Microstructural features in a laser clad TiB-Ti composite coating

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Abstract

The microstructure of a TiB/Ti composite coating, obtained by laser cladding a Ti-6Al-4V substrate with a Ti/TiB₂ powder mixture, was scrutinized using transmission electron microscopy (TEM). TiB showed three different morphologies: fine needles (200 nm diameter, 15 μm length), plates (thickness 1 μm, short length 3 μm and long length 15 μm) and coarse needles (diameter 3 μm and length 50 μm). All TiB is composed of both the stable B₂7 and the metastable Bf crystal structures. Intimate mixing of B₂7 and Bf is possible because B₂7[010] // Bf[001] that easily leads to stacking disorder. Aspects of disorder are quantitatively analysed using high-resolution transmission electron microscopy (HRTEM). Throughout the fine needles, extensive stacking disorder occurs. In the plates, a core of B₂7 (with relatively low stacking-fault density) is present, with faulted Bf on the outer surfaces that has a rough but fully faceted interface with the Ti matrix. The coarse needles consist predominantly of nearly defect-free B₂7. Noteworthy about the coarse needles is that they have a large core composed of Ti. On a much finer scale Ti is also dispersed in the plates and fine needles. It will be shown that the differences in microstructure among the three types of TiB morphologies provide important clues about the evolution of the TiB under the conditions of rapid growth.
1 Introduction

Titanium exhibits several excellent properties, e.g. a high strength-to-weight ratio and an excellent corrosion resistance [1]. However, the tribological properties of Ti are relatively poor. The wear resistance can be improved by reinforcing the loaded outer layer of Ti with ceramic particles. Suitable techniques to perform this task are laser melt injection (LMI) or laser cladding [2]. Some of our previous work concentrated on the LMI of SiC articles in Ti-6Al-4V resulting for instance in a reduction of the wear rate (weight loss) for abrasive wear by a factor 7 for the SiC embedded Ti alloy compared to the untreated material [3,4]. The present work is related to laser cladding of Ti-6Al-4V with a powder mixture of Ti and TiB₂ and focuses on the microstructure of the clad layer with (HR)TEM as the primary tool. An additional paper is devoted to the details of the laser-clad process and will be published elsewhere [5]. The present paper only shows results of cladding using a powder feeding system.

The analysis of different morphological types (fine needles, plates and coarse needles) of TiB present in the layer plays a decisive role in gaining an understanding of the TiB growth process. All the TiB present is intimately composed of two phases with the same composition but different crystal structures; stable TiB with the B27 structure and metastable TiB with the Bf structure. Here, the spatial distribution of these two phases within the TiB grains is accurately analyzed using HRTEM. Indeed, knowledge of this distribution for the different morphological types is instrumental for unraveling the evolution of the borides in the clad layer. The evolution of B27 and Bf type borides has been analyzed previously [6,7]. However, so far only one of the 3 morphological types of TiB (i.e. the plate type) was analyzed (in [6]) and HRTEM images of the mutual distribution of B27 and Bf were not reported (although accurate rigid atomic models have been presented). Further, more insight is gained at what stage during the solidification process B27 and Bf nucleate. Analysis including the two other morphological types is important to arrive at this insight. A comparison of the present results with [7] is not possible because the coarse monoboride needles analyzed in [7] contained a high concentration of Ta that stabilizes the Bf structure.

2 Experimental procedures

For the laser clad process a 2 kW continuous wave Nd:YAG laser (Rofin Sinar CW020) was used. The laser beam is transported by means of a Φ 0.8 mm fiber optics, resulting in a homogeneous intensity distribution. The focusing lens is watercooled and has a focal length of 100 mm. A spot size of about 2.5 mm was obtained on the specimen surface by defocusing the laser beam to 9 mm. Between the lens and the specimen a nozzle is located to supply a shielding gas (1 l/min Ar and 5 l/min He) for protection of the lens and for preventing oxidation of the specimen. The movement of the specimen was performed by a
CNC X-Y table. The laser power used was 1200 W and the scan velocity was 500 mm/min. A powder mixture of 65 vol.% Ti (particle size 40–90 μm) and 35 vol.% TiB₂ (particle size 10–40 μm) was continuously supplied by a powder feeding apparatus (Metco 9MP) to a Ti-6Al-4V substrate. More details about the laser cladding process will be given in [5]. Because the carrier gas for powder feeding (3 l/min Ar) can distort the melt bath a cyclone is used, in which the major gas flow escapes through the top-center outlet. Centrifugal forces prevent the powder to escape from this outlet. The powder is fed through the bottom outlet of the cyclone with an amount of gas depending on the ratio of the diameters of the two outlets.

For SEM a Philips XL30 operating at 15 kV was used. The TiB/Ti composite coating was deep-etched with Weck’s color etch (100 ml distilled water, 50 ml ethanol and 2 g. (NH₄)₂HF₂) or more gently etched with Titanium etch 3 (5 ml HF, 3 ml HNO₃ and 992 ml H₂O). Specimens for TEM were prepared by grinding, dimpling and ion-milling round 3 mm discs to electron transparency. The surface of the starting discs corresponded to the surface after laser embedding. By adjusting the amount of material removed from the top or the bottom of the discs, TEM specimen corresponding to a certain chosen depth in the melt pool could be prepared. In the present work the TEM samples are at a depth near the center of the clad layer thickness. Ion milling was performed using two beams of 4 kV Ar⁺ ions having an incidence angle of 6° with the bottom and top surfaces of the discs (using a Gatan PIPS 691). For (HR)TEM a JEOL 4000EX/II operating at 400 kV with a point-to-point resolution of 0.165 nm was used. (HR)TEM images were obtained by digitizing negatives using a CCD camera and the gray scale was adjusted to achieve reasonable brightness/contrast. For analytical TEM we used a JEOL 2010F, operating at 200 kV, equipped with X-Ray Energy-Dispersive Spectrometry (EDAX detector with super-ultra thin window) and with a Gatan Imaging Filter.

3 Results

An overview with SEM of the deep-etched TiB-Ti composite coating is depicted in Fig.1a, clearly revealing the morphology of the TiB phases. The total volume fraction of TiB in the coating is very high, i.e. amounting to about 40 Vol.%. Three basic morphologies of TiB can be distinguished. Most of the TiB is present in the form of fine needles with a mean diameter of 200 nm and a typical length of 15 μm. Also clear in Fig.1a are the much coarser needles that have a diameter and length of the order of 3 μm and 50 μm, respectively. These coarser structures are found more to the bottom of the re-solidified melt pool of the laser process. In Fig.1b a more detailed SEM image of such a coarse needle is shown. Noteworthy are the hollow core of the needle and the relative large area around the needle that is devoid of any TiB. SEM reveals that the core of the coarse needle is actually filled with Ti.
Fig. 1a SEM overview of a deep-etched Ti/TiB composite coating showing 3 basic TiB morphologies: fine needles (200 nm diameter, 15 μm length), plates (thickness 1 μm, short length 3 μm and long length 15 μm) and coarse needles (diameter 3 μm and length of 50 μm). Fig. 1b SEM image showing in more detail a coarse TiB needle with apparently a hollow core (was filled with Ti before etching) and a thin plate, both with relative large boride-free zones, surrounded by the thin needles.

This is an interesting finding in relation to Ref. 10 where it is stated that using solidification processes coarse TiB fibres tend to have hollow cores. In contrast, here we find coarse TiB fibres filled with Ti cores. Finally, in Fig. 1b the third morphological type of TiB that takes up a minor fraction can be discerned. It consists of a plate with rough surfaces with a thickness of the order of 1 μm, a short length of 3 μm and a long length (not visible in Fig. 1b) of about 15 μm.

Although a distinction between the 3 basic variants of TiB can be made in practice, intermediate stages between these 3 variants are possible. To unravel the details of the microstructure of the TiB-Ti composite and to reveal the atomic
structure of the three TiB variants, conventional, analytical and high-resolution TEM were performed.

Fig.2a (left) Bright-Field (BF) TEM image showing part of a TiB plate containing a core with B27 crystal structure and with Bf on the outer surfaces. In both TiB phases Ti precipitates are present; in Bf they are parallel to Bf(020). Note the rough but fully facetted Bf/Ti interface. Fig.2b (right) Selected-Area Electron Diffraction pattern showing the orientation relation and interface orientation between B27 and Bf: B27(200)//Bf(110) and B27[010]/Bf[001]. Note the strong streaking in the directions of Bf{110}.

Rough plates: In the bright-field TEM image of Fig.2a a part of a plate-shaped TiB particle is shown. The corresponding Selected-Area Electron Diffraction (SAED) pattern from the whole width of the plate is shown in Fig.2b. The image and SAED show the complex structure of the TiB plate. In the SAED, reflections from 3 phases can be discerned. Using a small SA aperture, the SAED from only a central part of the plate was obtained, which clearly revealed that it consists of TiB with the B27 structure viewed along the [010] zone axis. The most principal B27 reflections are indicated in Fig.2b by white arrows and in Fig.2a the corresponding B27 core is marked. Other dominating reflections in Fig.2b from outside this core stem from TiB with the Bf structure viewed along [001]. Also in this case the principal reflections are marked by overlaying a black circle on the corresponding spots. The Bf phase is present on both surface sides of the plate and shows a very rough, but fully facetted interface with the surrounding Ti matrix. Crystallographic information on these two TiB phases can be found in Ref.[6]. A third phase consisting of particles (more or less rounded in B27 and elongated parallel to (020) in Bf and mostly darker than the surrounding TiB but also in some cases brighter) is observed in Fig.2a that gives distorted spots in Fig.2b due to rotation around the viewing direction. The phase of these particles becomes apparent when looking at the energy-filtered images. Compared to the surrounding TiB the particles are enriched in Ti and B is absent.
It is concluded that the particles are Ti. No Al or V could be detected in this Ti when EDXS was performed in the TEM with a nanoprobe on the particles.

Fig. 2b reveals the orientation relation that also directly specifies the interface orientation between B27 and Bf: B27(200)/Bf(110) and B27[010]/Bf [001]. The interface between B27 and Bf appears to be flat without observable steps. The matching of B27 and Bf according to this interface orientation could be expected because coherency strains are minimum. The B27[010] axis is in principle crystallographically identical to the Bf [001] axis. The mismatch between the other orthogonal direction in the interface plane, i.e. B27[002] and Bf [110] is less than 0.4% according to their lattice constants [6].

Apart from the spots of the three phases, streaking is also evident in Fig. 2b. Streaking occurs in the direction of B27(200)/Bf (110) and also in the direction of Bf (1-10) and can be observed weakly around the central spot in the direction of Bf(020). This latter type of streaking originates from the many thin Ti plates on (020)Bf that are clearly visible in Fig. 2a. The other two types of streaking denotes some kind of stacking disorder of at least the Bf{110} planes and possibly also the B27(200) planes. In general the B27 core does not contain many defects, whereas the Bf has a high defect density.

Fine needles: The most interesting viewing direction of the fine needles in (HR)TEM is along the fibre axis. Because the needles have a typical diameter of 200 nm it is almost impossible to find and to orient individual needles in this single desired zone axis. Fortunately the needles in certain domains show collective behavior with similar orientation and tend to have an orientation relation with the surrounding Ti grains. Colonies of Ti grains with low-angle grain boundaries are observed containing TiB needles on their boundaries and in their interior; It turned out that when the Ti grains were oriented along <1120> groups of needles could be observed nearly end-on. In principle 3 Ti<1120> directions exist and in this way the needles can have a mutual tilt of 120°. Then, certain needles are end-on and others seem more plate-like, because ±120° inclined in the TEM foil elongating the projected section of the needle by a factor 2 in one direction; see for the latter case the BF-TEM image in Fig. 3a. Indeed, both orientations could be observed (sometimes) for closely separated TiB needles, but much less frequent than according to a 1/3 probability for end-on and 2/3 probability for ±120°. This implies that the TiB orientation is not determined solely by the OR with the surrounding Ti grains, but by a collective growth process where the needles tend to grow with the same orientation in the same direction.

In the bright-field image in Fig. 3a the Ti grain lies in the <1120> zone axis and from the contrast it is clear that the TiB out of a major zone axis. Stacking fault contrast can be observed throughout the width of the needle with inclined stacking faults that are not far from edge-on (due to the high density of SFs the typical bright and dark fringes of an individual stacking fault can not be observed). When the Ti grains were oriented in the <1120> zone axis a principal zone axis of the TiB needles was typically 10-15° off. For the end-on
observed needles this zone axis corresponded to \( B_f[001]/B_{27}[010] \). Thus, crystallographically the fiber axis of the needle is identical to the long axis observed for the plates above.

\[ \text{Fig.3a (left): Bright-field TEM image showing the large stacking disorder throughout the entire width of a fine needle.}\]

\[ \text{Fig.3b (right): BF-TEM image of end-on observed coarse TiB needle with corresponding diffraction patterns of the Ti core and TiB needle that consists fully of almost defect-free B27. Defected B_f is only present in a thin layer (100 nm) at the bottom facet of the needle. Although both diffraction patterns are recorded in zone axis, in practice a misorientation of about 2-3° was present. This value for the misorientation holds in general between the coarse needles and the Ti. Note that a misorientation between the Ti core and the Ti outside the needle was not detected (< 0.2°).} \]

Coarse needles: Due to their large size it was relatively easy to find and to orient the coarse TiB needles with the electron beam parallel to the fiber axis. Fig.3b shows an example of an end-on oriented coarse TiB needle. This TiB needle is almost completely composed of B27. \( B_f \) could only be observed in a relatively thin (a little bit less than 200 nm thick) layer on the (100) facets of B27, i.e. the horizontal downwards facets in Fig.3b. Similarly as for the fine needles the coarse ones have an orientation relation with the Ti. An interesting difference is that now a distinct inner core is also present. Both the Ti in the inner core and at the outside are in the \( <11\bar{2}0> \) zone axis as revealed by the SAED pattern bottom left in Fig.3b. No difference in orientation (within a few tenths of degree) between the inner and outer Ti could be observed. On the other hand the low index zone axis of the TiB turned out to be 2-3° rotated with respect
to Ti$<$11 2 0$>$ as was repeatedly observed for the coarse needles. Again, the fiber axis of the TiB corresponds to B27[010] as is shown by the SAED pattern bottom right in Fig.3b. Combining the SAED patterns and the bright field image in Fig.3b leads to the following observations: (i) the inner and outer facets of the TiB needle are nearly identical, (ii) the dominant facet is parallel to B27(200) and at the outer facet a thin layer of $B_f$ forms the interface with the Ti (however not at the inner facet), (iii) the second largest facet corresponds to B27(101)/Ti(1010), (iv) the third and smallest facet corresponds more or less to B27(101)/Ti(1015). In all coarse TiB needles observed, the stacking-fault density in the dominant B27 parts is in general low and large defect-free B27 crystals can be observed. Streaking in the SAED patterns of B27 is therefore absent. On the other hand the $B_f$, although only a thin outer layer of the B27(200) facets, remains full of defects [8][9].

4 Discussion

A logical evolution of the TiB phases is clearly revealed with their morphology transition i.e. from the coarse needles (with a Ti core) where B27 is dominant with only a limited influence of $B_f$ on the B27(100) facets, via the plates where a core of B27 is present with relative thick $B_f$ parts on the outer surfaces of the plates, to the fine needles in which $B_f$ is dominant and stacking faults occur throughout the entire width of the needles. An increasing coarseness of the TiB (i.e. not its length, but more dictated by its dimensions perpendicular to the length) directly relates to (i) an increased dominance of B27 in the structure, (ii) a relative decrease of the stacking fault density in the TiB and (iii) a decrease of the width of the transition region from $B_f$ to B27. These points are interrelated because the B27 that accounts for the increased coarseness of the TiB is relatively defect free. The $B_f$ present in all three morphologies is invariably rich in defects, i.e. containing stacking faults and thin layers of Ti. The coarse needles were formed first and the fine needles last during the solidification process. An increasing coarseness thus indicates a longer time that after nucleation the TiB spent at relatively high temperatures and the more time was available for the TiB structure to approach a kind of (although may be still far from an) equilibrium structure. Therefore, knowing that $B_f$ is metastable while B27 is, the observed evolution of the micro- and atomic structures of the three morphological types of TiB appears logical.

According to the binary Ti-B phase diagram [11], the composition (13.6 wt.% B) of the powder mixture used is located close to the intersection point between the liquidus and the peritectic transformation line of TiB formation. The choice of this composition, taking the dilution due to melting a thin surface layer of the Ti6Al4V substrate into account, ensures that TiB may form as high as 40 vol.% in the clad composite layer and that it is very unlikely that the solidification path of the layer runs through the two phase L + TiB$_2$ zone. This
implies that primary TiB phases should directly form from the melt without the necessity of a peritectic reaction between TiB₂ and the Ti-melt. According to the microstructural observations, the coarse needles are considered as the primary TiB phases that nucleate from the liquid by a heterogeneous mechanism. It is evidenced by the radial growth pattern of the coarse needles originating from the incompletely decomposed TiB₂ particles [5], which corresponds to the maximum thermal gradient existing around a TiB₂ remnant particle. The TiB-free zone surrounding the coarse TiB needles indicates the depletion of B elements in the adjacent melt that solidifies later as Ti halos analogous to the Al-halo observed in hypereutectic AlSi alloys [12]. Formation of such Ti halos eventually separates the coarse TiB needles from the remaining liquid and forces the TiB in the eutectic to nucleate cooperatively with the Ti at large undercoolings. The fast growth rate due to the large undercooling and the absence of additional time to approach an energetically more favorable state explains why the fine TiB needles have a high defect density compared to the coarse ones.

In Ref.10 coarse and fine needles were also observed. The presence of the fine needles was explained by a critical volume fraction of TiB (Vc). Below Vc, only coarse needles were present and, above Vc, coarse needles cause mutual hindrance of their elongation. Because growth in directions perpendicular to the length of the fibers is slow, secondary nucleation of fine needles occurs instead of coarsening of the primary needles. In that scenario the fine needles are connected (nucleate on) the coarse needles. We never observed this (cf. Fig.1). Furthermore, their scenario does not take the presence of the eutectic in the Ti-B phase diagram into account and does, therefore, not hold for our composites. Nevertheless, what is of greater importance for the present paper is that in all scenarios the coarse needles develop first and the fine ones later.

The increased hardness of the Ti/TiB composite coating compared to the Ti-6Al-4V substrate measured (500 HV versus 180 HV [5]) is substantial, but by itself of limited value. In a hard and brittle coating, particles may easily break out, ultimately leading to poor wear resistance. Therefore, the fracture toughness of the coating is also of principal importance. Luckily, the fracture toughness of Ti is excellent and a mixture of TiB with Ti can thus be expected advantageous, in particular with a proper spatial distribution of TiB and Ti. The large Ti cores in the coarse TiB needles are expected to be important to arrive at an optimal combination of hardness, fracture toughness and wear resistance. In general, the presence of Ti within all three basic morphologies of TiB will appear beneficial to the tribological properties. A nice example is exhibited in Fig.2a, where a crack in the B27 core of the TiB plate is present that is bridged and stopped by the Ti particles present.

5 Conclusions

In the TiB/Ti composite coating produced by laser cladding the following three basic TiB morphologies were found in order of increasing coarseness: (1) fine needles with a diameter of 200 nm and length of 15 µm (2) plates with a thickness of 1 µm, short length of 3 µm and long length of 15 µm, and (3) coarse
needles with a diameter of 3 μm and length of 50 μm. All TiB is composed of both the stable B27 and the metastable Bf crystal structures. Intimate mixing of B27 and Bf is possible because B27(200) planes fit excellently onto Bf (110) or (110) planes (with B27[010]/Bf[001]) easily leading to stacking disorder. The long (fibre) axis of all three morphologies corresponds to B27[010]/Bf[001]. The coarse needles and centers of the plates consist of relatively defect-free B27 and are formed in the proeutectic stage. The Bfrich fine needles show extensive stacking disorder throughout their entire widths and are formed cooperatively with the Ti in the eutectic. During this reaction the same defected Bfrich phase nucleates on the B27(200) facets of the coarse needles and plates. The width of the transition region between the B27 core of the plates and the Bf on the outer surface is smaller than the width of the mixed B27/Bf fine needles. The fine and coarse needles show a tendency to have an orientation relation with the neighboring Ti. The misorientation between the TiB fiber axis and the Ti[1120] zone axis is typically 10-15° for the fine and only 2-3° for the coarse needles. This value for the misorientation reflects that the coarse needles grew under conditions closer to equilibrium. The coarse TiB needles have a substantial Ti core, but on a very fine scale Ti is also dispersed in the other TiB morphologies. Experimental observations suggest that this Ti incorporated in the TiB is beneficial for increasing the fracture toughness of the composite coating. Together with the increased hardness of the coating, an important improvement of the wear resistance of Ti is anticipated.

References