A1-L1₂ structures in the Al-Co-Ni-Ti quaternary phase system

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Abstract
The phase constituents of alloys from the (Ni,Co)₈₅(Al,Ti)₁₅ plane of the Ni-Co-Al-Ti quaternary system were investigated following prolonged exposure at 750°C. Microstructural investigations confirmed the existence of a continuous A1-L1₂ two-phase region in the Ni-Co-Al-Ti quaternary system between Ni-Ni₃Al and Co-Co₃Ti. The lattice misfits of alloys from this quaternary system were determined using neutron diffraction. With increasing contents of Ti the positive lattice misfit increases up to +0.79% in the Ti-containing alloys, which leads to an increasing tetragonal distortion of the γ matrix phase due to the increasing coherency stresses.

Introduction
Efforts to improve the elevated temperature strength and creep resistance of alloys used for the manufacture of turbine discs have led to the investigation of new Ni-base superalloys with higher contents of Co and Ti than in commercially available Ni-base superalloys [1]. The enhanced high temperature properties reported for these alloys can be attributed to the known effects of the alloying elements Co and Ti in Ni-base superalloys. Ti increases the volume fraction and solvus temperature of the intermetallic L1₂ phase (γ’) and acts as a solid solution strengthener of the L1₂ phase. Co increases the volume fraction of the L1₂ by reducing the solubility of L1₂ forming elements Al and Ti in the A1 matrix phase (γ), acts as solid solution strengthener of γ and increases creep resistance through reduction of stacking fault energy (SFE) [2].

In recent work, Raghaven [3] and Cui [4] have reported the existence of a continuous L1₂ phase field between Ni₃Al and Co₃Ti, forming precipitates of the type (Ni,Co)₉₅(Al,Ti) across the entire composition line (see Fig 1). In these studies, EDX analysis of the L1₂ phase precipitates showed that the Ni+Co content was approximately 75 at% whilst the Al+Ti content was 25 at%. The identification of a single L1₂ phase field across this quaternary system offers the prospect of new Ni-Co-based superalloys that may take advantage of the benefits of elevated Co and Ti levels in nickel-base superalloys. In particular, it is known that the intermetallic L1₂ Co₃Ti phase possesses an increased strength over Ni₃Al above 730 °C [5]. Nickel based superalloys with high Co and Ti levels may therefore be anticipated to possess higher strength in this temperature regime. In addition, it is possible that these alloys may also overcome many of the key deficiencies associated with alloys based upon Co-Co₃Ti. These include the lower solubility limits for alloying elements compared with alloys based upon Ni-Ni₃Al as well as their predisposition to discontinuous coarsening [6]. Efforts to inhibit discontinuous coarsening in alloys based upon Co-Co₃Ti have not been sufficiently successful to allow their use at high temperatures. It has been suggested that discontinuous coarsening in these alloys may be influenced by their relatively high lattice parameter misfit compared to Ni-Ni₃Al alloys [7]. For A1-L1₂ it is generally accepted that a large lattice parameter misfit between the coherent γ’ precipitates and the γ matrix is beneficial for low temperature strength, whilst a low misfit is generally preferred for intermediate temperature creep resistance [8, 9]. In designing such alloys it is therefore critical that the effect of alloying on the lattice parameter misfit is understood.
In this work a series of alloys were prepared which lie within the continuous Al-L1_2 region connecting the two phase regions Ni-Ni_3Al and Co-Co_3Ti identified by Raghaven [3] and Cui [4]. In order to determine the relationship between alloy composition and the lattice parameter misfit between the γ and γ’ phase in the quaternary system a series of measurements were performed using neutron diffraction. Further investigations on the lattice misfit and the propensity of these alloys to discontinuous coarsening will be published elsewhere.

**Experimental method**

Compositionally homogeneous alloys along the compositional line between 85Ni-15Al at% and 85Co-15Al at% were produced by vacuum arc remelting (VAR) of pieces of two ingots which had the composition line end member compositions, namely 85Ni-15at%Al and 85Co-15at%Ti for the Al-Co-Ni-Ti quaternary system. The binary composition end members were prepared, from raw elements of 99.9% purity, or better, by means of vacuum induction melting (VIM). The alloys were chosen in order to have a reasonable (50-60%) volume fraction of L1_2 phase in equilibrium with an Al matrix.

The compositions of the alloys A to G in the Al-Co-Ni-Ti system are given in Table 1 and illustrated in Fig 1).

**Figure 1**: Quaternary phase diagram of Ni-Co-Al-Ti with γ - γ’ equilibrium between 1100°C and 750°C (adapted from [4]). The investigated alloys A-G (marked as dots) with their different compositions lie on a line between the phase fields of γ and γ’.

The alloys A-F were solution heat treated in the single phase Al region in order to minimise casting-induced microsegregation. The solution heat treatment temperatures were selected to be above the L1_2 solvus temperature but below the solidus temperature for each alloy, as determined from DSC thermograms. The solution heat treatments were performed in sealed silica tubes at temperatures of 1380°C (alloy A), 1330°C (alloys B and C), 1285°C (alloy D), 1245°C (alloy E) and 1195°C (alloy F) for 20 hours. Alloy G was heat treated at 1160°C for 20h in the two phase region liquid + A1. The solution heat treated alloys were aged at 750 °C for 1000 hours to obtain thermodynamically stable phase distributions at this temperature. Samples of the different compositions in the solution heat treated condition were analysed using neutron diffraction on the POLARIS beamline at the ISIS facility, UK. Fitting of the experimental neutron diffraction spectra was performed using the Carpenter-Ikeda function implemented in the graphic software IGOR PRO [10].
Table 1: Nominal compositions of alloys prepared from the Ni-Co-Al-Ti quaternary system in atomic (at%) and weight per cent (wt%).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nickel at%</th>
<th>Nickel wt%</th>
<th>Cobalt at%</th>
<th>Cobalt wt%</th>
<th>Aluminium at%</th>
<th>Aluminium wt%</th>
<th>Titanium at%</th>
<th>Titanium wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>85.0</td>
<td>92.50</td>
<td>-</td>
<td>-</td>
<td>15.0</td>
<td>7.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>70.0</td>
<td>75.35</td>
<td>15</td>
<td>16.21</td>
<td>12.35</td>
<td>6.11</td>
<td>2.65</td>
<td>2.32</td>
</tr>
<tr>
<td>C</td>
<td>55.0</td>
<td>58.57</td>
<td>30.0</td>
<td>32.08</td>
<td>9.71</td>
<td>4.82</td>
<td>5.29</td>
<td>4.63</td>
</tr>
<tr>
<td>D</td>
<td>42.5</td>
<td>44.86</td>
<td>42.5</td>
<td>45.04</td>
<td>7.50</td>
<td>3.64</td>
<td>7.50</td>
<td>6.46</td>
</tr>
<tr>
<td>E</td>
<td>30.0</td>
<td>31.39</td>
<td>55.0</td>
<td>57.78</td>
<td>5.29</td>
<td>2.55</td>
<td>9.71</td>
<td>8.28</td>
</tr>
<tr>
<td>F</td>
<td>15.0</td>
<td>15.53</td>
<td>70.0</td>
<td>72.78</td>
<td>2.64</td>
<td>1.26</td>
<td>12.35</td>
<td>10.43</td>
</tr>
<tr>
<td>G</td>
<td>-</td>
<td>-</td>
<td>85.0</td>
<td>87.46</td>
<td>-</td>
<td>-</td>
<td>15.0</td>
<td>12.54</td>
</tr>
</tbody>
</table>

Due to the high lattice misfit, $\delta$, exhibited by many of the alloys investigated, the $\gamma$ matrix phase was often observed to exhibit a tetragonal distortion. Accordingly the fundamental \{200\} peaks had to be fitted with three sub-peaks to represent the contributions of the $L1_2$ phase and the tetragonal distorted lattice of the $A1$ phase. By assuming plane stress in the thin films of the $\gamma$ matrix, the equivalent cubic lattice parameter could be obtained using the following equation:

$$a_{A1,cubic} = \frac{a_{A1,c} - Pa_{A1,a}}{1-P}$$  \hspace{1cm} (1)

where $a_{A1,c}$ and $a_{A1,a}$ are the lattice parameters of the tetragonal distorted $\gamma$ matrix phase and the parameter $P = -0.86$ (for details see [11]).

From this the lattice misfit, $\delta$, could be calculated by:

$$\delta = \frac{2 \times (a_{L1_2} - a_{A1,cubic})}{(a_{L1_2} + a_{A1,cubic})}$$  \hspace{1cm} (2)

where $a_{L1_2}$ is the lattice parameter of the $\gamma'$ precipitate phase.

For microstructural investigations the samples were prepared by sequential grinding and polishing before etching using Kalling’s reagent (CuCl$_2$, hydrochloric acid, water). Images of all of the samples were acquired with a JEOL 6340F FEGSEM.

Results and Discussion

**Microstructure.** In the solution heat treated condition, all the alloys A-F exhibited a two-phase $\gamma/\gamma'$ microstructure. Following aging at 750°C for 1000 hours no new phases were formed in these alloys. However, discontinuous coarsening was observed in the alloys with high Co and Ti contents. The microstructures of alloys C, D, E and F are shown in Fig. 2. These microstructural investigations are consistent with the existence of a two phase $A1$-$L1_2$ region connecting the Ni-Ni$_3$Al and Co-Co$_3$Ti binary systems.

**Lattice misfit.** Neutron diffraction data was acquired from all of the alloys in the as-solutioned condition and also after subsequent isothermal exposure at a range of different temperatures and durations. An example of one of the neutron diffraction spectra is shown in Fig 4. The two insets in this figure show expanded views of the \{200\} and \{111\} peaks. The differences between these two peaks is indicative of a tetragonal distortion of the $\gamma$ matrix phase as a result of the coherency stresses between the $\gamma$ and $\gamma'$ phases [12].
The lattice parameters of the L1₂ phase, \( a_{L1_2} \), and of the tetragonal distorted A1 matrix phase, \( a_{A1,c} \) and \( a_{A1,a} \), as well as the equivalent cubic lattice parameter, \( a_{A1,cubic} \), (see Eq. 1) determined from the diffraction spectra of all alloys investigated are plotted in Fig 5a. The calculated lattice misfits (see Eq.2) are shown in Fig 5b.

**Figure 2:** Alloys C, D, E and F a) to d) after solution heat treatment and aging for 1000h at 750°C.

**Figure 4:** Full spectrum neutron diffraction analysis from alloy composition E after solution heat treatment and an additional short term aging at 900°C for 60hrs. The line shows the overall modelled fit of the experimental data (dots). Inset are expansions of the \{111\} peak (right) and the \{200\} which shows the tetragonal distortion of the lattice of the matrix.
The measured lattice parameter and calculated lattice misfits for the binary alloys are in good agreement with literature data [7, 13]. The binary Ni-Al alloy, A has a positive lattice parameter misfit, i.e. the lattice parameter of the $\gamma'$ precipitate phase is bigger than that of the $\gamma$ matrix phase (Fig. 5a and b).

With increasing contents of Co and Ti the lattice parameter of both the $\gamma$ and $\gamma'$ phases of the solutioned heat treated samples rise continuously from Ni-Ni$_3$Al to Co-Co$_3$Ti. The lattice parameter of $\gamma'$ increases more strongly than $\gamma$ leading to an increasing lattice misfit from alloy A to alloy F (Fig. 5b). This is easily understood as Ti partitions preferentially to the $\gamma'$ precipitate phase and exhibits a positive Vegard coefficient for the Ni$_3$Al phase [2]. The increasing lattice misfit from alloy A to alloy G also leads to increased coherency stresses. Consequently the tetragonal distortion of the $\gamma$ matrix gets bigger from alloy A to alloy G which in turn causes an increasing difference between $a_{A1,c}$ and $a_{A1,a}$.

As the quaternary system possess a two-phase $\gamma/\gamma'$ microstructure over an extended range of compositions they may be used as model systems to investigate the factors, like the lattice misfit, that may influence discontinuous coarsening in Co and Ti rich alloys.

**Summary**

The quaternary phase system Ni-Co-Al-Ti was investigated in this work and following conclusions can be drawn:

- A continuous Al-L1$_2$ two phase region exists in the Ni-Co-Al-Ti quaternary phase diagram between Ni-Ni$_3$Al and Co-Co$_3$Ti at 750°C
- The positive lattice misfit in alloys of both quaternary systems increases with increasing contents of Ti.
- The increasing lattice misfit causes increasing coherency stresses and tetragonal distortion of the $\gamma$ matrix phase.

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References


