Light Metals 2014
Edited by: John Grandfield
TMS (The Minerals, Metals & Materials Society), 2014

PHASE FORMATION AND MECHANICAL PROPERTIES OF Al-Mg-Mn-Ti-B-Zr-Sc COMPOSITE MATERIAL

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Keywords: Aluminum matrix composite material, Radiation protection, Boron containing.

Abstract

In this work composite alloys Al-2Mn-1.5Ti-2B-0.25Zr-0.1Sc, Al-4Mg-1Mn-1.5Ti-2B-0.3Sc and Al-4Mg-1Mn-2B-0.3Sc were obtained using casting technology. Thermodynamic calculations showed that the most probable chemical reaction during composite alloys casting is the formation of titanium aluminide. Formation of titanium and zirconium borides is also possible, but undesirable. Analysis of the structure and mechanical properties of composite alloys confirmed the interaction between boron, zirconium and scandium. Metallographic researches showed that the particles AlB_2 transfer into composite alloys and look like compact agglomerations of inclusions. Also takes place the formation of acicular phases of scandium and zirconium borides, and possibly more complex phases.

Introduction

At present, great attention is paid to the theme of creating new functional and structural materials with enhanced properties [1]. Aluminum-matrix composites (AMCs) take special place in scientific researches, through a unique combination of properties: low-density, high specific strength, low cost, allowing them to be used in car and ship building, aerospace and nuclear industries [2-4].

AMCs are of particular interest as a neutron absorber material in the transport and storage of spent nuclear fuel because they have special capacity - radiation resistance [5]. Sometimes the absorption of thermal neutrons generates heat and material of the cask for the spent nuclear fuel storage may undergo long periods at a high temperature caused by the accumulation of heat from the spent fuels [6].

Development of lightweight AMCs capable of surviving high temperatures being thermally stable for long periods has recently become an urgent topic. Most commercial AMCs use a traditional alloy for the aluminum matrix, such as the 2xxx and 6xxx series, but their strength is limited at increased temperatures. The mechanical properties of these materials degrade quickly at elevated temperatures due to the rapid coarsening of strengthening precipitates [7, 8].

Al–Sc alloys are promising for use in items operating at high temperatures because they offer a significant strengthening effect and a high thermal stability due to the formation of a number of nanoscale and coherent Al_3Sc precipitates which remain coarsening-resistant up to temperatures of ~300 °C [9-13]. Above this temperature, the Al_3Sc precipitates coarsen and lose coherency, which leads to a weak thermal stability of the materials. Additional ternary alloying elements in Al–Sc alloys may further improve the precipitation strengthening and coarsening resistance of materials at high temperatures. It was reported that Zr could substitute Sc in Al_3Sc to form more stable $Al_3(Sc, Zr)$ precipitates resulting in an enhanced strengthening and a better coarsening resistance of precipitates [5, 14-16]. Therefore, addition Zr in Al–Sc alloys can advance the thermal stability [17].

However, the problem of production technology for AMCs alloyed with boron is not solved. Selection of the technology mode is due to many factors, the most important being: consolidation of the material, obtaining a uniform distribution of reinforcing component, good bond between the matrix and the filler, no chemical interaction at the interface [17-19]. Liquid-phase technology becomes more and more popular because it is often cheaper, easier and provides enhanced mechanical properties of the material due to the strong joint at the matrix-filler boundary [20, 21].

For heat-resistant aluminum alloys doped with Mg, Mn, Ti, B, Zr and Sc the application of liquid-phase technology may be complicated because of interactions between alloy components.

Thus, the aim of the work is to evaluate the possibility of obtaining thermally stable composite material based on the Al-Mg-Mn-Ti-B-Zr-Sc system by using liquid-phase technology, to be exact by casting, as well as to study of the structure and properties of prepared composite material.

Experimental

Composite preparation

Three experimental composites were prepared to analyze the structure and evaluate mechanical properties. Their chemical composition is listed in Table 1.

Table 1
Chemical composition of experimental composites

Number	Element (wt%)						
	Mg	Mn	Ti	B	Zr	Sc	Al
1	-	2	1.5	2	0.25	0.1	Balance
2	4	1	1.5	2	-	0.3	
3	4	1	-	2	-	0.3	

A prefabricated alloy Al-5 wt% B, manufactured by KBM Affilips, was used for the composite preparation. First, commercially pure Al (99.7%) and Al-5 wt% B were melted in an induction furnace. Master alloys Ti-20 wt% Na_3AlF_6 Al-2 wt% Sc, Al-10 wt% Mn, Al-15 wt% Zr were added into the molten aluminum and the melt was held at 900 °C for 30 min to dissolve the master alloys. Finally, a Mg-10 wt% Al master alloy was added into the melt and held for 5 min.

The composite melt was poured into a rectangular permanent graphite mold. The dimension of cast ingots was 38 mm × 120 mm × 220 mm.

Thermodynamic calculations

In many cases, spontaneous processes occur in nature in the presence of potential difference, for example, an electric potential difference, determine charge transfer. These processes finish at the potential minimum. The driving force of the chemical processes that take place at constant pressure and temperature is the isobaric - isothermal potential, called the Gibbs energy (G). Gibbs energy change in the chemical process can be expressed as:

$$\Delta G=\Delta H - T\cdot\Delta S \tag{1}$$

Where, ΔG - change of Gibbs energy of a chemical process;
ΔH - enthalpy change of a chemical process;
ΔS - entropy change of a chemical process;
T - temperature in Kelvin.
Equation (1) can be represented as:

$$\Delta H = \Delta G + T\Delta S \tag{2}$$

The first member on the right-hand side of Eq. (2) is the reaction heat spent on work execution (ΔG), and the other part is dissipated in environment ($T\Delta S$).

The Gibbs energy is the measure of the fundamental possibility of spontaneous reaction. If the reaction results in the Gibbs energy decrease ($\Delta G < 0$), the process can take place spontaneously in these conditions. Reaction process is impossible in the conditions when $\Delta G > 0$. The reaction is reversible, i.e. can flow forward and reverse, if $\Delta G = 0$ (thermodynamic condition of chemical equilibrium).

For a system where several reactions can occur in the same conditions, the most probable is the reaction with the most negative Gibbs energy. This thesis is used in the work to assess the probability of chemical reactions.

Standard heats of formation and entropies were taken from the reference book [22-24] and presented in Table 2. It should be noted, that reference data for Sc compounds are lacking.

In addition, Thermo-Calc software was used to calculate the liquid composition at a fusion temperature. We applied the fifth version of the software and TCAL1 database.

Table 2
Standard heats of formation and entropies at 298 K

Material	ΔH^0_f (298 K) cal / mole	S^0 (298 K) cal / mole	Reference
Mg		7,81	22
B		1,4	23
Ti		7,32	22
Mn		7,65	22
Zr		9,32	22
Al		6,75	24
MgB_2	-22	8,6	22
MnB	-18	7,75	22
ZrB_2	-77,4	8,59	22
AlB_2	-16	8,3	24
$TiAl_3$	-34	22,6	24
TiB_2	-66,8	6,81	23

Microstructural observation

Microstructural analysis of different conditions was carried out using optical and electron microscopes (JEOL JSM-6610LV and HITACHI TM1000).

The samples were prepared on Struers A-Roto Module grinder using abrasive paper made of silicon carbide. Grit of abrasive paper was -120 K3 , K3 -150 , K3 - 180, K3M -40. Final polishing was carried out using OP-S Suspension and silica colloidal suspension (40 nm SiO_2, ammonia, hydrogen peroxide), applied to the grinding disc.

Brinell hardness

Hardness of cast ingots was determined by the Brinell method according to standard procedure. Ball indenter, diameter 5 mm, was pressed into the sample (2 cm × 3 cm × 1.5 cm) with a continuously increasing load for 5 seconds. After the maximum load value (750 kilogram-force) the indenter dwell time was 30 s. Then, the applied load was removed and the diameter of the resulting print was measured. The values of the hardness were calculated as the average of 7 measurements.

Heat treatment and hot rolling

The cast ingots of two composites, No. 2 and No.3, were hot-rolled on a laboratory scale rolling mill at 350 °C. During rolling the samples were subjected to intermediate annealing at regime - 300 °C 3 h. + 450 °C 3 h. Heat treatments were conducted to yield the precipitation-strengthening for the composites. The precipitation-strengthening aging procedures for the castings were carried out in electric resistance furnace SNOL 10/10 with ± 5°C temperature variation.

The thickness of the cast ingot was reduced from the initial value of 38 mm to a final thickness of 2 mm, with a total deformation rate of 92%. After rolling sheets were annealed at 300 °C for 3 hours.

Tensile test

Sheets obtained after rolling, were subjected to uniaxial tensile test on a machine Zwick Z250. The mechanical properties of the samples were evaluated by the tensile strength, yield strength and elongation, which are determined by the standard method on a standard fivefold flat samples.

The values of the mechanical properties were calculated as the average of 5 measurements. To estimate the precision of the results we calculated standard deviation and confidence interval.

Results and discussion

Thermodynamics of chemical reactions

Thermodynamic calculations of the Gibbs energy and graphical results are shown in Table 3 and Fig. 1.

Table 3
Free energies for various reactions used in this study

Reaction	Gibbs free energy, cal / mole
Mg+2B=MgB2	$-22-2.01\cdot T$
Mn+B=MnB	$-18-1.3\cdot T$
Zr+2B=ZrB2	$-77.4-3.53\cdot T$
Al+2B=AlB2	$-16-1.25\cdot T$
Ti+3Al=TiAl3	$-34-4.97\cdot T$
Ti+2B=TiB2	$-66.8-33.31\cdot T$

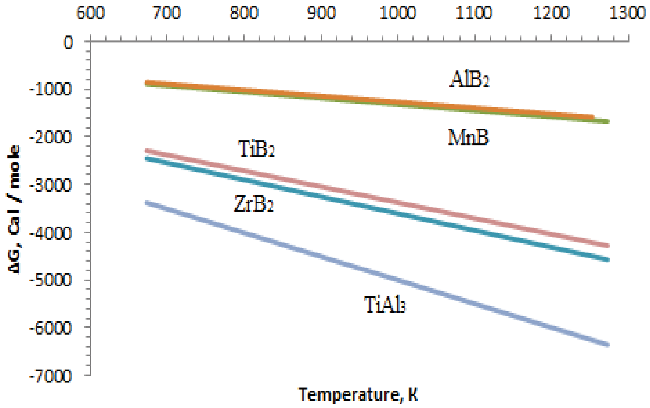

Figure 1. Gibbs energy of chemical reactions in the system Al-Mg-Mn-Zr-Sc-Ti-B.

It should be noted, that results of metallographic (Fig. 2) and x-ray analyzes showed that the Al-5 wt% B master alloy, used for obtaining composite alloys, contains boron as compound AlB_2 (Fig. 2).

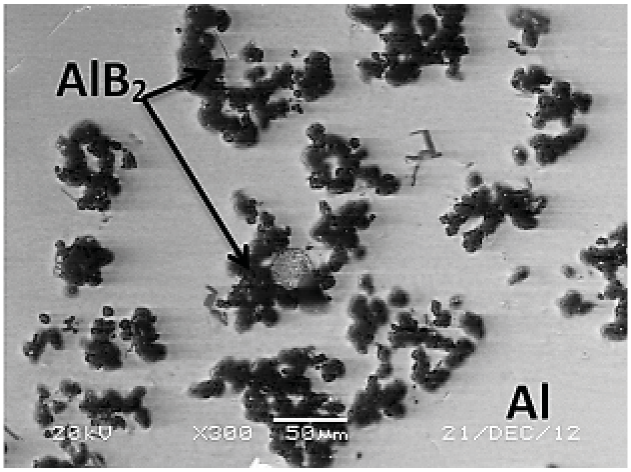

Figure 2. Microstructure of Al-5 wt. % B master alloy.

The result of thermodynamic calculations showed that, at the fusion temperature, the Gibbs energy of aluminum diboride is -1480 cal/mole. The values of manganese boride formation energy are in the same range, and they both have the highest Gibbs energy of chemical reactions in the system Al-Mg-Mn-Zr-Sc-Ti-B. It means that the additional formation of AlB_2 and MnB during melting is improbable.

The most probable is the formation of titanium aluminide by the reaction:

$Ti + 3Al = TiAl_3$.

The sequence of the reactions can be represented in the following way. Firstly, titanium aluminide is formed. Next titanium and zirconium borides would be formed. Zirconium diboride has a smaller value of Gibbs energy, so this reaction is more probable than the formation of titanium diboride, which Gibbs energy at 1173 K is 270 kcal/mol higher than that of zirconium diboride.

Table 4 shows the chemical composition for Al-3 wt % Ti-2 wt% B-0.25 wt% Zr-0.1 wt% Sc alloy, calculated using the Thermo-Calc software. Calculations show that the phase of unknown stoichiometry is forming, it contains Al, Ti, B, Zr. At the same time the melt does not contain zirconium, which prevents the possibility of obtaining an aluminum supersaturated solid solution during the crystallization, and thus prevents the formation of a dispersed, coherent phase Al_3Zr. Calculations show that the scandium does not form boron-containing compounds.

Table 4

Composition of Al-3 wt% Ti-2 wt% B-0.25 wt% Zr-0.1 wt% Sc alloy obtained using the Thermo-Calc software.

Temperature, °C	Phase composition	Chemical composition , wt. %				
		Al	Ti	B	Zr	Sc
1000	Liquid	99.65	0.00	0.25	0.00	0.10
	Phase of unknown stoichiometry	8.06	54.98	32.38	4.58	0.00
900	Liquid	99.76	0.00	0.14	0.00	0.10
	Phase of unknown stoichiometry	10.00	52.73	32.87	4.40	0.00
800	Liquid	99.83	0.00	0.07	0.00	0.10
	Phase of unknown stoichiometry	11.21	51.33	33.18	4.28	0.00

Structure and mechanical properties

Cast ingots hardness (Table 5) shows that the cast alloy No. 1 has a hardness comparable to the hardness of the standard alloy No. 4, given in the table for comparison. However, the results of the analysis showed that the alloy No. 1 was not hardened after heat treatment, which confirms the interaction between zirconium and boron.

The addition of magnesium to the alloy increases hardness of ingots. Substitution of zirconium for scandium concentration does not give the desired effect, the alloy is not hardened after the heat treatment. Elimination of titanium increases strength after annealing,

Table 5

Hardness of cast ingots

Alloy No.	Brinell scale hardness, BHN	
	cast	heat-treated
1	51±1	50±1
2	64±3	63±3
3	65±3	68±3
4* (Al-1.5Mg-1Mn-0.25Zr-0.1Sc)	50±2	79±2

*Alloy containing no boron and titanium for comparison

Sheets of composite alloys No. 2 and No. 3, obtained by rolling and heat-treated, were subjected to tensile test. Alloy No. 1 showed low hardness after heat treatment, so the analysis of the mechanical properties was not appropriate. The test results are shown in Table 6.

Table 6
Mechanical properties of composite alloys

Alloy No.	Tensile strength, MPa	Yield strength, MPa	Elongation, %
2	280±6	154±4	13.4±0,6
3	274±7	179±3	11.8±0,5
4*(Al-1.5Mg-1Mn-0.25Zr-0.1Sc)	275±4	248±3	6.1±0,3

*Alloy containing no boron and titanium for comparison

Samples 2 and 3 have low yield strength in comparison with alloy 4. Elongation for composite alloys No. 2 and No. 3 two times more than that for the alloy No. 4. Microstructural analysis shows that large clusters of particles AlB$_2$ (Fig. 3 and 4), from the master alloy, remain during fusion process. At the same time, acicular phase is formed, containing, according to calculations, boron, titanium, scandium and aluminum

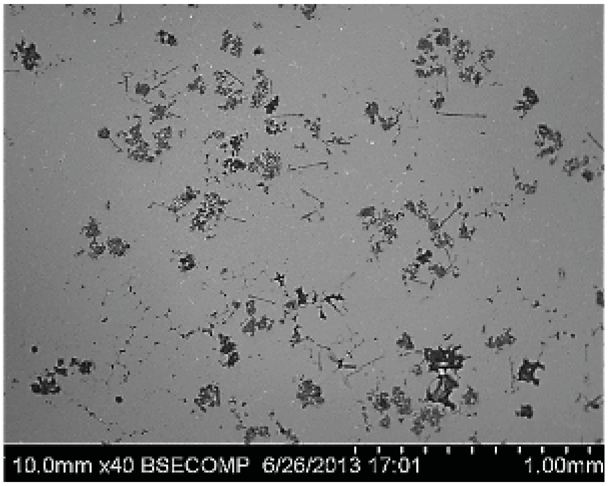

Figure 3. Microstructure of the composite cast alloy No. 2 (Al-4Mg-1Mn-1.5Ti-2B-0.3Sc).

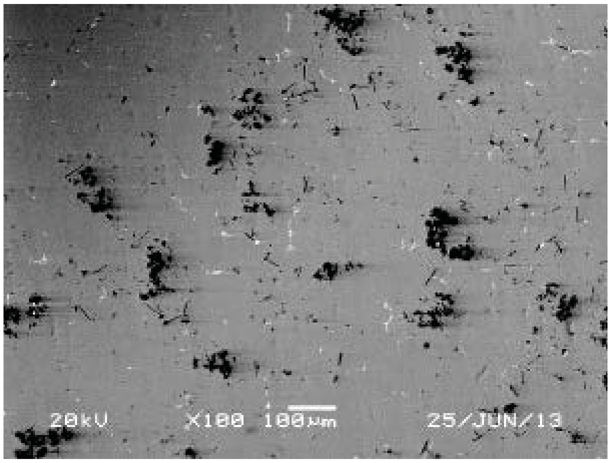

Figure 4. Microstructure of the composite cast alloy No. 3 (Al-4Mg-1Mn-2B-0.3Sc).

Conclusions

1. In this work composite alloys Al-2Mn-1.5Ti-2B-0.25Zr-0.1Sc, Al-4Mg-1Mn-1.5Ti-2B-0.3Sc and Al-4Mg-1Mn-2B-0.3Sc were obtained using casting technology.
2. 2. Thermodynamic calculations showed that the most probable chemical reaction, during composite alloys casting, is the reaction of titanium aluminide formation. Formation of titanium and zirconium borides is also possible, but undesirable. The calculation of the phase composition using Thermo-Calc software showed the formation of phase containing titanium, zirconium, aluminum and boron. To determine the stoichiometry of this phase requires further study. Interaction of scandium with other alloying elements makes it extremely difficult to obtain a boron-containing heat-resistant aluminum composite alloyed with zirconium and scandium produced by casting. Since the formation of nanoparticles Al3Zr, Al3Sc and Al3(Zr, Sc) is not possible
3. Analysis of mechanical properties revealed that the composite alloy is not hardened by heat treatment. Maximum mechanical properties of the alloy are: tensile strength – 274 MPa, yield strength – 179 MPa, elongation – 11.8 %
4. Metallographic researches showed that the particles AlB$_2$ transfer into composite alloys and look like compact agglomerations of inclusions. Also takes place the formation of acicular phases of scandium and zirconium borides, and possibly more complex phases.

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