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Refining as-cast β -Ti grains through ZrN inoculation

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Abstract

The columnar-to-equiaxed transition and remarkable refinement of β -Ti grains occurs in an as-cast Ti-13Mo alloy when a new grain refiner, ZrN, was inoculated at a nitrogen level as low as 0.4 wt. %. The grain refining effect is attributed to in-situ formed TiN particles that provide active nucleation sites and solute Zr that promotes constitutional supercooling. Reproducible orientation relationships were identified between TiN nucleants and β -Ti matrix, and well explained by the edge-to-edge matching model.

Keywords: grain refinement; titanium alloy; heterogeneous nucleation; inoculation

It is acknowledged that grain refinement of engineering alloys during solidification can significantly reduce casting defects, enhance mechanical properties and improve formability during subsequent thermomechanical processing [1]. In addition to the benefit to conventional cast and forged products, fine and equiaxed grains also play a critical role for

additively manufactured alloy components. Smart manipulation of the material's chemistry and laser/electron beam scanning strategies can convert commonly observed columnar grains, fully or partially, into equiaxed grains, reducing the microstructural anisotropy and suppressing the formation of hot cracks in as-built components [2-4].

Unlike other widely used engineering alloys, such as Mg alloys, Al alloys and steels, there is currently no commercial grain refiner available for Ti and its alloys. So far, the best grain refining efficiency was obtained through the additions of boron as a solute due to its strong segregating power [5,6]. However, in the absence of potent inoculant particles, trace boron addition as solute only is not able to deliver equiaxed prior β -Ti grains, but only decreases the width of columnar grains of additively manufactured Ti-6Al-4V components [7]. Another problem associated with boron additions is the formation of elongated TiB particles at dendrite arm boundaries and/or grain boundaries, which is usually detrimental to the ductility of Ti alloys [8]. It is worth mentioning that TiB₂ is a potent grain refiner for β -Ti in TiAl-based alloys (Al concentration is around 45 at. %) [9,10]. However, TiB₂ inoculation is not applicable in common Ti-based alloys, such as Ti-6Al-4V, because the TiB₂ is not stable in the liquid and will transform to TiB when the Al concentration is lower than 30 at.% unless an excessive amount of boron (over 8 at.%) is added [11].

It has been a long-standing challenge to seek potent nucleant particles that can serve as heterogeneous nucleation sites for prior β -Ti grains. This is mainly because very few intermetallic phases or even ceramic phases that could act as inoculants, survive in molten titanium which has very high chemical activity at temperatures above 1670°C. To address

this challenge, we shifted our focus towards peritectic forming elements because the pro-peritectic phase is thermodynamically stable in liquid titanium. For binary Ti alloys, one of the most common peritectic forming elements is nitrogen, which can form a pro-peritectic phase, TiN, in the Ti-N liquid when the nitrogen content reaches 5 wt. % [12]. It has been reported in an early US patent that nitrogen can reduce the prior β -Ti grain size by two to three times when 5 wt. % nitrogen was added in Ti-6Al-4V [13]. However, such a high concentration is far beyond the acceptance level for engineering applications due to nitrogen embrittlement [14]. In this paper, we present our recent discovery of the refinement of β -Ti grains at much lower nitrogen content through ZrN inoculation. The grain refining mechanisms of ZrN inoculation are discussed and the nucleation crystallography is determined.

A typical metastable β -Ti alloy, Ti-13Mo (wt. % hereinafter) was selected as a base alloy to retain β -Ti grains at room temperature. First, 99.7% pure Ti powder and 99.7% pure Mo powder were mixed with 99.5% pure ZrN powder (from 0 to 8 wt. %) and blended in a Turbula shaker mixer for half an hour. Another series of samples were made by mixing Ti, Mo powder and 99.5% pure TiN powder to study the individual effect of nitrogen. The total amount of powder mixture weighs 10 grams. The well blended powder mixture was then compacted into a cylindrical block with the pressure of 100 MPa. Cylindrical blocks were arc melted and cooled in a water-chilled copper crucible protected by an argon atmosphere. Each block was melted four times, with the ingot inverted between each re-melting, to enhance the homogeneity of the button ingot. As-cast button ingots were then sliced vertically followed by mechanical polishing. The polished samples were etched by Kroll's

reagent to reveal the grain boundaries. Energy dispersive spectroscopy (EDS) and electron back-scattered diffraction (EBSD) mapping were conducted at the centre of the vertical cross-section of the button ingots on an FEI Nova NanoSEM at 20 KV. ICP-AES analysis was used to determine the chemical composition of as-cast samples.

The measured alloy composition of the button ingots with different ZrN additions is shown in Table 1. For brevity, and because the Zr and N contents increase equally with ZrN addition, ZrN n ($n = 2, 4, 6, 8$) is used as the alloy designation where n represents the weight percentage of ZrN addition used in this study. The same alloy designation rule also applies to the samples inoculated with TiN. The morphology and size of the β -Ti grains at different addition levels of ZrN are shown by 1mm x 1mm EBSD maps in Figure 1. Large columnar grains (2 ± 0.5 mm long and 0.5 ± 0.1 mm wide) were observed in the base alloy. The grain morphology and size are not noticeably different in the ZrN2 and ZrN4 samples. In contrast, fine, equiaxed β -Ti grains appear in the ZrN6 sample where the average β -Ti grain size dramatically reduces to 104 ± 25 μ m. Further addition of ZrN only reduces the grain size slightly to 80 ± 15 μ m, however, large primary dendritic nitride particles can be seen inside the β -Ti grains in the ZrN8 sample (Figure 1e). The difference between Figure 1(a, b, c) and 1(d, e) implies that a columnar-to-equiaxed transition (CET) and significant grain refinement

Table 1 The chemical composition of the samples in the current study

Sample description	Designation	Ti	Mo	Zr	N	O
Ti-13Mo	base alloy	Bal.	13.3	---	0.03	0.14
Ti-13Mo + 2 wt.% ZrN	ZrN2	Bal.	12.9	2.00	0.14	0.19
Ti-13Mo + 4 wt.% ZrN	ZrN4	Bal.	13.4	4.11	0.26	0.26
Ti-13Mo + 6 wt.% ZrN	ZrN6	Bal.	13.4	5.84	0.40	0.32
Ti-13Mo + 8 wt.% ZrN	ZrN8	Bal.	13.5	7.78	0.52	0.34
Ti-13Mo + 4 wt.% TiN	TiN4	Bal.	14.0	---	0.53	0.28

Figure 1 EBSD map of β -Ti grains in the as-cast button ingot of (a) base alloy, (b) ZrN2, (c) ZrN4, (d) ZrN6, (e) ZrN8 and (f) TiN4.

occurred during solidification when the ZrN addition reaches the critical level of 6 wt. % (where the nitrogen content is 0.4 wt. %). Similar CET and grain refinement were also observed from as-cast Ti-13Mo-xN samples when the nitrogen content reaches a critical level of 0.5 wt. % (TiN4), as shown in Figure 1(f). Compared to the base alloy, the β -Ti grain size reduced to $200 \pm 36 \mu\text{m}$ when 0.5 wt. % nitrogen was added, but the grain refinement is not as substantial as that in the ZrN6 sample (Figure 1d).

For in-depth understanding of the grain refining mechanisms, local EBSD and EDS mapping were undertaken on the ZrN8 sample which had the best grain refining effect, as shown in

Figure 2 An equiaxed β -Ti grain in sample ZrN8. (a) secondary electron image. (b) EBSD map. (c-f) EDS map of Ti, Mo, Zr and N.

Figure 2. An equiaxed β -Ti grain contains a well-defined nucleant particle located at its grain centre. The distribution of four major elements, titanium, molybdenum, zirconium and nitrogen at the same location is shown in Figures 2(c) to 2(f), respectively. High intensities of both nitrogen and titanium were observed inside the nucleant particle whilst the molybdenum and zirconium intensities are very low. This implies that the nucleant particle located at the grain centre is TiN. EBSD analysis shown in Figure 2(b) also confirms this particle is TiN with a face-centred cubic (FCC) crystal structure. Figure 3(a) provides the pole figures of this TiN particle and its surrounding β -Ti matrix. It can be clearly seen that one of the $\{111\}_{\text{TiN}}$ planes shares the same orientation as one of the $\{110\}_{\beta\text{-Ti}}$ planes (circled in red)

in the pole figure while one of the $\langle 110 \rangle_{\text{TiN}}$ directions parallels one of the $\langle 001 \rangle_{\beta\text{-Ti}}$ directions (circled in blue). Accordingly, the $\beta\text{-Ti}$ matrix holds a well-defined Nishiyama-Wassermann (N-W) orientation relationship (OR) with this TiN nucleant particle, which can be expressed as

$$[001]_{\beta\text{-Ti}} // [\bar{1}01]_{\text{TiN}}, (\bar{1}10)_{\beta\text{-Ti}} // (111)_{\text{TiN}}.$$

Figure 3 Pole figures of a TiN nucleant and its surrounding $\beta\text{-Ti}$ matrix, which presents (a) N-W OR and (b) K-S OR.

Overall, reproducible ORs were observed from twenty one TiN particles at grain centres after investigating more than fifty $\beta\text{-Ti}$ grains. Among these twenty one particles, fifteen TiN particles hold the aforementioned N-W OR with their $\beta\text{-Ti}$ matrix while the second OR was identified from the other six TiN particles. The representative pole figures of the second OR are shown in Figure 3(b). This OR can be expressed as

$$[111]_{\beta\text{-Ti}} // [\bar{1}01]_{\text{TiN}}, (\bar{1}10)_{\beta\text{-Ti}} // (111)_{\text{TiN}},$$

which corresponds to the Kurdjumov-Sachs (K-S) OR, another common OR between FCC and body centred cubic (BCC) phases.

As an energetically favourable OR is always associated with a local minimum of interfacial energy, the edge-to-edge matching (E2EM) model [15,16] is used to examine the crystallographic matching across the interface between TiN and β -Ti. The lattice parameters of TiN and β -Ti are 0.4225 nm and 0.3278 nm, respectively, measured by XRD from the ZrN6 sample. There are two pairs of matching directions, $\langle 111 \rangle_{\beta\text{-Ti}} \parallel \langle \bar{1}01 \rangle_{\text{TiN}}$ and $\langle 001 \rangle_{\beta\text{-Ti}} \parallel [\bar{1}01]_{\text{TiN}}$ and two pairs of matching planes, $\{\bar{1}10\}_{\beta\text{-Ti}} \parallel \{111\}_{\text{TiN}}$ and $\{\bar{1}10\}_{\beta\text{-Ti}} \parallel \{020\}_{\text{TiN}}$ within the 10% misfit threshold. After grouping the matching directions and matching planes and applying the Δg parallelism rules [17], two independent ORs are predicted, i.e.

$[111]_{\beta\text{-Ti}} \parallel [\bar{1}01]_{\text{TiN}}$, $(\bar{1}10)_{\beta\text{-Ti}}$ 0.5° away from $(111)_{\text{TiN}}$, (OR A)

and $[001]_{\beta\text{-Ti}} \parallel [\bar{1}01]_{\text{TiN}}$, $(\bar{1}10)_{\beta\text{-Ti}}$ 1.0° away from $(111)_{\text{TiN}}$. (OR B)

Compared with the measured ORs, the predicted ORs A and B are fully consistent with the K-S and N-W ORs, respectively, within the experimental uncertainty.

In addition to the characterization of the nucleant particles, the distribution of solute elements was also studied. As can be seen from the EDS maps in Figures 2(e) and 2(d), the majority of zirconium segregates along the β -Ti grain boundaries whilst molybdenum is depleted from the grain boundaries. This indicates that substantial partitioning of both zirconium and molybdenum solute occurs across the solid/liquid interface during solidification. Solute zirconium and molybdenum partition in an opposite way because Ti-Zr

and Ti-Mo systems have an opposite sign for the gradient of the liquidus line on the Ti-rich side.

Based on the above experimental studies, the mechanisms of CET and grain refinement of β -Ti grains through ZrN inoculation can be attributed to the synergistic effect of in-situ formed TiN particles and enhanced solute segregation, as graphically illustrated in Figure 4. For the Ti-13Mo base alloy, the columnar grains nucleated from the bottom of the water-chilled copper crucible and grew in the opposite direction to the heat extraction direction, i.e. from the edge to the thermal centre of the melt pool. Because of the lack of potent nucleant particles in the melt pool, the critical undercooling required for nucleation, ΔT_n , is too large to be met by the constitutional supercooling, ΔT_{cs} , delivered by solute molybdenum. As a result, no equiaxed grains formed and large columnar grains grew across the whole vertical cross-section (Figure 4a).

When the alloy melt was inoculated with ZrN, it appears that the ZrN particles quickly decomposed when the powder compact was completely melted, as no ZrN phase was identified in the as-cast button ingot, i.e.

where $[\text{Zr}]_{\text{liquid}}$ and $[\text{N}]_{\text{liquid}}$ represent the solute zirconium and nitrogen released into the liquid titanium from the decomposition of ZrN. However, there is still no potent nucleant particle available in the ZrN2 and ZrN4 samples, and hence columnar grains still dominate

Figure 4 Graphic illustration of the mechanism of columnar dendrite formation in (a) base alloy, and mechanisms of CET and grain refinement in (b) Ti-13Mo-0.5N alloy (TiN4) and (c) Ti-13-Mo-6Zr-0.4N alloy (ZrN6). The constitutionally supercooled zone is shaded in light blue. The amount of ΔT_{cs} and ΔT_n is qualitatively represented by the length of green bar and red bar, respectively. T_E and T_A represent the equilibrium liquidus temperature and actual temperature profile, respectively. The average grain size is denoted by d_{gs} .

the microstructure. When the addition of ZrN induced 0.4 wt. % nitrogen (Sample ZrN6) or the addition of TiN induced 0.5 wt. % nitrogen (Sample TiN4) in the liquid, primary TiN particles start to form from the liquid prior to the formation of β -Ti, i.e.

These TiN particles provide potent heterogeneous nucleation sites for β -Ti with much smaller ΔT_n required for nucleation due to good crystallographic matching with β -Ti (Figures 4b and 4c).

When the first β -Ti dendrite forms in the liquid, the partitioning of both solute zirconium and molybdenum contribute to the formation of a constitutionally supercooled zone formed ahead of the solid-liquid interface. Once the development of ΔT_{cs} fulfils the ΔT_n of a TiN particle located in the constitutionally supercooled zone, this TiN particle will be activated as a nucleation site and a new equiaxed β -Ti dendrite is formed around it (Figure 4c). The formation of new equiaxed β -Ti dendrites effectively stops columnar grain growth through grain impingement. According to the Interdependence theory [18,19], when the first equiaxed β -Ti dendrite forms in the liquid, the constitutionally supercooled zone will continue to trigger successive heterogeneous nucleation events on the available potent TiN particles towards the thermal centre of the cooling melt pool. As a result, the microstructure is dominated by fine, equiaxed β -Ti dendrites when solidification is complete, leaving excess zirconium and depleted molybdenum along the dendritic arm boundaries and grain boundaries and active TiN nucleant particles at the centre of β -Ti grains.

186

187 The growth restriction factor (or Q-value) of individual solute elements is a common
188 parameter to evaluate their capability to developing constitutional supercooling [19]. Solute
189 molybdenum provides fairly high constitutional supercooling based on its Q-value of 85 K at
190 13 wt. % [20]. This explains why the CET and grain refinement can also be observed in
191 Sample TiN4 when only 0.5 wt. % nitrogen was added into the Ti-13Mo base alloy (Figure
192 4b). The segregation of solute zirconium offers additional constitutional supercooling so that
193 ΔT_n of the available TiN particles can be reached at a much shorter distance ahead of the
194 first β -Ti dendrite. This explains why the grain size of the ZrN6 sample (Figure 4c) is half as
195 small as the TiN4 sample (Figure 4b). It is also noteworthy that the Q-value of solute
196 zirconium itself is almost negligible (e.g. less than 2 K even at 6 wt. %) [21], which appears
197 contradictory to the strong partition of solute zirconium observed in the current study. This
198 implies that the actual constitutional supercooling in a multicomponent alloy cannot be
199 directly evaluated by simple addition of the Q-values from individual solute elements
200 deduced from a binary phase diagram. A more comprehensive investigation should be
201 undertaken to establish a more accurate phase diagram in the specific multicomponent Ti-
202 based alloy under consideration, so that the Q-value can be quantified rigorously by the
203 initial rate of development of constitutional supercooling [22].

204

205 The current study indicates that the critical amount of nitrogen to produce primary TiN
206 particles as heterogeneous nucleation sites of β -Ti grains is only 0.5 wt. % for the Ti-13Mo
207 alloy and it can be further reduced to 0.4 wt. % if ZrN is inoculated. In contrast to binary Ti-N
208 alloys where the minimal concentration of nitrogen to form pro-peritectic TiN phase is 5

wt. %, much less nitrogen is needed for refining the β -Ti grains in a β -Ti alloy. In addition, nitrogen embrittlement might not be an issue in β -Ti alloys. This is because nitrogen is an α -Ti stabilizer and stimulates α -Ti precipitation from the β -Ti matrix even at a fairly high cooling rate (in the order of 10^2 K/s) during the arc melting process (Figure 2a). At room temperature, the majority of nitrogen is apt to remain in the α precipitates, rather than in the β -Ti matrix (Figure 2f). Figure 5 shows the effect of ZrN addition on the hardness of Ti-13Mo base alloy. The hardness increases from 305 HV to 411 HV after 6 wt.% ZrN was added into Ti-13Mo. The remarkable hardness increment is attributed to the combination of

Figure 5 Vickers indentation on as-cast (a) Ti-13Mo and (b) ZrN6 samples after applying 1 kg load for 10 seconds. (c) Effect of ZrN addition on Vickers hardness of Ti-13Mo alloy.

217 additional solid solution strengthening from solute Zr, precipitation strengthening from α
218 precipitates as well as grain boundary strengthening from grain refinement. It should also be
219 noted that no cracks was observed around the corners of indentation in any ZrN inoculated
220 samples during Vickers hardness test, which indicates a reasonable ductility. Therefore,
221 smart manipulation of nitrogen and/or zirconium within a β -Ti alloy could offer a cost-
222 effective way to develop new high-strength β -Ti alloys.

223
224 In summary, coarse columnar β -Ti grains can be converted to fine equiaxed grains in as-cast,
225 Ti-Mo based β -Ti alloys when a brand new inoculant, ZrN is added into the molten Ti at a
226 nitrogen level as low as 0.4 wt. %. The substantial grain refinement is attributed to the
227 heterogeneous nucleation of β -Ti around in-situ formed TiN particles and enhanced
228 constitutional supercooling delivered by solute zirconium. In addition to the grain
229 refinement, addition of ZrN also induces remarkable hardness increment due to the extra
230 solid solution strengthening from solute zirconium and precipitation strengthening from
231 nitrogen-rich α precipitates.

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280

Table Title

Table 1 The chemical composition of the samples in the current study.

Figure Caption

Figure 1 EBSD map of β -Ti grains in the as-cast button ingot of (a) base alloy, (b) ZrN2, (c) ZrN4, (d) ZrN6, (e) ZrN8 and (f) TiN4.

Figure 2 An equiaxed β -Ti grain in sample ZrN8. (a) secondary electron image. (b) EBSD map. (c-f) EDS map of Ti, Mo, Zr and N.

Figure 3 Pole figures of a TiN nucleant and its surrounding β -Ti matrix, which presents (a) N-W OR and (b) K-S OR.

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Ti-13Mo + 4 wt.% TiN	TiN4	Bal.	14.0	---	0.53	0.28

(a)

(b)

(a) Ti-13Mo

(b) Ti-13Mo-0.5N

(c) Ti-13Mo-6Zr-0.4N

(a) Ti-13Mo

(b) ZrN6

(c)