Acta Materialia 131 (2017) 296–304

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

The effect of Ni:Co ratio on the elemental phase partitioning in γ-γ′ Ni-Co-Al-Ti-Cr alloys

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ARTICLE INFO

Article history:
Received 3 February 2017
Received in revised form
23 March 2017
Accepted 26 March 2017
Available online 28 March 2017

Keywords:
Atom-probe tomography
Nickel
Cobalt
Superalloys
Phase composition

ABSTRACT

Atom probe tomography has been used to characterise the effect of varying Ni:Co ratio on elemental phase partitioning at 800 °C in γ-γ′ alloys derived from the Ni-Co-Al-Ti-Cr system. In all alloys tested, Al and Ti were found to partition preferentially to the γ′ phase, whereas Co and Cr partitioned preferentially to the γ phase. However, above a critical Co content (~19 at.%), the extent of partitioning of Al and Ti to the γ′ phase reduced. Conversely, Cr partitioned more strongly to the γ phase with Co additions of up to ~19 at.%, above which this preferential segregation was less pronounced. This non-monotonic trend of elemental partitioning behaviour with increasing Co concentration was attributed to a transition in the chemistry of the $L1_2$ γ′ phase from $Ni_3(Ti, Al)$ to $(Ni, Co)_3(Ti, Al)$ and thus to a change in its solute solubility.

1. Introduction

In the drive to make air travel more sustainable, aero-engines must operate with greater efficiency and one method of achieving this is to increase the temperature of the gas entering the turbine. This imposes more stringent service conditions on the alloys from which aero-engine turbine components are fabricated, requiring new higher performance alloys to be developed that can sustain these higher operating temperatures. Currently, the polycrystalline Ni-based superalloys used for many such components typically comprise a Ni-rich solid solution (γ) exhibiting the face-centred cubic (A1) crystal structure strengthened by coherent particles of an intermetallic phase, $Ni_3(Al, Ti)$ (γ′), possessing the $L1_2$ superlattice structure [1]. One method by which superalloys can be designed with higher proof strength and greater creep resistance is through increasing the volume fraction of the strengthening γ′ phase for a given temperature [2,3]. This can be readily achieved through increasing the concentration of γ′-forming elements such as Al and Ti. Ti additions also offer the benefit of increasing the anti-phase boundary energy of the γ′ phase whilst not negatively impacting alloy density [4]. However, excessive Ti additions increase the propensity to form the Ni_3Ti (η) phase, which has the $D0_{24}$ crystal structure and is generally considered deleterious to alloy properties [5]. This issue may be overcome through the use of Co-Ti co-additions [6], enabling new superalloy compositions with improved high temperature strength and creep resistance.

In the binary Co-Ti phase diagram [7] a two-phase field exists above 600 °C between an A1 Co-rich solid solution and the $L1_2$ Co_3Ti intermetallic phase. As with Ni_3Al, the monolithic Co_3Ti compound exhibits an increase in proof stress with increasing temperature [8]. Indeed, the strength of Co_3Ti has been shown to exceed that of Ni_3Al at temperatures greater than 730 °C [9] and is thus anticipated to confer improved high temperature strength over conventional superalloys. Furthermore, the Co_3Ti intermetallic has the advantage of relatively low cost and low density compared with other candidate $L1_2$ intermetallics such as $Co_3(Al, W)$. Unfortunately, alloys based on the Co-Co_3Ti two-phase field are not currently considered as viable alternatives to Ni-based superalloys as their microstructures are often unstable, precipitating detrimental intermetallic phases and exhibiting discontinuous reaction products at elevated temperature [10–12]. A further barrier to the

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http://dx.doi.org/10.1016/j.actamat.2017.03.067
1359-6454/

commercial use of Co-Co_3Ti based alloys is the low solvus temperature of the γ'-Co_3Ti, which typically lies in the range of 815–872 °C [13]. However, simultaneous additions of Co and Ti to conventional Ni-based superalloys have been shown to enable the development of (Ni, Co)-based superalloys that exhibit improved high temperature properties over conventional superalloys.

A partial phase diagram of the quaternary Ni-Al-Co-Ti system has been experimentally derived for temperatures between 750 and 1100 °C [14–16]. It has been reported that a continuous $L1_2$ phase field exists between Ni_3Al and Co_3Ti (γ') along their near-stoichiometric compositions and that a continuous A1 phase field (γ) exists between the Ni-rich and Co-rich vertices of the phase diagram. Furthermore, for this range of temperatures, a continuous two phase field of γ and γ' has been shown to exist between the Ni-Ni_3Al and Co-Co_3Ti equilibria, such that any alloy composition within this two-phase field may produce the desirable A1-$L1_2$ microstructure [14–16]. Consistent with this result, a number of studies have shown that, by incorporating elevated concentrations of Co and Ti into commercial Ni-based superalloy compositions, it is possible to achieve a γ-γ' microstructure that possesses superior high temperature strength and creep resistance compared with conventional Ni-based superalloys [4,13,17–19]. This effect has been attributed to several mechanisms, most notably to an increase in γ' volume fraction as well as to an increase in the solid solution hardening of γ and γ' by Co and Ti respectively [17,19].

Critically, the relative concentrations of the different alloying elements in Ni-based superalloys determine the elemental partitioning behaviour between the γ and γ' phases and, therefore, the properties of the alloy. Previous studies have shown that Co partitions preferentially to the γ phase and has a significant influence on the solubility of other alloying elements in the γ and γ' phases of Ni-based superalloys [19–22]. For example, additions of Co have been found to increase the volume fraction of γ' in commercial Ni-based superalloys [20,23–25] and this has been attributed to the effect that Co has in reducing the solubility of Al and Ti in the γ solid solution [21,23]. This is consistent with a recent study by Oni et al. [22], who used atom probe tomography to highlight the differences in elemental partitioning between the γ and γ' phases in three Ni-Al-Co-Ti alloys with varying Co and Ti content.

Chromium is a critical addition in polycrystalline Ni-based superalloys as it imparts resistance to oxidation and hot corrosion via the formation of a protective (diffusion-resistant) Cr_2O_3-rich scale [2]. However, high Cr concentrations in the alloy increase the propensity to form deleterious topologically close-packed (TCP) intermetallic phases such as σ [1]. Therefore, it is desirable that the partitioning of Ni, Al, Co and Ti between the γ and γ' phases is assessed in the presence of Cr, as its concentration in the γ phase must be optimised to provide environmental resistance whilst also retaining microstructural stability. Elemental partitioning between the γ and γ' phases in such quinary alloys has been shown to affect their microstructure and resultant properties. Specifically, differences observed in the hardness of γ-γ' Ni-Co-Al-Ti-Cr alloys have been attributed to the effect of the Ni:Co ratio on the partitioning of the other elements [26]. Given the importance of elemental partitioning on the microstructure and properties of superalloys, an improved understanding of the phase equilibria is therefore critical if optimised compositions are to be designed. To this end, this study aims to elucidate the influence of the Ni:Co ratio on the elemental partitioning behaviour in alloys comprising Ni-Al-Co-Ti as well as Cr, as the latter is a critical addition in polycrystalline superalloys intended for service below 800 °C due to its ability to impart oxidation and hot corrosion resistance.

2. Experimental procedure

2.1. Material and heat treatment

The series of model superalloys investigated in the present study was based on the $(Ni, Co)_{75}Al_5Ti_5Cr_{15}$ (at.%) system in which the Ni:Co concentration ratio was varied from 1:0 to 1:3, Table 1. The concentration ratio of Al:Ti was kept at one to allow systematic assessment of the influence of Co on the partitioning of solute elements between the γ and γ' phases. Additionally, the total Al + Ti content was fixed at 10 at.% to achieve comparable γ' volume fractions in the alloys. The alloys were named according to their nominal at.% Co.

Vacuum arc melting was used to fabricate polycrystalline samples of the seven alloys from raw elements of at least 99.9% purity. Thermal analysis of the as-cast alloys was performed using differential scanning calorimetry (DSC) to determine the critical phase transformation temperatures, knowledge of which was required for the selection of suitable homogenising temperatures. DSC tests were performed using a Netzsch 404 heat-flux calorimeter operating at temperatures of up to 1450 °C with a heating rate of 10 °C min^{-1}. The alloys were sealed in quartz tubes under an Ar atmosphere before being subjected to a homogenisation heat treatment in the single γ phase field at 1250 °C for 24 h to minimise the effect of casting-induced micro-segregation. The homogenisation heat treatment temperature was chosen to be higher than the γ' solvus temperatures of all of the alloys but sufficiently lower than their solidus temperatures to avoid incipient melting. Following the homogenisation heat treatment, all alloys were subjected to an ageing heat treatment at 800 °C for 1000 h to attain the thermodynamically stable phase distributions at this temperature. The alloy specimens were then air-cooled.

2.2. Scanning electron microscopy (SEM)

Alloy specimens in the as-homogenised and fully aged conditions were mounted in conductive Bakelite and prepared for metallographical examination by grinding using wet SiC abrasive paper. They were then polished using progressively finer diamond suspensions down to 1 μm. Specimens were subsequently electrolytically etched using a 10% phosphoric acid solution in order to dissolve the γ matrices and to highlight the γ' particles. Microstructural examination of the alloys was performed using an FEI Nova NanoSEM 450 scanning electron microscope in secondary electron mode. Energy dispersive X-ray spectroscopy (EDS) was performed using a Bruker XFlash 6 solid state EDS system to identify the overall compositions of the alloys, Table 1, which were obtained from a minimum of 5 large area scans of at least 0.5 × 0.5 mm in size.

2.3. Differential scanning calorimetry (DSC)

DSC was performed to determine the γ' solvus, solidus and liquidus temperatures of the seven model superalloys after the ageing heat treatment of 800 °C for 1000 h. Small discs of 5 mm in diameter and 1 mm in thickness were extracted from each alloy in the fully aged condition using spark erosion. DSC tests on these aged alloy specimens were performed as for the as-cast alloy specimens using a Netzsch 404 heat-flux calorimeter operating at temperatures of up to 1450 °C with a heating rate of 10 °C min^{-1}. Data analysis was performed using Igor Pro 6.3 software [27].