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Grain Boundary Wetting in the Al–Mg System and Synthesis of Magnesium Diboride in Contact with Melt

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Abstract—The interaction between a Mg-containing melt and B under conditions of partial and complete wetting of Al/Al grain boundaries by Al–Mg melt has been investigated. The study was performed on Al polycrystals with Mg contents of 5, 10, 15, 18, and 25 wt %. Correspondingly, the Mg content in the melt was determined by the liquidus line and was in the range from 5 to 30 wt %. The obtained metal-matrix composites were investigated by light and scanning electron microscopy, electron-probe microanalysis, and X-ray diffraction. The possibility of synthesizing MgB_2 in the contact with a melt having a relatively low Mg content (from 15 to 30 wt %) has been demonstrated.

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INTRODUCTION

In 2001 magnesium diboride (MgB_2) was found to have a superconducting transition temperature of 39 K [1]. Since that time, this superconductor has figured prominently in the superconductor technology. Currently, MgB_2-based superconducting wire up to few kilometers long has been commercially produced. Magnesium diboride is a brittle compound; therefore, it is important to develop the fundamental bases of various technologies making it possible to form a plastic metal matrix of sufficiently high conductivity with MgB_2-filled channels or interlayers inside.

Currently, either MgB_2 superconducting channels are formed from a previously synthesized powder or MgB_2 is synthesized in situ. In the latter case, a mixture of boron and magnesium is placed in a tube made of a metal with a sufficiently high melting temperature (copper, niobium, iron, etc.) to react upon heating with the formation of MgB_2. The mixture is heated above the Mg melting point and then B reacts with the Mg melt. However, this method has a number of significant drawbacks.

First, heating should be performed to a temperature above the Mg melting temperature, which is fairly high (650°C). Second, high-temperature synthesis of MgB_2 is generally performed after rolling or drawing a metal rod or bar with the Mg–B reaction mixture inside. Since Mg has a hexagonal lattice, its deformability is low. Recently, an original method has been proposed to increase the deformability of pieces with a metallic shell and a reaction mixture inside to synthesize MgB_2 [2, 3].

In this method, not magnesium but its alloy with about 12 wt % lithium is placed in the mechanical shell before rolling or drawing. This alloy has a bcc lattice and is more plastic than pure magnesium. In this case, boron reacts not with molten magnesium but with the melt containing both Mg and Li. Nevertheless, it was shown in [2, 3] that this technique makes it possible to successfully synthesize continuous superconducting MgB_2 layers.

We proposed to use not only pure magnesium melt but also melts containing other elements, along with Mg, to synthesize MgB_2 in situ. To obtain composites with a plastic metal matrix and superconducting MgB_2-based interlayers, one can also use the effect of the so-called grain-boundary wetting, which has been recently found and investigated in detail by us.

The essence of grain-boundary wetting is that the liquid phase in a number of systems in the two-phase region of the solid solution + melt phase diagrams can completely wet the solid-phase grain boundaries. In this state (Fig. 1), liquid interlayers in equilibrium separate solid-phase grains. Changing the temperature, one can pass from complete to partial wetting and thus change the morphology of liquid channels in the solid matrix (Figs. 1b, 1c). In particular, this effect was found by us in the Al–Mg system [4, 5]. Thus, in a certain temperature range an Al–Mg alloy may consist of solid grains poor in magnesium and interlayers or channels of Mg-rich melt. The concept of this study is that boron would react not with pure magnesium but with a composite where an Al–Mg melt is confined between solid metal grains having a fairly high plasticity.

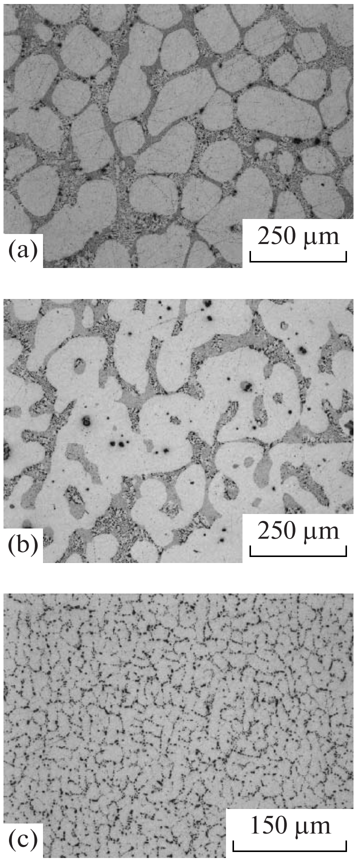

Fig. 1. Microstructure of Al–Mg polycrystals from the two-phase region ($S + L$): (a) Al–10 wt % Mg, 610°C, all grain boundaries are completely wetted by melt; (b) Al–10 wt % Mg, 581°C, some grain boundaries are completely wetted and the others are incompletely wetted; and (c) Al–15 wt % Mg, 490°C, completely wetted boundaries are absent.

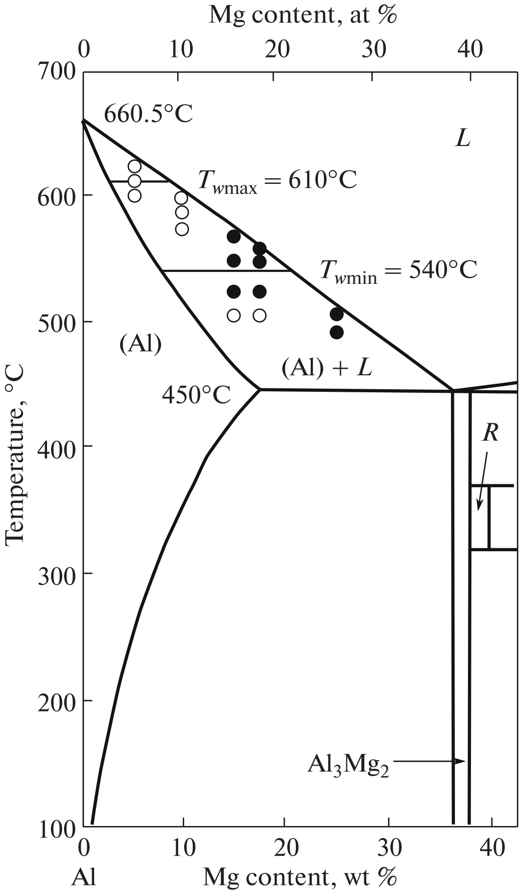

Fig. 2. Al–Mg phase diagram with lines of the bulk phase transitions (bold lines, [6]) and two wetting phase transition tie lines at $T_{w\max}$ = 610°C and $T_{w\min}$ = 540°C (continuous thin lines). The closed and open circles indicate the annealing conditions under which MgB$_2$ was formed and was not formed, respectively.

EXPERIMENTAL

Al alloys with different Mg contents (5, 10, 15, 18, and 25 wt %) were prepared for the experiments. Then cylindrical samples 7 mm in diameter and 4 mm in height were cut from each alloy piece. Holes 2 mm in diameter were drilled in the samples to be filled with boron powder. The annealings were performed in quartz ampoules with a residual gas pressure of 4×10^{-4} Pa. The Al–Mg alloy samples in contact with the boron powder were annealed in the two-phase Al + L region of the bulk phase diagram at temperatures below liquidus for 60 min. The annealing temperatures are indicated by circles in Fig. 2. After the annealing, the samples were ground and polished. The sample structure was studied by optical microscopy (Zeiss Axiophot microscope) and scanning electron microscopy (Tescan Vega TS5130 MM scanning electron microscope equipped with an energy-dispersive Oxford Instruments LINK spectrometer). The phase composition of the samples was analyzed by X-ray diffraction on a Siemens 500 diffractometer (FeK_α radiation).

RESULTS AND DISCUSSION

Figure 1 shows how the grain-boundary wetting phase transition affects the microstructure of Al–Mg polycrystals in the two-phase region ($S + L$) by the example of Al–10 wt % Mg and Al–15 wt % Mg alloys. The phase grains (Al), which remained solid at the annealing temperature appear bright in the lap. The sample regions that were molten at the annealing temperature undergo the $L \rightarrow$ Al + Zn eutectic transformation upon quenching and appear gray in the lap. For example, at 610°C (Fig. 1a) all boundaries are completely wetted by the melt, at 581°C (Fig. 1b) some grain boundaries are completely wetted (about 26%) and the others are wetted incompletely, and at 490°C (Fig. 1c) there are no completely wetted boundaries in the polycrystal. Grain boundaries completely wetted by the melt are absent in the polycrystals

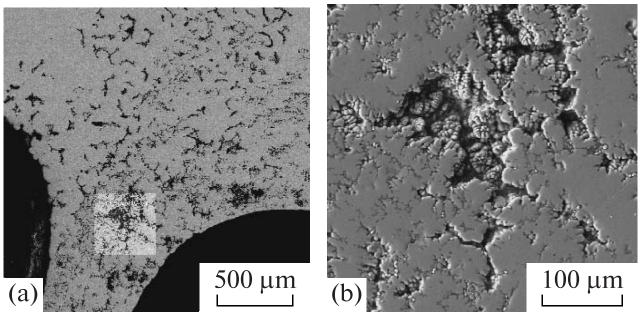

Fig. 3. Al–15 wt % Mg alloy with cylindrical holes filled with boron to react with Mg-containing melt after annealing at 520°C. A system of channels along the grain boundaries in the aluminum matrix can be seen, which were filled with the melt before the reaction with boron. Panel (b) is the enlarged fragment framed by a bright square in panel (a).

at temperatures below $T_{w\min} = 540°C$. In the range from $T_{w\min} = 540°C$ to $T_{w\max} = 610°C$, the fraction of completely wetted grain boundaries gradually increases from 0 to 100% with an increase in temperature and all boundaries become wetted above $T_{w\max} = 610°C$. These data made it possible to construct tie lines of the wetting phase transition at $T_{w\max} = 610°C$ and $T_{w\min} = 540°C$ (continuous thin lines) on the bulk phase diagram of Al–Mg (Fig. 2).

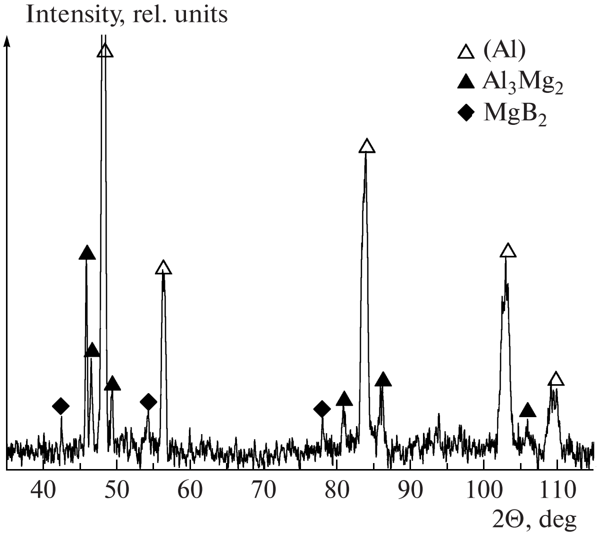

Fig. 4. X-ray diffraction pattern of the Al–25 wt % Mg alloy after reaction with boron at 500°C: (Al) peaks of the magnesium solid solution in aluminum with a lattice constant of ~0.41 nm (corresponds to a Mg content of 10.5 wt %, according to [7]); (Al_3Mg_2) intermetallic compound with a cubic lattice; and (MgB_2) hexagonal magnesium diboride (space group *P6mmm*).

The annealing temperatures of Al–Mg samples contacting with boron powder are indicated in Fig. 2 by circles. The Mg content in the melt at the reaction temperature corresponded to the liquidus in the Al–Mg diagram and ranged from 5 to 30 wt %. Figure 3 shows a typical sample microstructure after annealing in contact with boron. It can be seen that the Mg-rich melt partially flew out from the intergranular space into the holes filled with boron powder. The X-ray diffraction data (Fig. 4) indicate that MgB_2 can be produced as a result of the reaction of Mg-rich melt with boron. The annealing temperatures and the sample composition at which MgB_2 formation in contact with the Al–Mg melt was observed are indicated by closed circles in Fig. 2. It can be seen that MgB_2 was not formed at a Mg content in the melt below 15 wt %. Thus, the possibility of MgB_2 synthesis in contact with an Al-based melt with a relatively low Mg content (from 15 to 30 wt %) is demonstrated. Furthermore, we planning to optimize the process conditions in order to increase the reaction yield and obtain MgB_2 at interaction with the melt located directly between the grains of the Al-rich solid phase.

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