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Enhancing Titanium Alloys with Fe Microalloying: A Review

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Microalloying strategy can effectively enhance the overall performance of commercial pure titanium and TC4 alloy, expanding their applications in the petrochemical, aerospace, and biomedical fields. Iron, as a *β*-stabilizing and strengthening element, decreases the β transus temperature and refines as-cast microstructure of pure Ti and TC4 alloy. The effect of Fe microallying on microstructural evolution and performances of pure Ti and TC4 alloy have been summarized and analyzed from the perspectives of the first-principles calculations on the effects of multi-alloying elements on phase transformations, changes in microstructural morphology, variations in mechanical properties and fracture toughness. The strengthening factors of Fe microalloying is 223 MPa/wt.% for pure titanium and 481 MPa/wt% for TC4 alloy, which is resulted from the effective grain refinement and strong hindrance of crack propagation by the Fe-enriched *β* films at the phase boundaries.

Keywords: pure titanium, TC4, Fe microalloying, structure property, strengthening-toughening mechanism.

1. INTRODUCTION

Lightweight titanium and its alloys are widely used in many fields, such as petroleum, chemical industry, aerospace, and biomedicine, due to superior mechanical properties, outstanding corrosion resistance, and good biocompatibility [1 – 3]. However, in comparison to other conventional alloys, the widespread utilization of Ti and its alloys is constrained by the high cost of raw materials, low production efficiency, vacuum smelting requirements, and high prices. Pure Ti and TC4 (Ti-6Al-4V) are most widely used and representative. Many techniques, such as microalloying [4], optimization of melting and hot-working process parameters [5, 6], have been utilized to enhance the properties and improve the cost-effectiveness. Many Ti alloys, such as Ti-5Al-5Mo-5V-3Cr-0.6Fe (Ti-5553) [7], Ti-10V-3Al-2Fe (Ti-1023) [8], Ti-3.5Al-5Mo-4V-2Cr-2Zr-2Sn-1Fe (Ti-B20) [9], Ti-6.8Mo-1.5Al-4.5Fe (Ti-LCB) [10], and Ti-4.5Al-3V-2Mo-2Fe (SP-700) [11], have been developed by 1 – 5 wt.% alloying. The aforementioned alloys [7 – 11] are all classified as high-strength titanium alloys with tensile strengths beyond 1200 MPa. Microalloying is commonly defined as the alloying of element less than 1 wt.%. Numerous studies have demonstrated that the incorporation of minor alloying elements, such as Fe, into Ti alloys can enhance the tensile and yield strength without decay in the plasticity and toughness [12 – 14].

The TC-series Ti alloys consist of predominantly *α* and *β* phases, and *α* phases in particular exhibit high resistance to thermal deformation, which causes great challenges in manufacturing. Minor Fe incorporation in Ti alloys greatly decreases the flow stress and deformation temperature in the thermal deformation and ultimately enhances their hot working capabilities [15]. Fe microalloying can effectively decrease deformation resistance, as well as reduce energy consumption during annealing and heat preservation processes [12,13]. Fe alloying/microalloying can stabilize and increase *β* phases, and can further enhance the mechanical properties of Ti alloys [12]. Therefore, Fe microalloying is a highly effective method for designing Ti alloys with a balance of cost and performance. Excessive addition of Fe should be avoided, as it may lead to undesirable *β* flecks in cast alloys [16]. These *β* flecks are difficult to remove during further thermal processing, leading to a degradation in the uniformity of the alloy structure and a negative impact on its mechanical properties [17].

Effects of Fe microalloying on the microstructural evolution and the mechanical properties are summarized based on the published papers. The strengthening factor of Fe alloying/microalloying is defined and compared for pure Ti and TC4 alloys. The enhancing mechanisms of Fe microalloying are explored from aspects of microstructural evolution, the strength-toughness behaviors, corrosion resistance.

2. EFFECTS OF FE MICROALLOYING ON MICROSTRUCTURES OF PURE Ti

According to thr Chinese GB/T3621-2007 standard, the highest tensile strength of pure Ti is only 580 MPa for TA4G Brand. Pure Ti is susceptible to breakage and other issues resulting from inadequate strength as a load-bearing structural material. Pure Ti can be enhanced by a range of elements, thereby can meet the demands of practical applications. Higher Fe alloying in binary Ti-Fe alloy leads to finer microstructure and better strength and plasticity [18], which is achieved by inhibiting the α precipitation and stabilizing of more *β* phases.

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2.1. Phase transformation and property prediction of Fe-alloyed pure Ti based by the first-principles calculations

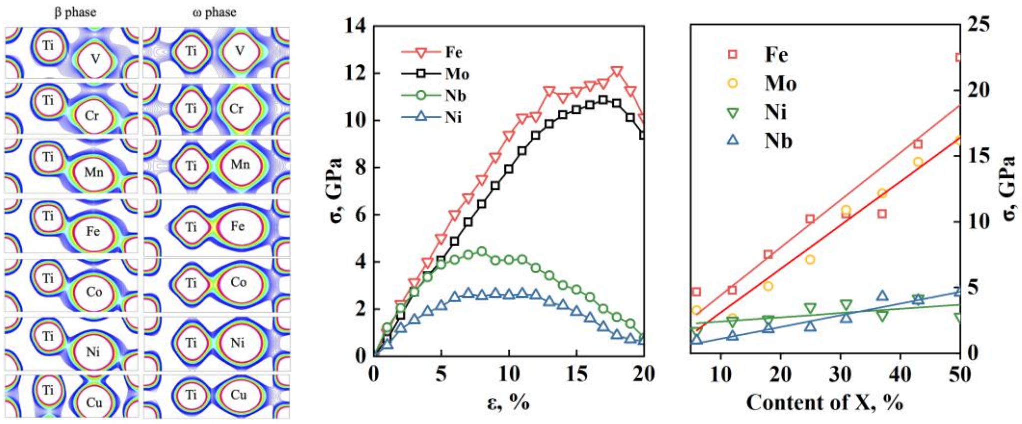
The trace O, N, C, and other impurity elements in Ti alloys can significantly impact their mechanical properties, particularly interstitial oxygen [19]. The tensile strength of Ti alloys increases, and the elongation decreases as the solid-solution oxygen content rises [20]. However, it should be noted that high concentrations of oxygen can lead to the embrittlement of Ti alloys and a decrease in the mechanical strength [21]. Excessive levels of oxygen, nitrogen, and other elements in the solid solution can have a detrimental effect on the mechanical properties of Ti alloys [22]. This can ultimately impact the viability of using Ti alloys in engineering applications, as quality issues may arise. The incorporation of β-stabilizing elements, such as Mo, V, Fe, serves as the nucleation sites for β phases, enhances the formation and growth of β phases, alters the paths and compositions of phase transitions, and effectively governs the overall mechanical properties of Ti [23]. With the addition of more β-stabilizing elements, the proportion of β phases in Ti alloys increases, resulting in an increase of the yield strength [24]. In order to identify the best alloying elements, Guo et al. [25] has analyzed the strengthening ability of 51 transition elements through the first-principle calculations. They discovered that the most powerful hybridization effect was between the Fe element and Ti, resulting in the highest β stability [25]. This is illustrated in the charge density contour plots of the ω and β phases of the doped 3d transition metals, as depicted in Fig. 1 a. The tensile stress-strain curves of Ti-6.25 % M alloy in Fig. 1 b demonstrates that Fe alloying has a best strengthening compared with Mo, Nb. The increase of the elastic modulus can be confirmed on the Ti-*x*Fe systems in Fig. 1 c. Amongst all the 51 transition elements, Fe emerges as the most effective alloying element for augmenting the tensile strength of Ti. Min et al. [26] has conducted a theoretical investigation into the effects of Fe doping in α-Ti, β-Ti, and ω-Ti using the first-principles calculations and discovered that Fe doping in Ti facilitates the phase transitions from ω to β or α to β, making them easier compared to pure Ti. Gouda et al. [27] has investigated the impacts of alloying elements (such as Cr, Mn, Fe, Zr, Nb, Mo, etc.) on the strength of Ti alloys, and concluded that the presence of Fe plays a crucial role in enhancing the strength of Ti alloys. Cheng et al. [28] investigated precipitation strengthening in binary Ti-*x*M (M = V, Cr, Fe, Nb, Ta, Mn, Ni, etc.) alloys and Ti55521 alloy by combining the elastic modulus and precipitation strengthening model, and concluded that Fe is one of the elements with strong precipitation strengthening effect. All of the aforementioned studies on material calculations consistently point to Fe as the preferred element for enhancing the overall mechanical properties of Ti alloys. Hence, the element Fe is meant to select due to its superior capability in stabilizing the β phase and enhancing the strength. Fe alloying or microalloying has promising potential for the advancement of new Ti alloys in the future.

2.2. Refinement of as-cast microstructure of pure Ti by Fe microalloying

Fe element can act as a grain refiner for pure Ti [29]. Fig. 2 illustrates the variation in the geometric feature size of the microstructure of pure Ti with the addition of Fe. With the increase of Fe content, there is a noticeable decrease in the size of β grains and α lamella. Drastic decrease in grains sizes occurs within the range of 0 – 0.5 wt.% Fe, followed by a more gradual decrease in size within the range of 0.5 – 4 wt.% [30]. The regression analysis of the relationship between β grain size (D_1) and Fe contents is conducted and presented in Fig. 2. The correlation between D_1 and Fe contents can be expressed by the following equation:

$$D_1 = 0.67152 \times (Fe\ wt\%)^{-0.60691}. \tag{1}$$

Eq. 1 has a degree of fitting of 0.98287. The tendency in Fig. 2. is largely consistent with the findings of Guo [31] and Tao [32]. The nuclei and solute play crucial roles in the grain refinement mechanism [33]. Potent nuclei play a crucial role in activating nucleation under low undercooling conditions, while the presence of solute Fe provides the necessary constitutional undercooling to activate adjacent nuclei [34].



a b c

Fig. 1. Ti-M (M is V, Cr, Mn, Fe, Co, Ni, Cu, Mo, Nb) binary system characteristics and mechanical properties prediction: a – the contour of the charge density for the ω phase and β phase doped with 3d transition elements [25]; b – stress-strain curves of the Ti-6.25 wt.%M; c – effect of alloying element concentration on tensile strength of Ti-M alloys. Data in b and c are unpublished

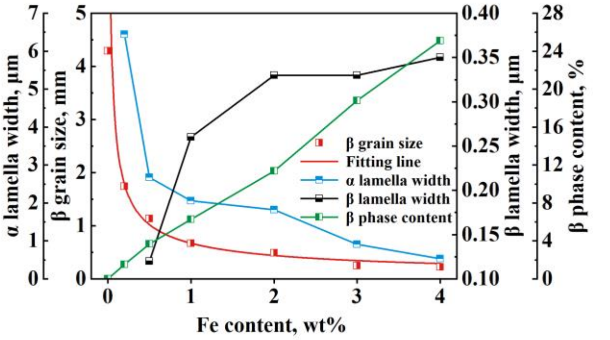


Fig. 2. The change curve of microstructure of pure Ti with Fe content. Data were collected from Ref. [30]

The more rapidly the constitutional undercooling zone forms, the greater the nucleation density per unit of time at the solid-liquid interface [35]. This ultimately leads to the formation of smaller grain sizes. In contrast to the grain size, the β-phase content exhibits an opposing trend, primarily attributed to the stabilizing influence of Fe on the β phases. When Fe concentration is below the maximum solubility of Fe in α-Ti of 0.5 wt.% [36], the solidification structure of pure Ti consists of single α phase. However, when Fe concentration exceeds the solubility limit of Fe in *α*-Ti, *β*-phase content gradually increases. Full *β* phases are formed as Fe ranging from 8 % to 20 %, while TiFe intermetallic compound is detected at Fe of 25 % [37]. It is crucial to prevent the formation of intermetallic compounds in the practical applications from the embrittlement and significant deterioration of fracture toughness, plasticity, and other mechanical properties.

2.3. Strength-toughness mechanism of pure Ti based on Fe microalloying

The mechanical properties of pure Ti are influenced by microstructure characteristics such as grain sizes, morphology, and volume fraction of phases [38]. Fe alloying into Ti can not only refine its structure, but also enhance of the mechanical properties [39]. As illustrated in Fig. 3., the dependency of the mechanical properties of as-cast Ti-*x*Fe alloy on Fe concentrations reveals that the strength rises with Fe contents.

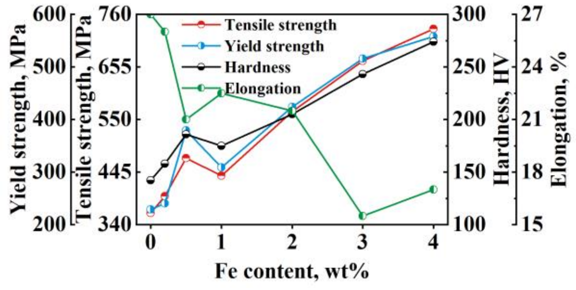


Fig. 3. The change curve of mechanical properties of pure Ti with Fe content. Data were collected from Ref. [30]

Conversely, plasticity demonstrates a contrary trend to strength, in accordance with the strength-plasticity inversion principle observed in Ti alloys. Pure Ti demonstrated the ideal balance of strength and ductility with Fe content below 0.5 wt.%. Fig. 4. illustrates the impact of various element contents on the tensile strength of pure Ti. Compared with Ag, Cu, Bi, Nb [41 – 43, 45, 46], Fe has the best strengthening ability for pure Ti.

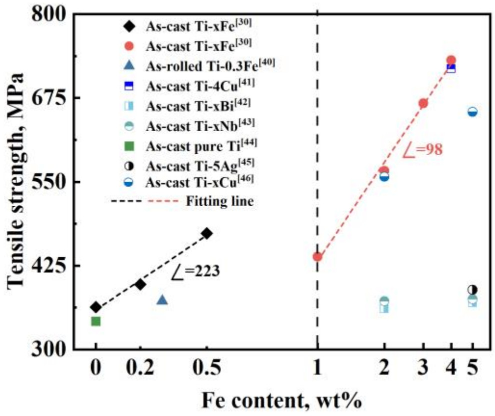


Fig. 4. Comparison of the effects of Fe and other elements on the tensile strength of pure Ti. Data were collected from Ref. [30, 40 – 46]

The enhancement in tensile strength resulting from Fe alloying is defined as the strengthening factor of the alloying element, in units of MPa/wt.%. The strengthening factor of Fe microalloying is 223 MPa/wt.% when its content is between 0 – 0.5 wt.%. When the Fe element content exceeds 1 wt.%, its strengthening factor is 98 MPa/wt.% for Fe alloying. The results above suggest that the effectiveness of strengthening enhances significantly with Fe microalloying ranging from 0 – 0.5 wt.%, compared to that with Fe content beyond 1 wt.%. The current strengthening mechanism of Ti-*x*Fe alloys can be primarily attributed to two factors: grain boundary strengthening and solution strengthening. Grain boundary strengthening primarily occurs through smaller grain sizes and a higher grain boundary densities. High-density of grain boundaries serves as an obstacle to the movement of dislocations, thereby restricting the creation and spread of microcracks caused by dislocations, which effectively enhances the strength. The yield strength is related to the grain sizes, following the typical Hall-Petch relationship [47]:

$$\sigma_y = \sigma_0 + k_y d^{-1/2}, \quad (2)$$

where σ_y is the yield stress; σ_0 is the lattice friction stress; k_y is the constant of yielding; *d* is the grain size. Therefore, as the grain size decreases, the yield strength increases. Another mechanism of solution strengthening can be achieved through significant 13.6 % differences in the atomic radius of Ti of 0.147 nm and that of Fe of 0.127 nm [48]. The lattice distortion resulting from the solid solution of Fe atoms in the α-Ti lattice increases the resistance to dislocation slip during deformation. The strength enhancement of pure Ti matrix is achieved through dislocation multiplication and dislocation pinning consolidation [49]. It is evident that Fe is the most effective strengthening element among alloying elements of Mn, Nb, Mo, and Fe. In summary, the advantages of Fe microalloying are as follows:

1. From a cost perspective, Fe has a wide range of sources and is relatively inexpensive compared to other alloy elements, giving it a cost advantage in raw materials.
2. In terms of the ability to stabilize the β phase, the Fe

element has the strongest β phase stability in Fig. 1 and Fig. 2.

3. In terms of strengthening factor, Fe microalloying method stands out as the most effective among the options considered in Fig. 3 b. Fe is considered one of the most optimal alloying elements for designing composition and regulating phase composition. Its practical significance and potential applications are profound and far-reaching.

3. INFLUENCE OF FE MICROALLOYING ON MICROSTRUCTURE AND PROPERTIES OF TC4 ALLOY

Compared with pure Ti, lightweight TC4 alloy with superior strength and ductility extends the appeal for various applications to meet the demand for higher performance [50]. Researchers are currently focusing on the development of a strength-ductility matched TC4 alloy, which has become a prominent research topic. Fe micro-alloying is considered to be one of the effective ways to improve the performance of TC4 alloy [12].

3.1. Effect of Fe microalloying on microstructure of TC4 alloys

Many scholars have studied the effect of Fe contents on β grain size, α/β phase size in TC4 alloy, and found that the grains of as-cast TC4 alloy are refined within a certain range of Fe content. As shown in Fig. 5, the change in β grain size, α/β phase size is dependent on Fe contents. In order to represent the relationship between the grain sizes (D_2) and the amount of Fe added, the green data points in Fig. 4 a are fitted to obtain the empirical Eq. 3:

$$D_2 = 1.28912 \times (\text{Fe wt.\%})^{-0.28179}. \quad (3)$$

Eq. 3 shows a good fit of 0.95942. A difference between the solidification structure size of TC4-*x*Fe alloy by simulation and experiment in Fig. 5 a is found [51]. The reason is that the simulation time is limited, while the TC4-xFe alloy completes the grain growth in the actual experiment, which ultimately leads to the experimental results being larger than the simulation results. It can be seen that the grain sizes are on the millimeter scale in Fig. 5 a [12], while the grain size in the article is on the micrometer scale in Fig. 5 b [52]. As the Fe content increases, the grain size gradually decreases [52]. The reason is that the Fe element can inhibit the grain growth of TC4-*x*Fe alloy during the thermomechanical deformation process.

The grain refinement mechanism of Fe microalloyed Ti alloys revealed that Fe elements can undergo segregation during solidification, and that segregation of solutes can provide constitutional undercooling, activate adjacent nuclei, and inhibit the grain growth [53]. Fe alloying not only enhances the thermodynamic stability of the β phases, but also limits the growth of the α lamella, which leads to a change in the content of the α and β phase, as shown in Fig. 6. The β-phase content tends to increase steadily, while the α-phase content decreases consistently with Fe addition. The correlation between α-phase content (V_α), β-phase content (V_β), and the amount of Fe added in Fig. 6. are used to derive Eq. 4 and Eq. 5:

$$V_\alpha = 95.24383 - 6.00282 \times (\text{Fe wt.\%}); \quad (4)$$

$$V_\beta = 4.95866 + 5.71717 \times (\text{Fe wt.\%}). \quad (5)$$

The goodness of fit for Eq. 4 and Eq. 5 is 0.97445 and 0.93695, respectively. The formula above demonstrates the significant impact of adding Fe element on the refinement of β grains, as well as the morphology and phase content of α and β phase in TC4 alloy.

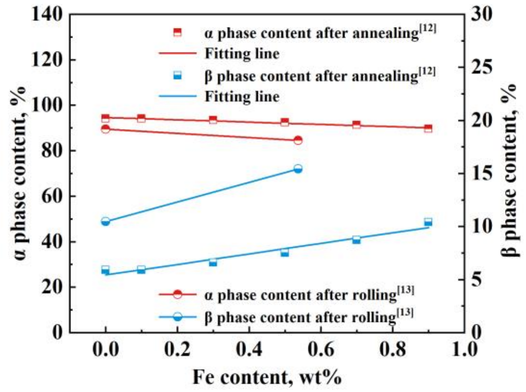


Fig. 6. Change of α/β phase content of TC4 alloy with Fe content. Data were collected from Ref. [12, 13]

3.2. Effect of Fe microalloying on mechanical properties of TC4 alloys

Fig. 7 summarizes the effect of different elemental contents on the tensile strength of TC4 alloy [12 – 14, 54 – 61]. It is evident that the incorporation of Fe element greatly enhances the tensile strength of TC4 alloys in Fig. 7. The analysis of the fitted data reveals that the strengthening factor of Fe microalloying is 58 MPa/wt.% for as-cast TC4 alloy, and is an impressive 481 MPa/wt.% for as-rolled TC4 alloy.

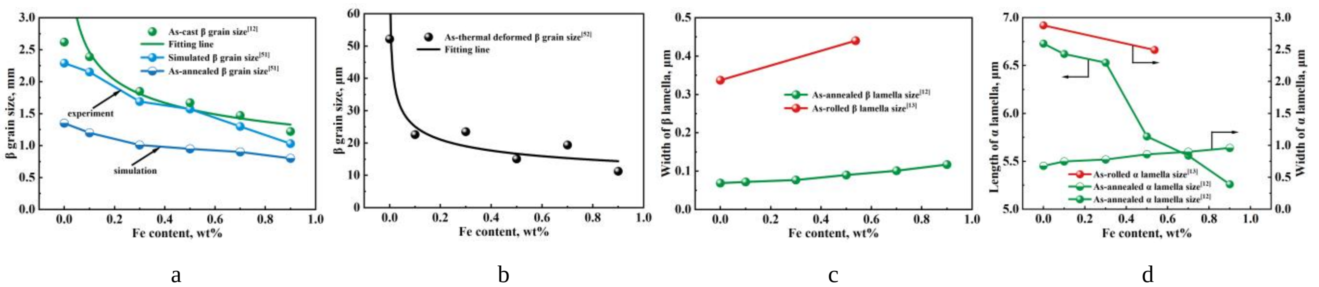


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Fig. 5. Dependency of grain sizes of TC4 alloy on Fe content: a – β grain size; b – β grain size after deformation; c – width of β lamella; d – length and width of α lamella. Data were collected from Ref. [12, 13, 51, 52]

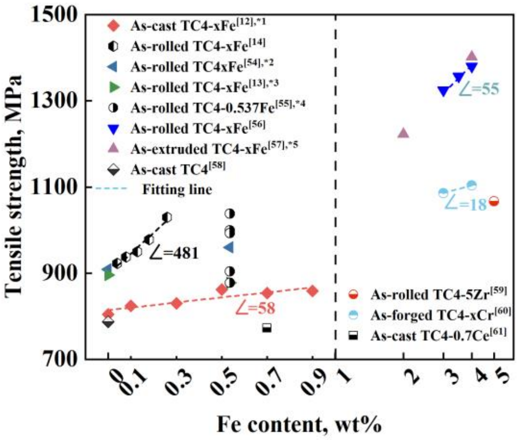

Fig. 7. Effect of alloying element contents on the tensile strength of TC4. Data were collected from Ref. [12 – 14, 54 – 61]: *1 – 800 °C/3 h/AC; *2 – 940 ºC/1.5 h/AC + 580 ºC/ 4h/AC; *3 – 1100 ºC/40 min, FC to 712 ºC, 712 ºC/2 h/AC, *4 – 1005 ºC/70 min/AC + 722 ºC/2 h/AC, 1005 ºC/ 70 min/AC + 732 ºC/2 h/AC, 1100 ºC/40 min/WC + 712 ºC/2 h/ AC, 1100 ºC /40 min/AC + 712 ºC/ 2h/AC, 1100 ºC/40 min/FC to 712 ºC + 712 ºC/2 h/AC; *5 – 700 ºC/6 h/FC. AC: air cooling, FC: furnace cooling, WC: water cooling

The strengthening factor is 55 MPa/wt.% for TC4 alloy with Fe element exceeding 1 wt.%, whereas the strengthening factor for Cr addition is only 18 MPa/wt.%. Strengthening the effectiveness of Fe microalloying (0 – 1 wt.%) is obviously better than that Fe alloying (> 1 wt.%). The presence of Fe in TC4 alloy serves to strengthen the matrixs by causing Fe atoms to congregate at the *α/β* boundary [62]. Fe atoms at phase boundaries strongly pin the dislocations in place, thereby increasing the resistance of the α/β boundary [63]. As a result, the *α/β* boundary is able to accommodate a greater number of dislocations, which in turn slows down the initiation of cracks. The incorporation of Fe can significantly reduce the rates of crack propagation under deformation [54]. The addition of Fe into Ti alloy leads to an increase in the lattice distortion energy, consequently enhancing the resistance to dislocation slip during deformation [64]. Based on Fig. 7, it is evident that the mechanical properties of Fe microalloyed TC4 alloy are influenced by heat processing deformation and heat treatment procedures. Through solid solution and aging treatments, TC4 alloy can be effectively strengthened through intricate phase transformations during heat treatments. Variations in the heat treatment processes can result in differences in the morphology, volume fraction, and size of the phases present in TC4 alloys [65]. Li et al. [66] concluded that $\beta \rightarrow \alpha$ phase transition curves of the equiaxed, bimodal, and lamellar microstructure of the TC4-0.55Fe alloy display an S-shape, suggesting that they are controlled by nucleation and growth. Furthermore, the TC4-0.55Fe alloy demonstrated a reduction in the thickness of the α phase lamella and a simultaneous enhancement in strength as the cooling rate increased during the continuous cooling [67]. Wang et al. [68] has reported that the activation energies for the $\alpha \rightarrow \beta$ phase transition of TC4-0.55Fe alloy and TC4 alloy were 200 and 251 kJ/mol, respectively. This suggests that the introduction of Fe is advantageous for lowering the activation energy of the phase transition reactions, consistence with data in Fig. 1 a. The studies on phase transitions in Fe microalloyed Ti alloys offer essential experimental data for advancing hot working processes, heat treatment procedures, and other aspects of Ti alloy development.

Recent studies [69, 70] conducted by researchers have determined that the TC4-0.55Fe alloy with a bimodal microstructure after double annealing exhibits superior mechanical properties. Liu et al. [55] found that high aging temperatures and low cooling rates resulted in low strength, high plasticity and fracture toughness. In conclusion, Fe stands out as the most promising element in the design and development of new Ti alloys. It not only enhances the mechanical properties but also contributes to reducing the overall cost of TC4 alloys. Unfortunately, the lack of in-situ analysis, the low microalloyed Fe content, and the inability to observe the dynamic redistribution of Fe elements make it challenging to fully understand the strength-toughness mechanism in Fe microalloying enhanced TC4 alloys. However, analyzing the strength-toughness mechanism of Fe microalloying enhanced TC4 alloys remains a challenging task. More effort still needs to be contributed to clarify the nature of the mechanism for Fe microalloying.

3.3. Effect of Fe microalloying on corrosion properties of pure Ti and TC4 alloys

Ti and its alloys have attracted much attention due to unique properties, such as high mechanical strength, biocompatibility and corrosion resistance [71]. The corrosion performance of Ti alloys depends mainly on the chemical composition, microstructure, and phase contents [72]. The presence of Fe content not only influences the composition of the phases but also serves as a grain refiner, resulting in changes in the grain size of the alloy structure. Hence, the corrosion resistance of TC4 alloys varies according to the amount of Fe. He et al. [73] concluded that medium Fe content (0.078 wt.%) formed a stable β phase deteriorating the corrosion properties of pure Ti in NaCl solution, while high Fe content (0.12 wt.%) formed a Ti*x*Fe intermetallic phase improving its corrosion properties. Seo et al. [74] found that the stability of TiO_2 against sulfuric acid decreases with increasing Fe content, leading to a decrease in the corrosion resistance of pure Ti. Gao et al. [75] has found that the addition of Fe element into Ti alloys decreased their corrosion resistance in NaCl and HCl solutions. Similarly, Zhao et al. [76] has revealed that TC4 with a higher Fe content (0.537 – 0.552 wt.%) exhibits inferior resistance to crevice corrosion compared to TC4 with a lower Fe content (0.035 wt.%), as illustrated in Fig. 8. The phenomenon is attributed to more doped Fe and higher defect density in the passivation films at higher Fe contents, and big difference in the volume expansion between FeO_x and TiO_x [76]. The studies mentioned above indicate that the addition of Fe elements to Ti alloys does not enhance their corrosion resistance as it does their mechanical properties. In fact, it is observed that the corrosion resistance decreases with the increasing Fe content. From an electrochemistry perspective, Fe exhibits a higher level of electrochemical activity compared to Ti, making it less likely to passivate.

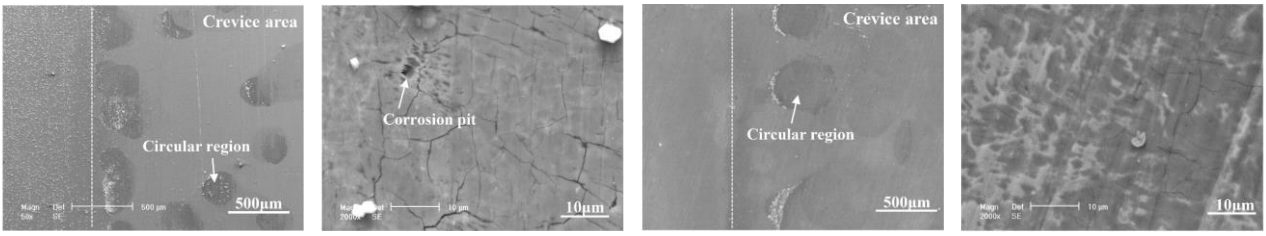

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Fig. 8. Corrosion morphologies after 11 d crevice corrosion measurements in 3.5% NaCl +8mMF- solution [76]: a, b – TC4-(0.537 – 0.552 wt.%) Fe; c, d – TC4-(0.035 wt.%) Fe

This difference results in the formation of a corrosion micro galvanic cells between Ti and Fe, ultimately causing galvanic coupling corrosion to take place [75]. By adding Fe element to TC4, the Fe element is selectively distributed to the *β* phase, causing an increase in the *α*/*β* interface. This phenomenon occurs because the *α* phase and *β* phase have different electrochemical stability, leading to the formation of harmful microgalvanic cells between adjacent *α* phase and *β* phase regions. The stability of the passivation film on the *β* phases is lower compared to that of the α phase surface. Under galvanic interactions, there is a preferential dissolution of *β* phases [77]. A weak tendency of inferior corrosion resistance exists for Fe microalloyed TC4 alloys.

4. STRENGTH-TOUGHNESS MECHANISM OF Fe MICROALLOYED TC4 ALLOYS

High-strength, high-toughness TC4 with excellent strength-plasticity matching has been a major demand for variuos applications. Toughness, especially fracture toughness, demonstrates the ability to resist crack propagation, thus reflecting its damage tolerance performance [78]. Recent research has demonstrated that Fe microalloying not only enhances the casting [79], sintering [80], hot working [81], and low-cycle fatigue [63] of TC4 alloys, but also has a beneficial impact on both their strength [48] and toughness [13]. Fig. 9 illustrates the correlation between tensile strength and fracture toughness of Fe microalloyed TC4 alloy.

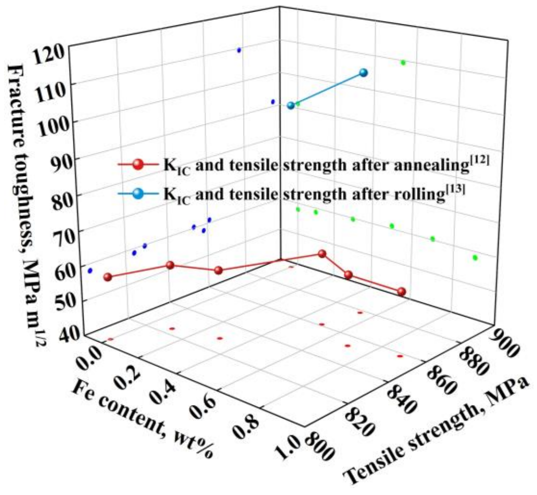

Fig. 9. Relationship between tensile strength and fracture toughness of Fe microalloying TC4 alloy. Data were collected from Ref. [12, 13]

The strength and toughness are improved when the Fe content is around 0.5 wt.% in Fig. 9. It is widely recognized that solution strengthening, grain boundary strengthening, dislocation strengthening, and second-phase strengthening are the primary mechanisms for enhancing the strength of Ti alloys [82]. Solute atoms have a grain refining effect on Ti alloys by Fe microalloying. The presence of these solute atoms results in the formation of large grain boundaries which effectively hinder dislocation motion within the alloy structure [12, 13]. A significant difference in size between solute and matrix atoms can distort the lattice structure and increase the resistance to dislocation movements. In the same way, the second phase influences deformation by limiting the movement of dislocations. Interactions of the dislocations hinder mobility through entanglements. The strengthening of TC4 Ti alloys by Fe microalloying can be attributed to several factors as follows:

1. The presence of minor amounts of Fe helps to refine the grain size [83]. This results in an increased area of obstacles within the microstructure, particularly at grain boundaries, which in turn enhances the effect of grain boundary strengthening.
2. Solute Fe atoms are dissolved in the Ti matrix, leading to lattice distortion and enhancing the resistance to dislocation movement [84]. These strengthening effects are attributed to the dislocation theory, which improves strength by providing obstacles to dislocation movements.

To meet the rigorous demands of aircraft structures, the development of high-strength Ti alloys with superior fracture toughness and excellent resistance to fatigue crack propagation is imperative. In recent years, there has been a growing interest in studying the fracture toughness of Ti alloys. Previous researches [85, 86] have demonstrated that lamella microstructure display superior fracture toughness compared to bimodal microstructure, indicating that microstructure plays a significant role in determining fracture toughness. Wen et al. [87] have reported that larger *α* colony sizes correspond to a greater presence of lamella *α* phase, which effectively hinders the initiation and propagation of cracks. This hindrance ultimately leads to increased strain, energy absorption, and subsequently, enhanced fracture toughness. Shi et al. [88] have discovered that the energy consumed in the plastic zone is also increased by increasing both the thickness and content of the lamella *α* phase in Ti-6Al-2Sn-2Zr-3Mo-1Cr-2Nb-Si alloys. This makes it more difficult for cracks propagation, ultimately enhancing the fracture toughness. A decrease in fracture toughness is caused by an increase in stress-strain incompatibility ahead of the crack tips at higher internal stresses [89]. Furthermore, the fracture toughness is directly proportional to the size of the plastic zone at the crack tips [90]. Another reason is that cracks in Ti alloys tend to turn at the point of fractures, leading to crack deflection, branching, and secondary cracking [89, 90]. These phenomena require additional energy for greater fracture toughness. The aforementioned studies demonstrate that factors such as microstructure, stress state at the crack tips, and the path of crack extension play a significant role in determining fracture toughness.

For the toughening mechanism of Fe microalloyed TC4, Liao et al. [12] pointed out that the agglomerates, *α*/*β* lamellae, and their phase interfaces play a crucial role in resisting crack propagations and enhancing the overall fracture toughness. Fig. 10 illustrates the various crack propagating paths observed in TC4 alloy microalloyed by Fe (denoted as TC4F) [12]. The overall fracture toughness, K_{IC}, can be thought of as the combined contributions to crack propagation resistance from various pathways. The value of K_{IC} can be expressed in Eq. 6 as following[12]:

$$K_{IC} = l_{csl}\% \times R_{csl} + l_{agc}\% \times R_{agc} + l_{agl}\% \times R_{agl}, \quad (6)$$

where R_{csl} is the crack propagation resistance per unit length for the case of traversing *α*/*β* lamellae; R_{agc} and R_{agl} are the crack propagation resistance along colony boundary and *α*/*β* phase boundary, respectively; $l_{csl}\%$ is the proportion of crack propagation distance that traverses the *α*/*β* lamellae to the total crack length, and $l_{agc}\%$, and $l_{agl}\%$ are the proportions for cracking along the colony boundary and the *α*/*β* lamellar boundary, respectively. When the alternately arranged *α* and *β* lamellae are considered, R_{csl} is simplified expressed as the average value of single-phase resistance per unit length, R_0^{α} and R_0^{β}, with lamella widths w_α and w_β as the weights. The values of R_{csl} can be calculated by Eq. 7 [12]:

$$R_{csl} = \frac{R_0^{\alpha} w_\alpha + R_0^{\beta} w_\beta}{w_\alpha + w_\beta}. \quad (7)$$

R_{agl} is assumed to be equal to R_0^{β} for simplicity since the slender *β* lamella is more vulnerable to interlamellar cracking. Therefore, Eq. 6 is reformulated as [12]:

$$K_{IC} = l_{csl}\% \times \frac{R_0^{\alpha} w_\alpha + R_0^{\beta} w_\beta}{w_\alpha + w_\beta} + l_{agc}\% \times R_{agc} + l_{agl}\% \times R_0^{\beta}. \quad (8)$$

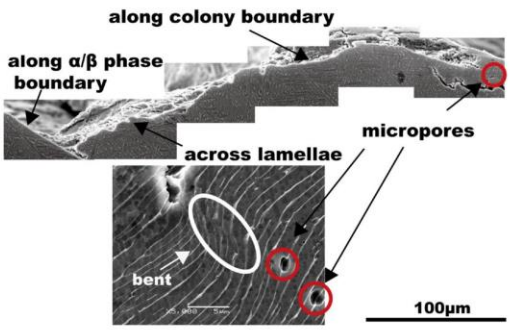

Fig. 10. SEM images of crack propagation and phase morphology near the cracks in the homogenization treated TC4-0.5Fe alloys [12]. The types of crack propagation pathways, namely, across α/β lamellae, along colony boundary, and along *α*/*β* phase boundary are shown

Among the TC4-*x*Fe (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 wt.%) alloys, the TC4-0.5Fe alloy has the longest crack extension distance through the *α*/*β* lamellae, the highest resistance to crack propagation, and the ability for the bending of the *α*/*β* lamellae to create additional energy dissipation [12]. This results in a notable increase in fracture toughness for the TC4-0.5Fe alloy. Furthermore, the presence of Fe can lead to the formation of nanoscale *β* films within the α lamella, contributing significantly to the enhancement of toughness in Fig. 11 [91].

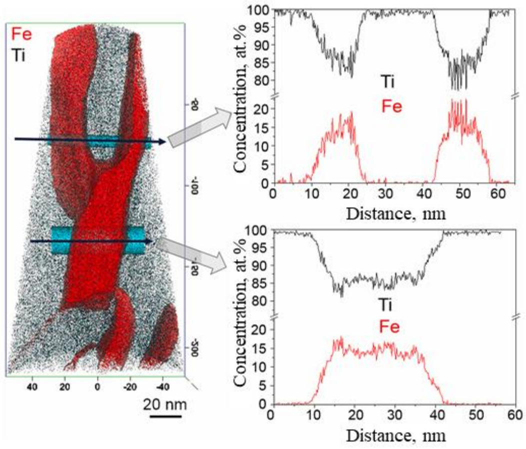

Fig. 11. 3-D APT reconstruction showing Fe (red) and Ti (black) atoms, the red surface represents an isoconcentration surface of 4 at% Fe (threshold value); 1-D concentration profiles through the β lamella of Ti-3% Fe 950 °C + 550 °C-WQ [91]

The *α*/*β* lamellae near the cracks in Fe-added TC4 alloys bent more severe than those of Fe-unadded TC4 alloys [13]. More bent *α*/*β* lamellae result in an enlargement of the plastic zone at the crack tips, a change in the direction of cracks propagation, and the consumption of additional energy. Moreover, the enrichments of Fe atoms in *β* phases enhances the cohesion between the α and *β* phases and helps to inhibit the interphase fracture to reach the better fracture toughness. A comparison schematic for crack propagation and bending of grain boundaries for TC4 and TC4F is depicted in Fig. 12.

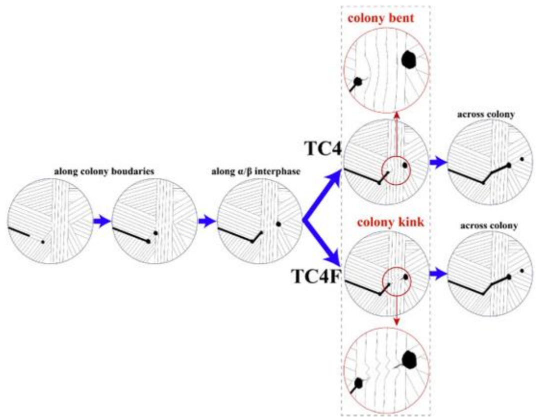

Fig. 12. The schematic drawing of crack propagation in TC4 and TC4F [13]. F represents the Fe element

The nature for the better K_{IC} might be due to the distribution of microalloyed Fe at the interfacial regions and the different response to the strains. Firstly, adding Fe to

TC4 alloys can increase their strength by utilizing a solution strengthening mechanism. This improvement in strength can enhance fracture toughness by increasing the energy needed for crack propagation under external loading. Secondly, the addition of Fe as a solute serves to refine the grain size, enhances the strength, and stabilizes the grain boundaries. By interacting with the grain boundaries, Fe effectively improves the bonding force. This reinforcement is crucial in preventing crack propagation, which typically occurs at the grain boundaries when subjected to external forces. The cracks growth is effectively inhibited by microalloyed Fe at the interfaces. Thirdly, the addition of Fe element increases the proportion of β phases good for a stronger absorption of strain energy and ultimate improving the fracture toughness.

4. CONCLUSIONS AND PROSPECT

Pure Ti and TC4 alloys are beneficial from Fe microalloying (< 1 wt.%) through grain refinements and distribution of Fe at the interfacial regions (grain boundaries). The strengthening factor was defined and extracted to be 223 MPa/wt.% for pure Ti and 481 MPa/wt.% for TC4 alloy. The enhancements in the strength, and fracture toughness for Fe microalloyed Ti alloys are attributed to the grain refinements, solution strengthening, grain boundary strengthening, and strong hindrance of crack propagation by the Fe-enriched β films at the phase boundaries. Better fracture toughening mechanism is ascribed to arise from both intrinsic (plastic region size) and extrinsic (crack extension path) factors. Future research on Fe microalloyed Ti alloys can be further explored as follows:

1. By utilizing a combination of material calculation methods, including crystal plasticity finite element analysis, molecular dynamics, and first principles, we can delve into the strength-toughness mechanism, interface reaction characteristics, crack initiation, and propagation mechanisms of Fe microalloying in Ti alloys like TC4 and other intricate systems at the atomic level.
2. Advanced characterization techniques, including in situ SEM, EBSD, TEM, are employed to gain a comprehensive understanding of the impact of microalloyed Fe elements on dynamic recrystallization, dynamic distribution, and dislocation reactions in Ti alloys during thermal processing.
3. Comparison of the effects of Fe alloying on microstructural evolutions in Ti alloys, including the effect of Fe on β phase stabilization and precipitation behavior during various manufacturing processes such as additive manufacturing with different cooling rates compared to conventional manufacturing methods.

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