TIBAL OUTPERFORMS TICAL IN GRAIN REFINEMENT EFFICIENCY OF ENHANCED EN AW-3003 ALUMINIUM ALLOY PREPARED BY TWIN-ROLL CASTING

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Abstract

Aluminium alloys are popular among automotive heat exchangers designers due to their high thermal conductivity, good corrosion resistance and excellent strength-to-weight ratio. Aluminium alloy EN AW-3003 and its modifications are commonly used in this field. This work investigates the importance that the grain refinement has in changing the microstructure of the enhanced EN AW-3003 alloy with content of Zr and Zn when producing the alloy by Twin-Roll Casting. The work compares the grain refining efficiency of the two most commonly used master alloys, Al–5 wt% Ti–1 wt% B (TiBAl) and Al–3 wt% Ti–0.15 wt% C (TiCAl), using cooling curves analysis, metallographic samples analysis and tensile tests. The results show higher nucleation effectiveness of Al–5 wt% Ti–1 wt% B master alloy when compared to its Al–3 wt% Ti–0.15 wt% C counterpart. In addition, the use of Al–5 wt% Ti–1 wt% B master alloy leads to final product with slightly higher mechanical properties and more uniform microstructure. However, the grain refinement of enhanced EN AW-3003 aluminium alloy is a more complex problem involving other aspects (technological, economic, etc.). This is an important point for future study.

Keywords: Grain refinement, fin stock foils, enhanced EN AW-3003, TRC

1. INTRODUCTION

Nowadays, aluminium alloys play a key role in automotive heat exchanger applications. These materials have an excellent strength-to-weight ratio, generally good corrosion resistance and, most importantly, high thermal conductivity. For heat exchanger tubes and fins, automotive designers frequently use aluminium alloy EN AW-3003 and its modifications. The alloy is based on aluminium-manganese system and it is often modified with small additions of other elements. One of these commonly used modifiers is zirconium which precipitates into Al_3Zr phases. The Al_3Zr pins grain boundary movement during recrystallization and thus improves recrystallization resistance and brazing ability of this alloy. [1, 2, 3]

Several ways how to modify aluminium alloys microstructure and thus achieve desired mechanical properties are available in industrial conditions. One of the most important is grain refinement by inoculation. In inoculation process, insoluble particles are added to the aluminium melt. The particles are released from so-called master alloys and they help to nucleate aluminium grains during the solidification process. Many types of master alloys are available on the market but aluminium producers prefer mostly an Aluminium–Titanium–Boron based alloy (Al–Ti–B; also known as TiBAl) or in some cases an Aluminium–Titanium–Carbon based alloy (Al–Ti–C; also known as TiCAl). [4, 5, 6]

The mechanism of promoting the aluminium grains nucleation differs between TiBAl and TiCAl. When added to the melt, TiBAl releases insoluble TiB_2 particles on which a thin Al_3Ti interlayer nucleates. In the second step, aluminium grains nucleate on the Al_3Ti interlayer. The nucleation mechanism of TiCAl, on the other hand, does not depend on the Al_3Ti interlayer formation, since none is present. In this case, the aluminium grains nucleate directly on the TiC particles that are released into the melt. [4, 7, 8, 9, 10, 11] The schematic particles behaviour during nucleation is shown in **Figure 1**.

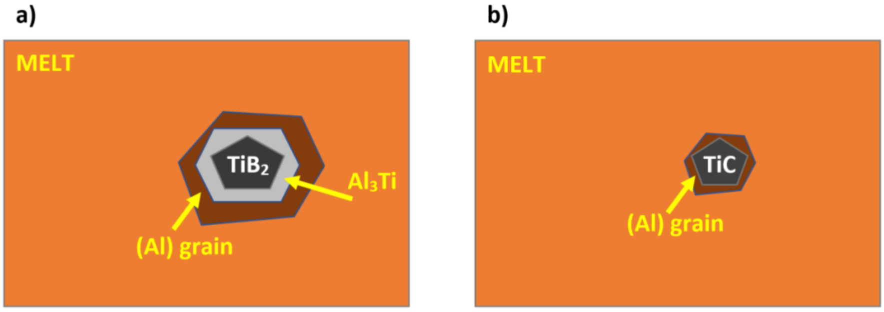


Figure 1 Mechanism of grain refinement by: a) AlTiB, b) AlTiC

The selection between TiBAl and TiCAl depends mainly on the alloy composition and the production technology. In general, TiBAl is more commonly used. TiCAl, on the other hand, is popular among manufactures of aluminium-magnesium alloys where TiB_2 particles promote thick oxide formation [5]. TiCAl also replaces TiBAl in the grain refinement of aluminium alloys with content of zirconium, chromium and/or manganese. These elements cause the so-called poisoning effect which decreases the grain refinement efficiency of Al_3Ti interlayer [7, 12, 13, 14]. The use of TiCAl may also be advantageous for other alloys produced by Direct Chill Casting technology. [4, 9]

However, there is very little data in the literature on the behaviour of TiCAl when used in Twin-Roll Casting technology. An experiment performed on 8111 aluminium alloy comparing the grain refinement efficiency of TiBAl and TiCAl during Twin-Roll Casting process indicates that TiCAl is far less efficient than TiBAl in such case. [15]

This work studies grain refining effect of TiBAl and TiCAl on the microstructure of enhanced EN AW-3003 alloy with content of zirconium, chromium and zinc. Experiments were performed under laboratory conditions as well as in the standard industrial process of Twin-Roll Casting. The aim is to determine which of the two above mentioned master alloys is more effective grain refiner when used under industrial condition and to say whether the laboratory experiments are able to provide similar results.

2. EXPERIMENTAL

Enhanced EN AW-3003 aluminium alloy with zirconium and zinc additions was produced by AL INVEST Břidličná, a.s. company (Czech Republic) by TRC. The composition of the standard alloy EN AW-3003 according to *ČSN EN 573-3+A1* [16] is given in **Table 1**.

Table 1 Composition of standard AW-3003 according to *ČSN EN 573-3+A1* [10]

	Si (wt%)	**Fe** (wt%)	**Cu** (wt%)	**Mn** (wt%)	**Zn** (wt%)	**Others**		**Al** (wt%)
						Each	**Total**	
Min.	-	-	0.05	1.00	-	-	-	Bal.
Max.	0.60	0.70	0.20	1.50	0.10	0.05	0.15	

Samples of the base alloy for laboratory experiments were taken before the grain refiner addition. Samples were remelted under laboratory conditions at 750–770 °C. Than grain refiner, in the form of a small piece of wire (Al–5 wt% Ti–1 wt% B – TiBAl or Al–3 wt% Ti–0.15 wt% C – TiCAl), was added into the melt. The melt was stirred and put back into the furnace for two minutes. Two series of samples were prepared – one for macrostructure (grain size) evaluating and the other for cooling curves assembling.

To evaluate the macrostructure, melt was poured into a steel form with cylindrical core (diameter: approx. 30 mm, height: approx. 60 mm). The cylindrical castings were cut from top to bottom and etched in solution of HNO_3, HCl, HF and H_2O (1:1:1:1 vol. %). Images were taken with a camera. The type and amount of grain refiner added are given in **Table 2**.

Table 2 Amount of grain refiner in prepared samples (macrostructure)

Sample	Base alloy (g)	TiBAl (g)	TiCAl (g)	TiBAl (kg per tonne)	TiCAl (kg per tonne)
No grain ref.	262.45	-	-	-	-
TiBAl (4 kg)	341.93	1.33	-	3.89	-
TiCAl (4 kg)	371.45	-	1.57	-	4.23

To assemble the cooling curves, the melt was poured into a small graphite crucible with a thermocouple. Thermocouple data was processed by DEWE-2010 than transfer to MS Excel to assemble cooling curves. Temperature was measured 20 times per second, but for better clarity only 2 measurements per second (each half a second) are included in the presented curves. The type and amount of grain refiner added are given in **Table 3**.

Table 3 Type and amount of grain refiner in prepared samples (cooling curves)

Sample	Base alloy (g)	TiBAl (g)	TiCAl (g)	TiBAl (kg per tonne)	TiCAl (kg per tonne)
No grain ref.	262.45	-	-	-	-
TiBAl (4 kg)	341.93	1.33	-	3.89	-
TiCAl (4 kg)	227.50	-	0.91	-	4.00

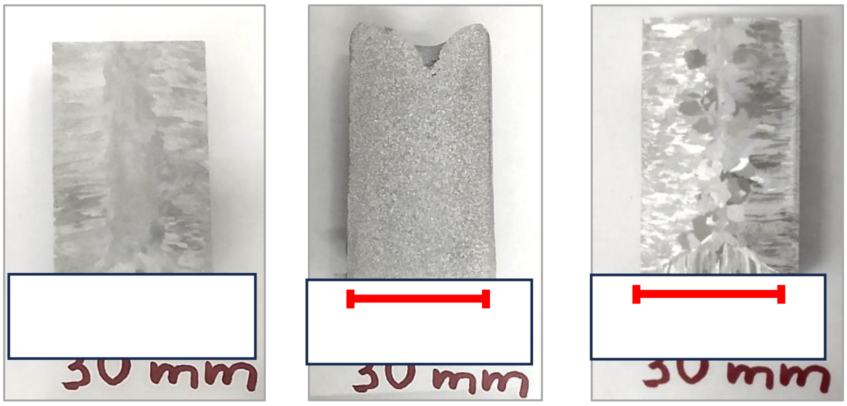
Samples of heat exchanger fin stock foils (thickness approx. 50 µm) were produced by AL INVEST Břidličná, a.s. via Twin-Roll Casting by standard processing route using different types of grain refiners (given in **Table 4**). Metallographic samples of the foils were prepared and they were electrolytically etched (voltage: 35 V) in a solution of HBF_4 and H_2O (9:400 vol%) for 45 seconds. The grains were analysed using an optical microscope OLYMPUS PME 3 in Polarized Light (PL) regime and NIKON NIS-Elements software. The mechanical properties of the foils were measured by MTS Insight 2 tensile test machine.

Table 4 Type and amount of grain refiner in prepared samples of the heat exchanger foils

Sample	TiBAl (kg per tonne)	TiCAl (kg per tonne)
Foil with TiBAl (4 kg)	4.00	-
Foil with TiCAl (4 kg)	-	4.00

RESULTS

The grain structures of cylindrical samples are shown in **Figure 2**.



a) No grain ref. **b) TiBAl (4 kg)** **c) TiCAl (4 kg)**

Figure 2 Grain structures of laboratory prepared samples with different addition of grain refiner

The cooling curves are presented in **Figure 3,** which shows critical solidification interval between 660 °C and 650 °C in detail.

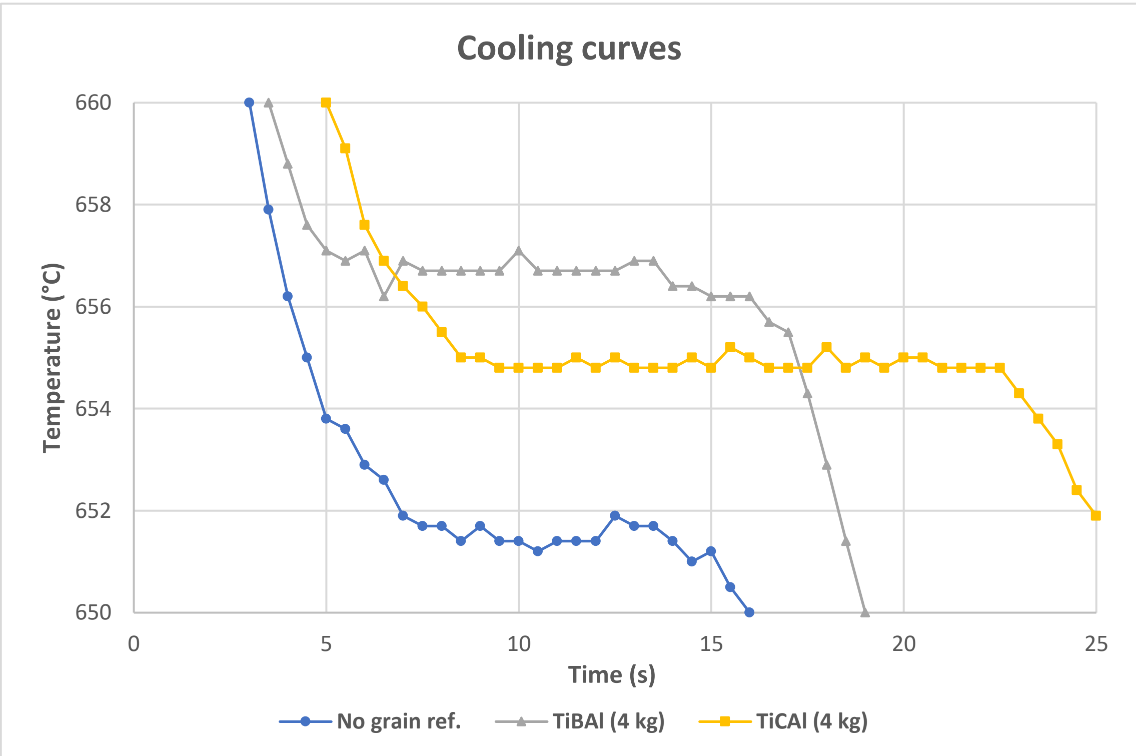
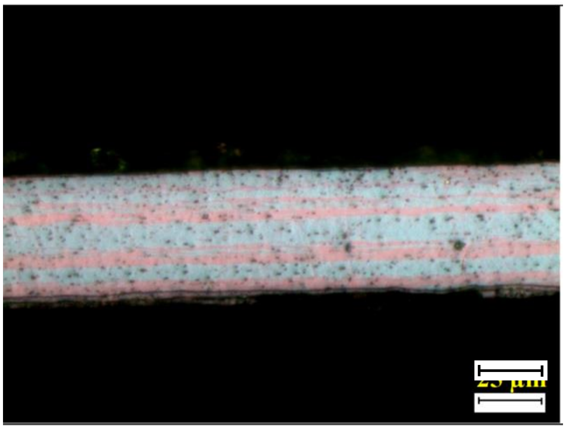
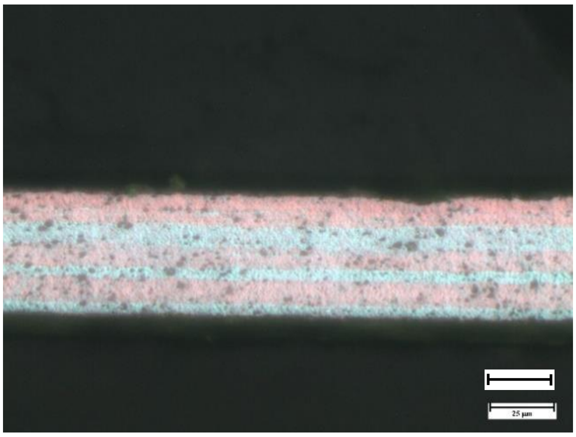


Figure 3 Critical interval (interval of solidification) of cooling curves

The samples of heat exchanger fin stock foils are presented in **Figure4.**





a) Foil with TiBAl (4 kg) **b) Foil with TiCAl (4 kg)**

Figure 4 Microstructure of heat exchanger fin stock foils

The mechanical properties of the foils are given in **Table 5**.

Table 5 Mechanical properties of heat exchanger fin stock Foils

	YS (MPa)	**UTS** (MPa)	**Elongation A_{50}** (%)
Foil with TiBAl (4 kg)	187	205	3.1
Foil with TiCAl (4 kg)	183	199	1.3

DISCUSSION

From **Figure 2** it can be clearly seen that the addition of grain refiner leads to finer and more uniform grain structure. Microstructure of the sample with no grain refiner (**Figure a**) consists of columnar and coarse grains which means that solidification process is slow and significant undercooling has to be achieved. The addition of 4 kg per tonne of TiBAl leads to evolution of very fine and equiaxed grain structure (**Figure b**). The addition of the same amount of TiCAl also leads to finer grain structure (**Figure c**) but the structure is coarser than in case of TiBAl. This does not necessarily contradict the claims in [9, 10, 12] of the generally higher (or at least equal) TiC nucleation site effectiveness compared to the TiB_2 nucleation site. One of the reasons could be higher concentrations of Ti and B in TiBAl (Al–5 wt% Ti–1 wt% B) than Ti and C concentrations in TiCAl (Al–3 wt% Ti–0,15 wt% C) implying different Ti:2B and Ti:C ratios. This means that fewer TiC nucleation sites are available in TiCAl (than TiB_2 nucleation sites in TiBAl).

This can be confirmed by analysing quasi-isothermal periods on the cooling curves in **Figure 3**. The sample with no grain refiner starts to solidify at the lowest temperature (652–651 °C) which corresponds to highest undercooling bellow the melting point. A much lower undercooling must be achieved in case of sample inoculated by 4 kg per tonne of TiBAl which starts to solidify between 657–656 °C. Sample inoculated by 4 kg per tonne of TiCAl starts to solidify at approximately 655 °C, which is less than in the case of sample with 4 kg per tonne of TiBAl, but still much more than in case of sample with no grain refiner. It can be also noticed that isothermal period is shorter in case of TiBAl than in case of TiCAl which is an incentive for further study.

Analyses of the real heat exchanger fin stock foils in **Figure 4** shows a similar trend that can be observed in the laboratory samples. The fin stock foil inoculated by 4 kg per tonne of TiBAlshows a more uniform and finer microstructure that in case of foil inoculated by the same amount of TiCAl. The sample of the foil inoculated by TiBAl also shows higher mechanical properties (Yield Stress, Ultimate Tensile Strength and Elongation) than its counterpart inoculated by TiCAl as can be seen in **Table 5**. This can be attributed to the finer grain structure and its reference to mechanical properties. (The influence of grain size on the Yield Stress according to Hall-Petch equation is well known.)

CONCLUSIONS

Based on experimental results following theses can be concluded:

- By analysing the cooling curves, it is clear that the addition of grain refiner causes a modification of the solidification behaviour of enhanced EN AW-3003 aluminium alloy which means that lower undercooling bellow the melting point has to be achieved.
- Solidification curves shows different times of isothermal solidification periods. For deeper understanding of the influence of grain refining on the solidification of aluminium alloys further study is necessary (e.g. via DSC measurement).
- Addition of 4 kg per tonne of TiBAl (Al–5 wt% Ti–1 wt% B) is more effective for grain refinement than the same addition of TiCAl (Al–3 wt% Ti–0.15 wt% C). This can be caused by several reasons one of which may be lower amounts of Ti and C in TiCAl than amounts of Ti and B in TiBAl.
- The heat exchanger foil inoculated by 4 kg per tonne of TiBAl shows more uniform microstructure than foil inoculated by the same amount of TiCAl despite potential role of Zr poisoning. Role of Zr poisoning in enhanced EN AW-3003 aluminium alloy should be examined in future studies.
- The heat exchanger foil inoculated by 4 kg per tonne of TiBAl shows higher mechanical properties that the foil inoculated by the same amount of TiCAl which is probably related to finer grain structure.
- It is necessary to find the appropriate amount of inoculant for both types of master alloys to achieve good equilibrium between thermodynamic driving force and solidification kinetics which is crucial for proper microstructural development.

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