. The addition of γ' stabilizers shows this even more clearly.

4. Conclusions

Experimental results obtained by TEM and APT calculations with ThermoCalc have enlightened the influence of the small additions of W, Mo and Ti to the microstructure of the Al8Co17Cr17Cu8Fe17Ni33 alloy. The following insights have been obtained:

- Ti was found preferentially in the γ' precipitates, as expected from Ni based superalloys.
- No preferential partitioning has been found for either W nor Mo. They are equally distributed in both the γ and the γ phase.
- Another important aspect is that the addition of W, Mo and Ti leads to the enlargement of the existence region of the γ' phase.
- The controlled formation of ordered particles inside a solid solution matrix enhances the microhardness of the alloy.
- The prediction of the phase formation by ThermoCalc simulation is valid for the high temperature region.

The modification of the Al8Co17Cr17Cu8Fe17Ni33 alloy by W, Mo and Ti additions was found to be an effective approach to stabilize and improve the microstructure with respect to high temperature applications.

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