SPECIFIC FEATURES OF STRUCTURE FORMATION IN Al-Ti-C POWDER MASTER ALLOYS AFTER THERMAL SYNTHESIS.

OSOBYENNOSTI STRUKTUROOBRAZOVANIYA PРИ TЕРМИЧЕСКОМ СИНТЕЗЕ ПОРОШКОВЫХ ЛИГАТУР СИСТЕМЫ Al-Ti-C.

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Abstract: In the present work, a method for fabrication of Al-Ti-C master alloys by thermal synthesis was developed. Titanium, aluminum and carbon powders were used as raw materials. It was shown that the different content of carbon and aluminum in the system leads to significant differences in the phase composition of the synthesized master alloys.

KEYWORDS: THERMAL SYNTHESIS, MASTER ALLOY, TITANIUM CARBIDE, PHASE COMPOSITION

1. Introduction

Particulate-reinforced metal matrix composites based on aluminum alloys are being used as structural materials due to their unique mechanical properties. Different particles such as SiC, Al2O3, TiB2, B4C, TiC have been recognized as potential reinforcements for aluminum alloys [1]. Even so, the authors [1] consider that among the mentioned additives the most attractive is titanium carbide due to its high hardness and elastic modulus, low relative density and good wettability of aluminum alloys. The lattice parameters of the carbide particles of transition metals, especially TiC, are close to the lattice parameter of aluminum solid solution [2]. Besides, titanium carbide particles are effective nucleating centers [1] in crystallization of cast aluminum alloys.

Particulate reinforced aluminum composites are conventionally prepared either by mechanical blending of elements or compounds with aluminum powder (powder metallurgy technique) or by direct introduction of reinforcing particles into the melt aluminum (in case of liquid metallurgy) [1].

However, these methods don’t allow entirely realize the potential of dispersion strengthening due to poor wettability of the titanium carbide particles with aluminum, because of oxide films on their surface [3;4].

The most preferred method is introduction the Al-Ti-C master alloy as strengthening phase into molten aluminum alloys [3]. Al-Ti-C master alloy synthesized by in-situ reaction between Al, Ti and carbon, which resulted to the formation of titanium carbide dispersed particles in aluminum at temperatures below 900 °C.

It is known [1] that for the effect of dispersion strengthening or for nucleation of TiC particles they must be stable in the melt, but according to the [3], titanium carbide can easy react with aluminum, the reaction products are brittle phases Al4C3, which leads to degradation of the composite properties. Whereas, the most common technological schemes of production such alloys include casting operation, the effect of dispersion strengthening in these materials tend to decrease.

Terefore, more attention has been paid to the preparation of master alloy from elemental powders of Al, Ti and C with its subsequently application for producing sintering (or additionally hot forming) composite mixed with aluminum powder. It is assumed that, as a result of in-situ reaction in the synthesized master alloy the grain boundaries between the particles of the strengthening phase and aluminum will be free of oxides, which greatly increases the interfacial strength, titanium carbide particles themselves are of submicron size and homogeneously distribute in the volume, which increase mechanical properties of composites [5].

The aim of this paper is to study the effect of carbon and aluminum on the microstructure in Al-Ti-C master alloys after thermal synthesis

2 Experimental procedure

Aluminum, titanium and graphite powders were used as raw materials for preparing the charge mixture which was subsequently thermal synthesized. To evaluate the effect of blending ratio on the structure and properties of the synthesized master alloys four compounds of raw charge mixtures were chosen. The materials used in this study are summarized in Table 1.

Table 1 Chemical composition of charge mixtures for the synthesis of master alloys

<table>
<thead>
<tr>
<th>Number</th>
<th>Composition, % (mass.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>1</td>
<td>35.0</td>
</tr>
<tr>
<td>2</td>
<td>35.0</td>
</tr>
<tr>
<td>3</td>
<td>40.0</td>
</tr>
<tr>
<td>4</td>
<td>45.0</td>
</tr>
</tbody>
</table>

The mixtures of powders were cold compacted in the 30 mm in diameter cylindrical matrix with 500 MPa pressure. To prevent the adhering of powder on the walls of the matrix the boron nitride soap solution was used as a lubricant. Thermal synthesis of charge mixture were carried out in a sealed chamber filled with technically pure argon, on the plant with indirect induction heating at 900 °C for 1 hour. Microstructure observations were made by metallographic microscope XJL-17AT. The specimens were etched for 1 hour. Microstructure observations were made by X-ray diffraction analysis (XRD) and subsequent differential thermal analysis (DTA).

3 Results and discussion

The samples after thermal synthesis (Fig. 1, a) have become rather hard, but divided into a layers (Fig. 1, b) and looks like the samples, which were obtained by self-propagating high-temperature synthesis (SHS), as shown in (Fig. 1, b). However, there is a volume growth of compact due to degassing of adsorbed and dissolved gases and the formation of macro pores and cavities during reactive sintering (Fig. 1, c).

The large difference between the partial diffusion coefficients of Ti and Al could be an additional source of pores. The synthesis of TiAl/Ti3Al phases via thermal synthesis follows a mechanism in which the diffusion flow moves from aluminum to titanium, while the titanium atoms haven’t time to diffuse into the aluminum, thus leading to the formation of diffusion pores [6;17].
Figure 1. Visual appearance of the initial compact (a), sample after thermal synthesis (b) and its macrostructure (c)

Figure 2 shows the microstructure of the master alloys, after thermal synthesis. A uniform distribution of the white particulate reinforcements with different dispersity and shape through the gray metal matrix is observed. The samples with the lowest carbon content (Table 1, №3) consist of white disordered elongated needle-like grains (Fig. 2, a), while all other samples consist of the white spherical particles (Fig. 2, b, c, d).

Quantitative analysis for the represented elements of the structure were made. The results were listed in Table 2. According to the results, it was confirmed that the gray field on the microstructure is intermetallic compounds based on Al and Ti (zone 2) or it is a mixture of Al and TiC particles (zone 8) [4], white spherical particles (zone 3, 5 and 7) correspond to stoichiometric composition of TiC and elongated needle-like grains (zone 1) is ternary carbide Ti₃AlC the percentage of elements in this phase is close to stoichiometric composition [8].

Zone 4 and 6 corresponds to the solid solution based on aluminum.

Table 2. Quantitative analysis in different zone of Al-Ti-C master alloys synthesized alloys of (Fig. 2)

<table>
<thead>
<tr>
<th>Zone</th>
<th>Al, %</th>
<th>Ti, %</th>
<th>C, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.31</td>
<td>78.81</td>
<td>5.88</td>
</tr>
<tr>
<td>2</td>
<td>63.473</td>
<td>36.527</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>3.714</td>
<td>78.336</td>
<td>17.950</td>
</tr>
<tr>
<td>4</td>
<td>92.861</td>
<td>2.839</td>
<td>4.299</td>
</tr>
<tr>
<td>5</td>
<td>0.409</td>
<td>77.313</td>
<td>22.278</td>
</tr>
<tr>
<td>6</td>
<td>91.731</td>
<td>2.145</td>
<td>6.124</td>
</tr>
<tr>
<td>7</td>
<td>0.585</td>
<td>81.857</td>
<td>17.558</td>
</tr>
<tr>
<td>8</td>
<td>57.821</td>
<td>38.723</td>
<td>3.457</td>
</tr>
</tbody>
</table>
This assumption is confirmed by X-ray diffraction analysis (Fig. 3).

Fig. 3 presents the XRD pattern of initial mixture and synthesized master alloys. It can be seen that the initial mixture contains Al, Ti and C as shown in Fig 3a. The XRD results revealed the presents of TiC and ternary carbides $\text{Ti}_2\text{AlC}$, $\text{Ti}_3\text{AlC}$ in all specimens after thermal synthesis. The formation of titanium aluminides depends on the percentage of components of the samples: $\text{40Al-6C-54Ti}$, $\text{35Al-13C-54Ti}$ - most likely $\text{Al}_2\text{Ti}$, $\text{AlTi}$, $\text{Al}_2\text{Ti}_3$ and ternary carbide $\text{Ti}_3\text{AlC}$; $\text{35Al-9.75C-55, 25Ti}$, $\text{45Al-11C-44Ti}$ - $\text{AlTi}$, $\text{AlTi}_2$, $\text{AlTi}_3$ and $\text{Al}_2\text{Ti}_3$. The X-ray analysis shows the presence of $\text{Ti}_4\text{AlC}$ as the trace phase in $\text{45Al-11C-44Ti}$ master alloy, besides the diffraction pattern of this sample indicates a very dispersed state of strengthening phase after thermal synthesis against the other samples, which is also seen from the microstructure (Fig. 2, b). Only in one sample $\text{35Al-13C-54Ti}$ the $\text{Ti}_3\text{AlC}$ carbide and the $\text{Al}_4\text{C}_3$ carbide were indicated. It is difficult to indicate the presence of TiC carbide in this sample because of overlaying of diffraction peak and due to close angles of reflection. However, the microstructure of $\text{35Al-9,75C-55,25Ti}$ master alloy (Fig. 2, d) shows white spherical particles in a matrix, according to the quantitative analysis (Table 2, zone 7), we can speak about the presence of TiC phase in the sample. No Al or $\text{Al}_2\text{O}_3$ phase was detected in the XRD patterns of synthesized master alloys. The large variety of titanium aluminides in master alloys after thermal synthesis connected with the cooling conditions of the samples after sintering (for example, changing the effective heat-transfer coefficient it is possible to get pure titanium monoaluminid or multiphase product) [9;10], so with intermetallic phase which is formed in the first place. As a rule, in samples with initially formed titanium aluminide $\text{AlTi}$ and where composition of the initial powder mixture close to stoichiometry of $\text{AlTi}$, the traces of $\text{AlTi}_2$, $\text{AlTi}_3$, $\text{Al}_2\text{Ti}_3$, $\text{Al}_3\text{Ti}_6$ phases was observed. The suggested mechanism of the above phases formation is through a series of solid-liquid and/or solid state reactions necessarily involving TiAl as one of the starting phases [6].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Diffraction patterns of the initial powder mixture (a) and synthesized Al-Ti-C master alloys (b, c, d, e)}
\end{figure}
The results of chemical analysis on carbon content is shown in Table 2, there is some amount of free carbon in master alloys after thermal synthesis.

Table 2. – The amount of carbon in the samples before and after thermal synthesis.

<table>
<thead>
<tr>
<th>Chemical composition, % (mass.)</th>
<th>C_{total}, % (mass.)</th>
<th>C_{free}, % (mass.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40Al-6C-54Ti</td>
<td>5,9</td>
<td>1,3</td>
</tr>
<tr>
<td>45Al-11C-44Ti</td>
<td>6,5</td>
<td>0,43</td>
</tr>
<tr>
<td>35Al-13C-52Ti</td>
<td>12,7</td>
<td>0,37</td>
</tr>
<tr>
<td>35Al-9,75C-55,25Ti</td>
<td>8,5</td>
<td>0,30</td>
</tr>
</tbody>
</table>

The content if combined carbon is usually decrease in comparison to the theoretical one after synthesis. Besides, there is a number of free, unreacted carbon C_{free} in real product. It is known that the closer the combined carbon content in the real product to the theoretical and the lower free carbon content in it, the better synthesized product [11].

The phase and structure formation mechanism in the Al–Ti–C system was investigated by means of DTA and calculations of the Gibbs free energy were carried out using the program HSC Chemistry 5.11. Thermodynamic analysis helps to understand what reactions are possible and which is the most favorable between Al, Ti and C. The changes of Gibbs free energy (ΔG) as a function of temperature were calculated for the following reactions:

\[
\begin{align*}
\text{Al} + \text{Ti} &= \text{AlTi} & \quad (1) \\
3\text{Al} + \text{Ti} &= \text{Al}_3\text{Ti} & \quad (2) \\
\text{Ti} + \text{C} &= \text{TiC} & \quad (3) \\
\text{TiAl} + 2\text{Al} &= \text{Al}_3\text{Ti} & \quad (4) \\
\text{TiAl} + \text{C} &= \text{TiC} + \text{Al} & \quad (5) \\
4\text{TiAl} + 7\text{C} &= 4\text{TiC} + \text{Al}_4\text{C}_3 & \quad (6) \\
4\text{TiAl} + 3\text{C} &= 4\text{Ti} + \text{Al}_4\text{C}_3 & \quad (7) \\
\text{Al}_3\text{Ti} + \text{C} &= \text{TiC} + 3\text{Al} & \quad (8) \\
1.333\text{Al}_3\text{Ti} + 4.333\text{C} &= 1.333\text{TiC} + \text{Al}_4\text{C}_3 & \quad (9) \\
1.333\text{Al}_3\text{Ti} + 3\text{C} &= 1.333\text{Ti} + \text{Al}_4\text{C}_3 & \quad (10)
\end{align*}
\]

As can be seen from the Fig. 4, the values of ΔG in all the reactions at given temperatures are negative, indicating that all these reactions could take place in view of thermodynamics. Moreover, the reactions (6), (9), (3), (2) and (1) are most favorable for Al-Ti-C system, because the absolute values of ΔG in these reactions are the largest.

![Figure 4](image-url) 

Fig. 4. Changes of Gibbs free energy as a function of temperature.

Fig. 5 shows the DTA curves of initial mixtures with endothermic and exothermic peaks. It was found that for the samples with 35 mass. % of Al, there is a broad endothermic peak at 640 °C and exothermic peak at 800 °C. The endothermic peaks at 635 °C and exothermic peaks at 812 °C and 800 °C respectively were observed in samples with 40 and 45 % Al (Fig. 5c, Fig. 5d). Endothermic effect occurred at temperatures of 635-640 °C due to the liquid phase formation at temperatures lower than the melting point of aluminum, which is connected with the formation of various titanium aluminides or AlTi during sintering. As a result of diffusion of Al atoms in Ti a significant amount of heat released and caused sample heating to the melting point of aluminum. The liquid phase increases interfacial surface, which leads to an increasing the temperature, but all the warmth connected with the intermetallic formation was expended on the process for aluminum melting and exothermic event on the DTA curves in this region, was not observed [7;12].

Exothermic peaks on DTA curves at 800 °C and 812 °C correspond to in-situ formation of titanium carbide by interaction between Ti and C in the liquid phase, which was formed during melting in the Al-Ti system [13;3]. The carbon reacts with molten titanium aluminide by reaction (7), which is the most thermodynamically favorable from all listed above.
It should be noted that in DTA curves there is no exothermic peak connected with the formation of $\text{Ti}_3\text{AlC}_2$, $\text{Ti}_4\text{AlC}_3$, detected during X-ray analysis. The formation of ternary carbides can occur either during slow cooling after $\text{TiC} + \text{TiAl} \rightarrow \text{Ti}_2\text{AlC}$ in $\text{Ti-Al-C}$ system [14-17] or $\text{Ti}_4\text{AlC}_3$, $\text{Ti}_3\text{AlC}_2$ formed simultaneously with titanium carbide particles and their exothermic peaks coincide [18-19].

**Conclusion**

According to the microspectral analysis, X-ray diffraction and differential thermal analysis of Al-Ti-C mixtures with different compositions the presence of TiC and titanium-aluminum complex carbides (ternary carbides) were determined after thermal synthesis. The predominant strengthening phase in specimens with high carbon content (10–13%) is titanium carbide, in samples with minimal carbon content (6%) and relatively high aluminum content (40%) in the structure of the synthesized material predominant disordered elongated needle-like grains of complex ternary titanium-aluminum carbides. The 45Al-11C-44Ti master alloy, where the percentage of aluminum and titanium are practically equal, characterized by very dispersed state of strengthening phase after thermal synthesis.

**References**