Full length article

On the effect of boron on grain boundary character in a new polycrystalline superalloy

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ABSTRACT

The role of boron in conferring the grain boundary character in a new polycrystalline superalloy suitable for power generation applications is considered. One boron-free and three boron-containing variants are studied using a suite of high resolution characterisation techniques including atom probe tomography (APT), high resolution secondary ion mass spectroscopy (SIMS) and transmission electron microscopy (TEM). The primary effect of boron addition is the suppression of Cr-rich $M_{23}C_6$ carbide and the formation instead of the Cr-rich M_5B_3 boride. The SIMS analysis indicates that the boride particles are distributed fairly uniformly along the grain boundaries, of length up to 500 nm along the grain boundary. The substantial majority of the boron added resides in the form of these M_5B_3 borides; some boron segregation is found at the γ'/M_5B_3 interfaces but interfaces of other forms — such as γ/γ', γ/M_5B_3, γ/MC and γ'/MC — show no significant segregation. Creep testing indicates that the optimum boron content in this alloy is 0.05 at.%.

1. Introduction

Boron is added to the nickel-based superalloys, in small quantities and has the significant effect of improving the mechanical properties of these materials, in particular creep performance [1–3]. But why? The received wisdom is that boron acts a grain boundary strengthening element; it is well known that it prefers to reside at the grain boundaries on account of its different atomic size and electronic properties [4,5]. But one cannot be satisfied with this explanation. Some important questions exist concerning this so-called boron effect, which deserve consideration.

For instance, in what state does boron reside at the grain boundaries? As elemental segregation or as a second phase? If the latter, which phase is prevalent? How much boron is necessary to impart optimised performance, and why? How do the properties vary around the optimum concentration? What happens if the boron is removed entirely? Moreover, these alloys contain a number of different phases other than the matrix γ — for instance the strengthening phase γ' as well as carbides as such MC and $M_{23}C_6$ which can also lie on the grain boundaries. Therefore, at which of the different interfaces is boron preferentially located?

Answers to these questions are needed to promote fundamental understanding of the boron effect. The principal overarching issue is one of better characterisation; systematic experimentation at high resolution is required. Here, complementary analytical techniques — specifically atom probe tomography, transmission electron microscopy and high resolution secondary ion mass spectroscopy — are used to study the boron distribution in a new experimental single crystal superalloy [6]. Using four variants — including one which is boron free — has provided new insights to begin to resolve some of the issues identified above.

2. Background

The role of boron in superalloy metallurgy is contentious. Various conflicting reasons have been put forward for its beneficial effects. Among them, the most popular include an increase in boundary strength and cohesivity [7,8]. For instance, Briant and Messmer [9,10] have emphasised the effect of chemical bonding on grain boundary embrittlement; thus when an impurity element resides at the grain boundary, it can be expected to alter locally the chemical bonding on the basis of a differing electronegativity. Such effects will draw charge from the metal atoms onto the impurity, and as a consequence less charge is available to participate in the

local metal−metal bonding. Thus embrittlement occurs. Elements such boron do not draw charge from the metal atoms but rather form covalent bonds, and hence cohesion might be increased at grain boundaries. In general, the more electronegative the impurity element with respect to the metal solvent, the greater the amount of embrittlement expected [9,10].

Boron has also been implicated in microstructural modifications of grain boundary character. For example, it has been proposed that minor additions of boron are advantageous to creep life and creep ductility by decreasing the agglomeration of $M_{23}C_6$ at the grain boundaries during protracted loading at temperature [7,11–14]. It has been proposed that continuous layers of $M_{23}C_6$ along the grain boundaries serves as a crack initiation site, presumably on the basis of the brittleness of this phase. It has been argued that boron may play a role in the transfer of slip from one plastically deforming grain to neighbouring ones, but without substantive proof [15]. In addition, boron has been found to segregate to the γ/γ' interface at grain boundaries, presumably due to its size and its low solubility in those phases [16]. Moreover, it can combine with elements such as chromium or molybdenum to form borides; however their precise composition and crystallography remain in doubt [7,17].

Moreover, it has been suggested that any strong interaction between boron atoms and dislocation cores might impede dislocation motion and hence increase resistance to fatigue cracking [18]. Indeed, a mechanism by which the grain boundary dislocation motion is encouraged by boron has been proposed [19]. It is well known that grain boundaries serve as obstacles to dislocation movement, creating dislocation pileups in the vicinity of grain boundaries. This results in strain concentration, initiation of microcracks and eventually to premature failure. Therefore, it has been suggested that some elements, for instance boron, may not improve the strength of the material, but on the contrary, soften it by facilitating grain boundary dislocation movement. Finally, it has been claimed that the segregation of boron may fill vacancies at grain boundaries, thus decreasing the grain boundary diffusivity. It is known that at high temperatures and low stresses cracks initiate at the boundaries due to diffusional phenomena [20]. As a consequence, as the grain boundary diffusivity decreases, the rate of void formation might be expected to decrease and simultaneously the occurrence of γ' denuded zones retarded, thus improving creep properties [7].

Note that each of the above mechanisms requires the presence of boron at grain boundaries. However, at this stage it is not clear whether the improved grain boundary strength can be ascribed to boron being segregated along the grain boundaries or alternatively incorporated into borides and/or carbides. Table 1 summarises

Table 2
Summary of chemical compositions of the different STAL15-CC variants investigated in this work (at.%).

Alloy	B	C	Co	Cr	Mo	W	Al	Ta	Hf
Boron free	<0.005	0.44	5.50	16.45	0.61	1.26	10.00	2.41	0.02
Low boron	0.03	0.47	5.60	16.43	0.58	1.27	10.11	2.41	0.02
Medium boron	0.05	0.47	5.50	16.55	0.59	1.26	10.09	2.40	0.02
High boron	0.08	0.53	5.53	16.64	0.60	1.21	10.01	2.43	0.02

available studies on the effect of boron in different superalloys [21–36]. Although one must take care in drawing conclusions particularly due to the well-known difficulty in characterising and quantifying boron levels, the most common observation finds boron to be segregated at grain boundaries, followed by studies supporting the presence of intergranular borides. In other studies, both segregation of boron and precipitation of borides have been observed, whereas the least common observation is the presence of boron in carbides such as MC and $M_{23}C_6$. What is clear is that application of high resolution characterisation techniques will aid in the rationalisation of the boron effect, and this is the focus of the present paper.

3. Experimental procedures

The prototype nickel-based polycrystalline superalloy STAL-15CC investigated in this study has composition as shown in Table 2. The chemical analysis was conducted in an independent laboratory where the carbon contents were measured using a LECO CS444 analyser and for the other elements the inductively coupled plasma OES (ICP-OES) method was utilised. In order to investigate the effect of boron on the grain boundary character, test-bars were cast containing various amounts of boron. In particular, test-bars with no boron (boron free − BF), low boron (LB − 0.03 at.% B), medium boron (MB − 0.05 at.% B) and relatively higher boron (HB − 0.08 at.% B) content were produced. Castings in the form of tapered rods were prepared at Doncasters Precision Castings Ltd., using casting stock melted by Ross & Catherall (Sheffield, United Kingdom). Conventional ceramic moulds were used, with additions of cobalt aluminate in the primary slurry in order to achieve the required grain size. The use of cobalt aluminate as nucleation catalyst in nickel-based superalloys casting has been thoroughly studied [37]. The ceramic moulds were de-waxed in a steam furnace for 5 min and then sintered at 1000 °C for an hour, prior to casting. All the castings were performed under vacuum conditions, where the temperature of the moulds was approximately 1000 °C.

Table 1
Summary of published studies of boron-containing superalloys, in which boron is claimed to be present either (i) in elemental form at grain boundaries, or (ii) as a boride.

Reference	Year	Alloy	Boron, at.%	Solid solution	Boride	Carbide
Tytko [21]	2012	617B	0.02	Yes	No	Yes
Hong [22]	2012	Alloy 263	0.015	Yes	No	No
Alam [23]	2012	(718) WE971/G727	0.059/0.064	Yes	No	No
Yan [24]	2008	Experimental	0.10	No	Yes	Yes
Zhang [25]	2008	Rene80	0.065	No	Yes	No
Zhang [26]	2008	IN738	0.060	No	Yes	No
Ojo and Zhang [27]	2008	Rene80	0.065	No	Yes	No
Lemarchand [28]	2002	N18	0.083	Yes	No	No
Cadel [29]	2002	N18	0.083	No	Yes	No
Chen [30]	1998	IN718 − Low/High boron	0.006/0.023	Yes	No	No
Huang [31]	1997	IN718	0.016	Yes	No	No
Blavette [32]	1996	Astroloy	0.11	Yes	Yes	Yes
Letellier [33]	1994	Astroloy	0.11	Yes	No	No
Letellier [34]	1993	Astroloy	0.11	Yes	No	No
Buchon [35]	1991	NA4	0.09	Yes	No	No
Delargy [36]	1983	IN939	0.05	No	No	Yes