Characteristic effects of alloying elements on \( \beta \) solidifying titanium aluminides: A review

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**ABSTRACT**

The high strength-to-weight ratio property of titanium aluminide (TiAl) based intermetallic alloys makes researchers regard this type of material as a potential replacement for the heavier superalloys of nickel. These alloys have been applied as turbocharger wheels of automobile and turbine blades of aircraft engines. A much recent alloy type of TiAl called the TNM alloy has emerged and primarily amenable to mechanical working; while providing the best combinations of mechanical properties that could be achieved through manufacturing processes with subsequent heat treatments. This is attained by solidifying entirely through the disordered \( \beta \)-phase (A2 structure). Effects of major alloying elements such as strength improvement, microstructural stability and phase formation demand the understanding of these alloying elements addition in TiAl-based intermetallic alloys. This review paper aims at encapsulating several works regarding the effects of major alloying elements on \( \beta \)-solidifying TiAl-based alloys and summarizing the characteristic effects of Si for these types of alloys. An impetus for future works on these types of intermetallic TiAl-based alloys is also presented.

**Keywords:**
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1. Introduction

Recently, an innovative variety of beta-solidifying (\( \beta \)-solidifying) titanium aluminide (TiAl) alloys have been developed by several researchers dubbed TNM and TNM\(^{\pm}\) alloys [1, 2, 3, 4, 5, 6]. In contrast to the peritectic solidification pattern prone to segregation, these alloys produce fine-grained homogeneous structures by solidifying entirely through the disordered \( \beta \)-phase (A2 structure) having a body-centred cubic (BCC) lattice structure [4, 7, 8, 9, 10, 11]. Oehring et al. [12], suggested the phase transformation pathway liquid \( \rightarrow \beta \rightarrow \beta + \alpha \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + (\beta) \) for \( \beta \)-solidifying alloy in achieving complete solidification. Also, Imayev et al. [8], realized that a TiAl-based alloy with 44 at.% Al content which contains boron (B) transforms through a solid-state solidification pathway as \( L \rightarrow L + \beta \rightarrow \beta + \alpha + \beta \rightarrow \alpha + \gamma \rightarrow \alpha_{2} + \gamma \). While Tian et al. [13], observed that Ti-48Al-2Nb-2Cr (at.%) alloy (4822) has a transformation path based on phase diagram which follows \( L \rightarrow L + \beta \rightarrow L + \beta + \alpha \rightarrow \alpha + \gamma \rightarrow \text{lamellae (} \alpha_{2} + \gamma \text{).} \) All compositions are presented in atomic percentage except stated otherwise. Cobbinah and Matizambuka [14], stated that a typical TiAl alloy solidifies entirely via the single \( \alpha \)-phase region as \( \alpha \rightarrow \alpha_{2} + \gamma \rightarrow \alpha_{2} + \gamma \) or \( \alpha \rightarrow \alpha_{2} + \gamma \rightarrow \alpha_{2} + \gamma \). It is understood that subject to the cooling rate and solidification path, distinct phase compositions and microstructures could be achieved. Hence, making it possible to control these microstructures in obtaining specific and desirable or peculiar material properties.

Apart from Ti and Al, TNM alloys contain alloying elements such as Nb, Mo and minor additions of B [8, 12, 15, 16, 17, 18]. This was developed primarily to be amenable to mechanical working while providing the best combinations of mechanical properties that could be achieved through manufacturing processes with subsequent heat treatments. TNM alloys are quite sensitive in varying the microstructural grain sizes, morphology and decomposition of lamellae depending on the alloying elements. Thus, the curiosity in understanding the microstructural evolution and phase compositions. At elevated temperatures, TNM alloys display satisfactory quantities of disordered \( \beta \)-phase because of the
β-stabilizing effects that Mo and Nb offer in promoting hot-workability of TiAl-based alloys [7, 15, 16, 17, 18]. TNM alloys containing micro-alloys of Si and C called TNM’ are said to demonstrate excellent creep resistance properties and exceeding the present service temperature limits for TiAl alloys [5]. This is a process-adapted alloy that allows for one-step heat treatment in the α-phase region to attain microstructure of fully lamellar. Different cooling rates during annealing results in adjustments of the α2/γ colonies and lamellar spacings.

Furthermore, it must be noted that the detrimental effects of the β-phase at the material’s service temperatures could be easily reduced and/or completely removed with appropriate heat treatment techniques [16, 19, 20]. This detrimental effect emanates from the disordered A2 structure transforming at ambient temperature to the ordered B2 structure ($\beta_0$-phase) which is brittle and harder than $\gamma$ and $\alpha_2$ phases. Also, the $\beta_0$-phase is incompatible with the $\omega_2$ (D019 structure) and $\gamma$ (L12 structure) phases leading to crack nucleation and propagation at the $\beta_0$/γ interfaces, thereby, causing a reduction in ductility at the service temperatures [16, 20, 21, 22]. This crack initiation has a significant influence on the fracture of TNM alloys [22]. However, in the study of Cui et al. [19], it was observed that the $\beta$-phase was not detrimental to the room-temperature ductility. Microalloying elements additions of B, Si and C were added to act as nucleation agents in TNM alloys during solidification and phase transformations. Moreover, B has proven to be the most effective for grain refinement [8, 12, 23]; while C and Si were more suitable in improving the maximum operating temperatures of TNM alloys giving rise to a promising alloy subclass known as TNM’ [1, 3, 4].

Another important phase (though it is minor) present in TNM alloys is the $\alpha_0$-phase [7, 24]. This phase is barely identified through a scanning electron microscope (SEM) because the phase has a fine nature that is mostly observed as precipitates in the $\beta_0$/γ-phases [24, 25]. The specific nature of occurrence and mechanism of its precipitation reactions are still not fully understood and it is still an ongoing discussion of research between scientists.

At room temperature, TiAl intermetallic alloys comprise of three major phases of intermetallics, namely: $\gamma$-TiAl (D019 structure), $\gamma$-TiAl (L12 structure) and $\beta_0$-TiAl (B2 structure) [1, 4, 7, 18, 20, 26, 27, 28, 29]. The $\gamma$-TiAl phase has L12 tetragonal structure while $\gamma$-Ti2Al has a D019 hexagonal structure [30, 31, 32, 33, 34]. Also, the $\gamma$-TiAl phase is formed at 49 to 66 at.% Al content [14] that could be stabilized up to its melting temperature (~1450 °C) [28]. It possesses high specific modulus, low density, good oxidation resistance, excellent fatigue, and creep properties [35]. The $\gamma$-phase ($L10_0$) of lattice parameters a = 0.4005 nm and c = 0.4070 nm has an ordered face centred tetragonal (FCT) structure [14, 34] and transforms to the disordered structure at about 1250 °C [29]. The ordered $\gamma$-phase has low ductility (up to 750 °C), thereby, decreases its plastic deformation capability likewise does the ordered $\alpha_2$-phase have low ductility (up to 600 °C) [30]. This is because of the limited number of slip systems, the occurrence of planar slip [30, 31] and lack of twinning [32] which makes these phases brittle.

The $\alpha_2$-Ti2Al phase has an ordered hexagonal closed packed (HCP) structure [33, 34] formed between 22 to 39 at.% Al content and transforms to an ordered structure from the disordered one at about 1180 °C with lattice parameters, a = 0.5782 nm and c = 0.4629 nm [14, 34]. It is known to exhibit extremely poor toughness and tensile ductility at ambient temperatures while possessing good oxidation resistance and excellent elevated temperature specific strength [28]. Typical Ti-based alloy microstructures consist of alternating $\alpha_2$ and $\gamma$ lamellae formed within the $\gamma$-phase region, present a non-twinned crystallographic relationship of (0001)-$\alpha_2$ || (111)-γ and <1120>-$\alpha_2$ || <110>-γ [24, 37]. The principal modes of deformation in $\gamma$-phase are <110> slip and (111)<112> twinning while $\alpha_2$-phases is between the $\gamma$ twinned phases [34]. The high Al content of the $\gamma$-phase makes it achieve higher resistance against oxidation than $\alpha_2$-phase [38]. Jian et al. [39], reported that the $\alpha_2$-phase shows strong metallic bond with low mechanical anisotropy; while $\gamma$-phase has a coherent bond with strong universal mechanical anisotropy. It is commonly known that to maintain the ordered D019 structure, a large interchange shuffling is required [32, 40]. The appearance of $\alpha_2$-phase deformation twinning could play a key role in high Nb-containing TNM alloys’ mechanical properties enhancement. This will help in understanding and further the development of $\beta$-solidifying γ-TiAl-based alloys. Furthermore, $\beta_0$-phase has a body-centred cubic (BCC) structure which is similar to conventional $\beta$-phase Ti alloys with B2 superlattice structure [33]. As stated earlier, the disordered elevated temperature $\beta$-phase changes to a very brittle and hard $\beta_0$-phase at room temperature (RT) [16]; while ordered $\beta_0$-phase dissolving to disordered $\beta$-phase at about 1175–1205 °C [29]. In typical Ti alloys, there are both high-temperature BCC $\beta$-phase and low-temperature HCP $\alpha$-phase [41].

It was reported by Jiang et al. [28], that addition of Nb as BCC $\beta$-stabilizer in both $\omega_2$-Ti3Al and γ-TiAl contributed to the development of ordered B2–Ti(Al, Nb) or orthorhombic O-Ti(Al, Nb) phases. Besides, Nb and Mo as $\beta$-stabilizing elements are added in TiAl-based alloys to enhance RT ductility through the formation of minor $\beta$-/B2 phase quantities [28]. It is well reported in literature that $\beta$-stabilizing elements such as Mo, V, Ta Nb, Mn, Zr and Cr are favoured to enter the Ti sites. Moreover, the addition of $\beta$-stabilizers into $\beta$-Ti inhibits $\beta$-Ti → $\alpha$-Ti transformation that leads to intermediate γ-Ti phase formation (hcp-Ab2 type) [28].

According to Singh et al. [31], TiAl intermetallic alloys lack hot-workability due to reasons such as (i) low dislocation mobility, (ii) shortage of independent slip system resulting in the materials’ plastic anisotropy, and (iii) lack of mobility at grain boundaries and diffusivity caused by retarded recrystallization and recovery. Also, the practical application of TiAl alloys is inhibited by poor oxidation at elevated temperatures [42]. Titanium aluminides are problematic to process due to their brittle nature, hence, limiting its widespread production. The intrinsic brittleness at RT and poor hot-deformability limit its application in manufacturing complex-shaped structural components [14, 31, 39, 42, 43, 44, 45, 46, 47, 48]. Consequently, conventional processing of TiAl-based alloys such as forging and extrusion are restricted; while casting is known to always produce coarse microstructure and arbitrary defects resulting in inhomogeneous mechanical properties [20, 47]. This is caused by high strain at elevated temperatures and poor RT ductility of TiAl-based alloys.

However, several heat treatment procedures and/or mechanical processing routes have been exploited based on the transformation of phases in manipulating the resultant microstructures. These processing techniques allows for a balance in desirable properties while gaining control of the colony sizes, lamellar spacing, grain size and grain growth. Chen and Li [30], reported that ordered structures of TiAl-based alloys and their morphological texture causes mechanical properties in-homogeneity. Four possible microstructures are usually formed by TiAl-based intermetallic alloys are shown in Figure 1. It is reported that the nearly fully lamellar and/or fully lamellar microstructures could provide the much-needed combination of mechanical properties using a viable production method and provide structural integrity during the components’ lifetime [5, 7, 14, 16, 22, 30, 46, 51, 52]. The duplex or equiaxed microstructure ($\gamma$+$\alpha_2$) provides adequate ductility and fatigue but it exhibits low creep resistant and fracture toughness; while the microstructure with fully lamellar (with alternating plates of $\gamma$ and $\alpha_2$ phases) demonstrates superior fracture toughness and creep resistant but demonstrates poor ductility [30, 31, 52]. Hence, the choice of final microstructure during processing is very essential to obtain the best combination of mechanical properties. This is because of the transpose correlation between fracture toughness and ductility in the different microstructures. To further understand these microstructures, the reader could refer reads [14, 48, 49, 50].

The gamma-TiAl (γ-TiAl) alloy is a novel type of lightweight material [53]. γ-TiAl-based alloys are potential substitutes for nickel (Ni) based superalloys especially in applications that require considerable weight saving and minimal redesigning [15, 28, 48, 54, 55, 56, 57, 58, 59, 60, 61, 62]. According to Ding et al. [63], γ-TiAl alloys with FL
microstructures creates decent stability in properties such as ductility, creep resistance and fatigue resistance which are often needed in several engineering applications. γ-TiAl alloys serve as a feasible substitute in aircraft engine applications for turbine blades and turbochargers wheels. However, oxidation resistance above 800 °C is another major drawback in expanding its usage in high-temperature applications [64].

Previous works have shown that enhance mechanical properties could be achieved by the dual-phase (α2/γ) alloys. Particularly, lamellar microstructures in respect of fracture toughness, higher strength and ductility when compared to either the single phases of γ or α2. The duplex and fully lamellar are the two most common microstructures of TiAl-based alloys for engineering applications. The α2 and γ phases display diverse behaviours during deformation owing to their distinctive crystal structures [63]. The Blackburn orientation relationship (BOR) expresses the crystallographic relationship between these phases [37, 65]. A semi-coherent interface would result from any slight difference in the lattice parameters of both γ and α2 phases. The transfer of dislocations from one phase to the other is difficult because α2-phase is a very brittle phase; thus, reducing the overall ductility in fully lamellar microstructures [31].

This has made researchers study the fundamental phenomenon in understanding the α2-phase of the dual-phase alloys which retains the highest levels of O impurity [59, 66, 67, 68]. Ren et al. [68], explained that microhardness and nano-indentation measurements revealed that significant precipitation hardening arises in γ/(α2+O) lamellar due to O phase present in α2 lamellae. This is attributed to the refinement of α2 lamellae in relation to the interface and phase transformation. This is because the elastic strain energy introduced between the adjacent γ-phase and modulated lamellae. This is also because of the thermodynamic equilibrium of O phase and retention of a high-volume fraction within the α2-phase. Hence, it is critical to control the microstructure and ensuing mechanical properties in producing a high-performance β-solidifying γ-TiAl alloy [68]. However, there are divergent views by researchers regarding the so-called “scavenging effect” stating that the γ-phase is ductile compared to α2-phases. The precipitation of fine-scaled oxides owing to excess O results in embrittlement because the solubility of O in the γ-phase of TiAl alloys is limited [7, 69]. Lefebvre et al. [69], maintained that O, C or N have a preference to dwell in the Ti6 octahedral sites which are situated in α2-phase. Moreover, if the composition of phases in γ changes to the Al-lean area of the stoichiometric composition, the excess Ti atoms occupy Al sites resulting in cavity formation of Ti6 octahedral. Other researchers like [24, 25, 50], used this conclusion to explain their observations of Nb, stating that excess Ti is generated as Ti2C is favourably substituted in the γ-phase by the Nb atoms that locate the Al sites. Thereby, raising the concentration of Ti6 octahedral site which acts unvaryingly to off-stoichiometry.

Titanium aluminides are potential engineering materials where lightweight is required including strength retention at elevated temperatures [65]. Due to a density between 3.8 to 4.3 g/cm3, TiAl-based alloys are ideal candidates in aircraft applications [16, 19, 24, 25, 50]. For the past three decades, titanium aluminides intermetallic alloys have been of major interests especially in the aerospace and automotive industries. This is essentially due to their attractive mechanical properties like high strength-to-weight, low density, excellent high-temperatures stiffness and strength retention [15, 28, 31, 43, 46, 47, 48, 50, 56, 62, 67, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80]. This makes TiAl-based alloys a type of material with very high prospects of replacing nickel-based superalloys typically used for making aircraft-engine turbine parts [43]. However, poor hot workability is a major problem concerning TiAl alloy.

The intermetallic Ti–Al ordered system is still a topic of extensive study because of its inherent applications for structural materials operating at elevated temperatures [6, 23, 47, 53, 54, 60, 69, 79, 80, 81, 82, 83, 84, 85, 86]. The successful integration of TiAl-based alloys parts into aircraft engines is predicted to tremendously decrease greenhouse gas emission and fuel consumption [5]. Thus, titanium aluminide has found application in making seal supports, cases and frames of aircraft engines where clearances are crucial [54]. Also, it is applied in turbocharger wheels and turbine blades of automobile and aero engines respectively.
Mengis, Grimme and Galetz [92], stated that high-temperature problems hindering its wider adaptability as aero-engine components adopted by General Electric (GE) to manufacture their LPT blades in engines from TiAl alloy [81]. The TiAl has been known to be the foremost mode of failure during machining of TiAl-based alloys because of the work-hardened layer. Considerable machinability of TiAl-based alloys. Castellanos et al. [77], reported that the partitioning tendency at β-stabilizing effects are not only important alloy additions of TiAl-based alloys for improving mechanical properties especially their fracture toughness and ductility at RT. This is usually achieved by deliberate microstructural alterations with slip and twin deformation of solute elements [34]. The addition of the β-stabilizing elements also causes grain refinement by changing the solidification pathway and formation of β-phase to enhance the workability of TiAl-based alloys [35]. Moreover, in understanding TNM alloys and related alloys, the effects of Nb and Mo are distinctly essential, because they are usually present as major alloying constituents [4, 7, 12, 15, 18, 24, 26].

Transition metals like V, Nb, Ta, Mo, Cr, Mn and W are common and important alloy additions of TiAl-based alloys for improving mechanical properties especially their fracture toughness and ductility at RT. This is usually achieved by deliberate microstructural alterations with slip and twin deformation of solute elements [34]. The addition of the β-stabilizing elements also causes grain refinement by changing the solidification pathway and formation of β-phase to enhance the workability of TiAl-based alloys [35]. Moreover, in understanding TNM alloys and related alloys, the effects of Nb and Mo are distinctly essential, because they are usually present as major alloying constituents [4, 7, 12, 15, 18, 24, 26].

In a study by Kainuma et al. [96], it was concluded that W, Ta, Mo, Cr and V partitions α2 or a phase at the α/γ and α2/γ phase equilibria while Zr does same in the γ-phase; but Nb, Cu, Ni, Co, Fe and Mn changes to α formers from γ formers as temperature increases. These phenomena of alterations in partitioning behaviour were attributed to the FCC and HCP lattice structural stability difference between the alloying elements. However, for the phase equilibria (β/α2, β/α, and β/γ) only Zr partitions the β-phase, unlike other elements partitioning at the γ, α2 or α phases. According to Kainuma et al. [96], the partitioning tendency at β/α equilibria is largely dependent on the interfacial energy between the HCP and BCC lattice structures in Ti-X (X = V, W, Nb, Co, Fe, Ta, Mo, Cu, Ni, Cr, Zr) binary systems. Bresler et al. [65], showed that domain boundaries and interfaces of γ/γ phases diminishes the movement of dislocations and plastic deformation but not like the α2/γ interface. Since the γ and α2 phases exhibit different slip systems, the movement of dislocations is restrained when compared to the γ/γ-interfaces. Hence, the mean
spacing between the interfaces of α2/γ affects the creep properties of TiAl alloys but not the colony boundaries and sizes. It has also been recognised that alternating microstructures of α2+γ lamellar leads to better resistance to creep in comparison to the equiaxed microstructures [54, 74]. This is related to the strong anisotropy of lath structures and large grain sizes, thus, high brittle-ductile-temperature-transition (BDTT) [74, 81]. Likewise, an increase in α2-phase and structural refinements is known to cause strengthening effects in the dual-phase α2+γ TiAl intermetallic alloys [50, 74].

Niobium (Nb) addition in γ-TiAl-based alloys stands out when compared to most alloying elements in providing a balance elevated temperature and RT properties [14]. These mechanical properties enhancement is ascribed to the combined influence of precipitation strengthening, solid solution strengthening, increase in γ-phase content and grain boundary strengthening [45]. It is well reported in literature that Nb plays a vital role in oxidation resistance and high-temperature strength improvements in TiAl-based alloys [15, 18, 25, 97]. Nb favours Al activities and prefers the formation of Al3O2 which act as a protective oxide surface, thereby, limiting oxygen diffusion into the alloy [35]. These beneficial effects of Nb manifest through increased propensity of the α2-phase basal slip, ductile β-phase stabilization, and oxidation resistance improvement [35, 55]. This is related to the Nb solid solubility which increases within the γ-phase and lesser diffusion in α2-phase; while segregation of Nb results in B2-phase formation [45]. The B2-phase is formed through a β-phase transformation and α-grains nucleation in the β-grains. Refinement of lamellar colonies and heterogeneous nucleation sites formation is promoted by the addition of Nb.

Nb being a β-stabilizer cause the retention of β0-phase at ambient temperatures, particularly for β-solidifying TiAl-based alloys. The β0-phase is an ordered derivative of the disordered β0-phase retained at RT [97]. Consequently, microstructural inhomogeneities as a result of strong partitioning lead to reduced fatigue and creep resistance. This is expected due to considerable difference of Nb distribution in the phases in comparison to the traditional dual-phase TiAl-based alloys [7, 97]. In TiAl-based alloys with high Nb content, the emergence of β0-phase leads to reduced RT ductility and the formation of ω-phase from the parent β0-phases. The ω'-ω0 and ω (D8h structure) phases occur at separate stages during the β0→ω0 or β0→D8h transformations [25, 40, 97]. Depending on the cooling methods adopted, the ω-related phases vary in morphology, size, and structure around the β0-phases [24]. Nb addition in TiAl-based alloys enhance the oxidation resistance, toughness at RT and creep resistance. Nonetheless, high amount of Nb would densify the alloy, thereby, limiting the alloy applications [10, 72, 95]. It has been observed that the composition of Al and Ti in β0 and α2 phases are in contrast with what is obtained in the γ-TiAl and α2-Ti3Al binary phases [9]. The different sites occupied by these metal atoms in the alloy causes this nonconformity. It was also reported from ab initio calculation of refs [2, 26], that transition metal atoms favours substitution of both Al and Ti sites in β0 and α2 phases respectively, showing stronger tendencies in the latter. Generally, Nb demonstrates a weak preference for the β0-phase but shows almost the same amount of distribution in other phase confirming Nb as a β-stabilizer in TiAl-based alloy systems [7].

Doping of Ti-Al binary system with Mo promote a rise in ionic or coherent bonds resulting in improved elasticity modulus and strength [98]. Based on the observations from literature [12, 24, 81, 99], Nb addition in TiAl-based alloys still retains substantial quantities of Nb in other phases even with the initiation of the β0-phases that are quite stable at ambient temperatures. However, Mo still favours the formation of more β0-phase but behaves differently by creating strong partitioning between phases. This is because Mo is a stronger β-stabilizer compared to Nb and broadly influences processing, which has been well reported by refs [9, 15, 24, 81, 94]. Also, hot-working is achievable using near conventional equipment because the disordered β-phase is stabilized at elevated temperatures with small additions of Mo [26, 82, 94, 100]. Moreover, heat treatment could be applied to decrease the β/β0 volume fraction due to the detrimental creep resistance effects [24, 99, 100]. The ordered β0-phase with A2 structure is reported to have high energy of formation, thus, making it more stable chemically when compared to the disordered β-phase having a B2 structure. However, the disordered β-phase has better mechanical stability than β0-phase [26]. Erdely et al. [9], investigated the precipitation behaviour of the γ-phase growth in a Ti–44Al–7Mo β-homogenised alloy within the supersaturated β0-matrix. The results showed that the transformation of β0 → γ phase occurred without forming any intermediate phase with diverse crystallographic structures. This β single-phase homogenisation treatment triggers the dissolution of α2 and γ. Subsequently, water quenching (WQ) invariably subdued the re-precipitation of α2 and γ which prevents martensitic or massive transformation. Thus, β0 single-phase microstructure is preserved at RT.

Several authors [4, 9, 24, 26, 61, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 100, 101, 102] have used a dual-stage heat treatment process in trying to reduce the β-phase. These TiAl-based alloys were first heated to a temperature above the γ solvus temperature (Tγsolv), held for a brief period to avoid grain growth with subsequent fast cooling. While the second heat treatment was conducted at a temperature higher than the predicted service temperature, held for a prolonged period followed by slow cooling (or furnace cooling). This is done because Mo barely stabilizes the ordered β0-phase but effectively stabilizes the disordered β-phase. In comparison to Ti and Al, Mo seems rather slow in diffusing the B2 structure. This is because the self-diffusion energies of Al and Ti for short distance diffusions are lower than the activation energy of Mo in the alloy [9]. Also, it results in phase fraction equilibria and regulated fine lamellar microstructure leading to phase transformation and improved oxidation resistance. Impurities observed in TiAl-alloys are most prevalent in the α2-phase as an interstitial element. This impurity dissolves in the α2-phase because of the Ti6 octahedral sites which favour the incorporation of these interstices [7]. The γ and β phases do not possess or contain any octahedral sites. According to Erdely et al. [9], the rationalization of diffusion role in the γ-phase formation at equilibrium is considered that: (i) partition of elements must take place between the phases, and (ii) owing to energetic reasons, atoms of Mo must relocate to the Ti sublattice in γ from the Al sublattice in β0. Consequently, it could be said that the redistribution elements instead of interfacial migration governs the growth of diffusion precipitates in the γ-phase.

In the work of Cui et al. [19], it was noticed that the difference in hardness between the β and γ phases was close. It was used to explain the lower hardness value recorded for β-phase which contributes to the superior tensile properties (RT elongation of about 1.5%) of Ti–43Al–2Cr–0.7Mo–0.1Y alloy with satisfactory hot-workability owing to high β-phase present. Moreover, the hardness values of TiAl-based alloys depend on the β-stabilizers and amount β-phase formed. It was also reported by Cui et al. [19], that alloys produced by Cr, Mn, and V had β-phase with low hardness; while Nb, Mo, or W resulted in β-phase of higher hardness values. The Reduction of hardness through alloying could be employed in designing compositions of β-solidifying TiAl-based alloys with excellent RT ductility.

Elements of zirconium (Zr) and Ti have the same atomic size and crystal structure belonging to group iv in the periodic table. Zr is said to refine TiAl-based alloy microstructures by dissolving completely in Ti within the β-phase region at elevated-temperatures and the α-phase region at ambient temperature [103]. Zr occupies the Ti sites in the crystal lattice of TiAl-based alloys like β-stabilising elements of Mo and Nb [102]. The combined addition of Zr and Cr in TNM alloys promotes ω-phase formation by increasing β-phase and decreases the amount of α2-phase [104]. It was also reported that Zr improves compressive strength [104], enhances fracture strain and yield stress at intermediate temperatures [65]. It has been reported that diffusion of Zr is much faster than Nb and consequently it has little benefit in retarding diffusion-controlled processes.

Bresler et al. [65], investigated the influence of Zr, Nb and Ta on the creep properties of Ti–44Al–5X (X = Zr, Ta, Nb) ternary alloy. The microstructure was reported to be fully lamellar microstructure. All three
alloying elements were said to be highly soluble in the Ti–Al system and showed different $\alpha_2/\gamma$ partitioning behaviour along with distinctive $\alpha_2$ and $\gamma$ phases lattice parameters. The atomic size difference and partitioning behaviour meant that the mean lattice parameter transformation misfits of $\alpha_2/\gamma$ occur by the addition of microalloying elements [65]. Ta and Nb increase the misfit of $\alpha_2/\gamma$ lattice, but Zr reduces it. Thus, the lesser the misfits of the lattices and coherent stresses, the more the dislocation emission decreases at the interfaces. According to Kainuma et al. [96], Nb partitioning is almost the same on both phases; while Ta partitioning occurs mainly at the $\alpha_2$-phase and largely at $\gamma$-phase for Zr which was also reported by Bresler et al. [65]. Microalloying and the rate of cooling has a substantial effect on the average distance of $\alpha_2/\gamma$-interfaces. It is understood that Zr and Ta show greater Nb segregation and the average spacing between the cores of dendrites were much smaller in the Ta-containing alloys compared to Zr- and Nb-containing alloys. The alloy (Ti–44Al–5Nb) had the least resistance to creep, whereas Ti–44Al–5Zr and Ti–44Al–5Ta exhibited almost the same creep resistance. Thus, it could be deduced that both Zr and Ta had enhanced creep resistance properties than Nb. It was proposed that due to the interfacial segregation of alloying elements and desaturated $\alpha_2$-phase dissolution during creep exposure, the slower kinetics of dissolution, rise in phase stability or decreasing misfits lattices could be responsible for the Nb, Ta and Zr $\alpha_2$-stabilizing effects.

Ta as an alloying element is also used in TiAl-based alloys, but not often as Nb. As stated earlier, Ta enriches the $\alpha_2$-phase, Zr enriches the $\gamma$-phase whereas Nb equally partitions between both phases. The strong solid solution hardening effect and high solubility of Zr in the $\gamma$-phase are attributed to the exceptional creep properties of the TiAl alloy containing Zr; while interdiffusion coefficient of Ta is responsible for the Ti-containing alloy [65]. Ta can equally substitute Nb since the positions of Ta in the periodic table suggests they both would exhibit similar chemical behaviours. Likewise, high melting point of Ta makes it offer high melting point of Ta, thereby, inhibiting Nb atom diffusion during solidification. The slower kinetics of dissolution, rise in phase stability or decreasing misfits lattices could be responsible for the Nb, Ta and Zr $\alpha_2$-stabilizing effects.

In an experiment conducted to examine the correlation between microstructure and addition of Ta to produce B2-phase within the lamellar colonies, Fang et al. [36], prepared Ti46Al8Nb2.6CxTa alloys (Ta = 0.8–4 at.%%) in Ti-46.5Al alloy produced by spark plasma sintered (SPS). The Ta-containing alloys showed the tendency of dissolving further within the lamellar colonies. It was reported to have vanished. This is ascribed to slow diffusion rate and the higher melting point of Ta. This led to the increase in volume fraction of the $\beta$-phase from 0% to 23% in the Ta-containing alloy. Moreover, the $\alpha_2$-phase lattice parameter increases, but that of $\gamma$-phase decreases. This is because Ta hinders the dispersion of Nb atoms from dissolving further within the lamellar colonies.

Furthermore, Ta is described to refine lamellar colony sizes of TiAl alloys [36]. This was attributed to the heterogeneous nucleation particles formed within the Ta addition. In related work, Fang et al. [36] further investigated the mechanical properties of Ti42Al6Nb2.6C alloy produced by vacuum arc melting. It was noticed that above 0.2 at.% of Ta, the B2-phase seems to have vanished. This is ascribed to slow diffusion rate and the higher melting point of Ta, thereby, inhibiting Nb atom diffusion during solidification. This causes the disappearance of the B2-phase. The compressive strain and strength increase by 2.2 and 1.2 times, respectively, as Ta increases. There was an increment of 405 MPa–472 MPa for the tensile strength and 2.3%–2.9% for the strain has Ta increases at 750 °C. The mechanical properties enhancement was due to the disappearance of the B2-phase and strengthening through Ta and Nb solid solutions [20]. Based on previous works, Ta and Nb display equal outstanding solubility in $\alpha_2$ and $\gamma$ phases. With additional solutes in $\gamma$-phase by the Nb atoms, more solutes of Ta are observed in the $\alpha_2$-phase. Zhang et al. [105], examined the formation of $\gamma$-phase in Ti–48Al–3Nb alloy with 0.5 at.% Ta after fast cooling from elevated temperature $\alpha$-phase region. A massive transformation was observed due to rapid cooling which displays sub-grains in $\gamma$-m-phase and fine nano-grain compared to retained $\alpha_2$-phase favoured in the Ti–48Al–3Nb alloy. It was reported that the solute atoms slow down the transformation of $\gamma$-m-phase during rapid cooling, which was analogous to the observation of other works in ref [20, 36, 55, 65].

Saeedipour, Kermanpur and Sadeghi [52], examined the high-temperature mechanical properties and microstructural re- 
finements of a Ti–46Al–8Ta alloy fabricated via vacuum arc re-melting with N addition up to 2 (at.%). The results presented demonstrated that N affects the as-cast alloys microstructure morphology, changes the transformation pathway, and caused notable microstructural refinement. From the viewpoint of thermodynamics, the solubility limit was exceeded by the N content leading to the formation of Ti3AlN. Furthermore, N extends the $\alpha$-phase field and up to 2 at.% addition does not affect the orientation relationship of $\alpha_2$ and $\gamma$ lamellae.
properties and strength at high-temperature, the ~8 vol% β-phase equivalent to 2 at.% Cr addition was a very encouraging composition.

In a multi-alloying system examined by Panin et al. [95], the β-solidifying TiAl-alloy which is a new Russian alloy (Ti-44.5 Al-2 V-1 Nb-2 Cr/1 Zr-(0.01) Gd) were investigated. It was determined that the phase composition of the TiAl alloy in the as-cast state (without Gd) was characterized by three principal phases: α2, β and γ. Alloys with Zr had a β-phase volume fraction that does not exceed 2–3%; while alloys with Cr showed β-phase volume fraction reaching 5–6% that was restricted along the transformed grain boundaries. It was discovered that the Zr-containing alloys showed grain boundaries lamellar colonies (γ+α2) sprouts.

As stated earlier, the β-solidifying TiAl-based alloys properties are extremely dependent on compositions, particularly the β-stabilizing elements in the alloy. The mechanical properties and high-temperature deformability of a new TiAl alloy containing Nb and Mn were studied by Wu et al. [107]. It was deduced that the alloy had good heat deformability based on recorded low activation energy (392 kJ/mol) and low deformation resistance of the alloy. The primary lamellae were transformed completely into fine equiaxial γ-grains when compressed at the optimal deformation conditions 1200 °C/0.01 s⁻¹. The billet microstructure composed largely of recrystallized γ-grains with high angle boundaries. It was reported that the alloy had UTS and elongation were 780 MPa and 1.44%, respectively, which benefits from the average size (4.9 μm) of the fine γ-grains.

Iron (Fe) is also known to be an effective β-phase stabilizer and could improve the liquidity of TiAl-based alloys. Fe leads to reduced lattice tetragonality of TiAl alloys because the atomic radius of Fe is smaller (1.27 nm) than Al (1.43 nm) [60]. It is known that γ and β phases increases as α2-β phase reduces in TiAl-based alloys when Fe increases from 0 to 1.1 [60]. Consequently, Yang et al. [60] investigated the addition of Fe (0–1.1 at.%) in Ti43Al5Nb0.1B alloy produced by arc melting technique. It was reported that increasing Fe content caused a reduction in the lattice tetragonality (c/a) and average columnar grain width of the γ-phase. Fe led to B2-phase formation that is Fe-rich for both inter-dendritic and dendrite fields. It was reported that the compressive strain and strength were 1958.4 MPa and 29.8%, respectively, for the TiAl-based alloy at Fe 0.7 at.%. When Fe content is increased above 0.7 at.%, the mechanical properties depreciated because of B2-phase formation which typically behaves as crack initiation sites. It was also realized that Fe refines the grains and results in RT super-plasticity. The refinement of the microstructure was attributed to the Fe-rich band-like B2-phase that diminishes the rate of grain growth. While the formation of B2-phase was credited to the high-temperature α-phase supersaturation that restrains the excess Nb and Fe. The Fe solid solution strengthening and grain refinement are responsible for the enhancement in the strain and strength.

2.2. Grain refinement

Owing to the dispersion strengthening effects of carbides, borides and silicides along with the formation of ternary compounds, C, B and Si are added to increase the physical, chemical, and mechanical properties of TiAl-based alloys. They also promote temperature characteristics like heat resistance, short-term and long-term strength components, durability, and hardness [108]. An element that has been of remarkable importance in TiAl-based alloys for grain refinement is boron (B) [12]. It was revealed by Imayev et al. [8], that thermally stable borides principally cause grain refinement effects and behave as heterogeneous nucleation sites during solidification and resultant phase transformations. This effectively promotes precipitation of homogeneous and fine microstructures in as-cast γ-TiAl-based alloys [12]. Grain refinement effects depend on the evolving order of phase transformation which is still an ongoing research topic. As an example, the effect of microaloaying on microstructure and phase stabilization could be understood by analysing the chemical composition of the borides. Oehring et al. [12], demonstrated that apart from borides, the rate of cooling also has a significant impact on the resultant microstructure and solid-state transformation of β/α phase. During transformation, the morphology stems were said to be based on a solid-state reaction of β → β + α → α + γ → α2 + γ. It was concluded that refinement of microstructures causes the inhomogeneous distribution of γ + α2 lamellae orientation followed by precipitation of α-phase. It was deduced that α nucleation at boride sites found in the inter-dendritic fields are larger in number than the orientations obtainable at the α-phase. This nucleation occurs as borides precipitated from the β-phase at elevated temperature. Figure 2 shows SEM images in back-scattering electron (BSE) mode of as-cast and heat-treated TNM alloys, showing phase morphologies formed. For better understanding of these phases, the reader is referred to ref [12]. In the work of Bazarnev et al. [104], Yttrium (Y) was added in the range of 0.02–0.6 at.% to a β-solidifying TiAl-based alloy and reported that Y promoted microstructural grain refinement. The presence of Y also contributed to increased strength and elongation. Due to its reactive element effects, Y also enhances heat resistance properties. It was concluded that 0.3 at.% addition of Y increases the hot-deformability of β-solidifying TiAl-based alloys. This is made possible because Y allows for the uniform oxide growth devoid of Ti and Al oxides layers. Imayev et al. [8], examined the effects of Al and the addition of additional micro-alloying elements in γ(TiAl)+α2(Ti3Al) alloys produced by casting. It was shown that the microstructure was predominantly homogeneous and fine with no segregation when solidifying through the β-phase field at certain alloy compositions. This behaviour was ascribed to the effects of alloying transformation kinetics of β→α by avoiding the peritectic solidification path. Figure 3 indicates β-phase located at the layers of lamellae boundary colonies (Figure 3a) and significant coarsening of lamellae width shown in Figure 3b. Beta (β) stabilizers like Mo, Nb, W and Cr do also contribute to refining microstructure grains by stabilizing the metastable B2-phase (ordered β-phase) at low temperatures, thereby, enhancing high-temperature deformability [9, 51]. Lately, the Ti–44Al–7Mo ternary alloy has drawn attention, with research works demonstrating that heat treatment procedure resulted in a considerable microstructural refinement with a substantial increase in hardness. In a review by Klein, Clemens, and Mayer [7], borides in TNM alloys was said to be off-stoichiometric caused by the alloying elements, thus, leading to vacancies or anti-site defects. The authors explained that Ti-borides in TiAl-based alloys barely display solubility for Al and consist basically of B rich lamellae which had columnar and equiaxed regions. However, a further increase in TiB2 content of 0.54 wt.% in the as-cast microstructure produces an alloy which had columnar and equiaxed regions. However, a further increase in TiB2 leads to complete equiaxed grains. This shows that TiB2 addition has a threshold value for the refinement of TiAl alloy. It was further established that the fluidity of 4822 alloy could efficiently be enhanced by TiB2 addition. It was concluded that 0.72 wt.% TiB2 led to a reduction of the temperature range in the solid-liquid two-phase region and microstructural refinement resulted in fluidity enhancement.
2.3 Formation of special phases (ω₀-phase)

To achieve good oxidation resistance, creep, and high-temperature strength, Nb is usually added as alloying elements in TiAl-based alloys [15, 25, 99]. However, this causes increased hardness and leads to the formation of ω₀-phase as an additional phase [19, 24, 99]. Typically, this ω₀-phase precipitates in the β-matrix of β-solidifying TiAl-based alloys, but not the same for alloys where α₂-phase precipitates [23, 25, 40, 99]. It is understood that the B₂-phase is a thermodynamically metastable phase susceptible to decompose into ω-related phases of trigonal-ω', D₈₈-ω and B₈₂-ω (ω₀) [25, 61]. The size and volume fraction of ω₀-phase is strongly influenced by heat treatment and alloying elements, and also related to the β-stabilizing elements' diffusion [61, 109]. According to Yang et al. [61], during long time annealing, ω₀-phase could be transformed to D₈₈-ω-phase even though during WQ, the formation of ω'-phase is unavoidable. Hence, the observation of B₂/γ transition with adjacent γ lamellar discontinuous coarsening by the γ-phase nucleation in the matrix of B₂-phase. Also, structures containing γ and ω-related phases are normally found in the B₂ region.

Transmission electron microscopy (TEM) and other high-resolution microstructural examination equipment are adopted by different researchers in investigating the distribution of ω₀. The β₀-phases are studied during the precipitation process that results in destabilization and stabilization of TiAl-based alloys. It was confirmed by Song et al. [25], that ordered ω variants were observed to precipitate homogeneously inside the β₀-phase field of as-cast Ti–45Al–8.5Nb–0.2B alloy. In another study by Song et al. [97], as-cast Ti–45Al–8.5Nb–0.2W–0.2B–0.02Y alloy annealed at 900 °C and 950 °C exhibiting particles of micron-level ω₀-phase precipitate in β₀-phases were investigated. It was discovered that the direct transformation of β₀(ω₀) → γ occurrence was only confirmed by TEM analysis. Also, the ω₀-phase is Nb-rich with low W content in comparison to β₀-phase with almost the same composition of β₀ and γ phases [97]. In alloys containing both β and γ stabilizers, there is no single α-phase field in the

Figure 2. SEM Images of TNM alloy (a) As-cast (b) Heat-treated at 1310 °C/2 h/OQ/1450 °C/1 h/AC (c) Heat-treated at 1310 °C/2 h/OQ (d) Heat-treated at 1310 °C/2 h/OQ/1450 °C/1 h/FC as reported by ref [88].

Figure 3. SEM Micrographs of TNM alloy (a) As-cast alloy (b) Heat Treated at 1450 °C/5 min/FC as reported by [8].

S.A. Raji et al. Heliyon 6 (2020) e04463
transformation sequence, instead there exist an $\alpha + \beta + \gamma$ three-phase regime [23]. Likewise, Schloffer et al. [24], analyzed the cause of precipitation reactions during annealing after heating a TNM alloy above the $\omega_0$ solvus temperature. Figure 4a displays the histogram of Ti, Al, Nb and Mo as major alloying elements based on calculations made by Klein, Clemens, and Mayer [7] to quantify the chemical compositions. The authors also presented an atom probe tomography (APT) image reconstruction of Nb and Mo elements indicated in green and red lines, respectively, as shown in Figure 4b. The iso-concentration surfaces showed phases present and the elements inhomogeneous distribution. The concentration gradient adopted by Klein, Clemens and Mayer [7] was used in creating the surface with the $\omega_0$-particles. This demonstrated an elongated parallel arrangement along the direction of growth based on the orientation relationship [76]. From Figure 4, it could be deduced that the Ti, Nb and Mo atoms are not homogeneous, but the Al atoms are very close to being homogeneous. Also, it was realized that $\omega_0$-particles grow because of the redistribution of Mo that significantly affects the actual decomposition of phases. Other authors [2, 24, 97] have also concluded that there was Mo rejection from the $\omega_0$-phase, thereby, enriching the $\beta$-phase matrix.

The occurrence of $\omega_0$ (ordered $\omega$) phase at intermediate temperatures in TiAl-based alloys is widely reported [40, 61, 109]. Song et al. [109], studied the phase transformation behaviour of $\omega_0$-phase at 750–900 °C. It was realized that the microstructures comprise of $\gamma + \omega_0$ with minor precipitates of $\alpha_2$-phase after ageing treatment followed by quenching from high temperature. A unique mechanism of twinning by the $\alpha_2$-phase was observed after ageing that seems analogous to the described mechanism of phase transformation diffusive-displacive in deformed TiAl alloys [40, 109]. This could provide a preferred site for $\omega_0$-phase initiation due to the twinned interface atomic structure being relative to the crystallographic arrangement of $\omega_0$-phase. Owing to the $\gamma$-phase precipitates from the stacking faults of $\alpha_2$-laths, a semi-coherent interface between $\gamma$ and $\omega_0$ phases are observed and high density of stacking faults is noticed inside the $\alpha_2$-laths. But the $\gamma$-phase direct nucleation from the matrix of $\omega_0$/$\beta_0$ keenly develops at higher temperatures. The $\omega_0$-phase nucleates heterogeneously inside the $\beta_2$-phase.

Apart from the $\beta_0$-phase, it is known that $\omega_0$-phase can be precipitated within the lamellar colonies after prolonged annealing by transformations of $\alpha_2/\omega_0$ or $\beta_0/\omega_0$ phases, Thus, it is essential for mechanical properties and microstructural stability. Besides the influence of V, Zr and Ta on microstructures, Song et al. [109] also investigated their influence on $\omega_0$-phase stability. It was noticed that very fine-grained microstructure was obtained because of the multiple variants of $\omega_0$, $\gamma$ and $\alpha_2$ phases formed from $\beta_0$-matrix at different orientation relationships. The overall orientation relationship based on interfaces formed is stated as: $(112)_{\omega_0}/(0001)_{\alpha_2}/(111)_{\gamma}$; $<0001>_{\omega_0}/<1120>_{\alpha_2}/<101>_{\gamma}$ [109]. The elements V, Zr and Ta were reported to harm the stability of $\omega_0$-phase, but the Ta appeared weaker than V and Zr.

### 2.4. Strength improvement

The addition of C as an alloying element for TiAl-based alloys’ high-temperature strength improvement has been widely studied. Moreover, C additions are usually employed for fatigue and creep resistance enhancement in TiAl-based alloys. Carbon controls the microstructure of FL ($\alpha_2+\gamma$) through the refinement of the lamellar spacing owing to dislocation interactions between the fine lamellae [6]. Carbide precipitations and solution strengthening are the two methods of carbon strengthen alloys since it is an interstitial atom [4, 20, 54]. For TiAl-based alloys, C is located at the Ti$_6$ octahedral cavities within Ti-atoms. In TiAl-based alloys for engineering applications, only the $\alpha_2$-phase possesses the Ti$_6$ octahedral cavity that can accommodate C. This is due to it’s intrinsic solubility in $\alpha_2$-phase which is not obtainable in both $\beta_0$ and $\gamma$ phases. Also, segregation of C at the $\alpha_2$/$\gamma$ interface deters $\gamma$-laths thickening thereby resulting in finer $\gamma$ lamellae. Moreover, lath thickening reduction and increase in nucleation sites are major reasons for lamellar microstructure refinement in C-containing TiAl-based alloys [34]. However, Liu et al. [89] noticed that Nb addition contributed greatly to the rise in solid solubility of C in TiAl-based alloy reaching 2–3 at.% C. A requirement for C maximum solubility is obtained in the case of $\gamma$-phase relative to Al concentration which increases C solubility for Al-lean stoichiometric compositions [7]. This is corroborated by the excess Ti atoms occupying Al sites and creating Ti$_6$ octahedral cavities to accommodate C. Addition of transition metals as an alloying element enhances the solubility within the $\gamma$-phase for interstitial elements [4, 54, 89]. This is because they prefer to occupy the Li$_6$ lattice of Ti sites. Nevertheless, the stoichiometric B2 structure has no site that can encourage the $\beta_0$-phase by substituting atoms of transition metals, thus, limiting solubility of interstitial atoms like C [7]. Schwaighofer et al. [110], studied the addition of 0.75 at.% C in a TNM alloy using APT to determine the phase compositions present which agreed with Klein, Clemens, and Mayer [7]. The latter explained that the incorporation of C increases

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**Figure 4.** Showing the (a) proximity histograms across the interfaces (b) APT reconstruction containing $\beta_0$ and $\omega_0$ phase Nb (green) and Mo atoms (red) were indicated as reported by [7].
nano-hardness by solution strengthening to form carbides within the α₂ and γ phases verified by APT. However, owing to poor solubility of C in the βₐₐₜ phase, an increase in the overall C content diminishes the nano-hardness of the β₀-phase. Hence, C is said to be an α₂-phase stabilizer [3].

In the work of Li et al. [6], the influence of C on the elevated temperature mechanical properties of Ti–43Al–6Nb–1Mo–1Cr alloys was investigated. It was reported that 0.5 at.% C increases both the elongation and UTS of the alloy; as 7.07% and 643.85 MPa (at 800 °C), 23.55% and 540.02 MPa (at 850 °C) with 40.5% and 389.82 MPa (at 900 °C), respectively. At elevated temperatures, a reduction in elongation is observed for C content between 0.5 to 1.0 at.% while the UTS increases. This is ascribed to the decreasing lamellar (α₂+γ) colonies sizes, equiaxed crystals transformation to columnar crystals, the disappearance of segregations and carbides developments. Since C is an α₂/stabilizer, it causes the eutectoid temperature to increase and shifts solidification path in TiN alloys to L/L → α−β/L−α+β from L/L→β/α+β [6].

Furthermore, Liu et al. [89] reported that C addition of 5 at.% changes the solidification pathway of Ti–46Al–7.5Nb–0.5Si–0.2B to L → L + H (Ti₅AIC) → L + α + γ + H → γ + α + H from L → L + β → β + α → α + γ → γ + α₂. The as-cast microstructure was reported to comprise of FL (α₂+γ) microstructure and eutectic silicide at the dendritic region. A large quantity of randomly dispersed primary Ti₅AIC particles was detected in the dendritic region. The Ti₅AIC primary carbide gave microhardness value of about 1068 HV leading to the increment from 325 to 917 HV of the matrix. Song et al. [111], investigated the effects of C on Ti–46Al–8Nb–0.7C alloy at intermediate temperatures. Equiaxed γ-grains at lamellar boundaries with decomposed α₂-laths were noticed at higher stress and creep temperatures. The induced H-carbide precipitation at the interface of α/γ lamellae resulted in the transformation of the α₂-laths. The high-temperature stabilization of P-carbides in the γ-internal structure reduces at high creep temperatures which barely affected the P-carbides precipitation and morphology development.

The influence of C addition on a dual-phase Ti–46Al–4Nb alloy with respect to hardness and microstructure was investigated by Cabibbo [34]. It was demonstrated that an increase in hardness leads to diminishing lateral size in the twinning of γ-phase invariably obstructing sliding of the dislocations. It was shown that hardness of TiAl alloy was largely dependent on α₂-phase volume fraction and quantity of C it dissolves. Bazhenov et al. [104], studied the effect of 0.8 at.% Zr+0.2 at.% Y and 2.3 at.% Y on mechanical properties of TiN-B1 alloys. The microstructural analysis revealed that α₂, γ, and β phases were low in Y content and Al₂Y contained virtually all the Y. The addition of Y reduces tensile strength and elongation property of the TNM-B1 alloy. Large Al₂Y-phase was observed after 2.3 at.% Y addition at the colonies α₂+γ boundaries; while increased β quantity causes a reduction in mechanical properties. The UTS and EL decrease due to Y addition of up to 2.3 at.% in the TNM-B1 alloy. Also, a slight reduction in mechanical properties was noticed with the combined addition of 0.2 at.% Y and 0.8 at.% Zr. The presence of massive quantities of Al₂Y and β phases is responsible for the reduction in TNM-B1 alloy mechanical properties.

Furthermore, β₀-phase tends to be partitioned by Mo, thereby, reducing β₀-phase and increasing Mo in this phase which restrains ω₀-phase formation. A reduction in the nano-hardness is effected through the privation of ω₀-phase within β₀-phase of the C-containing TiAl alloy as non-precipitation-hardening alloying. Studies investigating the influence of C in TiAl-based alloys have mostly been about decreasing the recrystallization kinetics and stabilization of the microstructure [112]. Klein, Clemens, and Mayer [7], also reported that C increases the stability of TNM alloys microstructure. This is due to solute-drag effects and strong partition of C by weak redistribution restraining recrystallization of new grains being formation. Precipitation initiates immediately the α₂-phase is saturated within the interstitial elements.

3. Characteristic effects of silicon additions in TiAl alloys

Si-containing TiAl alloys are potential materials for elevated temperature utilization in the aerospace and automobile industries. Addition of Si to TiAl-based alloys as an alloying element is often controversial. Discussions available in literature are usually on microstructural stability and creep resistant associated with Si addition [4, 54, 112, 113]. However, Si is known to be a highly promising alloying element in improving elevated temperature strength of Ti–Al alloy systems [38, 114]. This is due to the Ti₅Si₃-phase (ζ-silicide; HCP structure) formed that acts as a strengthening phase for composites’ reinforcement based on TiAl inter-metallic alloys [115]. Silicide (ζ-Ti₅Si₃) is an intermediate phase that has considerable stiffness with superb oxidation and corrosion resistance [38]. Thus, Si is well suited for enhancing oxidation resistance through the formation of Ti₅Si₃-phase. Ti–Al based alloying systems with Si are identified at the α₀/γ lamellar interfaces with precipitates of ζ-silicide (Ti₅Si₃) known to be responsible for diminishing the dislocation mobility and interfacial stability [7, 54, 116, 117]. Si addition of ~0.5 at.% results in the formation of fine Ti₅Si₃ particles while between 2.0-6.0 at.% of Si produces large Ti₅Si₃ particles or whiskers nucleated at γ/γ and γ/α₂ interfacial sites [3, 113]. This tends to align particles at the interface of lamellae, particularly for alloys that have low quantity of α₂-phase after heat treatments in the dual-phase region. The Ti₅Si₃ precipitate formation is desirable for resistance to creep through phase stability improvements and dislocation motion prevention [116]. The precipitation of Ti₅Si₃ from Si-bearing TiAl alloys in the γ-phase occurs heterogeneously and the nucleation depends on the dislocation types [113]. Owing to poor Si solubility in the γ-phase, precipitation of silicide emerges when the α₂-phase which dissolves most of the Si is reduced in quantity. According to Sun and Froes [113], a true-twin type γ/γ+ lamellar boundary is a Ti₅Si₃ precipitate-free γ/γ boundary because of its low boundary energy. Also, the growth of needle-like Ti₅Si₃ particles at the γ/γ boundaries is regulated through interfacial diffusion of Si. Moreover, the growth of rounded Ti₅Si₃ particles in the γ-matrix is controlled by the volume distribution of Si, where the Ti₅Si₃/γ interfaces are incoherent.

It has been reported by Du, Wang and Zhu [116], that Si added to cast TiAl-based alloys are found to be beneficial to creep resistance enhancement without sacrificing the tensile properties. Si of 0.3 at.% in Ti–47Al–2Cr–1Nb–0.8Ta-0.2W-0.15B-0.3Si alloy produced through powder metallurgy (PM) resulted in unfavourable resistant to creep effects. It was concluded that the creep mechanism was not affected by Si addition, but influences the microstructural stability. Si was reported to be situated at the lamellar interfaces with precipitates of silicide and recrystallized γ-phase. Generally, Si atoms are located inside the matrix as solute due to the powder metallurgy process. Thus, making the detrimental effects more serious than the benefits of Ti₅Si₃ precipitates given rise to poor creep resistance of the alloy. Also, Karthikeyan and Mills [112] assert that Si and C have considerable in TNM-B1 alloy produced through powder metallurgy (PM) resulted in unfavourable resistant to creep effects. It was concluded that the creep mechanism was not affected by Si addition, but influences the microstructural stability. Si was reported to be situated at the lamellar interfaces with precipitates of silicide and recrystallized γ-phase. Generally, Si atoms are located inside the matrix as solute due to the powder metallurgy process. Thus, making the detrimental effects more serious than the benefits of Ti₅Si₃ precipitates given rise to poor creep resistance of the alloy. Also, Karthikeyan and Mills [112] assert that Si and C have considerable influence at all creep stages in diminishing the strain rates through precipitation hardening. Microstructural stability before creep, increases creep resistance through the elimination of metastable α₂ precipitates nucleation and lowering dynamic recrystallization driving force in alloys containing Si and C. Silicon was also reported to improve oxidation resistance, but also reduce the oxidation resistance when Si quantity is increased. However, Jiang et al. [72] reported that Si and Nb combinations could be beneficial to improve TiAl alloy resistant to oxidation substantially.

Si-containing TiAl alloys usually have a high-temperature varying quantity of α₂ and β phases, respectively. A two-step heat treatment is suggested because these phases change the reaction sequences in TNM alloys due to Si addition producing nano-lamellar structures [3, 4]. This makes the γ-phase lamellar to be formed inside the grains of α₂ by adequate thermal activation owing to the alterations in crystal structure created by two Shockley partial dislocations [7]. Klein et al. [1], heat-treated Ti-43.5Al–4Nb–1Mo–0.1B–0.3C–0.3Si alloy for 15 min at 1350 °C with oil quenching. This was followed by annealing at 800 °C between 15 min
to 24 h and furnace cooled. The microstructural image is shown in Figure 5. The SEM image could not resolve the ultra-fine structure of the lamellar colonies of α2/γ phases. This was made known by the transmission electron microscopy (TEM) as observed in Figures 5a and 5b. However, only the prior β0-phase that decomposed into γ-platelets and ω-particles with few undissolved β0-phases during annealing could be resolved by SEM. The γ-lamellar formed from the transformation of α2-grains tend to align parallel through the mechanism known as the BOR [37]; that has been explained by several authors [51, 76, 81]. Also, it was observed by Klein et al. [1], that the ζ-Ti5Si3 precipitates were not noticed around the lamellar interface.

In a study conducted by Lee et al. [114], ternary Ti–Al–Si alloy was synthesized through mechanical milling followed by SPS to examine their plastic deformation behaviour. The microstructure was rich in thermodynamically stable phases of α2-TiAl3 and ζ-Ti5Si3 intermetallics formed through invariant reaction. The initial powder structural properties and plane defects of sintered product influenced the brittle-ductile transition, thereby, increasing the fracture toughness of the Ti5Si3 alloy. The Crystallographic patterns and microstructure exposed the stacking faults or twining brought about by the acute plastic deformation. This is attributed to the phases of Ti5Si3(HCP) or TiAl3(FCC) slip system which is dependent on the refined grains and intermetallics nucleated at ambient temperature. Based on the crystallographic nature of metallic materials, BCC and FCC demonstrate satisfactory slip system while HCP displays inadequate slip system with temperature-dependence.

Knaislova et al. [38], studied the oxidation behaviour of Ti–Al–Si alloys prepared by PM at elevated-temperature. The alloy (TiAl10Si30) having the highest content of silicon gave the best resistance to oxidation through repetitive heating and cooling. The chemical reaction of the alloy displays good adhesion with the oxide layer and diffusion growth which is influenced by the high Si content. The Ti–Al–Si alloy had high microhardness after annealing at 1000 °C for 400 h. The hardness values remain the same even with prolonged oxidation time. In a related study by Knaislova et al. [115], phase composition, microstructure and hardness of Ti–Al–Si alloy fabricated through MA + SPS were examined. After compaction, the alloy (TiAl15Si15) contained uniform microstructure of small quantity of TiAl3 and Ti5Si3 in TiAl-matrix. Due to fine Ti5Si3-g-phase, the alloy microhardness rises to 865 ± 42 HV5. Apart from the TiAl2-phase, the phase composition observed was the same as in Knaislova et al. [38], independent of preparation conditions. It was also reported that the porosity is exceptionally low but has better hardness, UTS, and abrasive wear resistance compared to the similar alloy in ref [38] produced through SPS combined with reactive sintering.

In another work by Knaislova et al. [117], mechanical properties, phase compositions and microstructure of ternary Ti–Al–Si alloys produced by arc melting were investigated. The findings were compared with Ti–Al–Si produced by MA + SPS. The arc melted alloy is had a structure of very coarse Ti5Si3 in TiAl-matrix with porosity and cracks. Fast cooling of the melting metallurgy was suggested to be responsible for the cracks observed in the alloy. The PM processed alloy had a regular structure of fine-grains, low porosity, and high value of microhardness. Microhardness value record for samples processed by MA + SPS was almost twice the values recorded by the arc-melted Ti–Al–Si alloys. It was concluded that the melting process needs to be optimized to reduce the material porosity.

It has been reported by various authors [1, 3, 51] that Si dissolves by substituting for Al as determined by ab initio calculations. This leads to Al deficiencies in Si-containing TiAl-based alloys, but strong β-stabilizers like Mo if present would substitute for Ti which relocates to the Al-sites. While the Ti is diminished for the off-stoichiometry α2-phases with increasing Al content. Interstitial elements like C and Si with substitutional elements such as Mo, Nb and Cr would tend to balance the TiAl-based alloy chemistry to provide an equilibrium between high-temperature creep resistance and ductility [54]. The crystal structure of the α2-phase with the energetical chemical environment makes Si preferentially substitute Al [3, 4]. Typical TNM alloys are composed of a significant amount of α2-phases far more than γ-TiAl with Al content between 45-48 at.%. The α2-phase of the TNM alloys stores almost all quantities of Si present; thereby, determining the overall solubility and/or precipitation of Si. Thus, limited or no interfacial precipitation occurs because of almost complete dissolution of Si within the α2/γ colony. However, the ordered structure of α2-Ti3Al and γ-TiAl made TiAl-based alloys brittle but studies have shown that elements like Nb, Mo, Mn, V and Cr could alter the volume of the unit cell, modify the density distribution of electrons and re-order bonding. Thus, producing TiAl alloys with better ductility and fracture toughness.

4. Applications and future outlook

This section succinctly enumerates the various fields of application where TiAl-based alloys are being employed and give an impetus for future works on these types of intermetallic alloys.

4.1. Typical application of TiAl-Based alloys

It is common knowledge that there is no ‘one cap fits all’ composition of alloys meant to serve for all purposes. However, alloy compositions are
typically adapted in combination with the appropriate production tech-
niques to accomplish desired properties for a specific use. Currently, Ti
alloys account for one-third of modern aircraft engines’ weight after
nickel-base superalloys; which is the second commonly used material
[103]. Although processing Ti alloys are expensive which hamper its
economic viability, the aerospace industry is a multi-billion-dollar
industry where performance and safety are paramount [83].

In the manufacturing of critical components subjected to corrosive
environments and high-temperatures, TiAl is a potential alternative
material employed in the field of automobile and aerospace [77].
Weight saving is of prime concern for flight and TiAl alloys have an
excellent strength-to-weight ratio in comparison to aluminum, nickel,
and steel alloys. This is expected to allow producers of the aircraft to
decrease the overall weight, thereby, minimizing fuel consumption and
expenses [14, 83]. In 2006 General Electric (GE) introduced
Ti-48Al–2Cr–2Nb alloy to fabricate LPT blades of their GeNex engines
used by aeroplanes of Boeing’s 747-8s and 787s [109, 111]. The
PW1100G Geared-TurboFan (GTF) engines’ LPT blades was developed
using a TiAl alloy. Also, the same TiAl alloy was used for LEAP™
engine LPT blades by SNECMA [14]. In comparison to other class of
engines, GeNex engines deliver 50% noise reduction, 20% increment in
fuel efficiency, and 80% NOx emission reduction [30, 83]. Although,
feasibility studies for the TiAl-based alloy high-pressure compressor
have been conducted by Snecma and Turbomeca. The GE 4822 alloy
LPT blade is the most commercially available intermetallic component in service. Pratt & Whitney including Volvo has also been
conducting thorough work on TiAl-based alloys to develop parts like
turbine damper, blade retainers, shrouds, and compressor blades [14,
30]. The potential of TiAl-based alloys for turbine engines is well
recognized by major manufacturers in the aerospace industry. Howev-
er, aerospace engineers are faced with the obstacle of overcoming poor
oxidation resistance at an elevated temperature when designing air-
craft’s engine components [83].

The automotive industry has also seen increased applications of TiAl-
based alloys. Some parts are now being fabricated using TiAl alloys
owing to high-temperature resistance, low density, and high fatigue
strength [83]. It is used for piston connecting rods of sports cars because
it reduces vibration in the damping system. Also, due to
high-temperature strength and low density, it is used for engine valves
allowing the formation of lasting, but valves with lightweight that could
improve engine operations. Owing to weight reduction, it has found
usage in making valve cups. Mitsubishi Motors was reported to have used
TiAl alloy in their diesel or gasoline engines of Lancer 6 model as turbine
wheels of turbochargers in high-performance racing cars [14].

They have found extensive use in gas turbines due to their attractive
mechanical properties [118]. Nevertheless, TiAl poor resistant to
oxidation above 800 °C is still inadequate. TiAl-based alloys are reported
to be extensively utilized for corrosion prevention in seawater environ-
ments and ideal in chemical and petrochemical industries; due to their
chemical and mechanical properties [83]. TiAl-based alloys remain one of
the highly biocompatible materials. Hence, it is used in biomedical
applications as implants for orthopaedic, dental, and cardiovascular
applications. This is because of its non-immunogenic, non-toxic, and high
strength-to-density ratio in addition to its remarkable corrosion resis-
tance property [119].

The past two decades have seen intense industrial collaborations to
advance and produce novel materials based on TiAl alloys. For instance,
Pratt & Whitney and General Electric (GE) are highly involved in
different collaborations. This is done to develop an innovative TiAl-based
alloy that could operate at higher temperatures for applications in
advanced aircraft turbine engines. Specifically, Pratt & Whitney had a
Cooperative Research and Development Agreement (CRADA) with
Lawrence Livermore National Laboratory to produce TiAl-based alloy
materials of improved ductility and toughness for commercial jet engines
[120]. Collaborations are however not limited to industries. Some other
research groups are participating tremendously towards the advance-
ment of novel TiAl-based alloys to further enhance the properties of
previously established TiAl alloys [22, 81].

4.2. Future outlooks, challenges and prospects

Intermetallic γ-TiAl-based alloys fulfill various crucial prerequisites
for lightweight structural applications in the automotive and aerospace
industries [9, 14, 22, 101]. As stated earlier, Ti–Al alloying systems are
potential weight saving high-temperature materials. However, they are
rather quite expensive to manufacture owing to their poor machinability,
hot-workability and castability [10, 17, 30]. It should be noted that
because of the inherent brittleness of TiAl, processing through the
wrought techniques must be conducted at elevated temperatures (nor-
mally above 1100 °C) and multistep operations of low deformation rates
[30]. This requires using distinct equipment in specific gas atmospheres.
Solidification during melting metallurgy has often led to microalloying
elements segregation and macroscopic columnar grains. This method has
been presented to demonstrate greater microstructural flexibility. Also, it
has the benefit of improved ductility through thermal-mechanical treatments, so that equiaxed or finer duplex microstructures could be
attained [30]. Nevertheless, the manufacturing of these alloys is still
problematic. Melting metallurgy is confronted with the issue of high
reactivity of melt with melting crucibles, high melting points of inter-
metallic phases, exothermic reactions during intermetallic phase forma-
tion and cracks and pores formation [115]. All these difficulties
associated with wrought processing motivated researchers to study addi-
tive manufacturing (AM) technology for producing TiAl-based alloy
products [11, 14, 30, 31, 101, 121].

The application of different additive manufacturing (AM) technolo-
gies to fabricated TiAl-based alloys in the past two decades have gained
considerable interests. The most widely used AM technology in pro-
cessing composites is Selective Laser Sintering/Melting (SLS/M), Laser
Engineered Net Shaping (LENS), Electron Beam Melting (EBM) and Fused
Deposition Modelling (FDM) [120]. The benefit of AM is the direct
production of complex shapes, near-net-shaped parts of high quality,
uniform components with minor post-processing and a significant
reduction in scraps [30]. Due to the high precision in AM techniques, it
could be used to make several aerospace components with complex
shapes from TiAl-based alloys. Among the AM technologies, LENS, EBM
and SLS have been successfully used in the development of TiAl alloys
[31, 43, 81, 101, 122, 123].

Even though these technologies display realistic capacity, most
works are still been focussed on achieving fully dense parts with least
defects through processing parameters optimization. Currently, EBM is
found to display maximum readiness in term of technical feasibility
[30]. Most AM suffers from high thermal gradient created by the high
cooling rate and low substrate temperature leading to complex phase
transformations due to high-energy input and thermal history [47]. Also,
even distribution and evaporation of Al result in inhomoge-
neous mechanical properties of TiAl alloy fabricated by AM technolo-
gies. This gives rise to density variations and subsequently leads to
reduced strength of final parts [120].

As reported earlier, β-stabilizing γ-TiAl-based alloys are gaining
awareness because they display outstanding workability with large-scale
production opportunities [124]. However, β-phase hardness is dependent
on the type of β-stabilizing element in the TiAl alloys. Cr, Mn, and V have
been reported to produce β-phase of low hardness while Nb, Mo and W
promote β-phase with high hardness in TiAl alloys. Consequently,
decreasing the β-phase hardness could prove to be helpful in the
enhancement of β-solidifying TiAl-based alloys’ ductility. Also, alloying
elements’ composition determines the resultant microstructures which
directly influences the elevated temperature mechanical properties of
γ-TiAl alloys. Thus, to improve its intrinsic ductility, it is essential to control the microstructural evolution. This could be achieved by adding alloying elements such as W, Mo, Nb, V, C and Mn which could also help in grain refinements or phase stability and further promote hot workability. This could be followed by a multi-stage heat treatment procedure and hot-pack or near-isothermal working. Previous works have shown that TiAl-based alloys’ plastic deformation is primarily restricted to the γ-TiAl phase. This is due to the ordinary dislocation glides, but the deformation mechanism occurs by mechanical twinning. Consequently, the γ-phase refinement would help enhance TiAl-based alloys’ mechanical properties [105]. Whereas, if the microalloying element diffusivity is lower than Ti, α2/γ phase boundary migration process could be hampered through discontinuous coarsening. Besides, the tendencies of alloying elements’ β-stabilizing order of effects would be very beneficial in the designing of TiAl-based alloys’ composition and microstructure to improve the mechanical properties; while mitigating the precipitation of the unwanted ω-related phases.

Briefly, the basis for the effective application of TiAl-based alloys as structural engineering materials is determined by efficiently adjusting the microstructure. This is attained through proper alloying and carefully tailored processing. This should improve the mechanical properties, especially ductility when the alloying element can stabilize and promote new microstructures. Therefore, it is pertinent and essential to recognize the basics of processing, alloy designs, microstructural characterization, the relationship between property and microstructure, characteristics of new alloys together with the effects during service. Moreover, it has been demonstrated that AM could be combined with hot deformation techniques in achieving good workability and microstructural flexibility. It expected that combination of a suitable AM technology such as EBM and LENS followed by multi-step heat treatment and hot working at intermediate temperatures would produce a unique combination of properties. This could be used for fabricating novel materials in the automotive and aviation industries. Finally, the increasing interests in structural engineering parts that could be used in automotive and aerospace applications are expected to consistently encourage more research in developing TiAl-based alloy components. Predictably, this same manner of inclination will continue for many more years to come.

5. Conclusions

1. The relatively newly developed γ-TiAl-based alloys are increasingly being applied into aero and automobile engines. Particularly, the β-solifying TNM alloys having balanced mechanical properties and hot workability.

2. The beta phase (β-phase) is a detrimental phase at the materials’ service temperatures which could be easily reduced and/or completely removed with appropriate heat treatment technique. This arises from the β-phase transformation to the hard and brittle β0 phase that is incompatible with the γ and α2 phases resulting in crack nucleation and propagation at the β0/γ interfaces. Hence, a decrease in the ductility at the service temperature.

3. Nb and Mo (both β-stabilizers) are vital alloying elements providing improved creep resistance, oxidation resistance and elevated temperature strength retention.

4. Apart from grain refinements, boron is also beneficial for both enhancement of strength and ductility specifically for materials with duplex phase microstructures.

5. The α0/γ phases precipitates within the β-matrix for β-solifying γ-TiAl-based alloys but not the same for alloys where α2-β phase precipitates. This α0-γ phase are not easily resolved by SEM analysis except by TEM and other high-resolution microstructural analysis equipment.

6. The addition of Si to TiAl-based alloys influences creep resistance and stabilizes the microstructures but Si as an alloying element is rather controversial.

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Additional information

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