Effects of Sn on the densification and microstructure of a Ti-48Al-2Nb-0.7Mn-0.3Si-1Sn alloy fabricated from cold-pressed powders through vacuum melting

John Jimmy Masache Ellard1, Maria Ntsoaki Mathabathe2*, Charles Witness Siyasiya1, and Amogelang Sylvester Bolokang2, 3, 4
1Department of Material Science and Metallurgical Engineering, University of Pretoria, South Africa
2Manufacturing Cluster, Advanced Materials Engineering, Council of Scientific Industrial Research, South Africa
3Department of Physics, University of the Western Cape, Private Bag X 17, Bellville 7535, South Africa
4Department of Physics, University of the Free State, P.O. Box 339, Bloemfontein, ZA9300, South Africa

Abstract. The density and microstructure of a modified second-generation γ-TiAl intermetallic alloy with a nominal composition of Ti-48Al-2Nb-0.7Mn-0.3Si-1Sn (at. %) were investigated and compared with similar low-Nb containing alloys reported in the literature. The alloy was successfully fabricated from blended and uniaxial cold-pressed precursor powders and subsequently arc re-melted under vacuum and heat-treated. From the obtained results, the alloy showed improved castability as evidenced by the absence of shrinkage cavities and the highest relative density of 99.87%. In as-cast condition, the microstructure comprised fine-grained dendritic structures of γ-phase and γ + α2 lamellae with a mean grain size of about 49 μm which transformed into a well-developed duplex structure consisting of γ grains and γ + α2 lamellae, and traces of Ti5Si3 precipitates after heat treatment. The alloy exhibited a more significant grain refinement in as-cast condition than its counterparts reported previously.

1 Introduction

Although the past decade has witnessed a market penetration of γ-TiAl alloys in aerospace and automobile industries, their applications remain limited owing to the complex processing route they undergo to minimise defects viz. pores and shrinkage cavities [1]. Güther et al., [2] reported that to produce sound γ-TiAl semi-finished products, the raw materials have to go through a series of processing stages viz. vacuum arc remelting (VAR), skull melting, centrifugal casting, feeders cutting and hot isostatic pressing. This complexity of the fabrication process increases the production cost, hence, inhibiting the use of γ-TiAl-based...
alloys as economically feasible structural materials [3]. To reduce the production cost, Mathabathe et al.,[4] employed a different approach by amalgamating the powder metallurgy to produce green compacts at room temperature and VAR to melt the compacts into ingots. However, the resulting ingots also contained shrinkage cavities and a significant level of porosity which diminished the relative densities of the alloys. Recently, Ellard et al.,[3] demonstrated that the level of porosity in these alloys can be minimised by the blending of precursor powders having different morphologies and a considerable size difference between them. The researchers elucidated that this kind of powder blending helps the packing density reach its maximum level during compaction by allowing the finer particles to fill the gaps left by the larger ones. Subsequently, the maximum density is inherited in the ingot during the melting of the alloys. Nevertheless, since fine metal powders are expensive [5], the powder characteristics blending approach for ingot densification may not be cost-effective. Therefore, there should be a way of cost-effectively minimising the shrinkage cavities and pores during the casting of γ-TiAl alloys.

It is well established in the literature that Sn profoundly affects the castability of Al and Mg alloys. Turen [6] reported that the addition of 0.5wt % Sn improved the castability of AZ91 magnesium alloy by increasing the fluidity. Moreover, the researcher noted the increase in tensile strength and elongation by the addition of up to 0.5wt % Sn. In another study, Jihua et al. [7] found that the addition of Sn to Mg-Zn-Al alloys improved the ambient and elevated temperatures’ strength. This was attributed to the formation of dispersed short rod-like Mg2Sn particles.

Concerning the additions of Sn to γ-TiAl-based alloys, Pan et al. [8] reported that a small amount of Sn addition was capable of increasing the density of the high Nb-containing TiAl fabricated by pressureless sintering. Moreover, the researchers attested that Sn addition significantly reduced the alloy’s melting point, and directly affected the sintering behaviour and with increasing Sn content, the optimum sintering temperature decreased. However, these results for high Nb-containing TiAl alloys produced by the pressureless sintering route may not be applicable to the low Nb-containing TiAl alloy systems. Moreover, the sintering route may not be suitable for other applications of the alloys.

It is important to note that the attainment of high density alone is not enough to obtain well-balanced mechanical properties from a material. For γ-TiAl-based alloys, it is established that only those with fine and homogeneous microstructures possess well-balanced properties. However, research has shown that in as-cast conditions and without the addition of grain refiners, γ-TiAl-based alloys consist of coarse columnar structures with grain sizes above 300 μm [9]. These coarse and inhomogeneous microstructures affect negatively the resulting mechanical properties and further processing of the alloys. Nevertheless, research has demonstrated that a small addition of boron (0.1-1 at.%) can improve the castability and refine the lamellar colonies of γ-TiAl-based alloys in the range of 50-150 μm [9]. Boron addition leads to the formation of TiB mono- or TiB2 di-borides which act as nucleating sites in the melt during solidification [10]. However, as demonstrated by Li et al., [11] the precipitation of curvy borides deteriorates the resulting ductility of the alloys. Furthermore, long refractory metal borides can form and cause premature failure during loading if solidification cooling rates are slow, which is often the case for thick cross sections. Therefore, alternative alloying elements that can refine the microstructures of the alloys and at the same time improve their castability must be explored. Mathabathe et al. [12] observed a significant grain refinement from 280 to 180 μm in as-cast condition when Nb was added to a binary γ-TiAl alloy. The mean grain size decreased further to 120 μm after adding both Nb and Cr to the binary γ-TiAl alloy. However, these alloying elements could not mitigate the shrinkage cavities [4]. Therefore, there is a need to obtain a suitable combination of alloying elements that could yield refined grains and minimise the shrinkage cavities as well as the level of porosity in the alloys.
It was therefore, the aim of this study to investigate the densification and microstructure of a modified second-generation $\gamma$-TiAl-based alloy of nominal composition Ti-48Al-2Nb-0.7Mn-0.3Si-1Sn (at. %). The alloy was fabricated from the cold-pressed precursor powders through the VAR process.

2 Experimental work

The Ti, Al, Nb, Mn, Si and Sn precursor powders with mean particle sizes of 31.25, 36.17, 74.83, 25.78, 8.12 and 10.38 $\mu$m respectively as also reported in [3,4] were uniaxially cold-pressed into a 53 mm diameter and 12 mm long cylindrical green compact using an Enerpac hydraulic press after being blended and mixed for 30 minutes in a tubular mixer. The applied compacting pressure was 380 MPa [3,4] and the press die arrangement is shown in Fig. 1a. The compact was then melted and cast three times under a vacuum of $1 \times 10^{-5}$ Torr [12] in a non-consumable electrode arc melting furnace fitted with a water-cooled copper crucible to synthesise a Ti-48Al-2Nb-0.7Mn-0.3Si-1Sn (at. %) button-ingot of dimensions 38×38×13 mm$^3$.

The as-cast specimen was heat treated at 1250 $^\circ$C (in the $\alpha + \gamma$ region of the TiAl phase diagram) for 4 hours in a protective argon atmosphere in a tube furnace with subsequent furnace cooling. To quantify the porosity in the alloy parts, the densities of the compact and button-ingot were measured using the Archimedes method according to ASTM B962-08 [3] and then compared with a reference value reported in [13]. To identify the stable phases at ambient temperature, the X-ray diffraction (XRD) technique was employed using the parameters reported in [3,4,12]. The scan step size and speed of 0.02$^\circ$ and 0.02$^\circ$/min respectively were used.

The green compact was characterised by a JEOL JSM-6510 scanning electron microscope (SEM) in a backscattered electron (BSE) mode and equipped with energy-dispersive X-ray spectroscopy (EDS) capabilities to determine the effect of cold-pressing on chemical distribution and to identify areas most likely to contain pores in the compact. The locations on the compact that were analysed were labelled A and B as shown in Fig. 1b. Furthermore, both the as-cast and heat-treated samples were analysed on a Zeiss Axio Imager.M2 light microscope (LM). A Line intercept method in ImageJ software was employed on the LM images to determine the average grain sizes [3]. To obtain the phase fractions in the heat-treated sample, the SEM electron backscattered diffraction (EBSD) technique was used. The EBSD parameters reported in [14] were adopted and the gathered data were processed with Aztec ICE software. Metallographic sample preparation for the LM characterisation was carried out according to what was reported in [14] which included grinding and polishing the specimens’ surfaces to a mirror-like finish followed by etching in a 24 ml H$_2$O + 50 ml glycerol + 24 ml HNO$_3$ + 2 ml HF solution [14]. The sample for EBSD analysis was mechanically ground and then electro-polished in a solution of 600 ml methanol, 360 ml butoxyethanol and 60 ml perchloric acid.
3 Results and discussion

3.1 Analysis of the green compact

The composition profiles for the two locations A and B (shown in Fig. 1b) on the surface of the green compact are shown in Fig. 2. As can be observed, the Ti atomic percentage is the highest at both locations A (Fig. 2a) and B (Fig. 2c), and the difference in Ti atomic composition between the locations is 3.5 (at. %). Al atomic percentage is higher at location B than at A. However, the difference in Al between the locations is as small as 2.5 (at. %). Mn atomic percentages are the same at A and B, whereas the percentages of Sn, Si and Nb are higher at B than at A with differences of 0.4, 0.3 and 0.3 (at. %) respectively. In general, one could infer that the elements of Ti, Al, Si, Sn and Nb were relatively evenly distributed on the observed compact surface while the elemental distribution for Mn was even.

Mathabathe et al., [4] also analysed the chemical distribution in the compacts of several γ-TiAl-based alloy systems. The researchers reported that the Al particles dominated the surface of the compacts as compared to the core. They attributed the behaviour to the spongy characteristics of Al with the presence of a small amount of Nb particles; hence the Al particles tended to migrate to the surface in contact with die facets and formed a strong weld on particles on the surface during cold-pressing. However, this tendency of Al particles was suppressed in this study as evidenced by the dominance of Ti particles on both locations observed. This could be due to the use of fine particles of Si, Sn and Mn which filled the gaps left by the larger ones during compaction [15], hence increasing the surface friction among the particles thereby preventing the Al particles from migrating to the surface.
Results and discussion

3.1 Analysis of the green compact

The composition profiles for the two locations A and B (shown in Fig. 1b) on the surface of the green compact are shown in Fig. 2. As can be observed, the Ti atomic percentage is the highest at both locations A (Fig. 2a) and B (Fig. 2c), and the difference in Ti atomic composition between the locations is 3.5 (at. %). Al atomic percentage is higher at location B than at A. However, the difference in Al between the locations is as small as 2.5 (at. %). Mn atomic percentages are the same at A and B, whereas the percentages of Sn, Si and Nb are higher at B than at A with differences of 0.4, 0.3 and 0.3 (at. %) respectively.

In general, one could infer that the elements of Ti, Al, Si, Sn and Nb were relatively evenly distributed on the observed compact surface while the elemental distribution for Mn was even. Mathabathe et al., [4] also analysed the chemical distribution in the compacts of several γ-TiAl-based alloy systems. The researchers reported that the Al particles dominated the surface of the compacts as compared to the core. They attributed the behaviour to the spongy characteristics of Al with the presence of a small amount of Nb particles; hence the Al particles tended to migrate to the surface in contact with die facets and formed a strong weld on particles on the surface during cold pressing. However, this tendency of Al particles was suppressed in this study as evidenced by the dominance of Ti particles on both locations observed. This could be due to the use of fine particles of Si, Sn and Mn which filled the gaps left by the larger ones during compaction [15], hence increasing the surface friction among the particles thereby preventing the Al particles from migrating to the surface.
Fig. 2: SEM-EDS elemental map analysis for the compact in which (a) and (b) are locations A and B respectively, on the compact’s surface. (i) electron image, (ii) EDS layered image, (iii) Ti Kα, (iv) Al Kα, (v) Nb Lα (vi) Mn Kα (vii) Si Kα (viii) Sn Lα and (ix) spectra with corresponding atomic compositions.

Furthermore, as observed in Fig. 2, the powder particles were deformed plastically by the compaction pressure during pressing, and the most affected ones appear to be Al and Sn particles as evidenced by the flattening of the particles which were spheres before cold-pressing. This could be ascribed to the soft nature of Al and Sn particles. Moreover, the fine Si particles which were attracted to Al and Nb coarse particles during blending and mixing as elucidated by Ellard et al.,[3] are observed to be welded to these particles as a result of compact pressure. In addition, as reported in [4], the inter-particle voids of irregular/angular-shaped Ti, Nb and Mn particles appear to be more readily closed when compared to the spherical Al and Sn powders. Ellard et al. [3] pointed out that irregular-shaped particles interlock mechanically during pressing and so improve the strength of the green compact.

The relative density results of the compact are compared with the ones reported previously by Mathabathe et al.,[4] as depicted in Fig. 3a (primary y-axis). The results indicate that the compact in this study (TiAlNbMnSiSn) possessed the highest relative green density of 86.99% despite the use of the same compaction pressure of 380 MPa. It is therefore imperative to infer that the level of porosity in the compact studied here was reduced. This can be primarily attributed to the improvement of powder packing during compaction as the finer particles filled the inter-particle voids left by the coarser ones. However, the analysis of the density progression from the tapped/apparent density of mixed precursor powders to the density of 86.99% despite the use of the same compaction pressure of 380 MPa. It is therefore reasonable to suggest that Sn was the element responsible for the elimination of the shrinkage cavity due to early wetting attributable to its low melting temperature in the ingot shown in Fig. 3b. During the melting and casting of the alloy, Sn increased the fluidity of the liquid metal [6] owing to the formation of some transient liquid phases at a lower temperature [8] such that any localized contraction of the molten metal during solidification was immediately compensated by the liquid metal flowing from elsewhere within the casting.

The secondary y-axis in Fig.3a shows that the alloy density of TiAlNbMnSiSn is the highest with a value of 99.87% compared with the density results obtained in [4]. Therefore, it can be inferred that the alloy in this study contained the least level of porosity majorly owing to the beneficial effect of Sn. As explained earlier, Sn addition increased the fluidity of the liquid metal which ensured the effective operation of the feeding mechanism to close the pores in the cast during solidification.

3.2 Analysis of the button-ingot

The vacuum arc-melted button-ingot is shown in Fig. 3b. It is evident that, unlike the VAR-produced button-ingots that were reported in [4], TiAlNbMnSiSn button-ingot shows no sign of shrinkage cavities. Recently, Genc and Unal [16], and Raji et al.,[1] reviewed the effects of several alloying elements in γ-TiAl-based alloys. The effects of the ones used in this study are summarised in Table 1. However, the effect of Sn in γ-TiAl alloys is still not clear. Therefore, it is reasonable to suggest that Sn was the element responsible for the elimination of the shrinkage cavity due to early wetting attributable to its low melting temperature in the ingot shown in Fig. 3b. During the melting and casting of the alloy, Sn increased the fluidity of the liquid metal [6] owing to the formation of some transient liquid phases at a lower temperature [8] such that any localized contraction of the molten metal during solidification was immediately compensated by the liquid metal flowing from elsewhere within the casting.

The secondary y-axis in Fig.3a shows that the alloy density of TiAlNbMnSiSn is the highest with a value of 99.87% compared with the density results obtained in [4]. Therefore, it can be inferred that the alloy in this study contained the least level of porosity majorly owing to the beneficial effect of Sn. As explained earlier, Sn addition increased the fluidity of the liquid metal which ensured the effective operation of the feeding mechanism to close the pores in the cast during solidification.
of the shrinkage cavity
Therefore, the effects of several alloying elements in the primary γ- TiAl are summarized in Table 1.

### 3.3 Identification of phases at ambient temperature

The stable phases at ambient temperature in the alloy were identified by the XRD technique (Fig. 4). The alloy was composed of the matrix phases of α2-Ti3Al and the predominant γ-TiAl. Furthermore, owing to the addition of Si, titanium silicates (Ti5Si3) were also formed. This is in agreement with Kahrobaee and Palm [17] who stated that adding about 0.3 at. % Si leads to the formation of Ti5Si3 at the α2/β lamellar interface. Moreover, Noda et al., [18] deduced that the Ti5Si3 phase precipitates during solidification through the $L \rightarrow \beta + Ti_5Si_3$ eutectic reaction. However, the Ti2Sn phase which was observed by Pan et al., [8] did not form in the alloy. This may be ascribed to the low addition of Sn.

![Graph showing relative green and alloy densities](image)

**Fig. 3:** (a) Relative densities of the green compacts and the arc-melted buttons (TiAl, TiAlNb and TiAlNbCr density results were reproduced from [4] with permission from Elsevier); (b) macrograph of as-cast TiAlNbMnSiSn button-ingot. The scale is in mm.

**Table 1:** Summary of effects of Nb, Mn and Si in γ-TiAl-based alloys

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>Improves strength and oxidation resistance [1,16]</td>
</tr>
<tr>
<td>Mn</td>
<td>Increases room temperature ductility [1, 16]</td>
</tr>
<tr>
<td>Si</td>
<td>Improves oxidation and corrosion resistance [1, 16]</td>
</tr>
</tbody>
</table>

![Image showing macrograph of as-cast TiAlNbMnSiSn button-ingot](image)
3.4 Microstructure characterisation

In as-cast condition, the microstructure of the alloy consists of dendritic structures that are made of many small parts that look like cells (Fig. 5a) with an average grain size of about 49 μm (Fig. 5c). The dendrites majorly consist of γ-phase whereas the inter-dendritic regions comprise γ + α2 lamellae. When the alloy was heat treated at 1250 °C for 4 hours with subsequent furnace cooling, a well-developed duplex microstructure (Fig. 5b) consisting of lamellar colonies of γ and α2 phases and coarse γ grains [19, 20] with lamellae oriented at 45° to the solidification direction was formed. Its measured mean grain size was about 162 μm which indicates that grain growth occurred during the heat treatment process. A systematic comparison is made in Fig. 5c between the mean grain size results of the as-cast alloy obtained in this study and the ones reported in the literature [12] of similar alloys and processing conditions. It is evident that the grain refinement in the alloy (TiAlNbMnSiSn) studied here was significantly improved owing to the dissolution of Sn in both γ and α2 phases [8]. This is consistent with the findings of Wang et al.,[21]. The researchers also reported that the size of lamellar grains of as-melted β-solidifying TiAl alloys decreased with increasing Sn content. Therefore, one could infer that Sn addition in γ-TiAl-based alloys refines the grains of the alloys.

Fig. 4: XRD phase identification of the alloy.
3.4 Microstructure characterisation

In as-cast condition, the microstructure of the alloy consists of dendritic structures that are made of many small parts that look like cells (Fig. 5a) with an average grain size of about 49 µm (Fig. 5c). The dendrites majorly consist of γ-phase whereas the interdendritic regions comprise γ+α2 lamellae.

When the alloy was heat treated at 1250 °C for 4 hours with subsequent furnace cooling, a well-developed duplex microstructure (Fig. 5b) consisting of lamellar colonies of γ and α2 phases and coarse γ grains [19, 20] with lamellae oriented at 45° to the solidification direction was formed. Its measured mean grain size was about 162 µm which indicates that grain growth occurred during the heat treatment process.

A systematic comparison is made in Fig. 5c between the mean grain size results of the as-cast alloy obtained in this study and the ones reported in the literature [12] of similar alloys and processing conditions. It is evident that the grain refinement in the alloy (TiAlNbMnSiSn) studied here was significantly improved owing to the dissolution of Sn in both γ and α2 phases [8]. This is consistent with the findings of Wang et al., [21]. The researchers also reported that the size of lamellar grains of as-melted β-solidifying TiAl alloys decreased with increasing Sn content. Therefore, one could infer that Sn addition in γ-TiAl-based alloys refines the grains of the alloys.

To further examine the microstructure and to reveal the presence of Ti5Si3 as detected by the XRD technique, and to determine the phase fractions in the heat-treated alloy, the SEM-EBSD technique was employed. The obtained EBSD maps are shown in Fig. 6 in which (a) is a band contrast, (b) a phase map, (c) an orientation map indicating inverse pole figure (IPF) in the x-axis, and (d) index maps with phase fractions. As can be observed, the γ-phase is predominant with a phase fraction of 96.18%. On the other hand, very small phase fractions of 0.5 and 0.46% for α2 and Ti5Si3 respectively were obtained. This provides evidence that the Al content in the alloy was very close to the γ-phase region. However, it will be critical for future investigation of this alloy to gain insight into how Sn addition affects the nucleation mechanisms of both α2 and Ti5Si3 phases.
Fig. 6: EBSD map of the alloy: a) band contrast, b) phase map, c) orientation map indicating inverse pole figure (IPF) in the x-axis, and d) index maps with phase fractions.

4 Conclusion

The densification and microstructure of a low Nb-containing γ-TiAl-based alloy with a nominal composition of Ti-48Al-2Nb-0.7Mn-0.3Si-1Sn (at. %) produced from cold-pressed precursor powders through VAR process were thoroughly investigated in this current work. The main aim was to improve the density of this difficult-to-cast material by minimizing the level of defects viz. shrinkage cavities and porosity in the microstructure as well as to further refine the grains of the resulting melted and cast ingot. From the investigation the following conclusions were drawn:

- The green density of the cold-pressed precursor powders was improved owing to the incorporation of powders having different morphologies and a considerable size difference between them which improved their packing during compaction as the finer particles filled the inter-particle voids left by the coarser ones.
- The alloy had better casting properties compared with similar alloys reported in the literature as evidenced by the absence of shrinkage cavities and the highest relative density of 99.87%. This was attributed to the effect of Sn which increased the fluidity of the molten metal to ensure effective operation of the feeding mechanism to close pores in the casting during solidification.
- At room temperature and in as-cast condition, the microstructure consisted of a fine dendritic structure of γ-phase and γ + α₂ lamellae. After heat treatment, a well-developed duplex microstructure consisting of Ti₅Si₃ precipitates, coarse γ grains and lamellar colonies of γ and α₂ phases with lamellae oriented at 45° to the solidification direction was formed.
- There was more grain refinement in the as-cast condition than in similar alloys reported in the literature.
Acknowledgements

The authors would like to acknowledge the Thuthuka National Research Foundation (grant no: 138314) for funding this work and The Council of Scientific and Industrial Research (CSIR) as well as the University of Pretoria (UP) in the Republic of South Africa for providing laboratory equipment.

References

1. S.A. Raji, A. P.I. Popoola, S.L. Pityana, O. M. Popoola, Heliyon, 6, 7 (2020)
17. Z. Kahrobaee, M. Palm, J. Alloys Compd., 924, 166223 (2022)
20. S. Magogodi, M. Mathabathe, A. Bolokang, C. Siyasiya, MATEC Web of Conferences, 370, 06008 (2022)