

# Master Alloy Report

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*Master Alloy for Refiner Mg Alloy*

*Master Alloy for Refiner Al Alloy*

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# Summary

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## Introduction

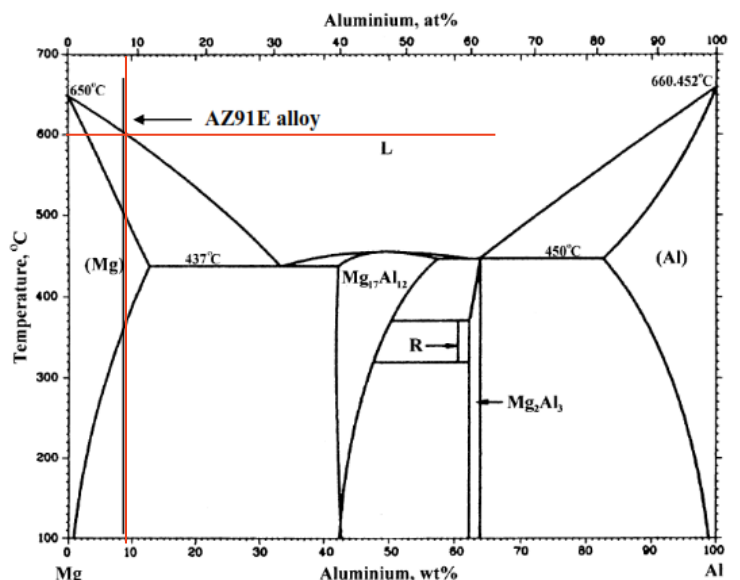
The mechanical properties of **Mg** alloys including modulus of elasticity, strength, hardness, creep resistance of commercial magnesium alloys (**Mg-Al-Zn-Mn**) decrease at temperature above 120°C due to the loss of grain boundary strength. This temperature is relatively low compared to other structural materials.

Molten metal reactivity, castability, grain structure, mechanical properties, chemical properties, physical properties, machinability, formability, and weldability of magnesium can be manipulated by adding alloying elements. Effects of some selected elements are discussed in the following:

**Aluminum** - Refines the as cast grain size of magnesium, because of growth restriction effect caused by constitutional undercooling and micro segregation effect in the interdendritic region. Al improves hardness of Mg alloys, because Al forms  $\beta$ -**Mg<sub>17</sub>Al<sub>12</sub>** phase along the grain boundaries. This phase is very hard and brittle. **Al** also increases corrosion resistance of **Mg** alloys, because the  $\beta$  phase is cathodic and acts as a barrier to corrosion. Further, **Al** improves castability, because it increases the freezing range of **Mg** alloys thus making the alloy/semi-solid for a longer period of time.

The maximum solid solubility limit of aluminum for binary **Mg** alloy is 12.7 wt. %. However, AZ91 is currently the highest **Al** containing (9 wt.%) of **Mg-Al** alloys in commercial applications.

Fig 1.1 - Mg-Al equilibrium phase diagram.



content. This grain refining effect of aluminum continues up to 5wt. % **Al**. Further increase of **Al** concentration has no effect.

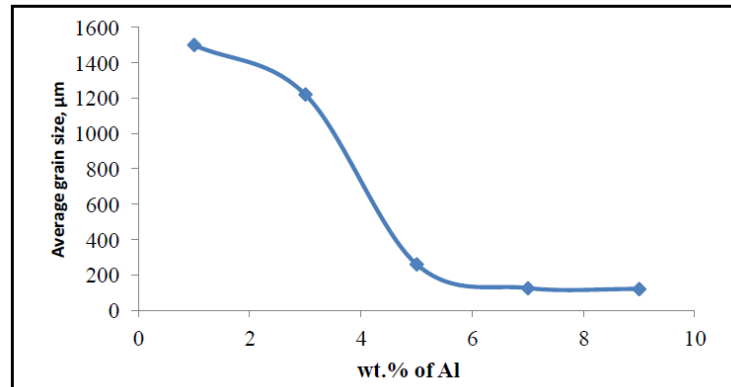


Figure 1.2 - Effect of Al addition on the grain size of pure Mg [1].

[1] Lee, Y. C., Dahle, A. K. and StJohn, D. H., "The role of solute in grain refinement of magnesium", Metallurgical and Materials Transaction A, Vol. 31A, N. 11, 2000, pp. 2895- 2906.

**Copper** - According to **Mg-Cu** binary phase diagram, the solubility of Cu is very low (<0.05%) in  $\alpha$ -**Mg** solid solution. **Cu** improves the high temperature strength of **Mg** alloys due to precipitation hardening. **Cu** is more cathodic than Mg and so high additions of copper may accelerate the corrosion of **Mg** alloys.

**Iron (Fe)** accelerates the corrosion of magnesium by galvanic corrosion. As shown **Mg** (-2.363V) has a greater electronegative potential than **Fe** (- 0.44V). As a result, **Mg** acts as sacrificial anode when connected with **Fe** and immersed in electrolyte. The maximum amount of iron that can be present in commercial grade alloys (**Mg-Al-Zn-Mn**) is 0.01 to 0.03 wt.%.

**Manganese (Mn)** increases the tensile strength of **Mg** alloys, because Mn addition causes grain refinement of magnesium. Due to the increased volume of grain boundaries, dislocation movement is hindered and alloy strength is improved [2].

[2] Matuoka, S., Oguri, M. and Mukai, T., "Mechanical properties and extrudability of Magnesium alloys", in proceedings of the 41st Annual Meeting, JSME Hokuriten Shinetsu Branch, 2004, pp. 215–216.

**Mn** addition to **Mg** alloy also transforms harmful impurities such as **Fe** into relatively harmless intermetallic compounds of **Al-Mn-Fe** [3]. As a result, it can be said that the **Mn** improves the corrosion resistance of **Mg** alloys. The solubility of manganese is relatively low, about 1.5 wt. % for commercial alloys (**Mg-Al-Zn-Mn**). The solid solubility of **Mn** is further reduced to 0.3 wt.% in the presence of aluminium.

[3] Sajuri, Z. B., Miyashita, Y., Hosokai, Y. and Mutoh, Y. , “Effects of Mn content and texture on fatigue properties of as-cast and extruded AZ61 magnesium alloys”, International Journal of Mechanical Sciences, Vol. 48, No. 2, 2006, pp. 198-209.

**Silicon** - The addition of Silicon (**Si**) to magnesium alloys enables the formation of **Mg<sub>2</sub>Si** phase, which has a high melting point (1085 °C) [2] and high heat of fusion (80 kJ/mol compared to 8.9 kJ/mol of **Mg**). As a result, **Si** increases the fluidity of magnesium alloys by reducing the solidification rate, due to the latent heat release of **Mg-Si** phases. Up to 1.5 wt.% **Si** can be added to **Mg** alloys. **Mg<sub>2</sub>Si** phase has high hardness (460 HV), high modulus of elasticity (120 GPa), low thermal expansion ( $7.5 \times 10^{-6}/K$ ) [2] and is very stable, and can thus obstruct grain boundary sliding at elevated temperatures. As a result, addition of **Si** improves the creep properties of **Mg** alloys. Silicon is also sometime added to refine the grain structure of magnesium alloys.

**Zinc (Zn)** increases the room temperature strength of **Mg-Al** alloys, because the solid solubility of **Al** in **Mg** decreases with the addition of **Zn**. Decreasing the solid solubility of **Al** increases the formation of eutectic  $\beta$ - **Mg<sub>17</sub>Al<sub>12</sub>** phase. This hard and brittle  $\beta$  - phase can act as a barrier for dislocation movement during deformation. Solid solubility of **Zn** in **Mg** alloy is 6.2 wt.%. However, maximum of 1 wt.% **Zn** is added in commercial **Mg-Al-Zn** alloys.

## Grain refinement of magnesium alloys

It is well established that grain refinement of polycrystalline materials can improve mechanical properties (e.g., yield strength and hardness), chemical properties (e.g., corrosion resistance of Mg-Al alloys), and improve manufacture ability (e.g., reduce hot tearing susceptibility during casting). However, large grain structure of magnesium alloys are also required in order to improve the creep resistance and use at high (above 150 °C) temperature applications.

There are two types of nucleation processes: **(1) homogeneous** and **(2) heterogeneous**. In a homogenous nucleation process, the nucleus arises from the bulk of the liquid. In heterogeneous nucleation, a foreign particle present in the liquid (***grain refiners - chemical grain refinement***, or metal oxide inclusions) acts as the nucleus.

*In the case of **chemical grain refinement**, the inoculant particles introduced into the molten metal must act as heterogeneous nucleation sites.*

However in many cases, very few of the added grain refiner particles acting as nucleate a grain, because of their segregation effect and poor surface contact with the matrix alloy.

Addition of solute elements into a matrix alloy controls the growth of the nucleated grains in two ways:

(1) microsegregation of solute in the interdendritic region can restrict the grain growth. During dendritic solidification, the dendrites push solute elements towards the interdendritic regions, where the solute elements act as barrier to grain growth.

(2) generating constitutional undercooling in a diffusion layer ahead of the advancing solid liquid interface slows down the diffusion of solute due to the lower freezing point at the interface. Thus, the diffusion of solute also limits the rate of grain growth.

The solute segregation effect can be quantified by the growth restriction factor (GRF),  $Q$ , defined as [4]:

$$Q = m_l \cdot C_0 \cdot (K_0 - 1)$$

Where  $m_l$  is the slope of the *liquidus* line.

Data obtained from binary phase diagrams were used to calculate the GRF values for various alloying elements in magnesium alloys and are shown in Table 1. A solute with a higher value of GRF is expected to have a stronger grain refining effect [5].

Table 1 - Slope of the liquidus line, partition coefficient and growth restriction parameter for various alloying elements in magnesium

Element	$m$	$K$	$m(K-1)$	Reaction type
Zr	6.90	6.55	38.29	peritectic
Ca	-12.67	0.06	11.94	eutectic
Si	-9.25	0.00	9.25	eutectic
Ni	-6.13	0.00	6.13	eutectic
Zn	-6.04	0.12	5.31	eutectic
Cu	-5.37	0.02	5.28	eutectic
Ge	-4.41	0.00	4.41	eutectic
Al	-6.87	0.37	4.32	eutectic
Sc	4.02	1.99	3.96	peritectic
Sr	-3.53	0.01	3.51	eutectic
Ce	-2.86	0.04	2.74	eutectic
Yb	-3.07	0.17	2.53	eutectic
Y	-3.40	0.50	1.70	eutectic
Sn	-2.41	0.39	1.47	eutectic
Pb	-2.75	0.62	1.03	eutectic

[4] Maxwell, I. and Hellawell, A., "A simple model for grain refinement during solidification". Acta Metallurgica, Vol. 23, No. 2, 1975, pp. 229-237.

[5] Lee, Y. C., Dahle, A. K. and StJohn, D. H., "The role of solute in grain refinement of magnesium", Metallurgical and Materials Transaction A, Vol. 31A, No. 11, 2000, pp. 2895-2906.

**There are two major methods which are widely used to refine the grain structure of Mg alloys:**

(1) Rapid cooling of liquid metal during solidification:

Rapid cooling prevents the diffusion of atoms from liquid phase to solid phase, which promotes establishment of constitutional undercooling.

(2) Chemical grain refinement method:

This method involves adding elements or compounds to the melt to promote heterogeneous nucleation.

Chemical grain refinement of magnesium alloys can be done by dividing the magnesium alloys into two groups:

**Group 1** - those alloys with aluminum.

**Group 2** – those alloys without aluminum.

The grain refinement of aluminum free magnesium alloys such as: ZE41, ZK60, WE43 and **ML10** (this alloy is used by Mr Victor – see Table 2 of composition and mechanical properties) can be accomplished by adding zirconium. This method is well established, because the powerful grain refining effect of zirconium is due to the similarity in crystal structure and lattice parameters with magnesium ( $a=0.320nm$ ,  $c=0.520nm$ ) and zirconium ( $a=0.330nm$ ,  $c=0.514nm$ ). This similarity in crystal structure creates smaller wetting angle, which decreases the barrier energy for heterogeneous nucleation.

Table 2 - Characteristics of the Mg alloy – ML10.

Chemical composition wt%										
Fe	Si	Ni	Al	Cu	Zr	Be	Mg	Zn	Y	Impurity
Max 0.01	Max 0.03	Max 0.005	Max 0.02	Max 0.03	0.4 – 1.0	Max 0.001	95.18 – 97.3	0.1 – 0.7	2.2 – 2.8	0.2
Mechanical properties										
				$\sigma_r$ (MPa)	$\sigma_c$ (MPa)	$\epsilon$ (%)				
				226 - 225	137	3				

However, the grain refining ability of zirconium is ineffective for **aluminum based magnesium alloys**, as the zirconium readily forms intermetallic compounds with aluminum.

**Consequently no zirconium is available for refining the grains.**

In Table 3 a variety of chemical elements to grain refinement Mg-Al alloys are presented.



Table 3 – Summary of grain refiners and mechanism for Mg and Mg alloys.

Alloys	Chemical elements	Proposed mechanism
<b>Mg</b>	Al, Zn, RE, Th, Si, Zr addition	growth restriction by solute effect and/or nucleant particles
	C inoculation*	nucleation by Al <sub>4</sub> C <sub>3</sub>
<b>Mg-Al(-Zn-Mn)</b>	Sr addition	growth restriction
	SiC addition	nucleation by SiC particles and/or restriction of growth
<b>Mg-Al-Mn(-Zn)</b>	Elfinal process**	nucleation by Fe-Mn-Al compounds
<b>Mg-Al-Mn (-RE-Mn)</b>	Elfinal process**	nucleation by Fe compounds
	Zr addition	nucleation by Zr particles
<b>Mg-Y (-Zn)</b>	Ca + Zr	growth restriction / nucleation by Zr particles

\*\* In the *Elfinal* process, anhydrous ferric chloride (FeCl<sub>3</sub>) is added to the molten magnesium alloy at a temperature range of 740 to 780 °C. According to Cao *et al.* [6], Fe-Al-Mn particles act as potential nuclei for -Mg. The main disadvantage of this process is that due to the addition of iron, it increases the risk of corrosion.

[6] Cao, P., Qian, M. and StJohn, D. H., "Effect of iron on grain refinement of high-purity Mg-Al alloys", Scripta Materialia, Vol. 51, No. 2, 2004, pp. 125–129.

The addition of other solutes (e.g., Sr, Si, Ca, Al) refines the grains, because of the microsegregation and constitutional undercooling effects. **However, addition of these solutes works effectively on grain refinement for lower wt.% Al (up to 3 wt.% Al) alloys.**

Among the above mentioned methods, addition of carbon containing agents is the most effective chemical grain refinement method. Carbon containing agents can be added to Mg-Al alloys at lower temperatures (700 °C), and:

- (1) The grain refiners experience less fading with long holding time.
- (2) Also, a large melt volume of Mg-Al alloys can be refined.
- (3) In addition to this, carbon containing agents can refine Mg-Al alloys up to 9 wt.% Al.

#### **\*Carbon inoculation**

This process involves the introduction of carbon into the molten magnesium at 700-800°C. Carbon can be added into the molten magnesium in the form of pure carbon such as graphite and carbon powder, carbonaceous gases (CO, CO<sub>2</sub>, CH<sub>4</sub>), wide range of carbon containing agents such as hexachlorobenzene (C<sub>6</sub>Cl<sub>6</sub>), hexachloroethane (C<sub>2</sub>Cl<sub>6</sub>), **silicon carbide (SiC)**, **aluminum carbide (Al<sub>4</sub>C<sub>3</sub>)**, calcium carbide (CaC<sub>2</sub>), and master alloys such as Al<sub>4</sub>C<sub>3</sub>-SiC/Al.

The grain refining mechanisms by carbon inoculation are not yet fully understood. When carbon is added into the molten Mg-Al alloys, it reacts with aluminium in the melt and forms a large number of Al<sub>4</sub>C<sub>3</sub> particles, which can act as effective heterogeneous nucleation sites for primary magnesium ( $\alpha$ -Mg).

*C<sub>2</sub>Cl<sub>6</sub> was reported as the most useful grain refiner for Mg-Al alloys.*

The only disadvantage is that the refining process by C<sub>2</sub>Cl<sub>6</sub> usually releases toxic gases, which cause serious environmental and workplace health and safety concerns.

*As a result, **SiC** particles have been selected by many researchers as an alternative to C<sub>2</sub>Cl<sub>6</sub> for grain refinement of Mg-Al alloys. In addition, SiC particles are relatively inexpensive and easily available.*

Early investigations [7,8] reported that the crystal structure and lattice parameters of SiC are very close to that of  $\alpha$ -Mg. Thus, SiC particles may act as heterogeneous nucleation sites for grain refinement.

[7] Luo, A., "Heterogeneous nucleation and grain refinement in cast Mg (AZ91) SiCp metal matrix composites", Canadian Metallurgical Quarterly, Vol. 35 No. 10, 1996, pp. 375– 383.

[8] Cai, Y., Taplin, D., Tan, M.J. and Zhou, W., "Nucleation phenomenon in SiC particulate reinforced magnesium composite", Scripta Materialia, Vol. 41, No. 9, 1999, pp. 967– 971.

According to some studies is demonstrated that the addition of  $Al_4C_3$ -SiC/Al above 0.5 wt.% had little influence on further refinement of the grain size of both AZ31 and AZ63.

*Addition of  $Al_4C_3$ -SiC/Al to the AZ91 had no influence on the alloy's mean grain size, because of the high Al content in AZ91 alloy, the grains are already refined due to microsegregation effect of Al.*

Easton *et al.* [9] added master alloys of 0.15 and 0.3 wt.% SiC with pure Mg to the molten Mg-Al alloys. The grain size of Mg-1 wt.% Al was drastically reduced with the addition of 0.15 wt.% SiC. No significant grain refinement was observed with the addition of 0.15 wt.% SiC to higher Al content Mg-Al alloys.

[9] Easton, M. A., Schiffli, A., Yao, J. Y. and Kaufmann, H., "Grain refinement of Mg-Al(-Mn) alloys by SiC additions", Scripta Materialia, Vol. 55, No. 4, 2006, pp. 379–382.

Also, according to Easton *et al.* [9] the grain refinement of Mg-Al alloys with the addition of SiC was due to the heterogeneous nuclei sites of  $Al_4C_3$ .

### **Effect of Al-SiC on average grain size of AZ91E alloy**

In Figure 2.1 is presents the final mean grain size of AZ91E alloy obtained by [10]. As shown in Figure, the final mean grain size of the unrefined alloy was 227.5  $\mu\text{m}$ . The grain size decreased to 197.5  $\mu\text{m}$  with the addition of

**0.1 wt.% Al-SiC.** Further addition of Al-SiC increased the mean grain size. With the addition of 0.2 wt.% Al-SiC, the grain size increased to  $360.9\mu\text{m}$ , while the addition of 0.5 and 1 wt.% Al-SiC increased the grain size to 326.3 and  $296.5\mu\text{m}$ , respectively.

[10] Amit Azad, "Grain Refinement of magnesium Alloy AZ91E". Thesis submitted for the Degree of master Of Applied Science. 2012

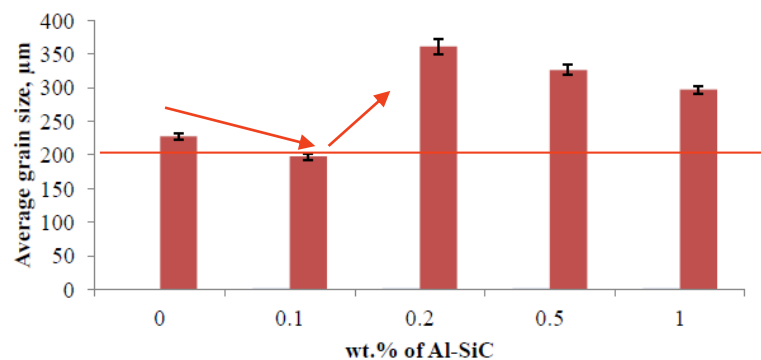


Fig 2.1 - Final mean grain size of AZ91E alloy at various wt.% of Al-SiC.

**It is also recognized that the grain size depends on the exact alloy composition and casting process.**

Thus the wt% of Al-SiC ideal can be little bit different.

#### **Others conclusions of this study:**

- (1) The increasing the wt.% of Al-SiC increased the amount of the  $\beta$ - phase ( $\beta$ - Mg<sub>17</sub>Al<sub>12</sub>).
- (2) For higher solute concentrations, Al forms the eutectic  $\beta$ - Mg<sub>17</sub>Al<sub>12</sub> phase. As a result, the total volume fraction of the  $\beta$ - phase in the alloy was seen to depend on the amount of aluminium in the system and appeared to increase with increasing amount of master alloy addition.
- (3) The increased amount of  $\beta$ -phase may potentially improve the room temperature properties of the new alloy. **However, it is known that for high-**

temperature applications  $\beta$ -phase is a contributing factor for the poor creep performance of aluminium-containing Mg alloys.

(4) It was found that increasing the addition level of Al-SiC had an effect on porosity. The porosities were found as interdendritic shrinkage porosity. The lowest mean area percentage of porosity was found with the addition of 0.1 wt.% Al-SiC, which agreed with the finest alloy grain size.

**Adding other additives**

Scandium (Sc) as element to refiner Magnesium Alloys

V. A. Shalomeev *et al.* [11] studied the effect of scandium on the structure and properties of magnesium alloys MI-5 and MI-10.

[11] V. A. Shalomeev, N. A. Lysenko, E. I. Tsvirko, V. V. Lukinov, V. V. Klochikhin, "Structure and Properties of Magnesium Alloys with Scandium". Metal Science and Heat Treatment. 50(1-2), 2008. p 34-37

Table 4 - Effect of scandium on the properties of magnesium alloys MI-5 and MI-10.

Alloy grade	Estimated quantity of scandium, %	Mechanical properties	
		$\sigma_r$ , MPa	$\delta$ , %
MI-5	–	216	5
	0.20	254	7
	0.50	239	7
	1.00	188	6
MI-10	–	235	4
	0.02	252	4
	0.05	245	6
	0.07	240	4
	0.10	254	6
	0.30	199	3
	0.50	235	4
	0.70	200	4
	1.00	187	3

The results of mechanical indicate (Table 4) that introduction of up to 0.5% scandium additive into alloy MI-5 slightly improves the mechanical

properties. Under a further increase in scandium content, the mechanical properties of the alloys deteriorate.

Scandium additive up to 0.1% in alloy MI-10 also increases its mechanical properties, and a further increase in scandium content decreases the mechanical parameters of this alloy.

**Observation:**

Improved mechanical properties and structural uniformity of Mg-based alloys can be achieved by use of grain-refining additives prior to casting. Ceramic particles of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and SiC can serve as such additives to refine the microstructure of Mg–Al-based alloys.



However, direct introduction of ceramic particles into Mg matrix is limited by the poor wetting of those particles by liquid Mg and their massive agglomeration.



**Solution:**

To use ultrasonic intensity based in MMM technology for:

- (1) Grain refinement with significantly improved and 3D uniformly distributed micro-crystallization.
- (2) Disintegration, wetting and dissolving of non-metallic and metallic inclusions, making smooth intermetallic transitional areas.
- (3) Alloys mixing with nano-particles, increasing density of alloys.

### Al-Ti-B and Sr as element to refiner Magnesium Alloys

Master alloys including **Al-4Ti-5B** [12] and **Mg-10Sr** [13] were added in Mg alloys to improve on grain refinement efficiency of Mg alloys.

[12] Wang, Y., Zeng, X. and Ding, W., "Effect of Al-4Ti-5B master alloy on the grain refinement of AZ31 magnesium alloy", Scripta Materialia, Vol. 54, No. 2, 2006, pp. 269-273.

[13] Yang, M., Pan, F., Cheng, R. and Tang, A., Effect of Mg-10Sr master alloy on grain refinement of AZ31 magnesium alloy, Materials Science and Engineering A, Vol. 491, 2008, pp. 440-445.

It was shown by Wang *et al.* [12] that the optimum addition level of master alloy Al-4Ti-5B was 0.3 wt. % for an effective reduction in grain size of AZ31, where the average grain size was reduced to 80 $\mu\text{m}$  from 1100 $\mu\text{m}$ .

**Wang et al. observed the sample under SEM and proposed that the grain refinement was due to the heterogeneous nucleation by TiB<sub>2</sub>.**

According to Yang *et al.* [13], the addition of Mg-10Sr into AZ31 had grain growth restriction effect, which has led to grain refinement of AZ31.

Recently, Elsayed *et al.* [14] **examined Al-5Ti-1B and Al-1Ti-3B master alloys as grain refiners for AZ91E**. They found 1.0 wt.% addition of Al-1Ti-3B reduced the grain size of the base alloy of AZ91E from 1000 $\pm$ 131 $\mu\text{m}$  to 361 $\pm$ 67 $\mu\text{m}$  and 0.1wt.% Al-5Ti-1B reduced the grain size to 323  $\pm$  59.

[14] Elsayed, A., Ravindran and Murty, B.S., "Effect of Al-Ti-B based master alloys on grain refinement and hot tearing susceptibility of AZ91E magnesium alloy", Material Science Forum, Vol. 690, 2011, pp.351-354.

According to description of Mr Victor the Alloy **ML5 is equivalent to AZ91E**, Also him reported in the email:

*We already applied (in December 2013) the master alloy modifier for aluminum Al-Ti-B, for industrial production (made by Puga). It is not necessary to prepare it at "home in Russia", since it must be very carefully mixed and stirred homogeneously, crushed to small particles (ultrasonically) and should not be drown. This is what Puga prepared for our experiment (in December 2013),*

and later we got certified laboratory test data, which fully meet requested technical conditions - strength gap (23kg/mm<sup>2</sup> or more), and other parameters were very good, and our customer is satisfied. We also applied ultrasound – which is clean and stable technology.

Thus according to the preliminaries results obtained in NIAT and results of others authors we are advance on the right way!

In table 4 are presented the Characteristics of the Mg alloy – ML5.

Table 5 - Characteristics of the Mg alloy – ML5.

Chemical composition wt%										
Fe	Si	Mn	Al	Cu	Zr	Be	Mg	Zn	Ni	Impurity
Max 0.06	Max 0.25	0.15 – 0.5	7.5 – 9.0	Max 0.1	Max 0.002	Max 0.002	89.1 – 92.15	0.2 – 0.8	Max 0.01	0.5
Mechanical properties										
			$\sigma_r$ (MPa)		$\sigma_c$ (MPa)		$\epsilon$ (%)			
			250 - 255		90 - 120		4 - 9			

The Figure 2.1 present the Influence of Al-5Ti-1B Addition Levels and Holding Time on the Grain Size of AZ91E [15].

[15] Abdallah Elsayed, “Novel grain refinement of AZ91E magnesium alloy and the effect on hot tearing during solidification”. Thesis to Master of Applied Science.

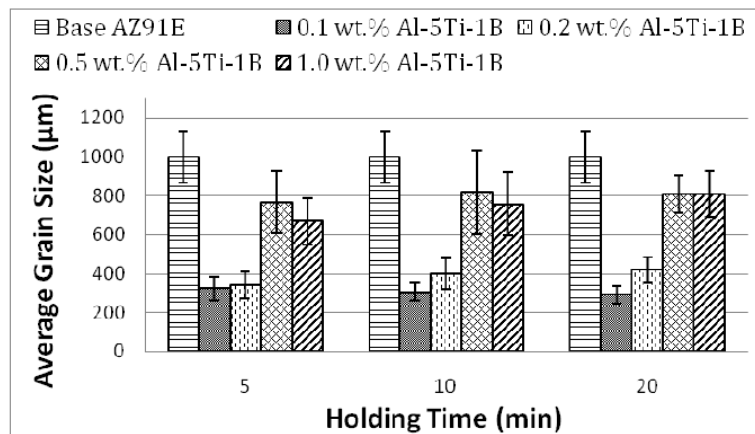


Fig 2.2 - Influence of Al-5Ti-1B Addition Levels and Holding Time on the Grain Size of AZ91E.



A quantitative summary of the average grain sizes with error bars representing one standard deviation is shown in Figure 2.2. It is believed that TiB<sub>2</sub> particles within the grain refiners provided heterogeneous nucleating sites during solidification.

The fading of the grain refiner could be explained by density differences between the Mg and TiB<sub>2</sub>. For each casting, the liquid metal was ladled from the top of the crucible. As time progressed the denser TiB<sub>2</sub> particles (4.38 g/cm<sup>3</sup>) likely sunk to the bottom of the less dense (1.74 g/cm<sup>3</sup>) Mg melt. Therefore, at longer holding times, fewer TiB<sub>2</sub> particles were available for nucleation.

At addition levels of 0.5 and 1.0wt.%, the poor grain refinement was attributed to TiB<sub>2</sub> particle agglomeration. Fine particles, such as TiB<sub>2</sub> tend to agglomerate to reduce their surface energy.

## Master alloys treated by US

The addition of grain refiners, **usually master alloys** containing potent nucleant particles, promotes formation of fine equiaxed grains by deliberately suppressing the growth of columnar and twin columnar grains. The finer equiaxed grain structure ensures [15-17]:

- (i) uniform mechanical properties (strength and ductility).
- (ii) reduced ingot cracking.
- (iii) improved feeding to eliminate shrinkage porosity.
- (iv) distribution of second phases and microporosity on a fine scale.
- (v) improved machinability
- (vi) improved formability during subsequent processing (extrusion and rolling).
- (vii) reduced need or time for homogenisation treatment.
- (viii) reduction of surface defects during extrusion and rolling.

[15] Z.H. Zhang, X.F. Bian, Y. Wang, X.F. Liu, and Z.Q. Wang, TEM observations of a rapidly solidified Al-Ti-C alloy, *J. Alloy Compd.*, **349**(2003), p. 121

[16] M.G. Chu. W. Schneider (Ed.), *Light metals 2002*, TMS, Warrendale [PA] (2002), pp. 899–907

[17] D.A. Granger. B. Welch (Ed.), *Light metals 1998*, TMS, Warrendale [PA] (1998), pp. 941–952

The main master alloy is based on the Al-T-B system, namely Al<sub>5</sub>Ti<sub>1</sub>B and Al<sub>3</sub>Ti<sub>1</sub>B, which essentially contain a mixture of TiB<sub>2</sub> and Al<sub>3</sub>Ti in the matrix. The microstructure of Al–Ti–B grain refiners consists of large Al<sub>3</sub>Ti particles and finer boride particles mostly agglomerated in clusters within the Al matrix, according Figure 3.1.

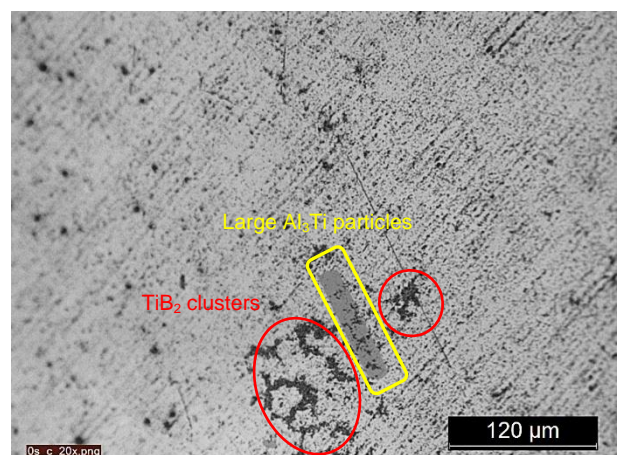


Fig 3.1 - Optical micrograph of an Al<sub>3</sub>Ti<sub>1</sub>B master alloy showing large **Al<sub>3</sub>Ti particles** and numerous **TiB<sub>2</sub> clusters** of particles within the (Al).

Propagation of high intensity ultrasound vibration in liquid metals leads to cavitation and acoustic streaming



*which can cause locally high temperature and pressure region and intense agitation in the melt.*

These non-linear effects can influence the degassing and solidification process greatly. Most of the previous reports on ultrasonic vibration are focused on the *as-cast* grain refinement of low-melting alloys or improvement on wetting of particles in composite fabrication.

**Important observation:**

The desirable characteristics for a good grain refiner may be summarized as follows:

- (i) small ( $\sim 1\mu\text{m}$ )  $\text{TiB}_2$  particle size.
- (ii) absence of large  $\text{TiB}_2$  agglomerates ( $< 50\mu\text{m}$ )
- (iii) low concentration of non-metallic inclusions.

It is known that Al-Ti-B grain refiners are widely used in the aluminum and magnesium industry. However, there are some problems with Al-Ti-B alloy, such:

- (i) agglomeration of the borides ( $\text{TiB}_2$ ).
- (ii) the existence of Zr, Cr, and V elements poisoning its grain refinement efficiency.

**However**, there are few papers on ultrasonic application in Al-Ti-B master alloy.

Until to the moment is possible to find **two types of experiments**:

**Experiments 1:** Ultrasonic treatment was applied in the remelting process of a commercial Al-5Ti-1B master alloy. The commercial Al-5Ti-1B master alloy was remelted at  $730^\circ\text{C}$  in a SiC crucible and held for 30min at this temperature.

Then, ultrasonic vibration based on the MMM technology was applied from the upper of the melt during 60 seconds and after the melt was poured into a permanent mold. *(Experimental made by H. Puga and M. Prokic. 2014)*

Figure 3.1 and 3.2 show the difference between micrograph of an Al<sub>3</sub>Ti1B master alloy before (conventional shape) and after processed by MMM ultrasound technology.

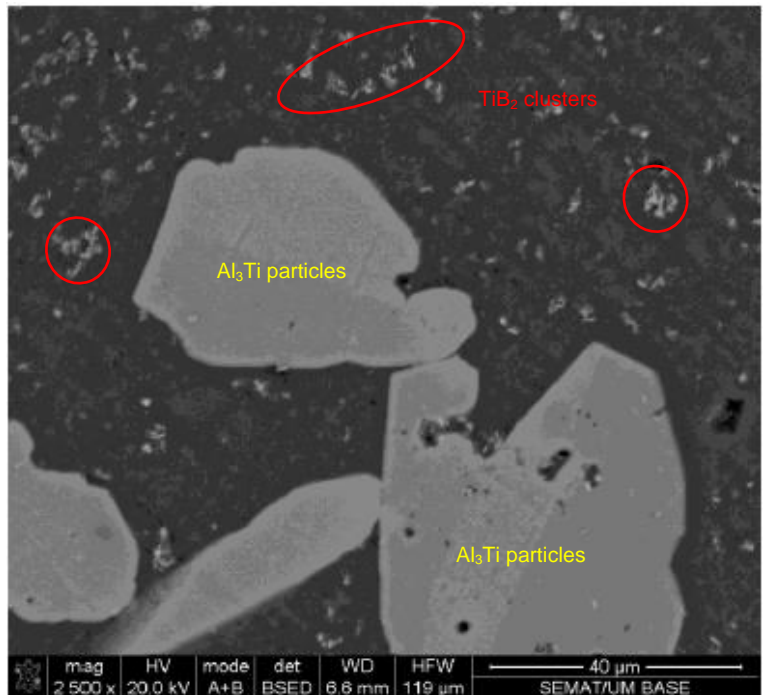


Fig 3.2 - SEM micrograph of an Al<sub>3</sub>Ti1B master alloy.

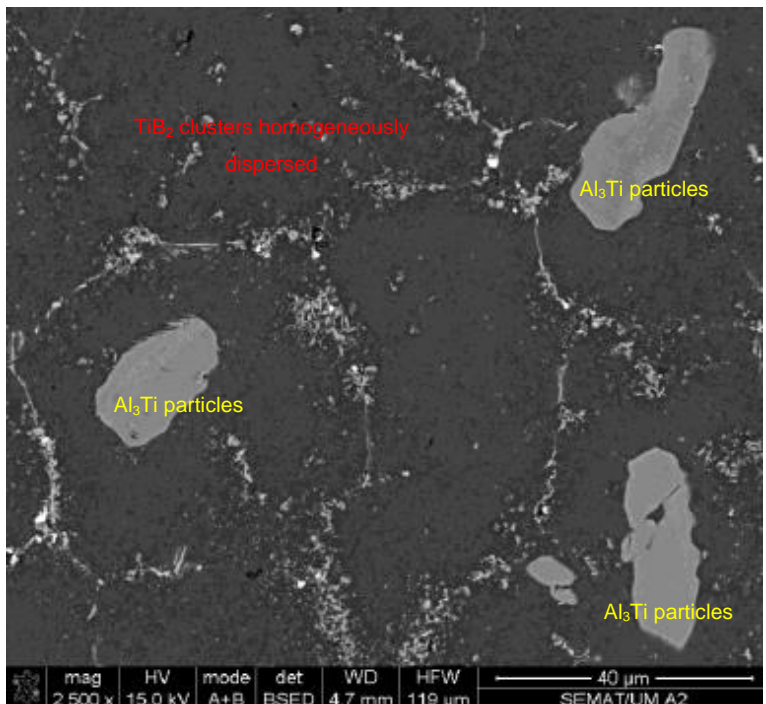


Fig 3.3 - SEM micrograph of an Al<sub>3</sub>Ti1B master alloy processed by US during 60seconds at 730C.

$TiAl_3$  particles are in rod-like form, the size of which is reduced. A strong treatment promoted by MMM technology promotes the breakdown of the  $TiAl_3$  particles as shown in Figure 3.4. The size of the black  $TiB_2$  particle agglomerations is also decreased, and the distribution of them is more uniform. Consequently, the agglomeration of  $TiB_2$  particles is significantly alleviated with ultrasonic treatment.

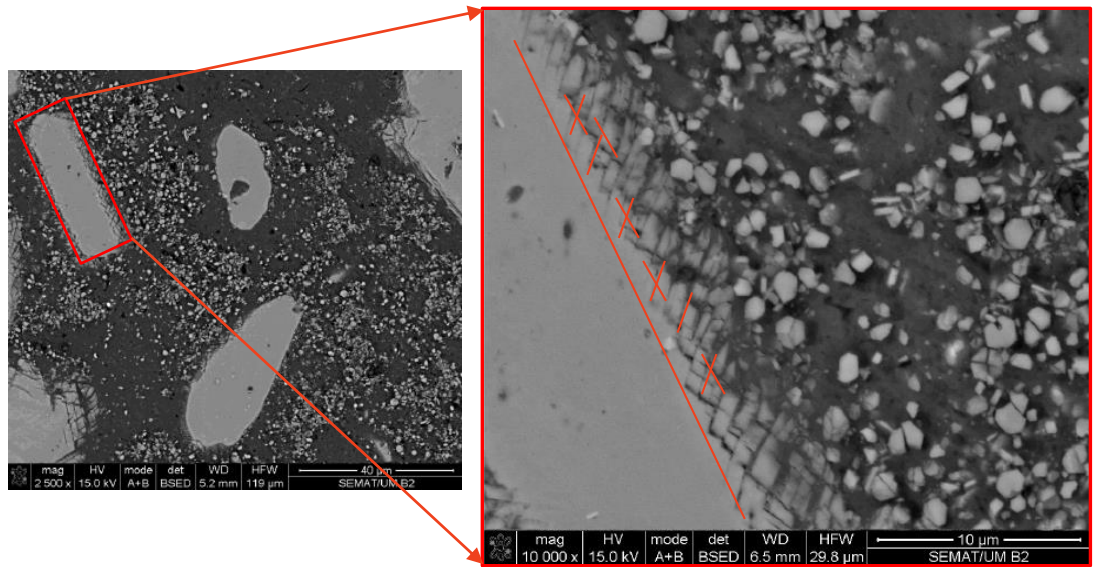


Figure 3.4 - Break of the  $TiAl_3$  particles promoted by MMM technology.

***Ultrasonic treatment on Al–Ti–B master alloy may improve the morphologies of  $TiB_2$  particles and  $TiAl_3$  phase and increase the grain refinement of the master alloy thereby.***

The Figure 3.5 and 3.6 show the optical microstructures of commercial purity aluminium with 2% of Al–5Ti–1B master alloy. It is shown that the commercial purity aluminium can be well refined by the addition of the new (Figure 3.5) or conventional (Figure 3.6) Al–5Ti–1B master alloy, while the grain refining properties of the new (Figure 3.5) Al–5Ti–1B master alloy is much better than that of the conventional (Figure 3.6) Al–5Ti–1B master alloy under the same addition level. This results are according to the results presented by Y. Han *et al* [18], according Figure 3.7.

Fig 3.5 - Refinement of commercial purity Al with 2% of Al-5Ti-1B of master alloy treated by ultrasound (process of remelting).

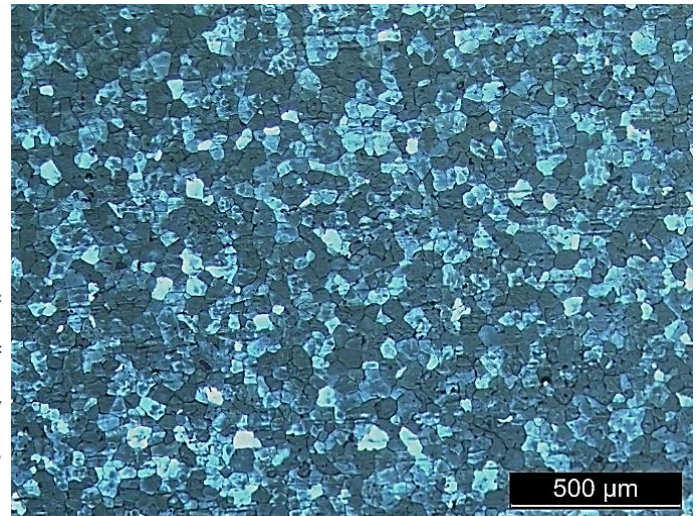


Fig 3.6 - Refinement of commercial purity Al with 2% of Al-5Ti-1B of master alloy commerciality available.

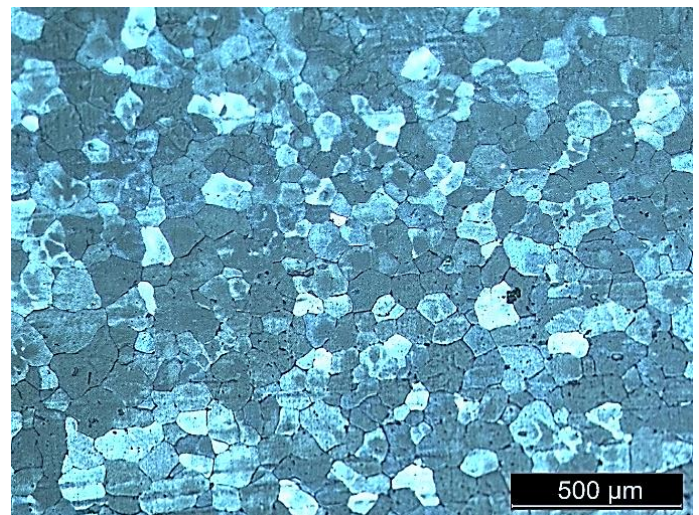
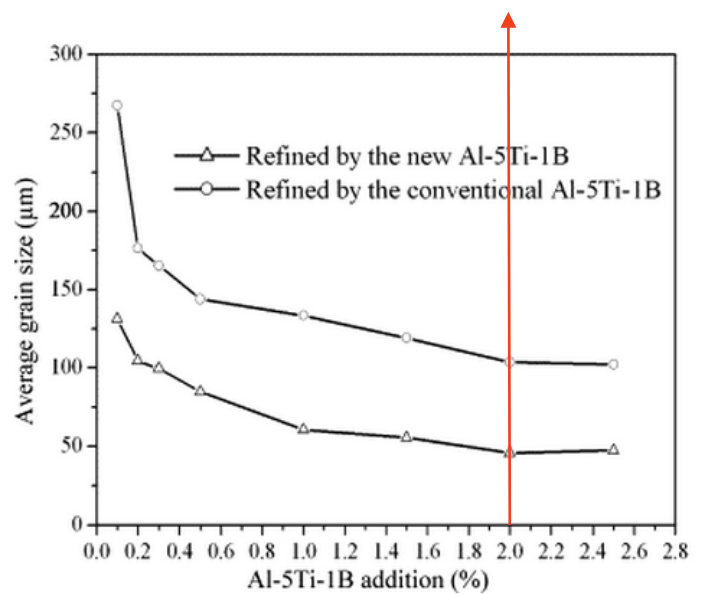


Fig 3.7 - Results presented by Y. Han et al [18].



Figures 3.8 and 3.9 show the effect of Al5Ti1B master alloy (Fig 3.8 - Commercial shape and Fig 3.9 - ultrasonically treated) on grain size of the AlSi9Cu3 alloy.

Fig. 3.8  
AlSi9Cu3 +1%of Al5Ti1B  
(Conventional master Alloy)

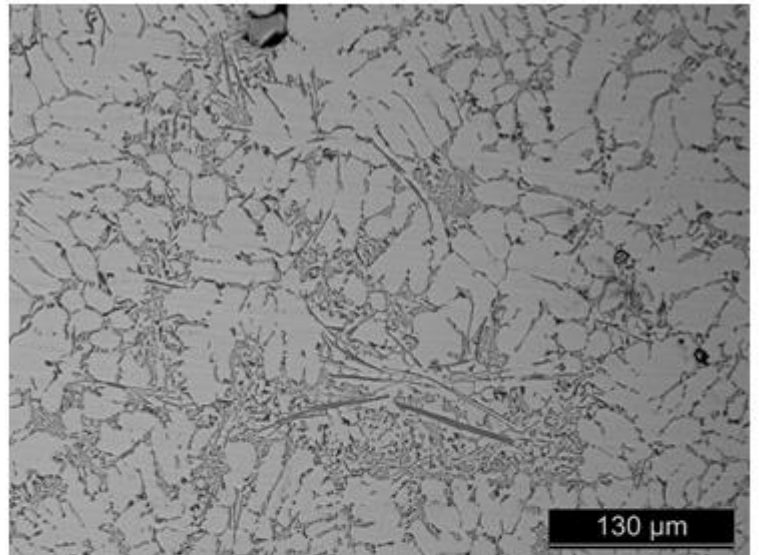
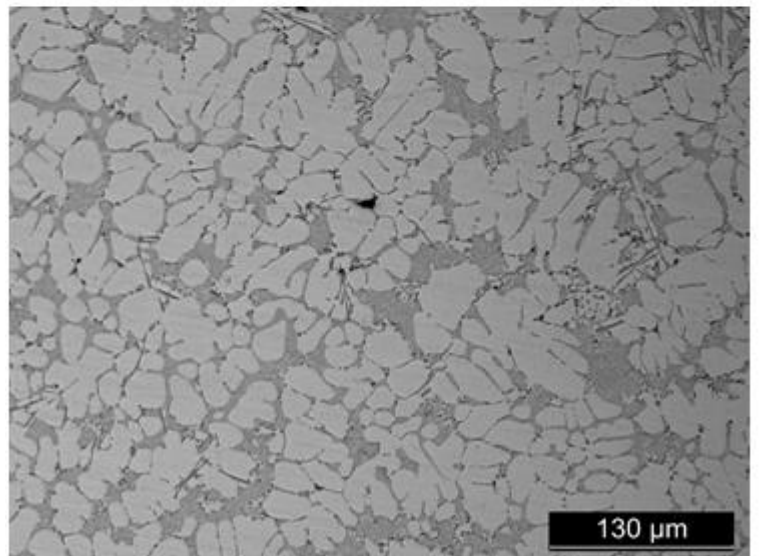


Fig. 3.9  
AlSi9Cu3 +1%of Al5Ti1B  
(Conventional master Alloy)



**Experiments 2:** Ultrasonic treatment can be applied in the preparation of an Al-5Ti-1B master alloy by the action of molten aluminium with  $\text{KBF}_4$  and  $\text{K}_2\text{TiF}_6$  at 820 °C in a resistance furnace.

*(Experimental conditions that Mr Jaco want to test)*

*What is expected?*

The ultrasound applied in the preparation of the Al–5Ti–1B master alloy mainly influences the reaction between the halide salts and the melt. Because of the cavitation and acoustic steaming effects of ultrasonic treatment, on one hand the general return circulation in the bulk of the melt gives the halide salts,  $\text{KBF}_4$  and  $\text{K}_2\text{TiF}_6$ , more opportunity to contact with each other, on the other hand the locally high temperature and pressure effects accelerate the reaction. These two effects jointly make the reaction complete shortly [18].

The ultrasonic vibration at the early fabrication stage and during the solidification can obviously improve the grain refining performance of Al–5Ti–1B master alloy [18].

[18] Yanfeng Han, Ke Li, Jun Wang, Da Shu, Baode Sun, "Influence of high-intensity ultrasound on grain refining performance of Al–5Ti–1B master alloy on aluminium", V 405 /1-2), 2005, 306-312



## Some Conclusions:

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- (1) The ultrasonic influence applied to a molten metal flow, creates a zone of acoustic cavitation in it, where additional modifiers in a shape of refiner rod are introduced.
- (2) During cavitation processing of the melt there is a destruction of nucleating agglomerates of disperse particles like  $TiB_2$  and activation of ultrafine particles of  $Al_3Ti$  that increases quantity of the effective particles participating in grain nucleation process.
- (3) The additional contribution to grain refinement is introduced also by activation of insoluble particles of aluminum oxides in the cavitation stream due to cleaning of their surface to an juvenile state and the subsequent wetting by melt.
- (4) Joint action of the above factors allows to receive non dendritic structure in ingots of aluminium alloys irrespective of the ingot size due to creation of excess number of the crystallization centers just before hit of a stream of melt in a mold.
- (5) Application of cavitation influence allows to decrease an expenses of a material to 30%.
- (6) By means of UT the agglomerates are broken off, the expense of refiner rod is decrease at identical amount of grains or the amount of grains increases. Additionally, there is a degassing and cleaning of the melt from oxide films."

***The morphology of the  $TiB_2$  particles is mainly decided by the manufacturing process of the Al-Ti-B master alloy***