Diffusion braze homogenisation and contraction during re-repair heat treatments of a single crystal nickel-based superalloy

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In this work, nickel-based braze reservoirs embedded in single crystal nickel-based superalloy substrates were cycled between one and four braze diffusion heat treatments to analyse the effect on microstructural transformation of the braze and substrate materials. Nickel-based superalloy turbine components can undergo several braze repair cycles during service life, and little has been reported on how previously repaired braze joints are affected in additional heat treatments. 1 mm wide braze joints with an initial composition of 6.8 at.% boron embedded in a single crystal substrate do not homogenise when brazed for 2.5 h above 1150 °C, resulting in the formation of eutectic boride phases. Subsequent heat treatments caused braze remelting and contraction leading to surface depressions with the potential to act as a stress raiser for crack nucleation, possibly requiring reworking which impacts on both profits and turnaround times. After four braze diffusion heat treatments, the braze had still not fully homogenised, even though four discrete bands of boride precipitates, separated by boride-free zones, could be observed in γ channels, indicating boron removal from the braze reservoir. Analysis of the metallurgy at the braze-substrate interface and the diffusion-affected zones showed that the most probable reason for controlling boron removal from the braze were: 1) decreasing boron concentration gradient across a thickening braze-substrate interface; 2) restricted boron transport across boride precipitates in the diffusion-affected zones; 3) slower transport of boron in γ', the area fraction of which changes over the braze cycle temperature range.

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1. Introduction

Ni-Based superalloy turbine components operate in harsh environments, and must endure high pressures, high temperatures, as well as highly-corrosive exhaust gases [1,2]. During service, the cyclic thermal nature of flight associated with aircraft take-off, cruising, and landing, coupled with the non-uniform heating of turbine vanes results in thermal mechanical fatigue cracking of these turbine components (TCs) [2,3]. The high intrinsic cost of single crystal (SX) Ni-based superalloy TCs can be attributed to the use of expensive materials and complex casting processes, and thus, during engine overhaul, it is more financially viable to repair these components multiple times rather than replace them [4].

Precipitation-strengthened Ni-based superalloys typically contain Al and Ti, which form a stable FCC Ni3(Al,Ti) gamma prime (γ') precipitate in a gamma (γ) matrix [1,2]. When the combined content of Al and Ti in these alloys exceed 6 wt%, welding difficulties arise due to heat-affected zone cracking [5]. Because of this, TCs are typically repaired using transient liquid phase bonding, or diffusion brazing. Ni-based diffusion brazes are doped with small quantities of melting point depressants (MPD), that lower the melting temperature of the braze to below that of the substrate [6]. The most widely used MPD for diffusion brazing of aerospace turbine components is boron. During this brazing process, a component is heated above 1000 °C where the braze melts. Capillary forces draw the braze into cracks, while the chemical potential difference causes boron to diffuse from the braze into the substrate [7]. As it diffuses, the melting temperature at the liquid-solid interfaces increase above the bonding temperature, and isothermal solidification begins [7,8]. Complete isothermal solidification
occurs when sufficient diffusion of MPD into the substrate occurs so that the entire liquid phase becomes solid at the bonding temperature [7,8].

The mechanical integrity of diffusion-brazed joints is highly dependent on process parameters. Thus, insufficient bond temperatures, combined with premature cooling, results in non-isothermal solidification and the formation of brittle, deleterious boride phases [9–11]. These undesirable phases provide a low resistance path for crack initiation and propagation, and should be avoided [12,13]. For example, it has been reported that during test engine runs of braze-repaired CFM56 low pressure turbine vanes, stress effects associated with thermal shock caused braze joints containing brittle phases to re-open [14].

Joint width is a critical process parameter for diffusion brazing. Wider braze joints have a greater propensity for boride phase formation than narrower joints, due to the larger volume of boron-enriched liquid braze [15,16]. To help address this issue, a technique referred to as wide-gap brazing (WGB) has been employed across the industry. This particular brazing technique sees the addition of a superalloy powder “high-melt” component to the braze, which remains largely unmelted during brazing [7,8]. This high-melt component reduces the overall amount of boron in the joint, improves capillary pressure and acts as a diffusion “sink” for boron [7]. However, even with the addition of the high-melt alloy, wide-gap diffusion braze can still be susceptible to boride formation. Thermal mechanical fatigue cracks to be repaired vary in width, meaning that some diffusion braze-repaired cracks may require longer holding times for sufficient boron diffusion and complete isothermal solidification. However, if this is not conducted, non-isothermal solidification of wider cracks will result in boride formation [10].

Turbine vanes can have an ultimate lifetime which can be more than three times that of the engine overhaul life, thus, a typical turbine vane can undergo three or more diffusion braze repairs over the course of its service life [4]. Each braze repair adds further boron to a turbine component [17], while it has been reported that borides may remelt if subjected to high-temperatures associated with a re-repair cycle [18]. It is advised that any re-repair is conducted at temperatures below the initial bonding temperature [11]; however, this is not typically feasible in industry. Thus, non-isothermally solidified braze containing deleterious borides may undergo remelting if re-heated during re-repair. However, little is covered in literature regarding the repeated repair of previously repaired braze joints.

The work carried out in this paper endeavours to obtain information on what effects, if any, repeated heat treatments emulating re-repair has on the microstructural integrity of diffusion braze embedded in SX substrates.

2. Materials and methods

Sixteen as-cast SX Ni-based superalloy samples approximately $7 \times 9 \times 25$ mm$^3$ were used as the substrate (see schematic in Fig. 1(a) and chemical composition in Table 1). Electro Discharge Machining (EDM) was used to produce identical channels approximately $1 \times 1 \times 15$ mm$^3$ and all specimens were fluoride ion cleaned using a proprietary cycle before brazing. The channels were then overfilled with a surplus of 50:50 ratio of high-melt-superalloy to low-melt braze mixture, where the chemical compositions of these materials are listed in Table 1. Fig. 1(b) illustrates the experimental steps used in this study. The sixteen identical samples were placed in a vacuum furnace with the braze-filled channels facing upwards, and underwent a proprietary two-stage braze diffusion & homogenisation vacuum heat treatment above 1150 °C for two and a half hours. The brazing temperature was approximately 1.1 times that of the low-melt liquidus. After this first furnace cycle, excess surface braze was ground away from all sixteen specimens to a 220-grit finish — typical of a first repair process. A vernier callipers was used to verify that surface braze was removed and the specimens had been returned to their starting geometry. Representative samples were removed from the batch for metallurgical evaluation, while the remaining specimens underwent either one, two or three additional respective braze diffusion heat treatments, simulating repeated repair.

Four cross-sections for each heat-treated sample type were hot-mounted in transparent Clarofast resin and ground and polished using SiC paper and an oxide polishing suspension with a final particle size of $1 \mu m$ using a Buehler Phoenix 4000 polishing system. Samples were analysed using a Hitachi SU-70 field emission gun scanning electron microscope (FEG-SEM), equipped with a backscattered electron detector, and an Oxford Instruments energy dispersive spectrometer (EDS). ImageJ was used for all measurements conducted on calibrated micrographs. The area fraction of particles observed was calculated using an average of 10 measurements per sample type. The average particle size was calculated by measuring 20 particles for each specimen type. The average band thickness for individual bands observed in the diffusion affected zone was calculated by taking between 6 and 30 measurements for each of the four bands observed. Vickers microhardness testing was conducted using a LECO M-400-G1, with a 100 gf load and 10 s indentation time. This testing was conducted in an area of interest adjacent to the braze, as indicated...
of the braze shows a complex heterogeneous microstructure of different phases. Large, equiaxed particles between 80 µm—120 µm in diameter are observed away from the-braze-substrate interface, with an appearance similar to islands, indicative of remnant high-melt particles. Surrounding these equiaxed Ni-based particles are a number of phases, which were semi-quantitatively characterised using SEM-EDS as Cr-rich borides (angular morphology), discrete Ta-based carbides (bright white) and a complex Ni-boron intermetallic system, some of which are indicated in Fig. 2(b). Very similar angular chromium boride phases have been reported by Nagy & Huang [19], and Mosallaee et al. [20], both reporting on Inconel 738 joints brazed with BNi-9 and BN-3 braze respectively.

A boride-depleted region, similar in contrast to the equiaxed high-melt particles, was observed in the braze material along the interface with the substrate, approximately 65 µm ± 5 µm thick.

### Table 1
Nominal weight percent and atomic percent chemical compositions of all materials used in this study.

| SX Substrate | High Melt (H) | Low Melt (L) | Braze 50H:50L |
|--------------|--------------|--------------|--------------|
|              | wt.% | at.% | wt.% | at.% | wt.% | at.% | wt.% | at.% |
| Ni           | 63.2  | 64.56 | 61.52 | 59.27 | 57.72 | 64.335 | 58.45 |
| Cr           | 7     | 8.07  | 16    | 17.39 | 13.58 | 15     | 15.38 |
| Co           | 7.5   | 7.63  | 8.5    | 8.15  | 8.56  | 9.25   | 8.36  |
| C            | 0.05  | 0.24  | 0.17   | 0.8   | —     | 0.085  | 0.37  |
| Ti           | —     | —     | 3.5    | 4.13  | —     | 1.75   | 1.94  |
| Al           | 6.2   | 13.77 | 3.5    | 7.33  | 3.5   | 6.54   | 3.5   |
| Mo           | 1.5   | 0.93  | 1.7    | 1     | —     | 0.85   | 0.47  |
| W            | 5     | 1.63  | 2.5    | 0.76  | —     | 1.25   | 0.36  |
| Ta           | 6.5   | 2.15  | 1.7    | 0.53  | 2.5   | 0.69   | 2.1   |
| Hf           | 0.05  | 0.01  | —      | —     | —     | —      | —     |
| B            | —     | —     | 0.01   | 0.05  | 2.75  | 12.83  | 1.38  |
| Zr           | —     | —     | 0.1    | 0.06  | —     | 0.05   | 0.02  |
| Re           | 3     | 0.96  | —      | —     | —     | —      | —     |
| Nb           | —     | —     | 0.8    | 0.48  | —     | 0.4    | 0.22  |
| Y            | —     | —     | —      | —     | 0.1   | 0.05   | 0.05  |

3. Results

3.1. Braze development during multiple repair cycles

Fig. 2(a) presents a representative cross-section of braze which underwent the initial braze-diffusion heat treatment, where excess surface braze has been ground away, showing a sharp flat interface between the grey specimen and the black mounting media. From atomic number imaging contrast, the darker braze material can easily be discerned from the brighter SX substrate. Closer scrutiny by SEM analyses.

A cross-section of a typical specimen that underwent a second heat treatment (2HT) — emulating one re-repair cycle — is shown in Fig. 2(c), referred to hereafter as a 2HT specimen type. Again, atomic number imaging contrast clearly discerns the braze material (dark grey) from the substrate (light grey) and mounting media (black). While the remnant high-melt particles were present in the braze material, they were less discernible than the 1HT specimen type. Additionally, the braze material again contained a similar number of Cr-rich borides, a Ni-boron intermetallic phase, as well as some discrete, blocky Ta-carbides as observed after the initial heat treatment. Wu et al., observed a similar braze microstructure consisting of high-melt particles embedded in an alloy of nickel solid solution with boride and silicide precipitates, when using WGB to join Inconel X-750 to 304 stainless steel with AMS4777 low-melt and Ni powder high-melt braze constituents [13]. Furthermore, the boride-depleted zone at the braze-substrate interface increased to 113 µm ± 6 µm, indicating that the braze

Fig. 2. Backscattered electron micrographs of (a) braze-substrate cross-section after one heat treatment (1HT), where the white rectangle indicates where Fig. 2(b) was captured; (b) braze material showing Cr-rich borides and Ni-based intermetallic phase; (c) braze-substrate cross-section after two heat treatments, showing a contraction in braze material; (d) top surface of a 2HT specimen beside the braze channel showing mounting media (black), braze material (dark grey) and SX substrate (light grey) containing discrete borides.
material and the substrate showed some level of homogenisation during the second heat treatment.

A striking observation made from Fig. 2(c) is the apparent loss of material from the top of the braze channel. This was observed in all twelve specimens that underwent one subsequent heat treatment after the initial removal of surface braze material. Fig. 2(d) shows a cross section taken at the top of the specimen, adjacent to the braze channel, where the black region shown in this micrograph is the mounting media. The interface between the mounting media and substrate shows a film of braze material — dark grey in contrast. This micrograph also shows a diffusion-affected zone (DAZ) consisting of discrete boride particles extending into the substrate. These discrete DAZ borides will be reported in more detail later in Section 3.2. Considering that the original surface braze was ground away from these specimens, it can be confirmed that braze material both remelted, and flowed away from the reservoir, onto the top surface of the specimens. This remelting was expected, as it is reported that braze material containing eutectic borides is prone to remelting at bonding temperatures [18,21]. However, this flow behaviour has not been reported before and is of concern to repair vendors, as it confirms that previously brazed cracks or joints which contain eutectic borides can remelt and reflow if subjected to a subsequent repair heat treatment, leaving voids within the braze joint which act as stress concentrators. Surface depressions can be captured using fluorescent penetrant inspections, leading to reworking of the component, negatively impacting turnaround time and profitability.

Fig. 3 (a) shows a typical microstructure for a specimen that underwent three heat treatments (3HT). The microstructure of the darker braze material comprised of Ni-solid solution, Cr-rich borides, Ni–B-intermetallic, and some Ta-carbides throughout the braze material. It is apparent from these microstructural observations that the remnant high-melt Ni-based grains in the bulk braze material have become more difficult to individually discern from one another — interdiffusing to form a network of conjoined particles. It was also noted that the boride-depleted region at the braze-substrate interface increased to 130 μm ± 8 μm in thickness, confirming further homogenisation of the braze material with the substrate. Contraction of braze material can also be observed in this micrograph. Again, closer scrutiny of the exterior top surface of the 3HT specimens away from the braze channel showed a layer of braze material (see Fig. 3(b)), discernible by its darker contrast. This surface layer of braze showed an apparently boride-depleted microstructure, while the substrate beneath again showed discrete boride precipitates.

The micrograph in Fig. 3(c) shows a typical microstructure of a four-heat treatment (4HT) specimen. Again, the braze microstructure imitates the behaviour of typical 2HT and 3HT specimens, where braze flows out of the channel onto the top surfaces, leaving a depleted braze region behind. The braze microstructure consists of Ni-solid solution, Cr-rich borides, Ni–B-intermetallic, and some Ta-carbides, as well as a boride-depleted region at the braze-substrate interface, approximately 144 μm ± 6 μm thick. Additionally, as with the 3HT specimen type, the high-melt particles in the braze are difficult to discern from one another, with the only indication of their presence being a partial outline of boride phases formed by the remanent low-melt material. This shows that both the interfacial region between the braze and the substrate, as well as the bulk braze material showed some level of homogenisation. Fig. 3(d) shows the interface between the top of the 4HT braze channel, and the exterior surface of the specimen. It is evident from this image that there has been some interdiffusion of the SX
substrate and the braze material, indicative by the rounded-corner of the DAZ. The presence of braze material along the top surface of the specimen is also notable in Fig. 3(d), as well as substrate carbides.

In summary then, as braze channels are subjected to more thermal cycles, they contract, while some minor homogenisation of the bulk braze material is observed. It appears that the contraction is a result of a molten boron rich eutectic flowing out of the braze channel and on to surfaces adjacent to the braze channel. A second process contributing to volume shrinkage in the braze is boron removal. In terms of the boron removal mechanisms, boron vaporisation during the vacuum heat treatment is unlikely given its vaporisation temperature at typical brazing vacuum pressures is several hundred degrees Celsius higher than Ni [22]. Thus, boron diffusion from the braze into the substrate across the boride-depleted layer is the mechanism which reduces boron content in the braze material. The boride-depleted layer thickens with increasing numbers of thermal treatments, showing homogenisation over the course of four heat treatments.

3.2. Effect of number of thermal treatments on microstructure of diffusion-affected zone

3.2.1. General observations and depths of boride penetration

The braze diffusion-affected zones (DAZs) were analysed for all specimen types, resulting in the identification of commonalities and differences between specimens which received different number of heat treatments. Firstly, it was noted that all specimen DAZs consisted of discrete sub-micron particles, where SEM-EDS analysis was used to semi-quantitatively indicate that these fine microconstituents are rich in boron, and also contained W, Mo and Re. These borides can be seen in Fig. 4(a) as discrete white pearls, embedded in the light grey γ channels between the dark grey γ’ precipitates. These DAZ borides are reported to form as a result of two relating factors: boron diffusion into the substrate during heat treatment, and the presence of boride-forming elements in the substrate [23]. As the concentration of boron diffusing into this region exceeds the solubility limit of boron in Ni, such microconstituents precipitate [9]. Fig. 4(b) shows a low-magnification image of the DAZ for a typical 1HT specimen, where it can be seen that there is a dense band of precipitates 5 μm—15 μm thick (arrowed in Fig. 4(b)), while there is a less dense band of discrete precipitates extending approximately 170 μm into the substrate. The location of the dense bands of precipitates at the braze-substrate interface is believed to be the remains of a fine grained polycrystalline recast layer which formed during the EDM fabrication of the braze channels. For the larger, less-dense band of precipitates, the fine discrete boride particles were observed to precipitate within the γ channels of the SX substrate alloy. Similar DAZ precipitates have been reported by other authors using a boron-based braze and an identical substrate alloy composition [21]. Hu et al. have analysed very similar morphology borides in a Ni–Cr–Co-based superalloy using transmission electron microscopy and electron energy loss spectroscopy, which identified these precipitates as tetragonal M₅B₃ borides, where M = Cr, W, and Mo [24]. In terms of turbine performance, the formation of these
discrete boride pearls is not of particular concern. Similar discrete borides have been reported by Ref. [25] in the DAZ of superalloy IC10 joined using a boride-enriched braze interlayer. These reported borides are of similar chemical composition and morphology to those observed in this paper, and it is reported that these are likely to be very stable, as the boride forming metals have high melting temperatures, and low diffusivity in Ni [25].

After a second heat treatment, it was observed that the DAZ grows to a maximum depth of approximately 235 μm into the substrate. However, this increase in DAZ thickness is manifested by the formation of an additional discrete band of particles which precipitated at the extremity of the original DAZ formed by the initial heat treatment. This second band, referred to as band 2, is separated by a boride-free zone, as shown in Fig. 4(c), where arrows indicate the direction of boride diffusion. It is also apparent from this micrograph that the precipitates in the newly-formed band 2 are smaller in size compared to those in band 1, but there is a higher number of particles per unit area. This trend continues with the 3HT (see Fig. 4(d)) and 4HT (see Fig. 5) specimens, which show additional third and fourth bands of precipitates with increased maximum DAZ depths of approximately 360 μm and 430 μm respectively. The increase in maximum DAZ precipitation depth is as expected, as the longer a brazed component spends at brazing temperature, the more boron can diffuse from the braze into the substrate provided there is a concentration gradient. This is corroborated by Ref. [25], who have also shown that the depth of boride precipitation in a Ni-based substrate DAZ increases with bonding time, where a Ni−Cr−B interlayer which was brazed for 15, 30 and 45 min showed the greatest DAZ depth for the 45 min heat treatment. However, it should be noted that there were significant fluctuations when trying to determine average diffusion depths in regions where interdendritic carbides formed. Additionally, the dense band of fine precipitates at the braze-substrate associated with the EDM recast layer became much less apparent with increased number of heat treatments – suggesting interdiffusion and homogenisation at the braze-substrate interface.

Fig. 4(d) shows the DAZ of a 3HT specimen, where interdendritic Ta carbides are indicated with arrows, and the edge of each DAZ band is highlighted with a dashed line. Examining the bands of boride particles in this region, it is apparent that this interdendritic carbide phase has restricted boron diffusion into the substrate. Additionally, the formation of a secondary phase with an accicular, needle-like morphology was observed within the DAZ, in close proximity to the interdendritic Ta-based carbide phase. This accicular phase was semi-quantitatively characterised using SEM-EDS as a carbo-boride precipitate. The formation of such a phase is reported to occur from a reaction between TaC, diffusing boron and refractory elements in the base alloy, where the boride phase consumes carbon as it grows, rejecting Ta into the surrounding region, which forms a γ′ envelop around the acicular phase [21]. The formation of such phases is of concern, as they are known to embrittle the base alloy, reducing life expectancy. The apparent restricted boron diffusion observed in Fig. 4(d) around the interdendritic carbides is expected, as it has been reported that the presence of intermetallics in the substrate can reduce local MPD diffusion coefficients, thus resulting in restricted diffusion [26]. Away from these carbides, the depth of boride precipitation from the braze-substrate interface appears to be greater. This observation can also be noted in Fig. 5, where it can be seen that the boride precipitation depths are less around interdendritic regions compared to within dendrites. In this case, the micrograph shows four bands of boride particles in the substrate, illustrated by dashed white lines, separated by boride-free zones.

3.2.2. Average width of bands, particle size & area fraction of boride precipitates

To investigate the relationship between the different number of heat treatments and specimen microstructures, a series of microstructure measurements were taken for each specimen DAZ, including overall average band thickness, average particle size (APS), boride area fraction, and local Vickers microhardness. These measurements are listed in Table 2. It was observed that the average bandwidth of newly formed bands diminishes as the number of heat treatments increases. In addition, the average width of each band type was very similar for different numbers of heat treatments. Thus, band 1 had similar widths after exposure to 1, 2 3 and 4 braze cycles, band 2 had similar widths after exposure to 1, 2 3 braze cycles etc. It can also be noted from Table 2 that particles in band 1 show an increase in APS with an increase in number of heat treatments, where 1HT specimen type has an APS of 330 ± 11.8 nm, while the 4HT specimen type has an APS of 686 ± 25.9 nm. Another trend which can be observed in Table 2 is the decrease in APS further away from the braze material (e.g. between band 1 and band 4 for the 4HT specimens). In this case, the APS for borides in band 1 of 4HT specimen type is 686 ± 25.9 nm, while the APS for band 4 is 174 ± 8.4 nm. As previously highlighted, the bands of boride particles were separated by boride-free zones. It was observed that at the edge of each band, the particles had a coarser morphology than those within the band. This can be observed in Fig. 6(a), where the direction of boron diffusion in this micrograph is from top to bottom, as arrowed. Fig. 6(b) shows band 4 of a 4HT specimen, where borides appear to be located at the γ − γ′ interface – indicative of nucleation close to the interfacial region. Hu et al., observed similar discrete boride nucleation at γ − γ′ interfaces in a Ni-based superalloy [24], and suggest that these discrete phases have a pinning effect on the γ − γ′ interface, resisting migration and potentially improving creep properties.

The area fraction of precipitate reported in Table 2 can be assumed to correspond with the volume fraction. The measured data shows that within each band, the volume fraction (Vf) of precipitates increases slightly with increasing number of heat treatments e.g. from 8.5 (HT1) to 10.4 vol % (HT4). In contrast, there is a significant difference in the boride precipitate Vf between bands, with reductions in Vf in bands deeper within the substrate. See for example the data for the 4HT sample where band 4 contains only 2.2 vol % precipitate compared to the 10.4 vol % for band 1.
For all specimens examined, the penetration depth does not change significantly for the individual bands of DAZ particles, however, particles are observed to coarsen with increasing time at elevated temperatures, while the number of particles per unit area was observed to decrease. To further investigate this phenomenon, and correlate the microstructural and mechanical properties, Vickers microhardness measurements were performed across the DAZs on all specimen types. As a baseline, the substrate alloy showed a mean hardness of $397 \pm 3.4$ HV$_{0.1}$ within the dendritic regions. While the locations of the indents were carefully controlled in the DAZ, it was not possible to completely avoid interdendritic carbides when testing. As a result, these microstructural anomalies were filtered from the data, as they skewed the microhardness readings. Microhardness values for the different bands of DAZs are shown in Table 2 and plotted in Fig. 7.

### Table 2

Average band thickness, average particle sizes, average area fractions and average Vickers microhardness plus respective standard errors for each band of borides for specimens which underwent between 1 and 4 heat treatments.

| Band  | Average band thickness (μm) | APS (nm) | Af of Borides | Microhardness (HV$_{0.1}$) |
|-------|-----------------------------|----------|---------------|---------------------------|
| 1 HT  | 139 ± 5.5                   | 330 ± 11.8 | 8.5% ± 0.2%   | 439 ± 3.3                 |
| 2 HT  | 96 ± 4.7                    | 448 ± 22.6 | 9.1% ± 0.3%   | 63% ± 0.1%                |
| 3 HT  | 55 ± 3.9                    | 440 ± 3.7  | 44 ± 2.0      | 437 ± 4.1                 |
| 4 HT  | 47 ± 2.4                    | 686 ± 25.9 | 10.4% ± 0.1%  | 437 ± 3.3                 |

### 3.3. Microhardness of boride containing zones

For all specimens examined, the penetration depth does not change significantly for the individual bands of DAZ particles, however, particles are observed to coarsen with increasing time at elevated temperatures, while the number of particles per unit area was observed to decrease. To further investigate this phenomenon, and correlate the microstructural and mechanical properties, Vickers microhardness measurements were performed across the DAZs on all specimen types. As a baseline, the substrate alloy showed a mean hardness of $397 \pm 3.4$ HV$_{0.1}$ within the dendritic regions. While the locations of the indents were carefully controlled in the DAZ, it was not possible to completely avoid interdendritic carbides when testing. As a result, these microstructural anomalies were filtered from the data, as they skewed the microhardness readings. Microhardness values for the different bands of DAZs are shown in Table 2 and plotted in Fig. 7.

Firstly, it can be observed from Fig. 7, that for each respective band, the microhardness increases with increasing number of heat treatments. This can be explained by the coarsening of borides with each heat treatment, as well as the increasing area fraction of precipitates closer to the braze interface. Similar behaviour was observed by Pouranvari et al., who observed that a decrease in boride precipitate size and density away from a brazed Inconel 718 joint resulted in lower microhardness values [27]. Additionally, it can also be observed from Fig. 7 that for each respective specimen, the microhardness decreases further away from the braze material. This can be explained by the APS, where precipitates decrease in size further away from the braze material, and thus, the boride Vf and microhardness also decreases.

### 3.4. Summary of diffusion affected zone observations

The schematic presented in Fig. 8 summarises the DAZ observations. For each specimen, the number of bands in the DAZ corresponded to the number of heat treatments received by the specimen. Bands closer to the braze reservoir had larger APS, while...
these bands are typically wider, penetrating deeper into the substrate. Bands further away from the braze material were thinner with smaller particles but more particles per unit area. Microhardness was shown to increase in the bands closer to the braze material, while the microhardness reduced in bands further away from the braze material. Additionally, at the periphery of each band observed, the deepest row of boride particles in each band showed a coarser morphology compared to the average boride particle size in each band. Finally, a boride-free region between each band of boride precipitates was observed.

4. Discussion

4.1. Effect of repeated heat treatments on braze volume and microstructure

It is clear from the results that contraction of the braze occurs after multiple heat treatments simulating additional repair cycles and that this is coupled with the presence of braze material on the outer surface of the specimens. During the initial braze diffusion heat treatment, the low-melt liquefied, and enveloped the high-melt particles which remained largely unmelted during the initial heat treatment. At the end of the initial furnace cycle, insufficient boron diffusion into the substrate and high-melt particles resulted in non-isothermal solidification of the boron-enriched liquid brazes. This results in the formation of eutectic borides, such as the angular Cr-rich borides and the complex boron-metal multiphase systems reported above, which surround the spaces between the remnant high-melt particles. Upon reheating, these eutectic boride phases remelt, and the braze becomes partially liquated as suggested by Duvall et al. [18]. While the majority of the liquified braze remains in the channel during the first re-repair cycle (2HT) interdiffusing with the substrate and high-melt particles, some liquid braze is drawn out of the braze channel by surface tension interactions, spreading along the exterior of the sample [28]. Upon cooling, the resulting braze microstructure after re-repair again showed the presence of Cr-rich borides as well as the complex Ni intermetallic phase. Over the course of 2HT, 3HT and 4HT, it was observed that the remnant high-melt component, which was easily discernible in the microstructure after the initial heat treatment, became somewhat homogenised with the bulk braze material as a network of conjoined particles as it interdiffused with the remnant low-melt alloy. While some boride-phase-outlines were observed, overall, less boron enriched material surrounded these fused Ni particles. The liquid braze component which spreads as a thin film across the specimens’ outer surfaces is boron-rich, and the large surface area of the substrate outer surface acts as a diffusion sink for the boron. This, combined with the lack of boride-forming elements in the low-melt, contribute to the formation of a boride-free braze film along the outer surfaces of the specimens as indicated in Figs. 2(d) and 3(b). The presence of significant boride formers in the SX substrate (e.g. Cr, W, Mo, Re) and boron diffusing from the braze gives rise to the formation of the discrete boride pearls in the substrate below the boride-free surface film.

Clearly, the fact that the braze volume slumps due to liquation and surface tension drawing the liquid onto the surface, is a result of the failure of the braze to isothermally solidify. It is well reported that complete isothermal solidification of braze material during heat treatment is desirable for producing strong, ductile braze joints [7,12,17]. To achieve such microstructures, the concentration of MPD in the braze material, in this case boron, must drop below the solid solubility limit of the bulk Ni matrix [8]. It is evident from the microstructures presented in this paper that braze material does not reach this critical boron concentration, even after four heat treatments, and thus, contains eutectic boride phases which facilitate the slumping of the braze volume. Thus, it can be clearly stated that eutectic boride phases remaining in the braze can remelt and have the potential to refloe if subjected to subsequent braze-repair heat treatments, causing surface depressions with the potential to act as stress concentrators and crack nucleation sites.

The second method of boron removal from the braze material, allowing its homogenisation, is its diffusion into the SX substrate, which is known to be slower than polycrystalline alloys due to the lack of high-diffusivity grain boundaries [29]. The thickness of the layer of boride-free braze material present at the braze-substrate interface, was observed to increase with increasing numbers of heat treatments, indicating local homogenisation of the braze material. The formation of this boride-free region is as a result of boron diffusing from the local braze site into the SX substrate such that the boron content falls to a concentration below saturation. The largest thickness increase was observed between one and two heat treatments, where the width of the boride-free region increased by approximately 75%. This was considerably greater than the increase after 3HTs and 4HTs, which showed a respective thickness increase of only 15% and 10% over the previous specimen. The major increase in boride-free layer thickness between the 1HT and 2HT samples can be explained by the fact that during the first heat treatment, the braze alloy was in dry paste form. Thus, until the point of melting of the low-melt component, there was a large number of voids between the braze and substrate, greatly restricting interstitial diffusion of boron from the braze [15]. As the braze subsequently melted and filled the reservoir during this heat treatment, the interaction time between the liquid braze and substrate was reduced compared to subsequent heat treatments. The rate of braze homogenisation decreased with each subsequent heat treatment. This is to be expected, as the concentration gradient and chemical potential between the braze and substrate decreases after each heat treatment, in accordance with Fick’s second law [30,31]. Accordingly, it is not surprising that the 1 mm wide braze joints with an initial composition of 6.8 at. % boron do not homogenise when brazed for two and a half hours above 1150 °C, nor after the brazing heating cycle is repeated to give 10 h in total above 1150 °C. This diffusion of boron from the braze into the substrate over a number of heat treatments may also contribute to contraction of the braze material and its likelihood of stress raiser creation due to

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1 While the melt temperature of the high-melt is above that of the furnace cycle, the interaction with boron as the liquid braze surrounds the particles can lead to substrate meltback [7].
molar volume decreases caused by boron removal.

4.2. Factors affecting the diffusion of boron within the substrate

Examination of the depth to which borides form in the DAZ was noted to have a linear dependence with the square root of numbers of heat treatments (N). As each braze cycle had the same thermal history it is possible to substitute N the number of braze cycles for the heat treatment time and accordingly the square root dependence indicates that the depth of boride precipitation in the substrate is diffusion controlled. It must be stressed that there were significant anomalies in the average penetration depths in regions where interdendritic carbides formed, with penetration depths being noticeably less. As noted in the results, these carbides are associated the formation of carbo-boride the needles. This is consistent with the findings of Hinchy et al. [21] who observed similar effects when brazing an identical base alloy. The formation of the needle-like carbo-boride phases in their case was associated with the formation of Ta enriched γ' around them. The reduction in penetration depths observed in these regions is most probably due to increased boron consumption due to carbo-boride needle formation, a slower diffusion rate in that area in γ', coupled with a reduction in interstitial sites available for boron diffusion due to the concentration of carbon in these interdendritic regions [6].

Examining factors which may affect the diffusion rate of boron into the substrate, a 10 μm thick polycrystalline recast layer was observed at the braze-substrate interface after the first heat treatment. The nature of this fine-grained polycrystalline layer is not likely to have a controlling effect on boron diffusion, due to the greater boron diffusivity in polycrystalline materials compared to SX nickel. One factor which may affect diffusion rates is the relative ratios of γ and γ' through the course of the heat treatment however, as temperatures exceed about 50% of the absolute liquidus temperature (550 °C using the liquidus value given by Ref. [32]), a decrease in γ' is expected. During heat up there will be a slight decrease in volume fraction of γ' with temperature until its solution begins to become rapid as indicated by Frederick et al. [33] using data produced by JMatPro. A schematic of this is presented in Fig. 9(a) and (b), where it can be seen that as the material is heat treated from room temperature to braze temperature, the γ' partially dissolves. The γ' solvus for the substrate alloy used in this work has been calculated by Neumeier et al. [34] using Thermocalc as being 1270 °C. Thus, while specific temperatures at which the γ' dissolution begins to increase rapidly with temperature are not known, it can be qualitatively predicted that as the temperature of the substrate alloy increases to above 1150 °C for brazing, the γ to γ' ratio increases. Using data for values of D0 (pre-exponential constant) and Q (activation energy) the diffusion coefficients of boron in Ni [35] and Ni3Al [36] at temperatures between 975 and 1325 °C were calculated. The calculations clearly showed the more rapid diffusion of boron in Ni by 2–3 orders of magnitude. Furthermore, it is to be noted that the calculations were carried out over a temperature range in excess of 0.75 \( T_m \) for Ni and so correspond to lattice diffusion by an interstitial mechanism. The data of [36] was obtained for volume diffusion and so corresponds to the same diffusion mechanism. Clearly, the substrate alloy comprises Ni and Ni3Al equivalents and so the diffusion rate of boron would be expected to be a summation of diffusivities based on relative amounts of γ and γ'. The relative amounts of γ will increase with temperature, as suggested above and thus a corresponding increase in boron diffusion rate will occur. By a similar argument, as temperatures decrease, boron diffusion rates would be expected to decrease due to the relative amounts of γ decreasing until the γ/γ' ratio becomes constant as dictated by the alloy chemistry.

Away from the interdendritic carbide regions, the presence of boride precipitates within the DAZ also affects the potential for diffusion of boron into the SX substrate. It is widely reported that due to its small size, boron occupies and diffuses through interstitial sites, along the path of least resistance [6,10,37]. For SX alloys, the lack of grain boundaries means that boron must diffuse through the bulk lattice. However, whilst very similar in lattice parameter, whether it is the γ or γ' lattice or both is not known, although this is discussed later in this section. What is known, is where the boride pearls precipitate and that they contain elements which prefer being within the Ni solid solution γ phase. As the boron content rises above the solubility limit in the substrate alloy during diffusion, the boron reacts with boride formers W, Mo and Re to form the pear like precipitates at the bonding temperature [38], as illustrated in the schematic in Fig. 9(c). The formation of these boride pearls in the γ channels along the γ/γ' interface can be explained by examining the partitioning behaviours of the W, Mo and Re in SX Ni-based superalloys. While W has been observed to partition in both γ and γ' for SX Ni-based superalloys, Mo and Re partition to the γ channels [39]. W and Re have also been observed to segregate at the γ/γ' interface for similar SX Ni-based superalloys [40]. In addition, the solubilities of boron in γ and γ' would strongly suggest that borides would be more likely to form in the γ channels since the maximum solubility of boron in Ni is 0.03 at. % [41], compared to at least 1.12 at. % in γ' [42]. While, it has also been reported that the presence of boride formers in the base metal accelerates the diffusion flux by causing in situ precipitation during brazing [43]. Thus, it could be expected that the diffusion rate of boron in the substrate alloy is controlled by the respective area fractions of γ and γ' in the diffusion plane and their diffusivities and the fraction of diffusion area occupied by boride precipitates and their diffusivity.

**Fig. 9.** — Schematic illustrating DAZ microstructural development during brazing (a) microstructure prior to brazing showing braze-alloy interface and cubic γ' precipitates. (b) At braze temperature, γ' partially dissolves below the solvus temperature of the alloy, and boron (B) diffuses as arrowed, while there is a reverse direction for boride forming elements W, Mo and Re, represented by ‘M’. (c) The formation of boride pearls at bonding temperature in the γ channels which are rich in boride elements M. (d) Upon cooling to room temperature, the γ' prime precipitates coarsen. Note the coarser boride particles at the front of the band where M diffused in opposite direction to boron.
Important and original observations from this work, relating to the DAZ, are shown schematically in Fig. 8, where it can be seen that additional boride-containing bands form during each heat treatment cycle and these bands are separated by boride-free regions. In addition, as there is little change in the width of the boride bands, they must remain during subsequent heat treatments. This means that band 1 borides formed during and after heat treatment one will remain after 2HT, 3HT and 4HT. Boride formation is, as indicated above, a result of the diffusion of boron into the substrate due not only to a chemical concentration gradient, but also a chemical potential gradient. The presence of the boride-free regions between each of the bands for all specimen types clearly indicates that the solubility of boron in these regions is insufficiently exceeded to precipitate borides or the rate of transport of Mo, W and Re to last row of particles is fast enough to "mop up" the available boron and cause them to coarsen as illustrated in Fig. 8(c) and (d). This clearly leads to a questioning of why the boride formers are transported to the borides faster than the boron diffuses further into the substrate. The latter would give a continuous layer of borides unbroken by the cooling and heating associated with each subsequent heat treatment. If, however, the boride forming elements were under a significant enough chemical potential change as temperatures decreased they would diffuse faster into the last line of borides and become denuded to a certain depth further into the substrate as a result. Comparing diffusion coefficients for Re, Mo and W [44] and boron in Ni based alloys [45,46] shows that they are six orders of magnitude slower for the refractory elements compared to boron. This must mean that the coarsening of the deepest "line" of boride particles, and the formation of a boride-free zone between bands on a subsequent heat treatment, are due to changes to the transport phenomena, which are increasingly controlled by the greater chemical potentials associated with boride formation at lower temperatures.

The fact that the thickness of each band of borides is similar and independent of the number of brazing cycles suggests that little else changes within the band. This is the almost the case for the Vf of borides and microhardness values too. Examining the microhardness data presented in Fig. 7, it can be seen that after each heat treatment, the microhardness for each respective band increases by a small but discernible amount. In addition, the Vf of precipitates in each band also increases but only by a small amount too. It is reported that the overall hardness in boride containing DAZs is controlled by the hardness of the substrate, the hardness of the borides, and their respective volume fractions [27,47]. Thus, the measured hardness, Hobs, can be described by the following:

\[ H_{obs} = \left(1 - V_f\right) H_M + V_f H_B \]  

(1)

Where \(V_f\) is the volume fraction of borides in each band, \(H_M\) is the hardness of the substrate material and \(H_B\) is the hardness of the boride phase. Equation (1) can be rearranged as:

\[ V_f H_B = H_{obs} - \left(1 - V_f\right) H_M \]  

(2)

Thus, plotting \(H_{obs} - \left(1 - V_f\right) H_M\) versus \(V_f\) should give a straight line relationship of slope \(H_B\). Fig. 10 shows this to be the case. On the one hand, this indicates consistency between the two sets of measurements, and on the other indicates a boride particle microhardness of the order of 878 Vickers microhardness. The microhardness value is consistent with values obtained for CrB and Ni3B by Riggs et al. [48], although it might be expected that the presence of refractory elements in the boride particles here would give rise to higher hardness.

Implicit in Fig. 8 is the discrete nature of each band and the fact that little change in \(V_f\) or microhardness occur. In contrast, as shown by the data in Table 2, particle coarsening occurs in each band subjected to a subsequent braze treatment. Since it is most likely that the boride formers are denuded almost completely in a boride band, particle coarsening is unlikely to arise by additional boride precipitating on to particle surfaces. This must be the case, otherwise significant increases in \(V_f\) and thus microhardness would occur. Accordingly, particle coarsening must occur via an Ostwald ripening process. The rate of this process is controlled either by diffusion rates between particles or the rate of interfacial solution or deposition. Which of these processes is rate controlling can be determined from Equation (3):

\[ (r-r_0) = Kt^n \]  

(3)

Where \(r = \) particle size after time \(t\), \(r_0 = \) the initial precipitate size and \(K\) is a rate constant. For diffusion controlled coarsening \(n = 0.33\) and for interfacial control \(n = 0.5\) (see Ref. [39]). Plotting \(\log(r)\) against \(\log(t)\) should give a straight line of slope \(n\). As indicated previously, knowing that each braze cycle had the same thermal history it is possible to replace \(t\) by \(N\) the number of braze cycles. Thus, using the data for particle sizes given in Table 2 and values of \(N\), a \(\log(r) - \log(N)\) was plotted for the data for bands 1 and 2. A line with slope 0.5 was determined for band 1 and for band 2 a similar slope was observed for 3 and 4 cycles. This means that the precipitate coarsening mechanism was controlled by an interfacial Ostwald ripening process.

Fig. 10. Graph plotting \(V_f\) against \(V_f H_B\) showing for each of the respective bands for each heat treatment, showing strong linear relationship.

The fact that the thickness of each of the bands of boride precipitates is very similar, strongly suggests that boron is transported around the boride pearls and through the alloy in that manner since transport through the borides is expected to be slower than in \(\gamma\) and \(\gamma'\), based on their strong bonding, high melting points and high activation energies reported for boride formation on molybdenum [49]. There is of course some particle coarsening and slight increases in \(V_f\) of borides in each band subjected to reheating, which will reduce the amount of boron being transported through the band, albeit by a slight amount. Once formed, the boride pearls decrease the effective area over which more rapid diffusion can occur. Solutions to Fick's laws correspond to diffusion across a unit area. Thus, any reduction in that area, due to boride particles, will result in a decrease in boron diffusion flux. This combined with increasing diffusion distances to the innermost point of boride precipitation and the reduction in boron concentration gradient across the layer formed at the braze - substrate interface accounts for the decrease in band thickness from band 1 to band 4.

The discussion above clearly shows that the factors which
control boron diffusion into a SX Ni-based superalloy are varied and complex. It is thus necessary to augment the arguments of Pouranvari et al. [43] that boron diffusivity is related to chemical potential for boron diffusion defined by boron concentration at the alloy surface and the concentration of boride formers in the alloy. In particular, a knowledge of phases present at the brazing temperature and their boron diffusivities would be very useful. The work in this paper shows that this information is not just necessary for explaining and predicting the remaining eutectic content after brazing, but how this content changes during re-repair cycles.

5. Conclusions

On the basis of this work, the following conclusions are made:

- Reheating of non-isothermally solidified WGB repairs in a SX superalloy results in braze remelting and contraction of the braze volume potentially causing a stress raiser and crack nucleation site.
- Boron homogenisation is impeded by a boride free layer at the braze-substrate interface which thickens with increased numbers of brazing cycles, reducing boron concentration gradients and thus diffusion rates.
- The diffusion rate of boron into the SX Ni-based superalloy is controlled by the respective area fractions of γ, γ' and boride precipitates in the diffusion plane and their diffusivities.
- The number of re-repair heat treatments corresponds to an equivalent number of bands of boride precipitates in the DAZ, where each band is separated by a boride-free region.
- A decrease in band thickness from band 1 to band 4 was caused by (1) decreasing boron concentration gradient across a thickening braze-substrate interface; 2) restricted boron transport across boride precipitates in the diffusion-affected zones; 3) slower transport of boron in γ', the area fraction of which changes over the braze cycle temperature range.

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