EFFECT OF YTTRIUM ON OXYGEN CONTENT AND MICROSTRUCTURE OF Ti-AL INTERMETALLICS

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Abstract
The influence of metallic yttrium with a purity of 99.9 % on the microstructure and properties of cast Ti-47Al alloys prepared by vacuum induction melting was studied. The prepared alloys exhibited relatively homogeneous composition with dendritic structure formed by lamellar dendrites and γ phase in interdendritic areas. The most yttrium rich phases were observed in the interdendritic areas, but were also observed within the dendrites. The composition of this phase corresponded to the Y2O3 oxide. It was found, that yttrium reduces the content of interstitial oxygen in the alloys due to high affinity to oxygen and also reduces primary and secondary arm spacing. Furthermore, the influence of yttrium on the solidification process of prepared alloys was studied by DTA (differential thermal analysis) and also was evaluated microhardness of prepared alloys.

Keywords: TiAl alloys; microstructure; yttrium; oxygen content; differential thermal analysis (DTA)

1. INTRODUCTION
Precise casting of lightweight alloys based on TiAl represents very promising technology for preparation of components for automotive, aerospace and power industries as turbine blades, turbochargers and valves, particularly in terms of low costs compared with other preparation technologies [1]. Mechanical properties of these alloys, especially toughness at room temperature and resistance to creep, depend significantly on the microstructure [1]. Alloys with fully lamellar or nearly lamellar microstructure are characterized by higher resistance to creep and higher toughness, compared to alloys with duplex microstructure but they have lower ductility and plasticity. Particularly low ductility at room temperature is a typical feature of γ-TiAl alloys, which prevents its wider use [1]. Impurities, such as oxygen, cause drop in mechanical properties and it is very difficult to prevent contamination due to the high affinity between metals and oxygen. Alloaying with a small amount of yttrium is one of the possibilities to improve oxidation resistance [2, 3, 4] and mechanical properties of γ-TiAl alloys [5, 6]. The purpose of the present work is to investigate the effect of yttrium on the oxygen content and also on the dendritic structure, particularly on the dendrite arm spacing of cast alloy TiAl. It is generally known, that reducing the dendrites arms spacing leads to an increase of mechanical properties and to reduction of segregation distance. Furthermore DTA analysis was evaluated for assessing the influence of yttrium for the solidification alloys. The microhardness measurements were also performed.

2. EXPERIMENT
Five types of TiAl alloys, the composition of which is shown in Table 1, were prepared by vacuum induction melting in a furnace LEYBOLD – HERAEUS IS1/FFF. Products and their preparation were described in another article [7]. Oxygen contents in alloys are shown in Tab. 2. Relatively high oxygen contents were found in the alloys probably for reason of leak in furnace. Therefore this fact was used to determine the
effect of yttrium as an absorber of interstitial oxygen. Samples were cut off in the longitudinal and transverse direction for metallographic observation. Determination of gas content in the samples was carried out at the VÚHŽ Dobrá on the analyzer LECO TC-436. The alloys were observed by optical microscopy on the microscope Olympus GX51 equipped with digital camera Olympus DP12 (OM), scanning electron microscopy in mode of scattered electrons (BSE) on the microscope SEM JEOL JSM - 6490LV, equipped with a probe EDS INCA X - ACT. DTA analysis was performed with using experimental equipment SETARAM SETSYS 18™. 

Table 1 Nominal and measured composition of alloys (EDS)

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Nominal composition [at. %]</th>
<th>Measured composition [at. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>Al</td>
</tr>
<tr>
<td>Ti-47Al</td>
<td>53</td>
<td>47</td>
</tr>
<tr>
<td>Ti-47Al-0.1Y</td>
<td>52.9</td>
<td>47</td>
</tr>
<tr>
<td>Ti-47Al-0.2Y</td>
<td>52.8</td>
<td>47</td>
</tr>
<tr>
<td>Ti-47Al-0.3Y</td>
<td>52.7</td>
<td>47</td>
</tr>
<tr>
<td>Ti-47Al-0.4Y</td>
<td>52.6</td>
<td>47</td>
</tr>
</tbody>
</table>

Table 2 Dependence of yttrium content on oxygen content

<table>
<thead>
<tr>
<th>Yttrium [at. %]</th>
<th>Oxygen [wt. ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5090 ± 234</td>
</tr>
<tr>
<td>0.1</td>
<td>3042 ± 122</td>
</tr>
<tr>
<td>0.2</td>
<td>2452 ± 59</td>
</tr>
<tr>
<td>0.3</td>
<td>2542 ± 89</td>
</tr>
<tr>
<td>0.4</td>
<td>3945 ± 457</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

Fig. 1 shows the detail of microstructure. The results of chemical analysis (EDS) in individual phases are shown in Tab. 3. All samples were formed by lamellar dendrites (L), which were composed by alternating lamellas $\alpha_2$ and $\gamma$. The lamellar structure was formed by precipitation of $\gamma$ lamellas in $\alpha$ matrix. Interdendritic spaces consisted of $\gamma$ phases ($\gamma$), which were formed by peritectic reaction between $\alpha$ and melt enriched with Al in accordance with the binary diagram [8]. A new phase was observed in the samples with the contents of yttrium. This phase is marked in Fig. 1 by white colour and the composition is in Tab. 3. According to the publications [2, 5], the solubility of yttrium in the $\alpha_2$ and $\gamma$ phases was less than 0.1 at.
% Higher contents of yttrium in the alloys leads to accumulation of yttrium at grain boundaries and fine particles of this metal are dispersed inside the grains. Yttrium should preferentially react with Al to form YAl$_2$ during melting [2, 5, 6]. However, this phase was observed only in the master alloys, which were prepared by plasma melting, where the oxygen content was not high [9]. The yttrium phases with high content of oxygen were observed in alloys after vacuum induction melting. This is due to the high affinity between oxygen and yttrium atoms [10]. Yttrium is highly susceptible to reaction with oxygen on Y$_2$O$_3$ during melting and casting process, and according to [3] at oxygen contents higher than 128 wt. ppm., yttrium acts as a collector, which can reduce the content of interstitially dispersed oxygen in the alloy. Possibility of this phenomenon in the prepared alloys was high, because the oxygen content was higher. This was confirmed by X-ray diffraction pattern, in which was identified Y$_2$O$_3$ phase in alloy Ti-47Al-0.4Y. X-ray diffraction patterns of Ti-47Al and Ti-47Al-0.4Y alloys are shown in Fig. 2. Further confirmation of this phenomenon is decreasing amount of oxygen with increasing yttrium content in the prepared samples, which is shown in Tab. 2. Values of oxygen contents were obtained by calculating the average of three pieces from each of the analyzed samples. Exceptions were the following: only a slight increase in oxygen content in the sample with 0.3 at. % Y and greater increase of the sample with 0.4 at% Y. The increased gas content in these samples might have been caused by bubble effect, which was registered during the analysis. It was caused by closed pores in the alloys.

Table 3 Results of chemical analysis in individual phases (EDS)

<table>
<thead>
<tr>
<th>Analysed composition [at. %]</th>
<th>Element</th>
<th>Small elipsoid oxides (Y-rich)</th>
<th>Lamellas (L)</th>
<th>Inter-dendritic $\gamma$ ($\gamma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td></td>
<td>23.7 ± 6.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>54.1 ± 6.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>11.3 ± 6.4</td>
<td>46.65 ± 1.10</td>
<td>51.17 ± 2.64</td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td>10.9 ± 5.4</td>
<td>53.35 ± 1.10</td>
<td>48.83 ± 2.64</td>
</tr>
</tbody>
</table>

Fig. 2 X-ray diffraction pattern of the samples Ti-47Al-0.4Y (4-V) and Ti-47Al (5-V).

1 … $\gamma$-TiAl, 2 … $\alpha_2$-Ti$_3$Al, 3 … Y$_2$O$_3$. 
As shown by Lapin, Vickers hardness measurements can be used as a good indicator for an increase of oxygen content in TiAl based alloys [11]. Tab. 4 shows the microhardness evolution with yttrium content in the alloys. The microhardness decreases with increasing yttrium content. By Lamirand [12], microhardness in TiAl based alloys is influenced by several factors: the \(\alpha_2\) volume fraction, interlamellar spacing, grain size and solid solution hardening of the \(\alpha_2\) and \(\gamma\) phases. In our alloys, there is no evolution of the \(\alpha_2\) volume fraction and interlamellar spacing when yttrium was added and also no evident variation in grain size [7]. Therefore from the results of microhardness measurements is evident that the decrease in microhardness is caused probably by reducing the amount of interstitial oxygen in the prepared alloys.

**Table 4** Dependence of microhardness on yttrium content

<table>
<thead>
<tr>
<th>Y [at. %]</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>HV 0.1</td>
<td>450.3 ± 34.2</td>
<td>424.6 ± 52.9</td>
<td>407.4 ± 48.7</td>
<td>396.5 ± 37.7</td>
<td>395.0 ± 31.9</td>
</tr>
</tbody>
</table>

Fig. 3 shows dendritic structure of the alloys Ti-47Al and Ti-47Al-0.4Y. Comparison of these figures shows that with increasing content of yttrium, the dendrites seem to be finer. Due to accurate assessment of these characteristics the distance of primary (PDAS) and secondary (SDAS) branches of dendrites was measured. Measurements of PDAS and SDAS were described more detailed in another article [13]. The results show (see Fig. 4) that both primary dendrite arm spacing and secondary dendrite arm spacing with increasing yttrium content had decreasing dependence. Decrease of PDAS and SDAS with increasing content of yttrium can be explained by the increasing content of yttrium-rich phases in the interdendritic spaces, which reduces heat transfer and mass transfer during cooling, as well as dendritic growth.

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Fig. 5 shows DTA curves obtained by heating of samples Ti-47Al and Ti-47Al-0.4Y. Moreover samples, which composition is Ti-40Al and Ti-50Al were also analyzed by DTA. These two alloys were prepared by plasma melting and their composition corresponds to nominal (analysed by EDS). Analysis of these two alloys was carried out to compare the solidification through \(\beta\) and \(\alpha\) as primary solidification phases. The oxygen contents in these 2 samples are about 400 wt. ppm.
Fig. 5 DTA curves for samples Ti-47Al, Ti-47Al-0.4Y, Ti-40Al and Ti-50Al

Tab. 5 shows temperatures of transformations detected by DTA in prepared samples. The temperatures of the invariant phase reactions were usually taken from the extrapolated peak-onset on heating. From the resulting values can be determined, that β phase is primary solidification phase of sample Ti-40Al, but determined liquidus and solidus temperatures are lower than it should be according to binary diagram [8]. However, this temperature is still high enough to confirm the β phase as the primary solidification phase. Detected liquidus temperature of alloy Ti-50Al is 1485 °C. According to [8] is evident, that this sample solidified through α phase. This phenomenon was confirmed by observing the symmetry of the dendrites, which can determined primary crystallization phase [14], because alloy Ti-50Al exhibits six-fold symmetry of dendrites. In samples Ti-47Al and Ti-47Al-0.4Y the six-fold symmetry of the dendrites are defined. From transformation temperatures obtained by DTA, the liquidus temperatures of these alloys are 1510 and 1505 °C. It corresponds rather to solidification through β phase, but no dendrites with four-fold symmetry were observed. This can be explained due to high oxygen content. From these facts can be suggested, that in alloys with 47 at. % Al and high oxygen contents is stabilized α phase and β phase occurs only in very small temperature range. During next peritectic transformation the β phase is totally covered with the growing α phase. This assumption will be verified by directional crystallization with rapid quenching of a solid–liquid interface and formation of mushy zone, which allows observation and accurately determination of the evolution of solidification.

Table 5 Overview of the transformation temperatures detected by DTA

<table>
<thead>
<tr>
<th>Composition [at. %]</th>
<th>Marking</th>
<th>Phase transformation</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-40Al</td>
<td>1–2</td>
<td>α₂ + γ → α</td>
<td>1125 - 1156</td>
</tr>
<tr>
<td></td>
<td>3–4</td>
<td>α → β</td>
<td>1329 - 1374</td>
</tr>
<tr>
<td></td>
<td>5–6</td>
<td>β → β + L</td>
<td>1526 - 1548</td>
</tr>
<tr>
<td>Ti-50Al</td>
<td>1–2</td>
<td>γ → α + γ</td>
<td>1265 - 1276</td>
</tr>
<tr>
<td></td>
<td>3–4</td>
<td>α + γ → α</td>
<td>1432 - 1454</td>
</tr>
<tr>
<td></td>
<td>4–5</td>
<td>α → α + L</td>
<td>1454 - 1485</td>
</tr>
<tr>
<td>Ti-47Al</td>
<td>1–2</td>
<td>α + γ → α</td>
<td>1270 - 1370</td>
</tr>
<tr>
<td></td>
<td>3–4</td>
<td>α → α + L</td>
<td>1460 - 1508</td>
</tr>
<tr>
<td></td>
<td>4–5</td>
<td>α + L → β + L</td>
<td>1508 - 1510</td>
</tr>
<tr>
<td>Ti-47Al-0.4Y</td>
<td>1–2</td>
<td>α + γ → α</td>
<td>1251 - 1380</td>
</tr>
<tr>
<td></td>
<td>3–4</td>
<td>α → α + L</td>
<td>1453 - 1504</td>
</tr>
<tr>
<td></td>
<td>4–5</td>
<td>α + L → β + L</td>
<td>1504 - 1505</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Five alloys based on TiAl, with different contents of yttrium were prepared by vacuum induction melting in Al₂O₃ crucible, modified by mechanical Y₂O₃ coating, followed by casting into graphite molds. Microstructure of prepared alloys was dendritic. Dendrites were formed by alternating lamellas α₂ and γ. The Y₂O₃ phase was occurred in interdendritic areas. It was found by analysis of gas content in combination with microanalysis of chemical composition, that the presence of yttrium in the alloy reduces content of interstitially bound oxygen, which bonds to itself. Addition of yttrium resulted in reduction of primary dendrite arm spacing and secondary dendrite arm spacing. It was found that yttrium not too much affected the temperature of phase transformations, which was investigated by DTA analysis.

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REFERENCES