The Wyckoff positional order and polyhedral intergrowth in the M₃B₂- and M₅B₃-type boride precipitated in the Ni-based superalloys

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Ni-based single superalloys play a crucial role in the hottest parts of jet engines. However, due to the complex geometry and macro-segregation during the solidification process, the cast defect such as stray grains is inevitable. Therefore, the transient liquid phase (TLP) bonding which can join several small single crystalline castings together is gradually believed to be an effective method for improving the yields of production of the complex components. The melting point depressant element B is always added into the interlayer filler material. Consequently, borides including the M₃B₂ and M₅B₃ phase usually precipitate during the TLP bonding process. So a comprehensive knowledge of the fine structural characteristics of the borides is very critical for an accurate evaluation of the TLP bonding process. In this work, by means of the aberration-corrected transmission electron microscopy, we show, at an atomic scale, the Wyckoff positional order phenomenon of the metal atoms in the unit cell of M₃B₂- and M₅B₃-type boride. Meanwhile, the defect along the (001) plane of the above two types of boride are determined to be the polyhedral intergrowth with complex configurations.

Single crystal (SX) turbine blades are widely used to increase the efficiency of advanced aero-engines in the past a few decades⁴⁻⁵. It is universally accepted that the temperature capability of a superalloy increases with the overall contents of solid solution strengthening elements such as W, Mo, Ta, Re and Ru. However, owing to the complex geometry of turbine blades and the relatively lower diffusivity of the heavy elements, macro-segregation is unavoidable during the directionally solidified process. Thus, the cast defects such as stray grains, small-angle grain boundary and freckles frequently occur. In order to improve the yields and to decrease the cost, the transient liquid phase (TLP) bonding which joins several smaller SX castings together gradually becomes an effective and promising method⁶⁻⁷. As a melting depressant element (MPD), boron (B) is usually introduced into the jointing materials. During the TLP bonding process, a great number of borides tend to precipitate in vicinity of the joint because of diffusion of B into the parent material from the molten filler⁸⁻¹⁰. Therefore, a comprehensive knowledge of the microstructural characteristics of the borides is of great importance for better assessing of the TLP bonding process.

Several boride precipitates in superalloy such as M₃B₂¹¹⁻¹³, M₅B₃¹⁴⁻¹⁶ and M₂B¹⁷⁻¹⁹ are often observed, where M denotes metal atoms. Nevertheless, the fine structural characteristics in M₃B₂ and M₅B₃ phases are known little. Based on X-ray diffraction (XRD) analysis, Beattie¹¹ proposed the concept of ordered occupation phenomenon for metal atoms in M₃B₂-type boride. However, various precipitates in superalloy usually coexist and the total content of the precipitates is always so little that XRD cannot detect. In contrast, electron diffraction including rotation electron diffraction (RED)¹⁰⁻²² is able to determine the crystallographic information from rather small domains. Particularly, the recently developed aberration-corrected scanning transmission electron microscopy (STEM) is capable of displaying the morphological information at a sub-angstrom resolution. This development enables many existing structural problems to be directly imaged at an atomic scale²³⁻²⁵. In this work, we extensively investigate, by means of aberration-corrected high angle annular dark field (HAADF) Z-contrast STEM imaging mode, the structural details in the M₃B₂- and M₅B₃-type borides that precipitate during the TLP bonding
The structure and composition of the M$_3$B$_2$-type boride. In contrast to the TEM mode, the STEM mode is very convenient for micro-chemical analysis. Fig. 1a is an HAADF image revealing a lath-shaped M$_3$B$_2$ precipitation in the matrix during the TLP bonding process. Compared with the matrix (γ/γ'), M$_3$B$_2$ phase shows brighter contrast under HAADF imaging mode due to the relatively higher average atomic number (Z). The framed area corresponds to the EDS image-scan zone and the composition is shown in Fig. 2d–i. For a detailed structural determination of M$_3$B$_2$ phase, it is necessary to obtain a series of electron diffraction patterns (EDPs) by large-angle tilting. The acquired EDPs from the M$_3$B$_2$ phase are shown in Fig. 1b–g, which correspond to [001], [101], [100], [112], [111] and [110] zone-axis, respectively. Due to the tilting angle limitation of the used TEM, the EDPs were acquired from more than one grain. Moreover, at least two EDPs were acquired in each grain. All the hkl reflections in [001], [101], [112], [111] and [110] EDP are present, which imply a primitive unit cell. In the [100] EDP, only 0kl reflections with k even appear agreeing with b-glide on (100) plane. Based on extinction rules in these EDPs, lattice type of M$_3$B$_2$ phase is derived as a primitive tetragonal structure with the space group of P4/mbm and lattice parameters of a = 0.57 nm and c = 0.30 nm. It has a D$_5_2$-type structure (Strukturbericht notation) based on the information of atomic occupations in M$_3$B$_2$ phase.

The energy-dispersive spectrum (EDS) shown in Fig. 2a–c displays the compositional information of γ, γ' and M$_3$B$_2$ phase, respectively. It is seen that the γ phase is composed of Ni, Co, Cr, W; γ' of Ni, Al, Cr, W and M$_3$B$_2$ of W, Cr, Mo, Ni, Co. The boron-K edge peak from the M$_3$B$_2$ phase is given by the electron energy loss spectrum (EELS) shown as top-right inset in Fig. 2c. Moreover, EDS image-scanning is performed on the framed area in Fig. 1a to display the element distribution in the boride and the matrix. The element maps of Ni, Co, Cr, Al, Mo and W are shown in Fig. 2d–i, respectively. It is seen that, compared with γ phase, γ' phase is rich of Al and W and lack of Co and Cr. Ni and Mo are homogeneously distributed in γ and γ'. Moreover, compared with the matrix (γ/γ'), M$_3$B$_2$ precipitate is abundant in W, Cr, and Mo. To detect the light element distribution of boron, energy filtered TEM (EFTEM) was performed. Fig. 2j is a zero-loss peak map image with elastic electrons showing the overall distribution of the matrix and boride. Fig. 2k and l correspond to Cr-L and W-M filtered map, which exhibit the similar contrast difference between the matrix and the boride as that shown in EDS maps (Fig. 2f and i). The nano-particles marked with arrows in Fig. 2k are secondary γ' phases precipitated during the furnace cooled process. The B-K map in Fig. 2m shows B segregation in the boride. Ti is not detected both in the matrix and in the M$_3$B$_2$ precipitates due to its low volume in the present alloy.

**Figure 1** | Structural determination of the M$_3$B$_2$-type boride. (a) HAADF image displaying the M$_3$B$_2$ phase that precipitated at grain interior during the TLP bonding process. The γ, γ' and M$_3$B$_2$ phase are denoted. The orange square frame indicates EDS image-scan area as shown in Fig. 2. (b)–(g) Electron diffraction patterns (EDPs) of M$_3$B$_2$ phase, they are indexed as [001], [101], [100], [112], [111] and [110] zone-axis, respectively. The M$_3$B$_2$-type boride with space group of P4/mbm is determined according to the EDPs. Because of dynamic diffraction, the forbidden reflections occur and some are marked with square frames.
The crystallographic considerations. To establish the structural relationships of M₃B₂ (D5ₐ), M₅B₃ (D₈₁) and M₂B (C₁₆ for Strukturbericht notation), detailed crystallographic data of binary borides with the above structures are given in Table 1. It is seen that the parameter of \(a\) in the above three tetragonal lattices are nearly the same. Moreover, \(c_{\text{M5B3}}\) nearly equals to 2\(c_{\text{M3B2}}\) and \(c_{\text{M2B}}\).

It is known that the structure of boride can be described by the stacking of polyhedron with metal atoms in vertexes and B atoms in

Figure 2 | Composition information of the matrix (γ/γ') and M₃B₂-type boride. (a)–(c) STEM-EDS spectrum displaying the chemical composition of γ, γ', and M₃B₂ phase, respectively. The top-right inset in (c) is a TEM-EELS spectrum for absorption edge of B-K at 188eV indicated with an arrow, which was acquired from the M₃B₂ phase. (d)–(i) Elemental maps of Ni-K, Co-K, Cr-K, Al-K, Mo-L and W-M, respectively. The EDS image-scan area is indicated with an orange frame in Fig. 1a. (j)–(m) Energy filtered TEM image corresponding to zero loss peak map, Cr-L, W-M, and B-K, respectively. The arrows in (k) indicate the secondary γ' precipitates in γ matrix.

Figure 3 | Structural determination and composition information of the M₅B₃-type boride. (a) HAADF image showing the M₅B₃ phase that precipitated at grain interior during the TLP bonding process. (b) STEM-EDS spectrum showing the chemical composition of M₅B₃ phase. (c)–(h) EDPs of M₅B₃ phase, indexed as [001], [101], [100], [111], [221], and [110] zone-axis, respectively. The M₅B₃-type boride with space group of \(I₄/mcm\) is determined according to the EDPs. Because of dynamic diffraction, the forbidden reflections occur and some are marked.
these phases with the crystallographic orientation relationship of M3B2//M2B//M5B3. The close relationship among the three structures actually results from the close relationship among the lattice parameter for the above three structures. Considering the same atomic number density (AND) of atomic columns can be divided into two groups, as indicated by the red (marked as 1) and green (marked as 1’) arrows. Considering the same atomic number density (AND) of atomic columns can be divided into two groups, as indicated by the red (marked as 1) and green (marked as 1’) arrows.

The ordered occupation of metal atoms in M3B2-type boride. As seen in above sections, M3B2-type boride possesses the D5a structure and contains more than one metal element. Meanwhile, the metal atoms can be classified into two groups, namely, heavy elements with large atomic radius such as major W, minor Mo and relatively lighter elements with smaller atomic radius such as major Cr, trace Co, Ni.

**Table 1** | The structural type, space group, lattice parameters, Wyckoff positions and fractional atom coordinates in W2B, V3B2 and Cr5B3 phase

| Structure | Space group | Unit cell (nm) | Atom | Fractional coordinates |
|-----------|-------------|----------------|------|------------------------|
| W2B       | I4/mcm (no. 140) | a = 0.557 | Cr (8h) | 0.169 0.669 0.000 |
| C16       | P4/mmbm (no. 127) | c = 0.474 | B (4d) | 0.000 0.000 0.250 |
| V3B2      | I4/mcm (no. 140) | a = 0.576 | V (4h) | 0.173 0.673 0.500 |
| D81       | C16         | c = 0.304 | V (4a) | 0.000 0.000 0.000 |
| Cr5B3     | I4/mcm (no. 140) | a = 0.546 | Cr (16l) | 0.166 0.666 0.150 |
| D81       | C16         | c = 1.064 | B (8h) | 0.625 0.125 0.000 |
| M3B2      | D5a         |                | B (4d) | 0.000 0.000 0.250 |

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**Figure 4** | Polyhedron stacking in M3B2-, M5B3- and M2B-type boride. (a)–(c) Schematic illustrations showing the atomic configurations in M3B2 (D5a), M5B3 (D81), M2B (C16) phase, respectively. The basic polyhedron of trigonal prism and anti-square prism in each structure are shadowed.
as 1) and green (marked as 1') arrows. Although the AND of atomic column 1 and 1' in Fig. 5b are the same along [100]_M3B2 direction, the atomic column 1 is occupied by large metal atoms and atomic column 1' by small metal atoms. Thereby, the atomic column 1 has brighter contrast than atomic column 1'. The structural projection along [100]_M3B2 direction of the ordered M3B2 phase is shown in Fig. 5f. In Fig. 5c, three different contrasts for the atomic columns can be seen as highlighted with red (marked as 1), green (marked as 1') and white (marked as 2) arrows. The atomic column 1 and 1' in Fig. 5c have the same AND along [110]_M3B2 direction. But the atomic column 1 is occupied by large metal atoms and the atomic column 1' by small metal atoms. Thus the atomic column 1 has brighter contrast than the atomic column 1'. However, for the atomic column 1 and 2 in Fig. 5c, although they are all occupied by large metal atoms, the AND of the atomic column 1 is twice as that of the atomic column 2. So, the atomic column 1 has brighter contrast than the atomic column 2 in Fig. 5c. The structural projection along [110]_M3B2 direction of the ordered M3B2 phase is shown in Fig. 5g, where the shadowed atomic column 2 indicates half AND of the atomic column 1. Such an ordering of metal atom occupation in M3B2 phase was proposed in an XRD study.

The ordered occupation of metal atoms in M3B2-type boride. Similarly, to display the atomic occupation of metal atoms in M3B2-type boride, atomic scale Z-contrast imaging is performed. Fig. 6a is an atomic HAADF image obtained along the four-fold [001]_M3B2 direction of the M3B2 phase. In Fig. 6a, contrast difference of the atomic columns can be classified into two groups, as indicated by red (marked as 1) and green (marked as 1') arrows. Considering the same AND of the atomic column 1 and 1' along the [001]_M3B2 direction in D81 structure, the contrast difference between the atomic column 1 and 1' in Fig. 6a should be ascribed to the ordered distribution of metal atoms in M3B2-type boride. The unit cell of M3B2 with ordered metal atoms is given in Fig. 6d where blue balls represent large metal atoms (designated as L) and green balls represent small metal atoms (designated as S). Therefore, the ordered M3B2 phase should be treated as a ternary boride with the chemical formula labeled as L4SB2. Fig. 6e displays the structural projection of the ordered M3B2 phase (L4SB2) along [001]_M3B2 direction. For more details, atomic HAADF images along the other two major directions of the tetragonal lattice, namely, [100]_M3B2 and [110]_M3B2 direction, are shown in Fig. 6b and c, respectively. In Fig. 6b, two different contrasts of the atomic columns can be seen as indicated by the red (marked as 1) and green (marked as 1') arrows. In spite of the same AND of the atomic column 1 and 1' in Fig. 6b, the atomic column 1 is occupied by large metal atoms and atomic column 1' by small metal atoms. Thus, the atomic column 1 has brighter contrast than the atomic column 1'. The structural projection along [100]_M3B3 direction of the ordered M5B3 phase is shown in Fig. 6f. In Fig. 6c, the contrast difference is proposed to result from different atomic occupations taking into account of the same AND of the atomic column 1 and 1' along [110]_M5B3 direction. That is to say, the atomic column 1 is occupied by large metal atoms and the atomic column 1' is occupied by small metal atoms. But the contrast difference where the same large metal atoms occupy the atomic column 1 and 2 is proposed to result from different ANDs. The AND of the atomic column 1 is twice as that of the atomic column 2 along [110]_M5B3 direction. The structural projection along [110]_M5B3 direction of the ordered M5B3 phase is shown in Fig. 6g, where the shadowed atomic column 2 indicates the half AND of atomic column 1.

Polyhedral intergrowth in the M3B2- and M5B3-type boride. Based on the above crystallographic considerations, it is seen that M3B2-,
M$_2$B- and M$_3$B$_2$-type borides are closely related. Along [001] direction, the M$_3$B$_2$ and M$_2$B phase are completely composed of trigonal prism layers and anti-square prism layers, respectively. Furthermore, considering the fact that the M$_5$B$_3$ phase is composed of an alternating array of both trigonal prism layer and anti-square prism layer, it is proposed that trigonal prism layer and anti-square prism layer can inter-grow along [001] stacking direction without destroying local coordination environment of the B atoms. Thus, the intergrowth of one or more polyhedral layer along [001] direction inside the M$_3$B$_2$/M$_5$B$_3$ phase is expectable. Moreover, due to conservation of polyhedrons consisting of metal and B atoms, the resultant interface by the polyhedral intergrowth is proposed to possess a lower energy. Fig. 7 displays an atomic HAADF image of the M$_3$B$_2$ phase projected along [100]M$_3$B$_2$ direction. The polyhedron stacking along [001]M$_3$B$_2$ stacking direction is indicated. Compared with trigonal prism layers designated as T, the trigonal prism layers denoted by T' have a 36.7° rotation about [001]M$_3$B$_2$ stacking direction. This defective structure can be described as TTTAT'T''T'' as indicated in Fig. 7. Since an anti-square prism is composed of two sections which have a 36.7° rotation apart from each other along the four-fold direction, the intersection of one anti-square prism (A) leads to the stacking of trigonal prism layer from T to T''.

Fig. 8a is an atomic HAADF image acquired along [110]M$_5$B$_3$ direction of the M$_3$B$_2$-type boride. The polyhedron stacking along [001]M$_5$B$_3$ direction is denoted by the basic polyhedral units (T, T', A, A'), where an intergrowth of an anti-square prism layer is identified. For the sake of simplification, such a defective structure can be described as AT'A'TAA'TA. Due to the local intersection of one...
anti-square prism layer, a unit cell of M₂B₃-type boride is derived with stacking of AA'⁹. Fig. 8b is an HAADF image of M₅B₃ phase projected along [100]M₅B₃ direction. Based on the designation of the basic polyhedral units (T, T', A, A'), an intergrowth of two trigonal prism layers was identified. This defective structure can be described as AT'T'AT'T'ÁT' as indicated in Fig. 8b. Due to the local intergrowth of two trigonal prism layers, a small-scale M₃B₂ (L₂SB₃)-type boride is derived with stacking form of T'T'T'. This polyhedral intergrowth in M₃B₂/M₅B₃ phase is similar to the intergrowth of various phases in Ti-B system reported by De Graef³⁸ and Kooi³⁹, respectively.

Figure 8 | Polyhedral intergrowth in M₅B₃-type boride. (a) Atomic HAADF image along [110]M₅B₃ showing the intergrowth of one anti-square prism layer inside the M₅B₃ phase. (b) Atomic HAADF image along [100]M₅B₃ displaying the intergrowth of two trigonal prism layers inside the M₅B₃ phase. The perfect M₅B₃ phase is composed of an alternating array of trigonal prism layers and anti-square prism layers stacking along [001]M₅B₃ direction. The stacking sequence of the basic polyhedral units (T, T', A, A') along [001]M₅B₃ stacking direction is indicated. Compared with anti-square prism layers designated as A, the anti-square prism layers denoted by A' have a 36.7° rotation about [001]M₅B₃ direction.

Besides the local polyhedral intergrowth, large scale intergrowth of M₃B₂ with M₅B₃ also occurs in our sample as shown in Fig. 9a–b, which are obtained along the [100]M₅B₃ and [110]M₅B₃ direction, respectively. The interface between M₃B₂ and M₅B₃ is coherent and lattice misfit dislocation is not identified.

Discussion

On account of above crystallographic considerations, it is seen that there are two kinds of Wyckoff positions (designated as 16l and 4c) for metal atoms in the D₈₁ structure. They are occupied in order by the metal atoms with different atomic radius. The Wyckoff position

Figure 9 | Large-scale intergrowth of the M₃B₂- and M₅B₃-type boride. Atomic HAADF images along (a) [100]M₃B₂ or [100]M₅B₃ and (b) [110]M₃B₂ or [110]M₅B₃, respectively, reveal the large-scale intergrowth of the M₃B₂ and M₅B₃ phase. The stacking sequence of basic polyhedral units (T, T', A, A') for M₃B₂ and M₅B₃ along [001] stacking direction is indicated. The red and green arrows in (a)–(b) represent layers of large metal atoms (indicated by L) and layers of small metal atoms (indicated by S), respectively.
16l is occupied by large metal atoms while Wyckoff position 4c by relatively smaller metal atoms. Since the ordering happens at different Wyckoff positions inside the unit cell, the space group of the ordered structure remains unchanged. This Wyckoff positional order phenomenon is also applicable to the ordering in the M1B2 phase. The Wyckoff position 4h in M1B2 phase is occupied by metal atoms with large atomic radius, while Wyckoff position 2a by metal atoms with relatively smaller atomic radius. The LS-B2 (LS-B2) phase with the D8h (D5h) structure, in which Wyckoff position 4c (2a) is occupied by large metal atoms and Wyckoff position 16l (4 h) by relatively smaller metal atoms, is not observed in our samples. This selective ordering agrees well with the proposal given by Steeds et al. that the ordered LS-B2 phase is not usually seen. In fact, the ordered occupation of the metal atoms at different Wyckoff positions in M1B2- and M2-type boride may indeed lead to the difference, in contrast to the disordered structure, in the intensity of some diffraction reflections. However, these tiny intensity differences are always screened because the intensity for diffraction spots is usually inaccurate, which is strongly affected by numerous factors such as the sample thickness, exposure time, and deviation for the exact zone-axis orientation.

Although B atoms are invisible in the HAADF images due to its weak scattering ability, the structural characteristics of M1B2- and M2-type boride can be clearly displayed as shown in Fig. 9a–b. Along [001]M3B2 direction, there is only one layer of large metal atoms between two layers of small metal atoms. However, in the M2-type boride, two layers of large metal atoms are present between two layers of small metal atoms. This indicates that the fraction of the large metal atoms (or heavy elements) is larger in M2-type boride than that in M1B2-type boride.

In summary, we have carried out a systematic analysis on the composition and microstructures in the M1B2- and M2-type boride that precipitated in Ni-based single superalloy during the TLP bonding process. We find that the metal atoms in the lattice of M1B2 and M2B2 phase are occupied in an ordered manner. The M1B2 and M2B2 phase with ordered occupation can be treated as the ternary boride with the chemical formula of L5SB2 and L5SB2, respectively, where L represents metal atoms with large atomic radius and S indicates metals with small atomic radius. This ordering phenomenon is actually Wyckoff positional order inside the unit cell of the M1B2- and M2B2 phase. By introducing the concept of polyhedron stacking, the planar defects along [001] of L5SB2 and L5SB2 are interpreted in terms of the polyhedral intergrowth. Since the interface between the trigonal prism layer and the anti-square prism layer is coherent, the interfacial energy of L5SB2/L5SB2 is proposed to be very low, which rationalize the present observation of large-scale intergrowth of L5SB2 and L5SB2.

Methods

Bulk sample preparation. The 16 mm diameter cylindrical samples with nominal composition of 6.0 Cr, 7.5 Co, 1.2 Mo, 5.8 W, 5.9 Al, 1.1 Ti and balance Ni, in wt% were directionally solidified along [001] direction. Then the 8 mm high and 300 μm wide gap parallel to the [001] direction was cut in the center of the 10 mm high specimen. After cleaned, the specimen with a gap was filled using the gas atomized metal powder with nominal composition of 15.0 Cr, 3.5 B and balance Ni, in wt%. Finally the specimens were bonded in a vacuum furnace at 1200 °C under the pressure of 5 × 10⁻⁵ Pa for 4 h, following by furnace cooled to room temperature. TEM specimens were prepared by cutting, grinding, punching and dimpling to 10 μm. The ion-milling was carried out in a Gatan precision ion polishing system (PIPS) with a liquid-nitrogen-cooled stage for avoiding preferential thinning effects. The specimen was plasma cleaned in the Advanced Plasma System Gatan Solarus 950 before loading in the TEM for preventing the surface contamination.

Composition analysis and STEM imaging. Micrometer scale structural investigations were performed in the Tecnai G² F30 transmission electron microscope, equipped with a high-angle annular dark-field (HAADF) detector, X-ray energy-dispersive spectrometer (EDS) system and Gatan imaging filter (GIF) system, operated at 300 kV. Electron energy loss spectra (EELS) were collected with 0.3 eV per channel dispersion. The energy filtered TEM (EFTEM) images were recorded by the three-window method. The atomic Z-contrast images were recorded using the aberration corrected scanning transmission electron microscopes Titan G² 60-300 fitted with a high-brightness field-emission gun (X-FEG) and double Cs correctors from CEOS, and a monochromator operated at 300 kV. In the scanning transmission electron microscopy (STEM) mode, the convergence angle of the electron beam is approximately 25 mrad, which yields a probe size less than 0.10 nm. And the collection angle is from 50 mrad to 250 mrad. The final resolution approximates 0.08 nm under the STEM mode. According to thickness map acquired from EFTEM, the final thickness for atomic Z-contrast images varies from 20 nm to 80 nm. The average background subtraction filter (ABSF) and Wiener filters were used to subtract the signal from the atomic HAADF images from the morphous layer at the surface of the specimen. The Fast Fourier Transform (FFT) pattern of the HR-STEM image was used to determine the exact direction of the projection.
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**Author contributions**
The project of fine structural analyses for borides precipitated in superalloy was conceived by X.L.M. and Y.L.Z.; bulk sample was prepared by N.C.S.; thin foils preparation and TEM/STEM observations were performed by X.B.H.; all the authors participated in discussion, interpretation of the data and producing the final version of this paper.

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