# CHAPTER 5 DISCUSSION

## 5.1 The as-cast structures

The structures of all of the alloys confirmed that Nb was significantly soluble in comparatively large amounts in $\gamma$ and $\alpha_2$ phases, which has been found to be particularly advantageous for $\gamma$-TiAl alloys. The as-cast microstructures of Ti-46Al and Ti-48Al binary alloys revealed columnar and equiaxed structures aligned with the direction of heat flow of the button ingot; the alloys with higher Al and Nb contents resulted in a finely equiaxed structure, a fine fully lamellar microstructure, and the $\gamma$-TiAl, $\alpha_2$-$Ti_3Al$ were all observed. According to a study by Küstner et al., 2003 as cited by Appel et al. [24], binary alloys with Al concentrations $\geq$ 45 at.% exhibited structures consisting of relatively large equiaxed grains. Alloys with higher Al contents showed columnar grains which grew in the opposite direction to that of heat extraction. However, after the addition of Nb in Ti-46Al and Ti-48Al binary alloys led to an increase in volume fraction of the $\gamma$ phase which is confirmed by the results obtained from XRD (Figure 2.5-2.10). Based on the results of a study by Scheual et al. [72], additions of Nb into TiAl alloys can yield a resulting crystal structure with both Ti and Nb atoms on Al sites. This leads to a reduction in the c/a ratio of the tetragonal $\gamma$ TiAl cell to approximately 1, and according to the results of Liu et al. [75], Nb can be a solute in the $\gamma$ TiAl phase.

With respect to the as-cast microstructures, all alloys were found to have lamellar structures. In the alloys with high Al contents (the Ti-48Al alloy set), the specimens have grain sizes with lamellae smaller than those found in the low-Al content (Ti-46Al) alloys. Ti-46Al-10Nb alloy has a fully lamellar structure which is in agreement with the results of Liu et al. [75]. They also found that a decrease in Al content results in an increase in the volume fraction of the $\alpha_2$ phase, which leads to a decrease in lamellar spacing of the lamellar structure. The results is also in agreement with that of Yamaguchi et al. [68] who found that additions of Nb have the effect of decreasing volume fraction of $\alpha_2$ phase. This promotes and stabilizes the lamellar microstructure because the $\alpha_2$ to $\gamma$ transformation proceeds by the migration of $\gamma/\alpha_2$ lamellar boundaries. Additionally, the motion of ledges along these boundaries is accomplished by the process of elemental migration. Nb atoms have a large size difference compare with Ti and Al atoms, and hence, Nb atoms segregate to the ledges along the $\gamma/\alpha_2$ lamellar boundaries. Nb has the lowest diffusivity among the major alloying elements in both $\gamma$-TiAl and $\alpha_2$-$Ti_3Al$ phases. Therefore, the addition of Nb reduces the mobility of the ledges during the transformation. Hence, Nb also assists the reduction of ledge mobility.

## 5.2 The solution-treated microstructures

The microstructures of the samples formed by solution treatment showed that the four alloys occurred in two structural types (i.e., fully lamellar and small random regions of equiaxed $\alpha_2$ phase and $\beta$ phase). Ti-46Al-2Mo and Ti-46Al-4Nb-2Mo alloy specimens have a finer colony size than Ti-46Al-2Cr and Ti-46Al-4Nb-2Cr alloys. Ti-46Al-4Nb-2Cr alloy exhibited the highest volume fraction of the transformed equiaxed microstructure at the grain boundaries. Sreenivasulu et al. [9] reported that decreasing Nb content and increasing Mo content was sufficient to increase the volume fraction of the transformed equiaxed microstructures compared with Ti-46Al-4Nb-2Cr specimen.

Therefore, the kinetics of the lamellar to equiaxed transformation is decreased by Nb and increased by Mo. The addition of Mo resulted in an increased stability of β phase. BSE images revealed that Mo more strongly segregated into β phase compared with Nb and Cr (Figure 4.14 (c) and (d)). Imayev et al. [79] found that Nb and Mo effectively stabilized β phase along the α grain boundaries while hindering the growth of α grains. Indeed, the addition of Mo expands the β phase region toward the α-phase and γ-phase regions in the isothermal section of the ternary phase system [14]. When heat-treated, the diffusion of Mo and Al occurs in opposite directions, which tends to equilibrate the gradients, and distinct microstructural zones exist, depending upon the extent to which diffusion has occurred. Interestingly, alloys with Cr and Mo additions solidified in a single-phase β region. Although segregation existed within β grains (forming a complete solidification stage), the composition gradients were not notably strong, and the structures observed within the β grains were uniform. The distribution of the β phase was dominated by primary post-solidification transformation, which resulted in the formation of a lath in Mo-lean alloys and the occurrence of γ plates, which directly formed from β phase in Mo-rich alloys [65].

## 5.3 Intermediate and slow-cooled microstructures

Similar microstructures, mainly $\gamma+\alpha_2$ phase structures, were observed in all alloys obtained from furnace cooling and air cooling after solution treating. However, detailed observations revealed that both Ti-46Al-2Cr and Ti-46Al-4Nb-2Cr alloys exhibited a coarsening of lamellar microstructure after cooling in the furnace, while Ti-46Al-2Mo microstructure was a duplex with small equiaxed grains located at the grain boundaries.

Duplex structure coarsening, with large colonies of equiaxed grains around the full lamellae, was found in Ti-46Al-4Nb-2Mo alloy after furnace cooling. In the case of air cooling Ti-46Al-4Nb-2Mo alloy possessed a fine duplex structure, which was very different from the other three alloys. For air-cooled Ti-46Al-2Mo alloy, its microstructure was fully lamellar, while Ti-46Al-2Cr and Ti-46Al-4Nb-2Cr alloys had duplex structures with small equiaxed colonies at the grain boundaries. Interestingly, the structures of these two air-cooled alloys, Ti-46Al-2Cr and Ti-46Al-4Nb-2Cr, were likely to contain small Widmanstätten laths with orientations related to the γ grain boundary (Figure 4.18 (b) and (d)). Generally, Widmanstätten laths can occur by nucleation under intermediate cooling rates; if so, they are generated with specific misorientations with respect to the parent lamellar structure. According to the studies of Dey [40], Dey et al. [61], Zhang et al. [63], and Hu et al. [64], which discuss the specific crystallographic orientation relationships between Widmanstätten laths and lamellae, it appeared that between the $\alpha_2$ phases of Widmanstätten laths and lamellar structures, approximate 65° misorientations around the $\langle 1\bar{1}00\rangle_{\alpha 2}$ axes were found, which are related to a hexagonal twinning system ($\{11\bar{2}2\}\langle\overline{11}23\rangle$) in the prior α phase. Earlier, this was defined as the $\alpha_{2W}/\alpha_{2L}$ 65° ($\alpha_2$-Widmanstätten denoted as $\alpha_{2w}$ and $\alpha_2$-lamellar denoted as $\alpha_{2L}$) misorientation. Additionally, a second relationship between the γ laths of Widmanstätten laths and lamellar structures was found with approximately 50° rotation around $\langle 110\rangle_{\gamma}$ axes. This minimum angular rotation is actually close to the Σ11 coincidence site lattice (CSL) boundaries (approximately 50.48° around the $\langle 110\rangle_{\gamma}$ axes). When comparing the experimental results obtained from Ti-46Al alloy with Cr and Mo additions, it can be concluded that Nb and Cr additions promote the development of Widmanstätten laths. Additionally, these additions facilitate twinning deformation due to a decrease in superlattice intrinsic stacking fault energy in $\gamma$ phase [8]. However, the morphology of the feathery-like structures of Ti-46Al-2Cr, as shown in Figure 4.17 (b), grow in two types as (i) $\gamma_f$-structure attached to the grain boundaries, which will further be denoted as the "$\gamma_{f\text{-}gb}$ structures," and (ii) $\gamma_f$-structures found inside the grains, which will be further referred to as the "$\gamma_{f\text{-}int}$ structures."

## 5.4 Rapid-cooled microstructures

The rapid cooling rate experiment was focused on the two quaternary alloys (Ti-46Al-4Nb-2Mo and Ti-46Al-4Nb-2Cr), which were subjected to solution treatments and cooled by oil and water quenching. It is found that the phase transformations resulted in the same microstructures (i.e., massive-$\gamma$ with $\alpha_2$ matrix). Interestingly, the addition of Cr in Ti-46Al-2Cr ternary alloy had a greater effect on the massive transformation. Mo additions yielded a massive structure with some lamellar structures. When comparing the effect of quenching media on the quantity of massive structure formed, the volume fraction of massive-$\gamma$ formed by oil quenching was greater than by water quenching for both Ti-46Al-4Nb-2Mo and Ti-46Al-4Nb-2Cr.

In contrast, Ti-46Al-2Cr ternary alloy was different in that the resulting structure was a $\alpha_2$-massive matrix with smaller $\gamma$-massive phase, upon water quenching. This result indicated that the rapid cooling either promoted the formation of $\alpha_2$-massive or retained the $\alpha_2$. According to a study by Hu et al. [57], in some alloys, the massive transformation regime is either too narrow or is shifted to a very high cooling rate side, which is not easy to reach in practice. Thus, in a given alloy, a totally massive microstructure will be formed for a specific cooling rate range. If the cooling rate is increased, some regions of the sample will contain retained $\alpha_2$, whereas if the cooling rate is decreased, some regions will form feathery/lamellar microstructures. When additions of Nb were made to TiAl alloys, $\gamma$-massive developed in all alloys subject to oil- and water-quenched processes. Because Nb has a low diffusivity in TiAl alloys, the formation of diffusion-related feathery/lamellar transformations is suppressed, allowing the massive transformation to occur [57]. The addition of Nb also extends the massive regime in TiAl alloys toward the rapid cooling rates observed between oil and water quenching. The additions of Mo and Cr in TiAl alloys were found to form similar feather-type microstructures as those of the massive-$\gamma$ formed by both oil and water quenching.

## 5.5 EBSD analyses

The massive-$\gamma$ transformation mechanism has proved difficult to explain. The observation of the nuclei of the massive formation has been especially difficult to explain because the massive-$\gamma$ structure can nucleate from lamellar structure above the usual massive transformation temperature [80]. Additionally, the massive-$\gamma$ structures can nucleate from single atom jump diffusional $\alpha \rightarrow \gamma$ phase transformations and spread in all directions with no large-scale compositional changes [65]. Some proposed mechanisms have indicated that the transformation to massive-$\gamma$ occurs because of a twinning mechanism between the massive transformation processes. Thus, one strategy that can be used to explore the massive transformation phenomenon is to observe the formation of twins in the (111) plane because this plane is the nucleation site of the massive-$\gamma$. If the twinning does occur at this point, the relationship could reveal the orientation between the massive transformation and the alpha matrix [67]. In the present study, we found that the massive-$\gamma$ formation was related to $\alpha$-parent phase in all alloys with either water or oil quenching. The orientation relationship in this study was found to indicate the same orientation with $\{111\}_{\gamma}//\{0001\}_{\alpha}$, which is confirmed in Figures 4.24-4.27 (panel d in all figures). The probability mechanism that could explain the relationship of the orientation in this study was the formation of massive-$\gamma$. This massive-$\gamma$ transformation was nucleated at the grain boundary of the prior $\alpha/\alpha$ grain, which confirmed this massive transformation mechanism (see Figure 4.27). Although the initial nucleus may be coherent, if twinning occurred on the {111} plane which is not the original interface, it would result in a massively transformed gamma that no longer had a simple orientation relationship with the alpha matrix [81]. The formation of massive-$\gamma$ is clearly explained in earlier publications [e.g., Refs. (81, 56)], which identified a competition between the growth of lamellae and the growth of massive-$\gamma$ under the cooling conditions that were used to refine the microstructures. The results of all cooling rates of two different compositions (i.e., Ti-46Al-4Nb-2Mo and Ti-46Al-4Nb-2Cr) indicated that the alloy with Cr addition as the quaternary alloying element promoted a massive transformation mechanism, which was greater than that produced by Mo addition. However, Mo promoted the formation of lamellae more than Cr [82]. The use of Nb as the alloying element generally retards the formation of lamellar microstructures which could be due to low diffusivity, and Nb is a slow diffuser in both TiAl and $Ti_3Al$. Indeed, Nb has a diffusion coefficient that is approximately an order of magnitude lower than that of Ti [83,84]. Interestingly, Cr is also a slow diffuser in both TiAl and $Ti_3Al$, similar to Nb [83]. Thus, Nb and Cr both effectively extend the regime of the nucleated massive-γ transformation of Ti-46Al-4Nb-2Cr, more than in Ti-46Al-4Nb-2Mo. Further, we found that increasing the quenching rate (from OQ to WQ) led to a reduction in the volume fraction of massive-γ for all of the compositions which confirmed the results of previous research [e.g., Ref. (65)].

## 5.6 Microhardness

The results of the microhardness tests of the as-cast binary and ternary systems revealed that the fully lamellar structure exhibited higher hardness values (Ti-46Al-10Nb ternary alloy) than all as-cast alloys. In considering the microhardness in the heat-treated alloys, it was found that all alloys have higher microhardness values than the as-cast alloys. Thus, the results for the microhardness of massive structures are higher than those lamellar structures. A study by Saage et al. [65] found that mechanical properties of these types of structures and reported that their tensile properties are far better than those of either duplex structures or as-cast structures, and exhibit enhanced ductility and tensile strength which is in general agreement with the present study. Additionally, according to the report by Wu et al. [85], duplex microstructure can have ductility as high as 4% but possesses a low ultimate tensile strength and poor creep properties.

## 5.7 Future work

1) The mechanical property of TiAl alloys in this research was microhardness only because the work was limited by the melted size and weight of the

samples. Other high temperature properties should be investigated in the future.

2) The orientation relationship between the product phase (γ-massive) and the parent phase (α-phase) was confirmed with Kikuchi maps and pole figures only. Further characterization by other means is needed to observe this relationship, such as the combination of TEM with EBSD.

Due to the limited access to analytical instrumentation, i.e., a hot isotactic press (HIP), a high vacuum arc furnace, a skull induction furnace, a transmission electron microscope (TEM), further investigation from these perspectives will be valuable.