Journal of Alloys and Compounds 688 (2016) 542–552

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

# The microstructure and hardness of Ni-Co-Al-Ti-Cr quinary alloys

K.A. Christofidou [a, *], N.G. Jones [a], E.J. Pickering [a, b], R. Flacau [c], M.C. Hardy [d], H.J. Stone [a]

[a] Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, CB3 0FS, UK
[b] School of Materials, The University of Manchester, Manchester, M13 9PL, UK
[c] Canadian Neutron Beam Center, Chalk River Laboratories, Chalk River, Ontario, Canada
[d] Rolls-Royce plc, PO Box 31, Derby, DE24 8BJ, UK

## ARTICLE INFO

*Article history:*
Received 21 April 2016
Received in revised form
14 July 2016
Accepted 15 July 2016
Available online 18 July 2016

*Keywords:*
High-temperature alloys
Metals and alloys
Microstructure
Neutron diffraction
Metallography

## ABSTRACT

The effects of Ni:Co and Al:Ti ratios on the room temperature microstructure, hardness and lattice parameter of twenty-seven quinary Ni-Co-Al-Ti-Cr alloys have been evaluated. All of the alloys exhibited a uniform $\gamma$-$\gamma'$ microstructure. Differential scanning calorimetry (DSC) showed that the liquidus and solidus temperatures of the alloys increased with greater Al:Ti ratios, decreased with Cr concentration and remained largely unchanged with respect to the Ni:Co ratio. Neutron diffraction measurements of the $\gamma$ and $\gamma'$ lattice parameters revealed that the lattice misfit in all of the alloys was positive and increased with Ti concentration (i.e. lower Al:Ti ratio) regardless of the concentration of Cr, or the ratio of Ni:Co. Importantly, alloys with a Ni:Co ratio of 1:1, were found to have consistently greater lattice misfits than alloys with Ni:Co ratios of either 1:3 or 3:1. The measured lattice misfits were found to be strongly correlated with the Vickers hardness of the alloys, suggesting that lattice misfit plays a key role in the strengthening of $\gamma$-$\gamma'$ alloys of this type.

## 1. Introduction

Superalloys based on the Ni-Al-Cr system and comprising up to 12 alloying elements are widely used for components in the hottest sections of gas turbine engines. In civil aviation, regulatory and economic pressures are driving the design of new gas turbine engines towards higher operating temperatures and faster rotation speeds [1–3]. Currently available alloys are already working close to their temperature and strength limits, thereby necessitating the development of new materials capable of withstanding the inimical conditions that will be encountered in the hottest sections of future, more efficient, engines. However, despite significant research to develop alternative materials [4–8], the exceptional balance of properties offered by superalloys with fine scale dispersions of $L1_2$ $\gamma'$ precipitates in an A1 $\gamma$ matrix, continues to make them the preferred solution for high temperature structural applications. Therefore, identifying alloying strategies that can extend the capabilities of A1-$L1_2$ superalloys continues to be a key research activity in the aerospace industry.

Cobalt is an attractive option for next generation A1-$L1_2$ superalloys as its metallurgy is remarkably similar to that of nickel, with the added advantage of a higher melting point. Co-based alloys containing $L1_2$ precipitates were identified in the Co-Ti and Co-Ta systems in the 1960s [9,10]. However, as a consequence of the successful development of Ni-based superalloys, and the uncertainty in the global supply of Co at that time, commercial interest in these systems waned. In the 1970s, Viatour et al. [11] developed multi-component Co-based alloys reinforced with $Co_3Ti$ precipitates, but these alloys were unable to compete with the balance of properties offered by their Ni-based counterparts. More recently, Sato et al. [12] reported the existence of an A1-$L1_2$ two phase field between a Co solid solution and the $Co_3(Al,W)$ phase in the Co-Al-W ternary system. In the ten years since this discovery, considerable work has been performed to gain an enhanced understanding of the behaviour of these materials and develop commercially viable alloys. This research has included studies of the phase equilibria and the effect of alloying [13–27], evaluation of their deformation behaviour [22,28–41], and assessment of their environmental resistance [42–44]. However, despite exhibiting several beneficial attributes, further development is still required before any of these alloys can compete with existing Ni-based superalloys.

At the same time as the discovery of the Co-$Co_3(Al,W)$ system, separate research efforts investigated the properties of Ni-based superalloys with high Co and Ti concentrations to induce the precipitation of the $L1_2$-$Co_3Ti$ phase [45,46]. Such modifications were

---

* Corresponding author.
*E-mail address:* kc424@cam.ac.uk (K.A. Christofidou).

http://dx.doi.org/10.1016/j.jallcom.2016.07.159

shown to confer benefits to both the strength and microstructural stability of both cast and wrought [47–51] and powder processed [52,53] alloys. In parallel, fundamental studies of the underpinning Ni-Co-Al-Ti system were performed and determined that the A1-$L1_2$ two-phase field is continuous between Ni-$Ni_3Al$ and Co-$Co_3Ti$ [54,55]. More recently, Oni et al. [56] employed a range of advanced characterisation techniques to study the site occupancies and lattice misfit strains in quaternary Ni-Co-Al-Ti alloys, and demonstrated a more complicated partitioning and site occupancy behaviour for Co than initially expected. However, whilst co-additions of Co and Ti are clearly beneficial to the properties of Ni-based superalloys, the origins of these effects have not yet been conclusively established.

To gain further insight into the physical metallurgy of Ni-based superalloys with elevated Co and Ti concentrations, several compositions from within the Ni-Co-Al-Ti-Cr quinary system have been examined following a super-solvus homogenisation heat treatment. In this condition, all of the alloys were found to have a $\gamma$-$\gamma'$ microstructure and their transition temperatures, microstructural characteristics, hardness and lattice parameters have been evaluated. From these data, the effects of varying the Ni:Co and Al:Ti ratios at three distinct Cr concentrations were assessed.

## 2. Experimental

Twenty-seven alloys were selected from the $(Ni,Co)_{90\text{-}x}(Al,Ti)_{10}Cr_x$ system, where x = 10, 15 or 20 at.%. At each Cr concentration, the relative ratios of Ni:Co and Al:Ti were independently varied from 3:1, to 1:1 to 1:3. The nominal compositions of the alloys are shown in Table 1. The naming convention of the alloys was chosen to reflect the composition ratios as follows: the first 2 numbers denote the chromium content in the alloy, for example an alloy containing a nominal 15 at.% Cr was named 15##; the subsequent number reflects the ratio of Ni:Co, number ‘1’ was used to denote a Ni:Co ratio of 1:3, ‘2’ denoted a Ni:Co ratio of 1:1 and ‘3’ denoted a Ni:Co ratio of 3:1, similarly, the last letter was used to identify the Al:Ti ratio, with ‘a’ indicating a ratio of 1:3, ‘b’ indicating a ratio of 1:1 and ‘c’ indicating a ratio of 3:1.

The alloys were produced by arc melting elements of ≥99.9% purity under an inert atmosphere. Each ingot was inverted and remelted a total of five times to minimise compositional inhomogeneity. Differential scanning calorimetry (DSC) data was acquired from 3 mm diameter, 1 mm thick samples using a SETARAM SETSYS Evolution DSC/TGA instrument. The heat flux was measured on heating between 700 °C and 1450 °C under an inert atmosphere using a heating rate of 10 °C $min^{-1}$. The solidus temperatures were identified from the DSC thermograms in line with the NIST recommendations [57]. This enabled homogenisation heat treatment temperatures to be identified close to the solidus, whilst avoiding incipient melting. Due to the logistics of heat treating 27 separate ingots, the alloys were grouped and heat treated at three temperatures; 1150, 1200 and 1250 °C, for 48 h, followed by air cooling. To protect the samples from oxidation during the homogenisation heat treatments, each ingot was encapsulated in an argon backfilled quartz ampoule.

The homogenised bars were also characterised using DSC, with the same protocol as the as-cast samples, to determine the liquidus, solidus and solvus temperatures of the alloys in this condition. In order to compare the measured transition temperatures with those predicted using thermodynamic models, calculations were performed on all 27 compositions using the Thermo-Calc software with both the TCNi5 and TTNi8 thermodynamic databases. No phases were omitted in conducting these calculations.

Microstructural characterisation was performed on samples which had been polished and electrolytically etched using a 10% phosphoric acid solution at ≈3 V. Imaging was conducted using an FEI Helios Dual Beam system and a JEOL FEG6340 scanning electron microscope (SEM), whilst quantitative compositional analysis was performed on a JEOL 5800 SEM equipped with an Oxford instruments energy dispersive X-ray spectroscopy (EDX) system. Bulk

**Table 1**
Summary of actual alloy compositions measured using electron dispersive X-ray spectroscopy (EDX). The transition temperatures obtained from differential scanning calorimetry (DSC) of the as-homogenised samples are also included along with the homogenisation temperature for each sample.

| Alloy | Actual composition (at%) | | | | | Temperatures obtained by DSC (°C) | | | Homogenisation temperature (°C) |
|---|---|---|---|---|---|---|---|---|---|
| | Ni | Co | Al | Ti | Cr | Liquidus | Solidus | $\gamma'$ solvus | |
| 101a | 27.2 | 50.7 | 3.1 | 8.1 | 10.9 | 1376 | 1278 | 1062 | 1200 |
| 101b | 19.7 | 58.5 | 5.4 | 5.3 | 11.0 | 1402 | 1288 | 963 | 1200 |
| 101c | 19.7 | 59.1 | 7.5 | 2.6 | 11.1 | >1450 | 1361 | 903 | 1250 |
| 102a | 39.8 | 38.9 | 2.8 | 7.6 | 10.8 | 1378 | 1298 | 1082 | 1200 |
| 102b | 39.2 | 38.1 | 5.9 | 5.3 | 10.5 | 1396 | 1307 | 1064 | 1250 |
| 102c | 39.7 | 39.6 | 7.5 | 2.6 | 10.8 | >1450 | 1364 | 999 | 1250 |
| 103a | 58.3 | 19.5 | 3.2 | 8.2 | 10.8 | 1371 | 1302 | 1122 | 1250 |
| 103b | 59.5 | 19.8 | 4.5 | 5.6 | 10.9 | 1392 | 1337 | 1099 | 1250 |
| 103c | 58.4 | 19.6 | 8.6 | 2.7 | 10.7 | 1410 | 1357 | 1077 | 1250 |
| 151a | 18.3 | 54.7 | 3.0 | 7.8 | 16.2 | 1378 | 1251 | 1055 | 1200 |
| 151b | 18.3 | 53.4 | 5.0 | 5.2 | 16.1 | 1393 | 1295 | 985 | 1200 |
| 151c | 19.0 | 54.7 | 7.1 | 2.7 | 16.5 | 1411 | 1342 | 916 | 1250 |
| 152a | 37.1 | 35.6 | 3.1 | 7.9 | 16.3 | 1359 | 1264 | 1147 | 1200 |
| 152b | 36.8 | 36.5 | 5.4 | 5.2 | 16.1 | 1385 | 1305 | 1094 | 1250 |
| 152c | 36.1 | 36.6 | 8.6 | 2.7 | 16.0 | 1406 | 1350 | 1014 | 1250 |
| 153a | 54.3 | 18.0 | 4.3 | 7.7 | 15.7 | 1371 | 1294 | 1135 | 1250 |
| 153b | 54.9 | 18.3 | 5.6 | 5.3 | 15.9 | 1379 | 1301 | 1120 | 1250 |
| 153c | 54.8 | 18.4 | 8.0 | 2.7 | 16.1 | 1399 | 1342 | 1074 | 1250 |
| 201a | 17.3 | 50.3 | 3.1 | 7.9 | 21.5 | 1361 | 1225 | 1078 | 1150 |
| 201b | 17.0 | 50.7 | 5.5 | 5.0 | 21.4 | 1400 | 1351 | 1080 | 1200 |
| 201c | 17.2 | 50.5 | 7.8 | 2.6 | 21.8 | 1401 | 1311 | 899 | 1250 |
| 202a | 34.2 | 32.6 | 3.6 | 8.1 | 21.5 | 1349 | 1248 | 1135 | 1200 |
| 202b | 34.4 | 33.5 | 5.7 | 5.2 | 21.2 | 1370 | 1284 | 1071 | 1200 |
| 202c | 34.0 | 33.5 | 8.2 | 2.7 | 21.6 | 1392 | 1302 | 1011 | 1250 |
| 203a | 50.7 | 17.4 | 2.7 | 7.9 | 21.9 | 1341 | 1261 | 1154 | 1250 |
| 203b | 51.2 | 15.7 | 6.0 | 5.5 | 21.6 | 1359 | 1273 | 1152 | 1250 |
| 203c | 50.6 | 17.4 | 8.5 | 2.5 | 20.9 | 1392 | 1324 | 1088 | 1250 |