

## Improved Boralcan™ MMC Materials for Elevated Temperature Applications

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### Abstract

Boralcan™ aluminum matrix composites using nuclear grade B<sub>4</sub>C have been used as neutron absorbing materials for dry and wet storage applications for over 10 years. AA6351 has been successfully supplied for extruded applications and has provided low density and good stiffness, adequate strength and compatibility with the extrusion process. However, improvements in strength, at elevated temperature, were required to more easily satisfy regulatory property requirements whilst still working within the AA6351 composition limits. Through careful optimization of the major alloying elements, Mg, Mn and Si, Rio Tinto Aluminium developed and commercialized 6351CO (“composition optimized”), which provides a 15% improvement in yield strength at 300°C. For designs not restricted to AA6351, further improvements in elevated-temperature strength have been achieved by the use of an Al-Mn-Mg AA3004 based material, which is compatible with both sheet and extrusion product forms.

This paper describes the pilot and production scale development for these new materials conducted by Rio Tinto Aluminium. Mechanical properties at both room and elevated temperatures (25 to 300°C) are presented and rationalized in terms of the underlying metallurgical mechanisms.

### Introduction

Boralcan™ aluminium matrix composites using nuclear grade B<sub>4</sub>C have been increasingly used as neutron absorbing materials to fabricate the transport and storage containers of spent nuclear fuels because of their special capacity for capturing neutrons. In service, Al-B<sub>4</sub>C composites absorb the neutrons and generate heat and hence they can be exposed to evaluated temperatures (250-350°C) for an extended period. Therefore, the continuous improvements in mechanical properties, especially at elevated temperatures, are required to better satisfy regulatory property requirements in the nuclear industry.

Typical AA6351, without reinforcement, used in the structural extrusion industry, has been optimized through experience to give an optimum balance of extrudability and the ability to meet AA6351T6 room temperature mechanical properties. A typical composition, in use today, is 0.58wt%Mg-1.05wt%Si-0.50Mn-0.20Fe. This is designed to be solution treated during the standard extrusion process and then provide a strong precipitation hardening response during artificial ageing. Al-Mg-Si alloys have limitations when used at elevated temperatures; the MgSi precipitate structure coarsens and the volume fraction of precipitate decreases due to the increase in solubility of Mg and Si. Rio Tinto Aluminium developed 6351CO<sup>(1)</sup> such that while still complying with AA6351 composition limits, alternate strengthening mechanisms that are more stable at elevated temperatures are activated. These include solid solution and dispersion strengthening and were promoted by increasing the levels of Mg, Mn and Fe while decreasing the Si content. This product was successfully commercialized as a matrix for B<sub>4</sub>C materials for nuclear waste storage, providing a 15% improvement in yield strength at 300°C. Further improvements in elevated-temperature strength are required by the nuclear industry. A natural extension of the approach taken with 6351CO was to move away from a precipitation hardening system and to use alternate strengthening mechanisms. In recent years, the dispersoid strengthening in 3xxx aluminium alloys that can improve the mechanical properties at both room and elevated temperatures has been discovered. Although Al-Mn-Mg 3xxx alloys are usually classified as non-heat-treatable alloys, the precipitation of thermally stable  $\alpha$ -Al(MnFe)Si dispersoids during heat treatment and hence the enhancement of high temperature properties have been reported<sup>(2-4)</sup>. Based on this knowledge, AA3004 was selected as a matrix as it is effectively an extension of 6351CO with a further decrease in Si content and corresponding increases in Mn and Mg. Available high temperature property data<sup>(3-5)</sup> indicates that AA3004 exhibits excellent thermal stability at elevated temperatures and is compatible with existing extrusion and rolling processing routes. Such an approach, based on AA3004 matrix, has been tested on pilot and commercial scales. This paper describes the development of AA3004 based Boralcan™ materials and compares their performance with 6351CO and traditional AA6351 based materials.

## **Pilot Scale Testing**

### **Experimental**

The bulk composition based on AA3004, listed in Table 1, was batched at 740°C in a 36-kg electric furnace and stirred using a graphite impeller. The furnace was sealed and the B<sub>4</sub>C particles, with a median particle size of 17.5 microns, were injected into the liquid alloy to produce a 10.5% by volume composite material. After five minutes of stirring, the furnace was opened. The liquid composite was held for 60-120 min, at 700-720°C, to simulate the length of a commercial DC casting batch. Afterwards, the metal was poured into a 106 mm dia. x 500 mm long steel permanent mould and solidified to produce individual billets. The initial composition prior to the B<sub>4</sub>C powder addition contained a deliberate titanium (Ti) addition<sup>(1)</sup> to form a protective layer of Ti containing

reaction compounds. This layer prevents further reaction between the B<sub>4</sub>C particles and the aluminium alloy and allows fluidity to be maintained. The matrix composition after the B<sub>4</sub>C addition, shown in Table 1, was determined by filtering a sample of the liquid composite through a porous ceramic disc (known by the trade name PoDFA).

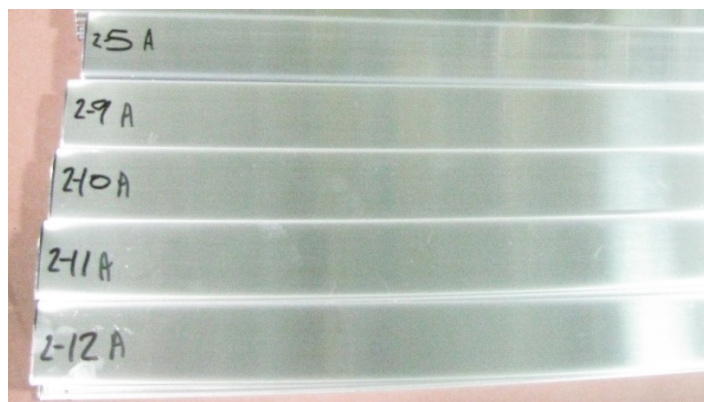
**Table 1 Composition of AA3004 based composite**

Alloy	Condition	Si	Fe	Cu	Mn	Mg
W3004N	Matrix before B <sub>4</sub> C addition	0,24	0,41	0,14	1,11	0,99
W3004N.10.5B	After B <sub>4</sub> C addition and holding for 60 min	0,26	0,41	0,14	1,04	0,92

The resulting ingots were machined into 101.6 mm diameter x 200 mm long billets. Two billet heat treatments were then applied:

- as-cast (none),
- 4 h/550°C cooled at 300°C/h.

The material was extruded into a 3 x 42-mm profile using the Rio Tinto Aluminium experimental 780-tonne extrusion press. The billets were induction preheated to a temperature of 430-440°C in ~ 3 min, and a ram speed of 2 mm/s was applied corresponding to an exit speed of 8 m/min. The extrusion ratio was 70/1. A standard nitrided H13 steel die was used with a 60-mm diameter feeder pocket. Exit temperatures at the press exit were in the range of 500-540°C. The profile was forced air cooled at a rate of ~ 8°C/s. Excellent surface quality was achieved using these press parameters, as shown in Figure 1. The W3004N material required ~ 10% higher extrusion pressure than the 6351CO material.



**Figure 1 As-extruded surface appearance of W3004N extrusions**

Samples of the profiles were then exposed for 100 h at 150, 200, 250 and 300°C. They were afterwards tensile tested at the same temperatures according to ISO 6896-2: 2011(E).

For comparison purposes, a composite with a matrix composition corresponding to a version of AA6351 optimized for high temperature strength (6351CO) <sup>(5)</sup> also containing 10.5% B<sub>4</sub>C was produced by a similar route (Table 2). However, as the material was 6XXX based, the thermal processing conditions differed from those used for the Al-Mg-Mn alloy described above. The billets were homogenized for 2 h at 560°C. Following extrusion, the profile was water quenched and artificially aged for 8 h/170°C. Identical thermal exposure and tensile testing protocols, as those used for the AA3004 based alloy, were then applied.

**Table 2 Composition of 6351CO based composite**

Alloy	Condition	Si	Fe	Cu	Mn	Mg
W6351N(CO)	Matrix before B4C addition	0,71	0,47	0,08	0,73	0,77
W6351N.10.5B(CO)	After B4C addition and holding for 60 min	0,76	0,46	0,08	0,68	0,69

## Results

### Mechanical Properties

Figure 2 presents the yield strength (YS) values at elevated temperatures up to 300°C after 100 h of thermal exposure. Up to 200°C, the 6351CO was stronger than the W3004N due to the residual effects of the Mg-Si precipitate structure. It is expected that the strength of 6351CO would deteriorate with extended times due to continued coarsening of that structure, which is a typical behavior for 6XXX based alloys above 150°C <sup>(5)</sup>.

At 250°C and higher, the W3004N based composite exhibited an increase in strength over the 6351CO for both billet conditions showing improvements of 4-18%, at 250°C, and 31-50%, at 300°C. Comparing the different billet conditions for the W3004N, the as-cast condition tended to give the highest strength. The trends in YS were mirrored by the UTS values, as shown in Figure 3.

Room temperature properties for the 6351CO and W3004N composites, without any thermal exposure, are compared in Figure 4. The 6351CO gave typical strength levels expected from conventional AA6351 wrought material in the T6 condition, although the elongation was lower at 5%. The W3004N was significantly softer with yield strength levels of 99-128 MPa and UTS values of 199-216 MPa. In line with the lower strength, the W3004N elongation values were correspondingly higher than 6351CO, at 9-13%. This difference in the room-temperature strength is to be expected as the 6351, in the peak aged condition, has a significant strength contribution from precipitation hardening whereas as-extruded W3004N is essentially in the annealed condition.

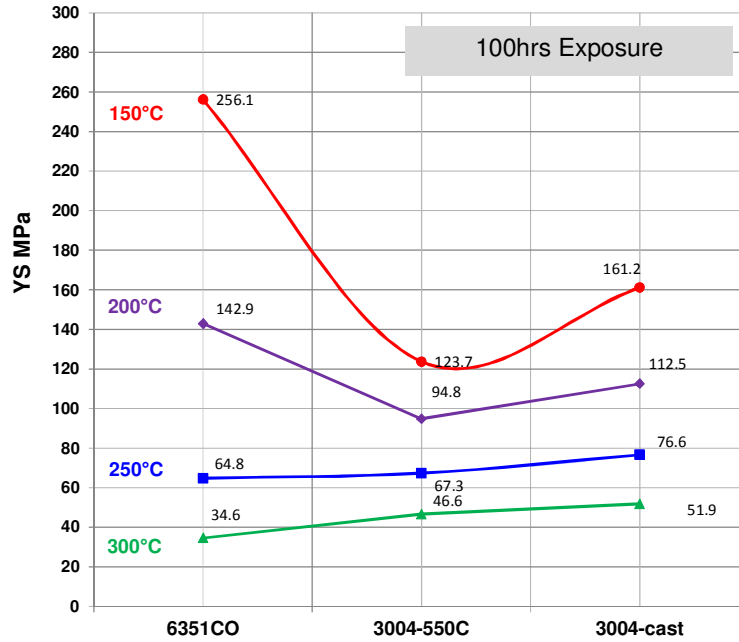


Figure 2 Elevated temperature YS values for 6351CO and W3004N with 10.5% B<sub>4</sub>C

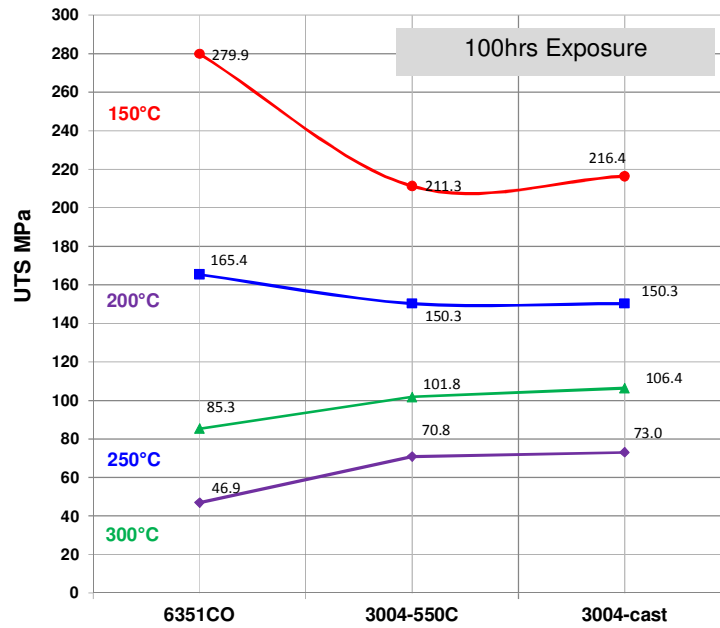
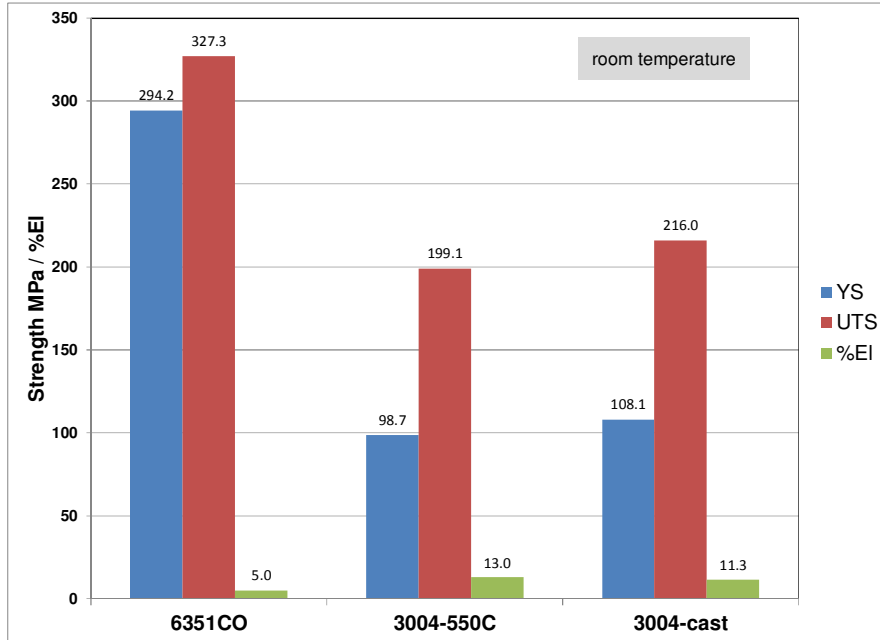


Figure 3 Elevated temperature UTS values for 6351CO and W3004N with 10.5% B<sub>4</sub>C



**Figure 4 Room temperature tensile property comparison 6351CO and W3004N with 10.5%B<sub>4</sub>C**

## Industrial Scale Testing

### Casting Details

An industrial scale, 6-tonne cast, of the Boralcan™ W3004N.10.5B was produced in June 2016, in Rio Tinto Aluminium Dubuc Plant in Saguenay, Quebec, Canada.

The aluminium matrix was prepared in an induction furnace, at 740°C, according to the targeted composition listed in Table 3.

An amount of titanium was also added to prevent a reaction between the aluminium and the B<sub>4</sub>C as well as to increase the fluidity of Boralcan™ composites during casting <sup>(1)</sup>. B<sub>4</sub>C powder with a median particle size of 17.5 µm was injected into the molten matrix in order to reach an equivalent of 10.5% volume in the final product.

During casting, metal samples were filtered by the means of PoDFA filters to analyse the metal composition using the optical emission spectrometry (OES) method, and the resulting composition is shown in Table 3. A chemical analysis by inductively coupled plasma (ICP) confirmed the results.

**Table 3 W3004N metal matrix composition of the cast**

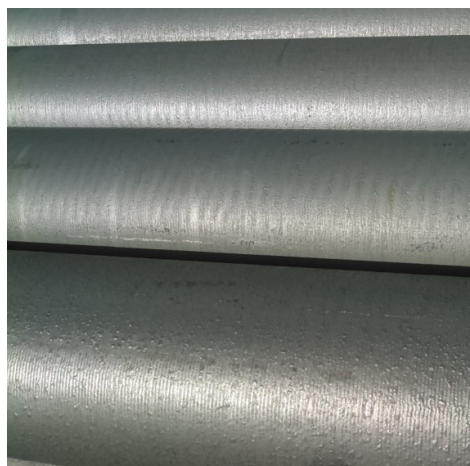
Alloy	Cast	Method	Si	Fe	Cu	Mn	Mg
W3004N.10.5B	Target	Nominal	0,20	0,30	0.10 max	1,1	1,0
W3004N.10.5B	16C00636A	SEO	0,23	0,31	0,002	1,06	1,00
W3004N.10.5B	16C00636A	ICP	0,22	0,30	0,002	1,10	1,04

The metal matrix composite (MMC) was then cast in eight individual billets of 228 mm of diameter and 5900 mm long using vertical DC casting equipment, as shown in Figure 5.



**Figure 5 DC casting installation**

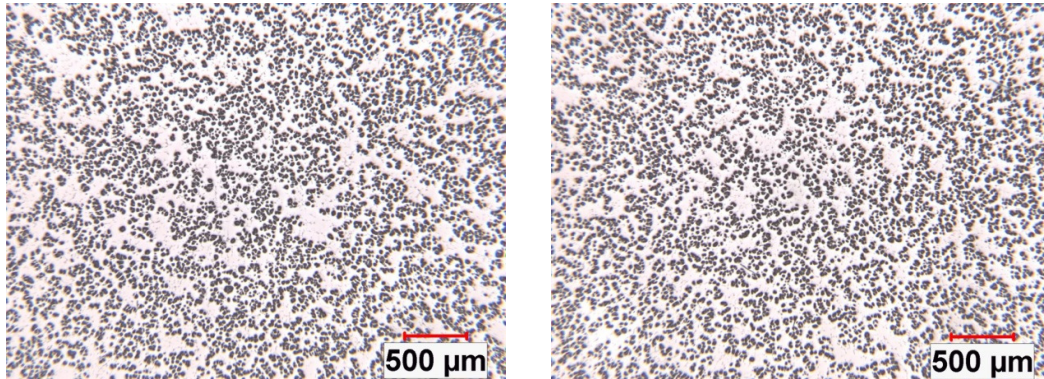
The casting behavior and the billet surface of the W3004N were similar to that of the existing 6351CO material, as shown in Figure 6.



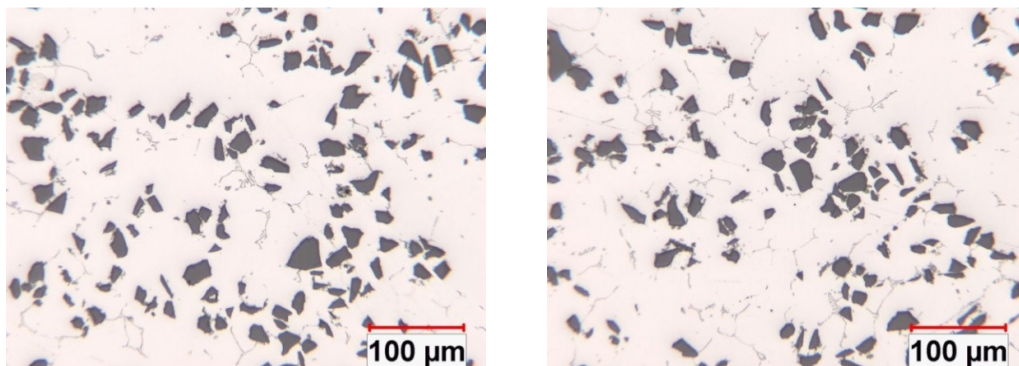
**Figure 6 W3004N billet surface**



The internal quality of the W3004N cast material were equivalent to that of the existing 6351CO, and the B<sub>4</sub>C powder was well distributed throughout the cast length, as illustrated in Figures 7 (low magnification) and 8(high magnification).



**Figure 7 Internal quality of the W3004N billet, samples at 300 mm and 5500 mm**



**Figure 8 Internal quality of the W3004N billet, samples at 300 mm and 5500 mm**

Two product forms were investigated: extrusion and rolled sheet.

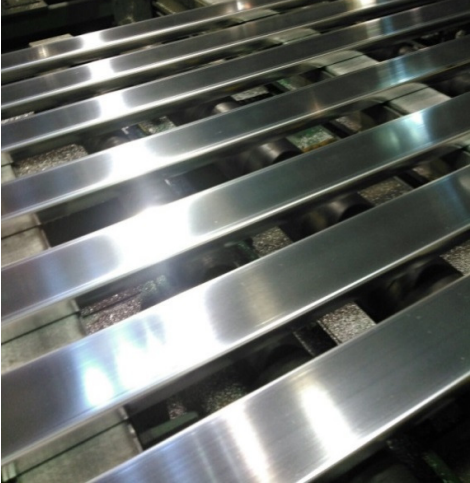
### **Extrusion Details**

The regular AA6351 matrix was given a typical commercial homogenization of 4 h at 550°C to provide low flow stress. Since the AA3004 is a non-heat-treatable alloy, a test was performed with and without this homogenization treatment in order to determine which condition is the most suitable for superior mechanical properties at elevated temperature and extrudability. The extrusion tests were conducted in June 2016 at Metra (Laval, Québec). Two logs of W3004N10.5B were extruded into a 23 x 78 mm profile and water quenched.

The billet preheat temperature used for extrusion was 430°C for the homogenized material which resulted in an exit temperature of 430-450°C. A slightly higher temperature of 480°C was applied for the as-cast material, due to its slightly higher flow stress, which gave a press exit temperature of



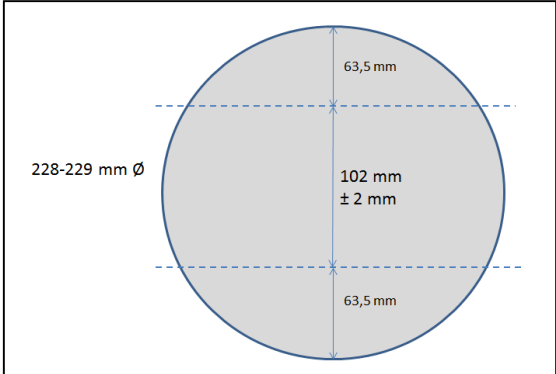
530-555°C. As the 3004 matrix does not rely on traditional precipitation hardening, there is no solutionizing requirement during extrusion and therefore no minimum exit temperature. Generally, it was possible to run W3004N at comparable extrusion speeds to 6351CO with excellent surface finish for both billet conditions, as shown in Figure 9.



**Figure 9 Typical W3004N extruded surface finish**

**Rolling Details**

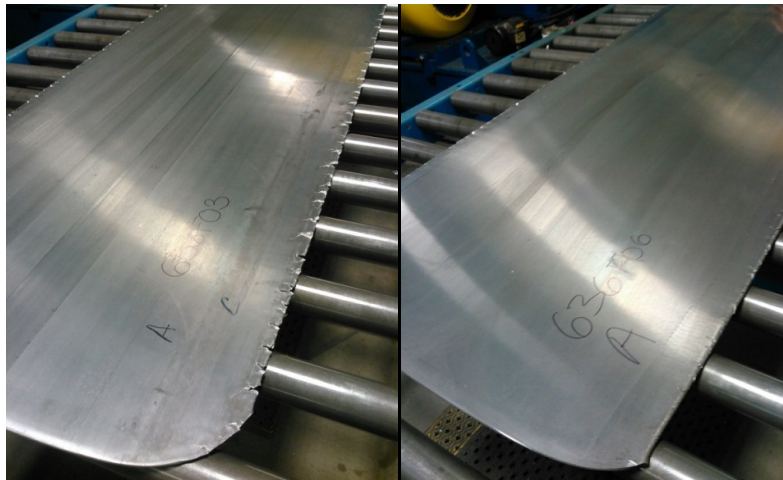
The AA3004 alloy is widely used in sheet form due to its good formability and corrosion resistance. Four billets of 228 mm were used for a rolling test. Ceradyne Canada, a 3M Company, located in Saguenay (Quebec), collaborated with Rio Tinto Aluminium for this test, due to their wide experience in rolling Borcalcan™ with a matrix of W1100N from 10 to 25% of B<sub>4</sub>C. Since the rolling ingot shape is usually 152 mm x 152 mm square, the available 228 mm diameter cast billets were machined to obtain two parallel flat surfaces in order to facilitate the rolling process, as shown in Figure 10.



**Figure 10 Billet shape for rolling process**

Two different sheet thicknesses were produced, 6 and 12 mm. To obtain a sheet surface after rolling of about 500 mm by 1500 to 2000 mm, two billet lengths were used: 381 mm, for the 6 mm plate, and 559 mm, for the 12 mm sheet, as shown in Figure 11. Billets were preheated for 12 h at 540°C before the hot rolling process. A cooling fluid was used between each pass.

Due to its stronger mechanical properties compared to the W1100N, the W3004N requires higher rolling force but remained within the available process limits. There was no difficulty to roll the W3004N using the similar rolling conditions to W1100N. An acceptable level of edge cracking was observed, and surface quality was similar to the existing W1100N rolled product.



**Figure 11 Appearance of 6 and 12 mm thick rolled sheets of W3004N**

### **Mechanical Properties**

A division of the National Research Council Canada (NRC), Aluminium Technology Centre (ATC), located in Saguenay, Quebec, performed the tensile tests on the sampled material. The following conditions were tested:

- Extruded Profile:
  - fresh (as-extruded) tested at room temperature,
  - after thermal exposure for 100 h at 300°C, tested at 300°C.
- Rolled Sheet:
  - As-rolled material tested at room temperature,
  - after thermal exposure for 100 h at 300°C, tested at 300°C.

A thermal exposure treatment of 100 h at 300°C, prior to tensile testing at the same temperature, was applied in order to simulate the effect of long exposure periods (e.g. 40 years) in a short timeframe,

according to Larsen-Miller parameters. The thermal exposure treatment was performed in a forced convection furnace maintaining the temperature at  $\pm 1^\circ\text{C}$ .

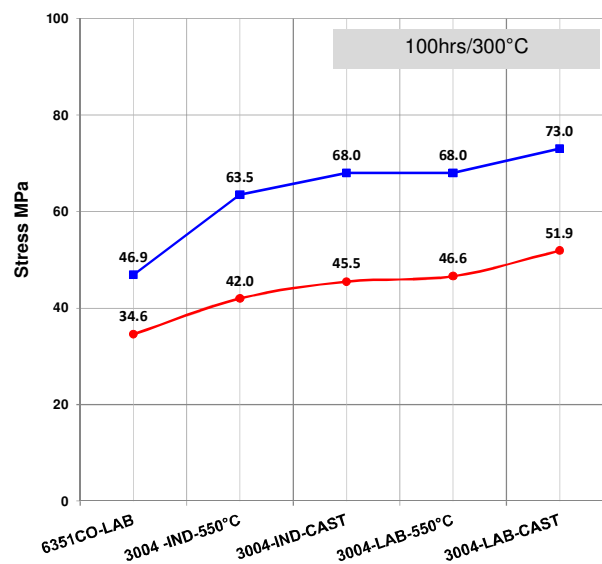
Two types of samples were machined from the transformed Boralcan™:

- round 5 mm section machined from the extrusion profile, taken along the extrusion direction,
- flat 12.5 mm x sheet thickness taken along the rolling direction.

Tensile testing was performed on a 50 kN tensile machine with a mechanical extensometer having a gauge length of 25 mm, in accordance to the following standard:

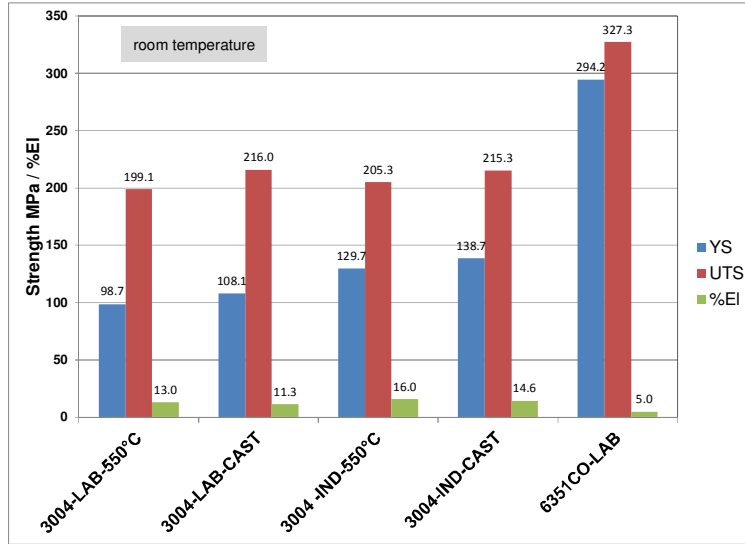
- ISO 6892-1: 2009 at room temperature,
- ISO 6892-2: 2011 method A at elevated temperature.

Figure 12 summarizes the 300°C test results for the extruded material and compares them with the lab scale results for W3004N and 6351CO. The industrial scale W3004N material exhibited slightly lower strength than the pilot scale material, which may be due to differences in ingot size and press preheating practice. The cast material consistently gave higher yield and tensile strengths than the material homogenized at 550°C. Compared to the existing 6351CO, the industrial scale W3004N exhibited attractive increases of 32%, in yield strength, and 45%, in tensile strength.



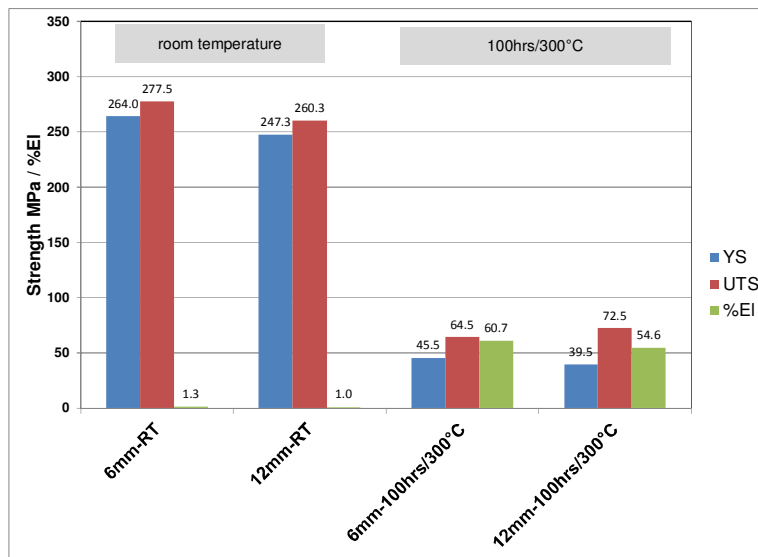
**Figure 12 Yield strength and UTS of extruded W3004N, industrial scale vs pilot scale**

The corresponding as-extruded room temperature properties are shown in Figure 13. As expected, the 6351CO material was stronger than the W3004N due to the effectiveness of MgSi precipitation hardening. In this case, the pilot scale material was softer than the industrial material indicating that different strengthening mechanisms operate at ambient and elevated temperatures.



**Figure 13 Tensile properties of as-extruded materials tested at room temperature**

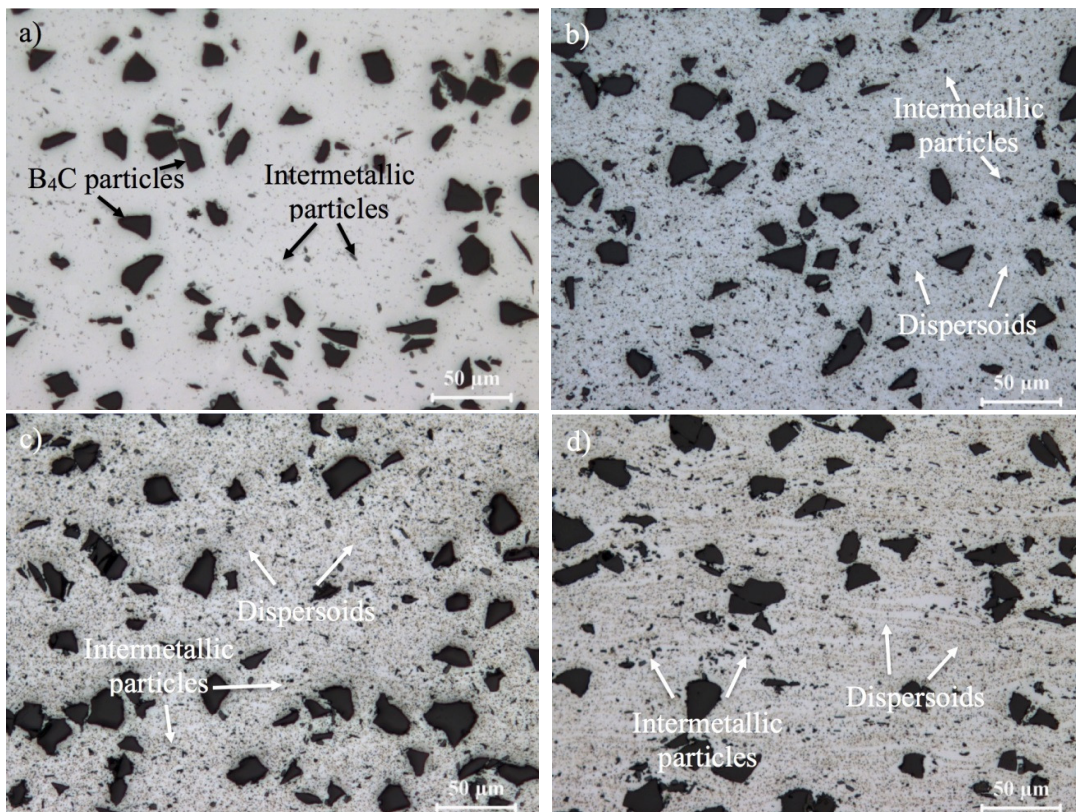
Figure 14 presents the tensile properties for the as-rolled sheet at room temperature and after 100 h/300°C. The elevated temperature properties were similar to the values measured on the extrusions. The YS ranged from 39.5 to 45.5 MPa, for the two gauges compared with 45.5, for the “as-cast” W3004N extrusion.



**Figure 14 Tensile properties of as-rolled W3004N tested at RT and 300 °C**

## Microstructure of Extruded and Rolled W3004N Materials

In the microstructure of as-cast billets of W3004N composites, besides  $B_4C$  particles, there are a number of Fe-rich intermetallic phases, in the form of semi continuous networks, distributed in the aluminum grain boundaries (Figure 8). During extrusion and rolling, those Fe-rich intermetallic networks were broken down into a number of fine intermetallic particles (Figure 15a). They were uniformly distributed in the aluminum matrix, and their size ranged from 1 to 5  $\mu m$ , which can act a strengthening phase. Moreover, during preheating of cast billets and extrusion process, the Mn, Fe and Si precipitated out of the supersaturated solid solution to form a large number of  $\alpha-Al(MnFe)Si$  dispersoids<sup>(3)</sup>, which act as the main strengthening phase in W3004N matrix (Figure 15b). In the extruded samples with a homogenization treatment at 4 h/540°C, the  $\alpha-Al(MnFe)Si$  dispersoids can be formed during homogenization and further well distributed during extrusion (Figure 15c). Similarly for rolled samples, a reasonable amount of  $\alpha-Al(MnFe)Si$  dispersoids were formed during homogenization of cast billets and further well mixed with aluminum matrix during multi-pass rolling (Figure. 15d).



**Figure 15 Optical microstructures: a) extruded without homogenization (as-cast), no etching samples, b) extruded without homogenization (as-cast), etched with HF 20 s, c) extruded with homogenization at 4 h/540°C, etched with HF 20 s and d) rolled 6 mm samples, etched with HF 20 s**



## Discussion

In the T5 or T6 aging conditions, the 6351 matrix is strengthened by precipitation hardening of fine  $Mg_2Si$  precipitates. In general, the precipitation hardening works well for enhancing room-temperature mechanical properties. Therefore, the mechanical properties at room temperature of W6351N are much better than those of W3004N (Figures 4 and 13). However, when the temperature increases above 200°C, the  $Mg_2Si$  precipitates rapidly coarsen resulting in a significant deterioration of mechanical properties. In contrast, the W3004N matrix is strengthened by dispersoid hardening. Through a proper selection of alloying elements and favourable conditions during extrusion and rolling, a large amount of dispersoids (both  $\alpha-Al(MnFe)Si$  dispersoids and Fe-rich intermetallic particles) can be formed (Figure 15). Due to their relatively large size of the order of several tens nanometres, the W3004N matrix possesses a moderate strength at room temperature. However, both  $\alpha-Al(MnFe)Si$  dispersoids and Fe-rich intermetallic particles are thermally stable even after a long-term exposure at 300°C<sup>(3)</sup>. Therefore, the W3004N provides superior mechanical properties at elevated temperatures (250-350°C). Due to a higher volume and finer size of  $\alpha-Al(MnFe)Si$  dispersoids compared to Fe-rich intermetallic particles, the  $\alpha-Al(MnFe)Si$  dispersoids are the main strengthening phase in the W3004N matrix, while the fine Fe-rich intermetallic particles provide a minor strengthening effect.

It is interesting to observe that the elevated-temperature properties of extruded samples without homogenization treatment (as-cast) are better than those with a homogenization treatment at 4 h/540°C. The precipitation of  $\alpha-Al(MnFe)Si$  dispersoids in W3004N matrix starts at about 350°C<sup>(3)</sup>. It appears that during preheating of cast billets, the  $\alpha-Al(MnFe)Si$  dispersoids can fully precipitate out without a need of the homogenization treatment prior extrusion, which is also confirmed by the microstructure results (Figure 15). Therefore, the homogenization treatment is not necessary for 3004, in this type of application. In addition, there is no need for the solution and aging treatments required for 6xxx materials, providing an additional benefit of cost saving in the production.

Compared with conventional 6xxx materials, the significant benefit of W3004N is for applications at elevated temperatures due to its high thermal stability. Results of pilot and industrial scale trials confirmed that a considerable improvement of yield strength at 300°C of 30-50% is easily achievable in comparison with the existing matrix of 6351CO. Further improvement of elevated-temperature strength is still expected through the optimization of chemical composition and thermomechanical process.

The processing window for extruded and rolled Boralcan™ W3004N is equivalent to that for existing extruded W6351N CO and rolled W1100N, containing a similar level of  $B_4C$ . In addition, the similarity in the tensile properties of both extruded and rolled W3004N, at an elevated

temperature of 300°C, provide new opportunities of using both materials in a storage assembly for spent nuclear fuels. The availability of both extruded and rolled product forms also provides the opportunity for more complex designs to be utilized in future assemblies.

### **Acknowledgments**

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