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# Analysis on the Formation of ALN Particles via Gas/Liquid Reaction In-Situ

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***Abstract* - AlN particles were successfully synthesized by the reaction in-situ between nitrogen gas and liquid aluminum. At high temperature nitrogen molecules decompose into atoms and react with Al to create AlN. The most important technological factors such as nitrogen gas rate, temperature of the melt and reaction time were investigated. Their optimal values were found: nitrogen rate 0.2 l/min, melt temperature 1150 0C, blowing time 2 hours. EDX diffraction shows that wight ratio of the particles fully coincides with the ratio of standard atomic mass between Al and N (about 2), confirming that these particles are AlN. The SEM pictures show that AlN particles size varies from several hundreds nanometers to some micrometers, depending on the contact time between gas bubles and liquid metal. A simple model shows that the growth rate of the AlN particles (0,148 nm/s) at the early stage is only a half of that at finishing stage (0,305 nm/s), may be due to the difficulty of the nucleation at the early stage. The formation rate of AlN was calculated based on the X-ray diffraction and shows the same tendency, as the growth rate.**

***Keywords* - Gas injection, microstructure formation, aluminum alloys, aluminum nitride; metal composite; In-situ methods, kinetics.**

## I. INTRODUCTION

Aluminum casting alloys conventionally used in the automotive and aero space industries (i.e., Al-Zn-Mg, and Al-Cu-Mg systems) are able to achieve excellent tensile strength at room temperature. However, at high temperature, such alloys lose dimensional stability and their mechanical properties rapidly degrade. Aluminum-based nanocomposites show the potential for enhanced performance at high temperatures. Many composite manufacturing ex-situ methods have been used, however, they have certain limitations such as high cost of the product, application scope is limited. That is why today the attention is focused on the *in-situ* methods, such as thermogravimetry method [1], melt spinning [2], liquid nitridation [3], stir casting process [4] and so on. In this work a novel fabrication process via gas/liquid reaction *in-situ* to synthesise AlN particles in the aluminum matrix was studied.

The nitrogen-bearing gas was injected into the melt at high temperature (1150 $^0$C) through a refactory ceramic tube and AlN particles were synthesized via chemical reaction. The AlN particles were proven to be very good reinforcement for aluminum alloys in comparison with others (table 1).

**Table 1:**
**Mechanical properties of AlN and some other reinforcements [5].**

| Properties | AlN | $Al_2O_3$ | BeO | SiC |
|---|---|---|---|---|
| Density (g/cm$^3$) | 3.25 | 3.89 | 2.90 | 3.217 |
| Bending strength (MPa) | 340–490 | 304–314 | 245 | – |
| Hardness Vickers (GPa) | 11–12 | 23–27 | 12 | 24 |
| Compressive Modulus (GPa) | 202–237 | – | – | – |

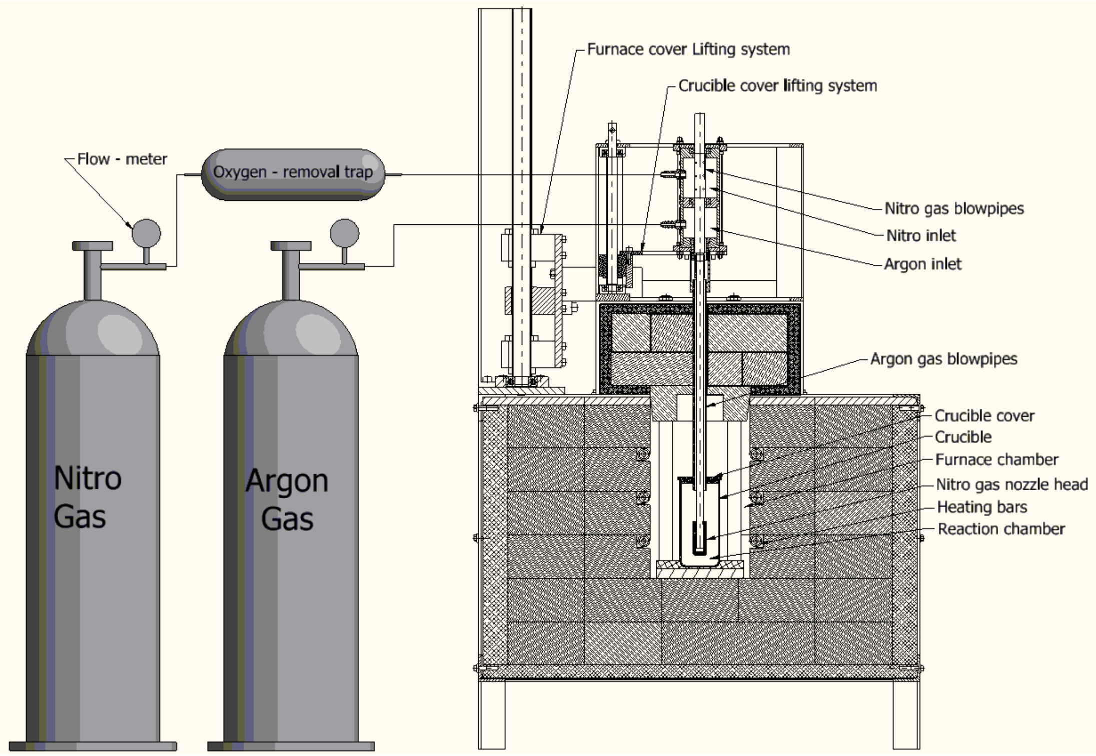
The formation of AlN particles can be proceeded by two routes [6]:

- Direct mechanism: $2Al + N_2 \rightarrow 2AlN$
- Indirect mechanism via intermediate compound $Mg_3N_2$, which is synthesized via reaction: $3Mg + N_2 \rightarrow Mg_3N_2$ (1), which then reacts with liquid aluminum to create AlN via reaction $Mg_3N_2 + 2Al \rightarrow 2AlN + 3Mg$ (2).

## II. EXPERIMETAL

The aluminum – 15% Mg alloy was use for experimental procedure. The equipment for synthesis of AlN is shown in the figure 1, including:

1. The furnace with automatic temperature control, which can raise the temperature until 1200$^0$ C.
2. The cup made of ceramic for melting aluminum alloy (about 350 gr).
3. The ceramics tubes for blowing nitrogen gas and protective Ar-gas.
4. The mechanical system to lift the ceramic cup.
5. The oxygen getter.
6. Temperature control device.




The blowing of nitrogen gas begin when the temperature reaches the given value and is maintained at given rate during whole blowing time (from 15 minutes to several hours). After that the melt was poured into a metallic mold, the cut for microstructure characterization and mechanical test. Figure 2 shows the moment, when the ceramic cup with melt is raised up after gas blowing.

**Fig. 2: The cup with liquid metal is taken out from the furnace after gas blowing process.**

The experimental procedure is demonstrated in the figure 3.

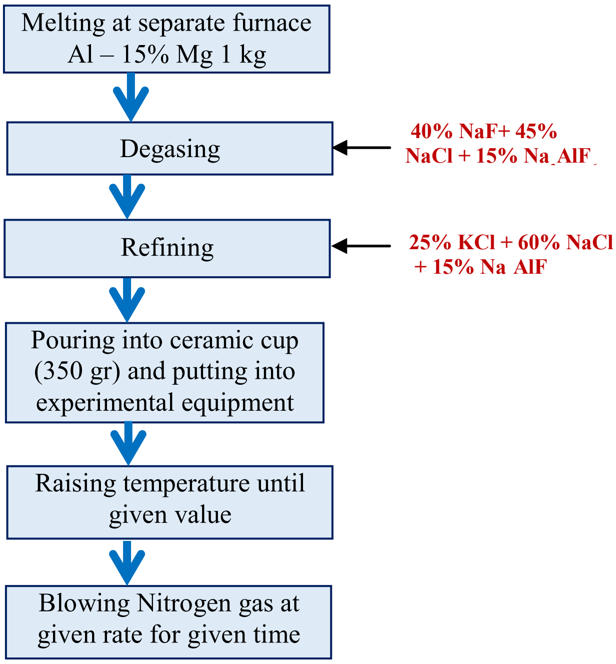



**Fig. 3: Experimantal procedure**

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## III. RESULTS AND DISCUSSIONS

The technological parameters to be investigated are:

1. Nitrogen gas velocity, varying in the range of 0.2 – 1.5 litres/minute.
2. Gas blowing temperature: 1050 – 1150$^0$ C.
3. Gas blowing time: 15' – 6 hours

### *3.1. Gas velocity*

Figure 4 shows the EDX pattern of the specimen M1 (1.5 litres/minute, 1050$^0$ C, 2 hours), on which there's no N peak.

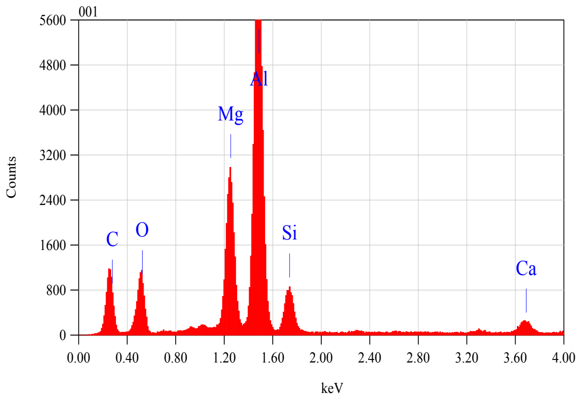


**Fig. 4. EDX pattern of the specimen M1**

Increasing the blowing time until 6 hours does not change the result: in the X-ray pattern of the specimen N3 (1.5 litres/minute, 1050$^0$ C, 6 hours) there's not the N peak too (figure 5).

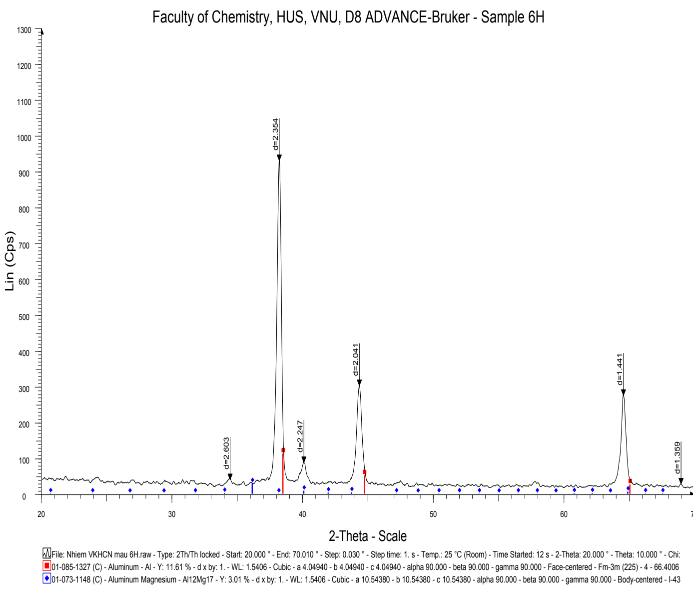


**Fig. 5 X-ray pattern of the specimen M3**

Increasing blowing temperature to 1100$^0$ C and reducing gas velocity to 0.8 litres/minute with the same blowing time (6 hours) – specimen M4 - do not change anything: the optical microscopy picture shows that only α-Al crystals and intermetallic compounds $Al_8Mg_5$ occur (figure 6).

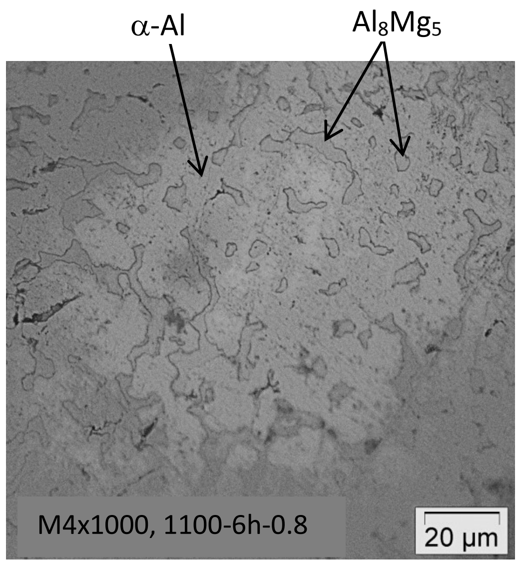


**Fig. 6. Optical microscopy picture of specimen M4**

The reason obviously must be found in the gas velocity, which appears too high so the gas bubbles rise very quickly to surface and the reaction for synthesis of AlN does not have enough time to occur. As known, the formation of AlN by in-situ reaction includes 4 processes [7]:

1. Diffusion of $N_2$ molecules to the bubble surface;
2. Absorption of $N_2$ molecules into gas/liquid interface;
3. Decomposition of $N_2$ molecules into atoms;
4. Reaction Al(liquid) + N(gas) → AlN (solid) in gas/liquid interface and in liquid bulk as the N-atoms diffuse.

All of these processes require some times. The simulation by blowing nitrogen gas into hydraulic oil (it's accepted commonly that the viscosity of liquid aluminum at high temperature is comparable with that of heavy hydraulic oil at room temperature) shows that the gas bubbles rise very quickly at gas velocity 1.5 litres/minute (figure 7).

The authors of [7] propose a formula to calculate the "residence time" of the gas bubble in the liquid as:

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**Fig. 7. Simulation with hydraulic oil.**

$$\tau = \frac{h_L}{u_B} = a d_{no}^{\left(-\frac{n+1}{3n}\right)} h_L$$

Where $h_L$ is the hight of the liquid bulk, $u_B$ is the bubble rising rate, a is the coefficient depending on the liquid and gas bubble properties, n is the index of energetical equation and $d_{no}$ is the size of blowing tip. But because the coefficient "a" depends on many factors, such as gas/liquid interface energy, gas and liquid densities, power-law index, drag correction factor…the determination of the residence time of gas bubbles in liquid is quite difficult, if not inpossible.

Based on the experimental and simulation results obtained above, the gas blowing velocity must be reduced into more reasonable value. In the next experiments it is reduced step by step and finally kept at 0.2 litres/minute.

### *3.2. Gas blowing temperature*

Figure 8 shows the microstructure of specimen M8 (0.2 litres/minute, $1100^0$ C, 3 hours), in which one can see only α-Al grains, $Al_8Mg_5$ and $Al_{15}Mn_3Si_5$ intermetallic compounds. Increasing gas velocity until 0.3 litres/minute does not change the result: EDX pattern of the specimen M10 (0.3 litres/minute, $1100^0$ C, 3 hours) that the Nitrogen peak is very week, almost zero (figure 9). These results can be explained as follows: at room temperature Nitrogen is chemically inert, because it possesses strong tri-bond N≡N with high enthalpy as 944.7 kJ $mol^{-1}$ (note that the enthalpy of single bond N-N is only 163 kJ $mol^{-1}$, or of H-N, found in $NH_3$, is 390.8 kJ $mol^{-1}$), so at $1100^0$ C the decomposition of $N_2$ molecules into N atoms is not clear (some authors [8] believe that even at $3000^0$ C the decomposition of $N_2$ molecules is not clear).

It's clear that rising temperature until $3000^0$ C is not realistic in our experiments, so based on some other reports [9, 10], the blowing temperature is increased to $1150^0$ C.

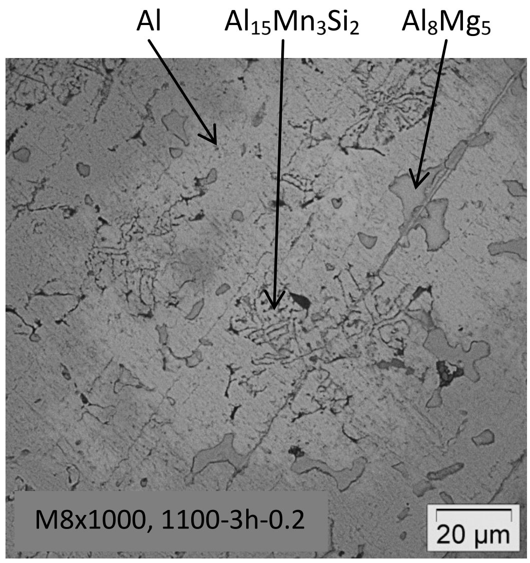


**Fig.8. Optical microscopy picture of specimen M8**

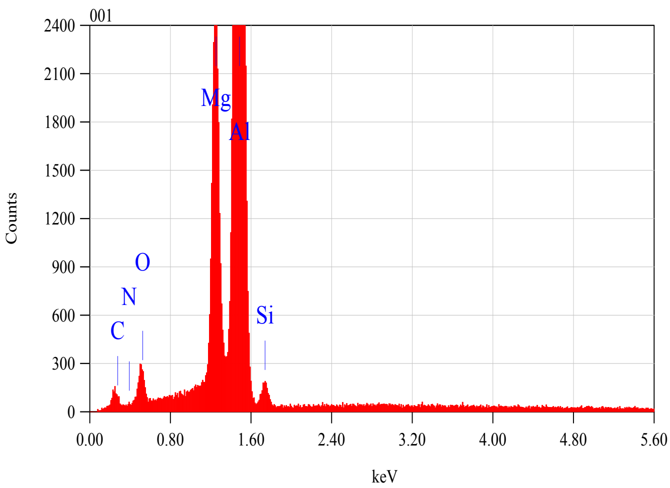


**Fig.9. EDX pattern of specimen M10**

### *3.3. Gas blowing time*

In the next experiments the gas velocity is fixed at 0.2 litres/minute, blowing temperature fixed at $1150^0$C and blowing time varies from 15 minutes to 6 hours. Figure 10 shows the optical microscopy picture of specimen M18: as seen, the only phases occurred are α-Al and $Al_8Mg_5$ intermetallic compound.

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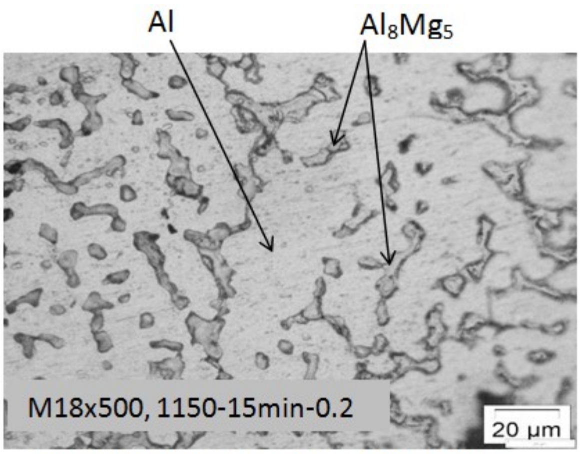


**Fig.10. Optical microscopy picture of the specimen M18**

It's obviously that the blowing time is too short so not any of 4 processes mentioned above can completed.

However, increasing blowing time to 1.5 until 3.5 hours gives good results.

Figure 11 shows the EDX pattern of the specimen M29; the spectrum 12 shows that wt.% of Al is 61.3 and of N is 30.5, so their ratio is ≈ 2, that is well correspond to the standard atomic weight ratio between Al and N (27/14 ≈ 1.93), indicating that these particles are AlN. The same confirmation can be done for the specimen M30 – figure 12 – where one can find the weight ratio Al:N = 63.2:32.8 ≈ 1.927 (spectrum 15).

As seen in the SEM picture after deep etching for the specimen M29 (figure 13), the AlN particles were formed of size from some hundreds nanometers to 1 µm, but they are still scattered and distributed mainly at grain boundary.

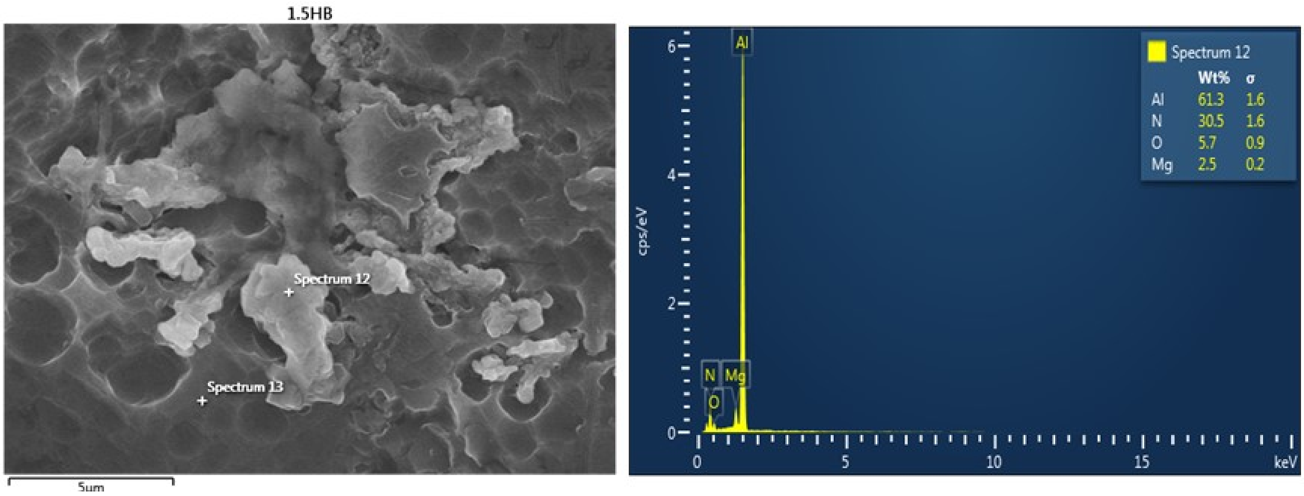


**Fig. 11. EDX pattern of the specimen M29 Blowing time: 1.5 h; $N_2$ velocity: 0.2 l/min; blowing temperature: 1150 $^0$C**

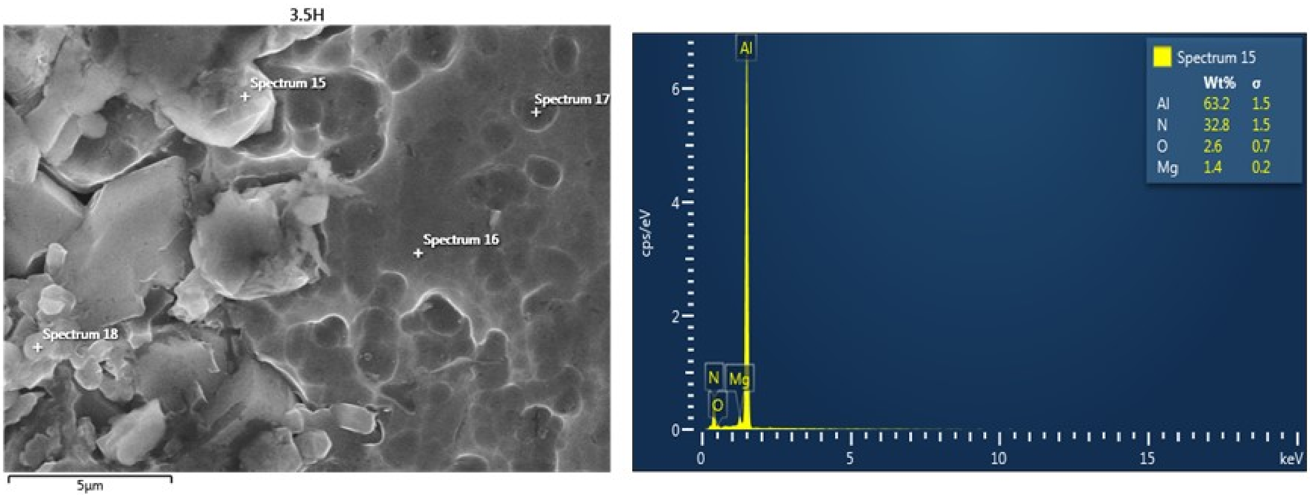


**Fig. 12. EDX pattern of the specimen M30 Blowing time: 3.5 h; $N_2$ velocity: 0.2 l/min; blowing temperature: 1150 $^0$C**

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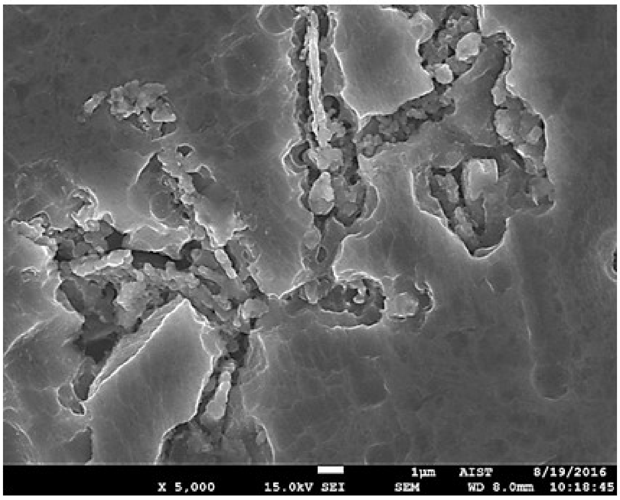


**Fig. 13. SEM picture of the specimen M29**

These particles can exert a pulling force on grain boundary and preventing it from migration at high temperature [11] – figure 14 - so the grain coarsening process should be restricted, but this consideration have to be examined with heat treatment and mechanical tests, that is not discussed here.

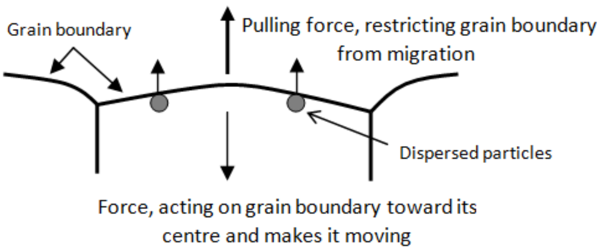


**Fig. 14. Scheme illustrated the forces acting on the grain boundary.**

Increasing blowing time to 3 and 3.5 hours with the same other parameters gives the particles more abundant with the size a little bit greater (about 1 – 3 µm) – see figures 15, 16 for specimens M26 and M30, correspondingly. As seen, these particles distributed not only on the grain boundaries, but also throughout the volume. Their coarsening can be explained by the fact that they are in contact with liquid aluminum more long time.

Increasing gas velocity more (until 0.3 litres /minute) with other parameters unchanged (blowing temperature and time: $1150^0$ C and 3.5 hours), applied for specimen M19 does not give clear effect (figure 17).

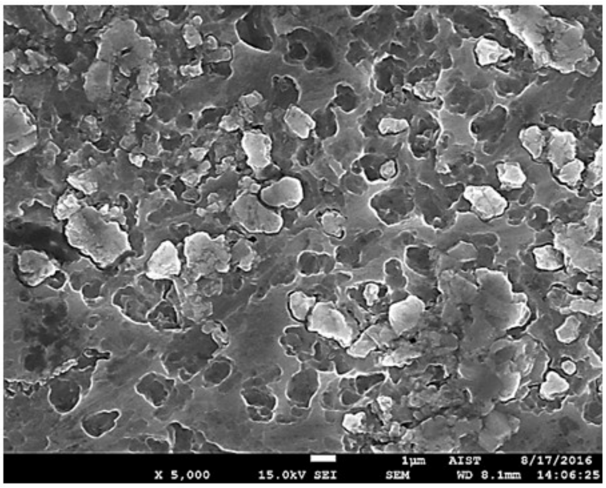


**Fig. 15. SEM picture of the specimen M26**

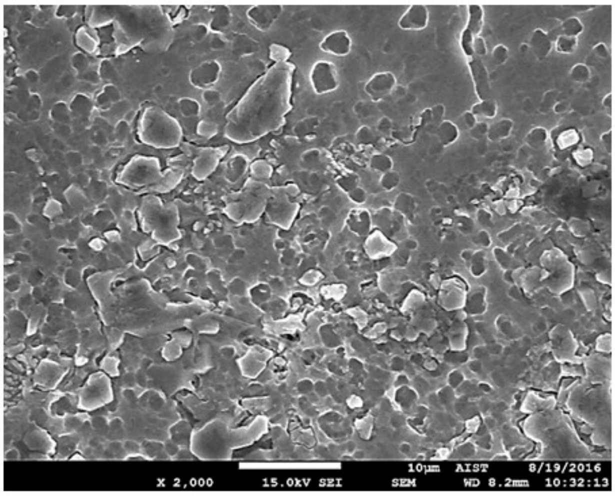


**Fig. 16. SEM picture of the specimen M30**

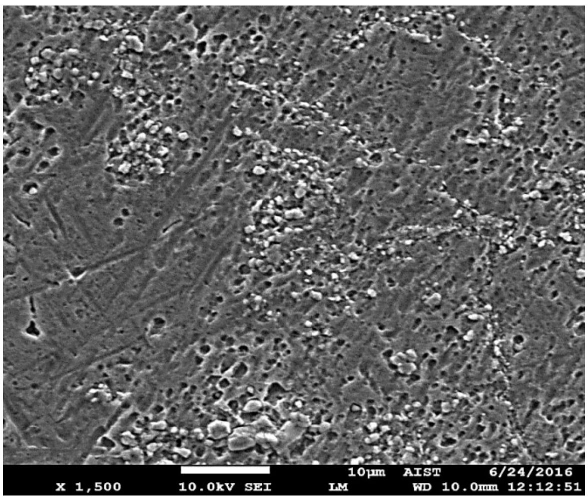


**Fig. 17. SEM picture of the specimen M19**

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*3.4. Effect of magnesium*

Magnesium plays important role in the synthesize process. As seen from Ellingham diagram [6], direct route: $2Al + N_2 \rightarrow 2AlN$ is difficult to proceed, because the change in Gibbs free energy, known as driving force, is small (figure 18) at all temperature range. Indirect route is probably easier: at high temperature Mg vaporizes and reacts with N to form $Mg_3N_2$, which then reacts with liquid aluminum to create AlN.

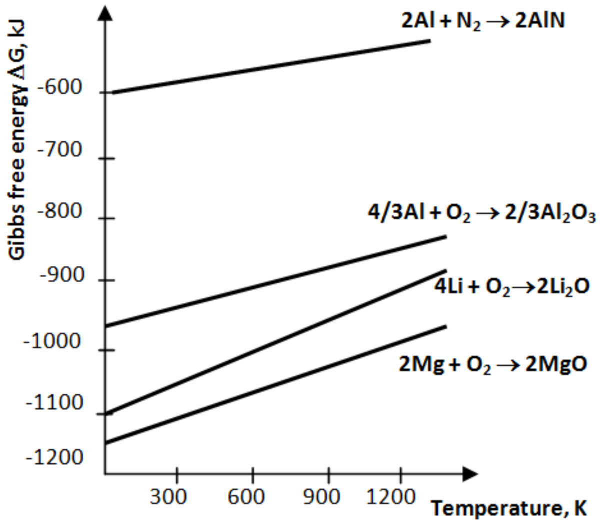


**Fig. 18. Elingham diagram**

From Ellingham diagram, it can be seen also that Mg can react with oxygen easily, so it serves as excellent oxygen getter to avoid the formation of aluminum oxide by reaction: $2Al + 3/2O_2 \rightarrow Al_2O_3$.

The above consideratons were proved by experimental results. As seen in the figures 19, 20, 21 and table 2, as it exists some amount of N, the amount of Mg must decrease dramatically (the initial content of Mg is 15%). One can pay the attention on the same tendency with silicon: it should be better if Si does not exist in the melt.

**Table 2.**
**Content of elements in specimens.**

| Specimen | N, % | Mg, % | Si, % |
|---|---|---|---|
| M1 | 0 | 11,12 | 0,49 |
| M3 | 2,19 | 8,97 | 0,94 |
| M2 | 11,04 | 1,64 | 0 |

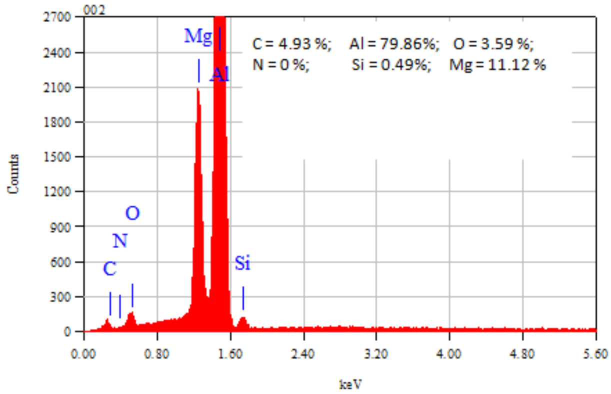


**Fig. 19. Field EDX pattern of the specimen M1 Blowing time: 2 h; $N_2$ velocity: 0.2 l/min; blowing temperature: 1100 $^0$C**

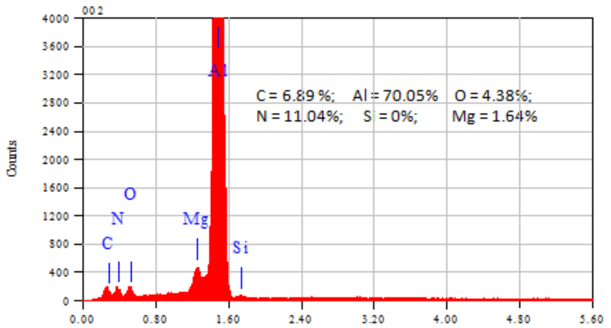


**Fig. 20. Field EDX pattern of the specimen M2 Blowing time: 2 h; $N_2$ velocity: 0.2 l/min; blowing temperature: 1150 $^0$C**

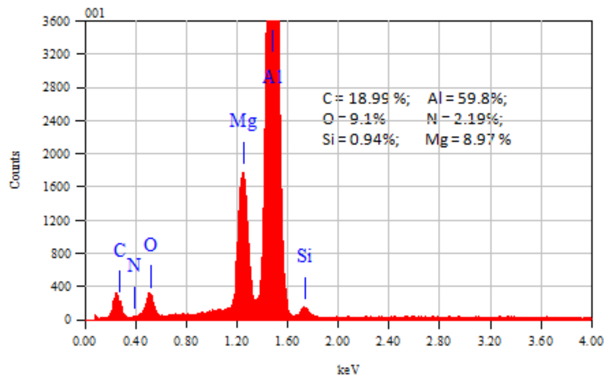


**Fig. 21. Field EDX pattern of the specimen M3 Blowing time: 3 h; $N_2$ velocity: 0.3 l/min; blowing temperature: 1100 $^0$C**

## IV. CONCLUSIONS

1. AlN particles can be sythesyzed by gas/liquid reaction in–situ. The presence of magnesium is necessary to enhance the synthesis process.

2. High velocity of nitrogen gas leads to rapid bubble rising and the synthesis process has not enough time to proceed. It seems that it should not exceed 0.2 litres/minute. Increasing this value to 0.3 litres/minute does not give a clear effect.
3. Due to very strong nitrogen tri-bond N≡N the blowing temperature should higher than $1100^0$ C to ensure the decomposition of nitrogen molecules.
4. Blowing time of about 2 hours is sufficient; after that the amount of Mg in the melt, allowing the realization of easier indirect mechanism, will become exhausted, meanwhile the direct route is not favorable. Beside, increasing blowing time can make the AlN particles coarser.
5. The AlN particles are formed of size from some hundreds nanometers to some µm, depending on the blowing time and can serve as the reinforcement for work at elevated temperature due to grain boundary pinning effect, that should be examined by heat treatment and mechanical test at high temperature.
6. The Al-alloy with synthesized AlN particles can be mixed after with conventional aluminum casting alloys such as A356 or A380 to produce nano-structure composite working at elevated temperature.

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