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Reaction of boron to transition metal impurities and its effect on conductivity of aluminum ①

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[Abstract] The effects of boron on electrical conductivity of aluminum and the action mechanism have been investigated. The results indicate that, by combining with the trace amounts of transition elements Ti, V and Zr to form two kinds of insoluble borides, boron can significantly improve the electrical conductivity of commercial aluminum. One of the borides contains 54.42% B, 13.70% Al and 23.39% (mole fraction) transition elements (including Ti, V, Zr and Fe) and is in the form of fine particles. The other one, in hexagonal shape, contains 78.59% B, 14.97% Al and 2.56% (mole fraction) transition elements (including Ti, V and Fe). Neither Cr nor Mn is found in these borides. The conversion of some transition metal impurities from solid solution state to the boride precipitates form leads to a decrease in electrical resistivity, and this decrease constitutes 86.2% of that can be achieved by complete removal of transition element impurities from aluminum melts.

[Key words] boron; electrical conductivity; commercial aluminum
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1 INTRODUCTION

Al-B master alloys have been successfully used for a number of years to increase the electrical conductivity of aluminum conductor alloys[1~5]. They are considered to form insoluble compounds with trace amounts of transition elements and then precipitate out. However there are some doubts about the roles of boron in aluminum conductor alloys. It was reported that boron could combine with the trace amounts of transition elements Ti, V, Cr and Mn in aluminum melts to form insoluble compounds[1]. Others considered that boron could remove the transition elements Ti, V, Cr and Zr from the aluminum melts[2~4]. There are also other contradictory results. Devgun et al[6] found that, at fixed titanium contents of 0.0014% and 0.0025%, the increasing additions of boron produced a linear increase in the electrical resistance of the resultant aluminum. Up to now, the action mechanism of boron in removal of transition metal impurities from aluminum is not known clearly.

In this work, the authors investigate the effects of boron on the electrical conductivity of aluminum, by studying the morphology and chemical composition of borides formed by boron and transition element impurities, which will help to clarify the action mechanism of boron.

2 EXPERIMENTAL

2.1 Settling ingot preparation

In order to extract the borides, settling experiments were conducted to make the probable boride particles to agglomerate and settle down. The compositions of aluminum and Al-B master alloy used for the experiments are shown in Table 1. About 2 kg aluminum was weighed respectively into two graphite crucibles previously lined in a resistance furnace. The size of the crucibles is shown in Fig. 1. Once the aluminum was melted and its temperature reached 700 ℃, 0.06% B in the form of Al-B master alloy was added into one of the crucibles. Then the melts in both crucibles were stirred for 30 s and maintained at (700 ±10) ℃ for 2 h. Finally, the crucibles were taken out of furnace with minimal disturbance of the melts. After the melts solidified in the crucibles, the settling ingots A (boron-added) and F (boron-free) were obtained.

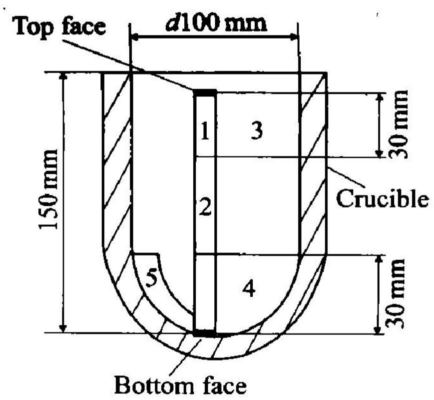

Fig. 1 Size of settling ingots and its sectioning

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Table 1 Chemical compositions of materials used for tests(mass fraction, %)

Material	Fe	Si	Cu	Mg	Ti	V	Zr	Cr	Mn	B	Others	Al
Commercial aluminum	0.196	0.05	0.002 3	0.006	0.005	0.010	0.002	0.004	0.004		0.050	99.7
Al-B master alloy	< 0.20	< 0.16								3.35		Bal.

The settling ingots were cut into specimens as shown in Fig. 1 for the following characterization.

Section 1, 2: microstructure examination (top surface in section 1; bottom surface in section 2); Section 3, 4: resistivity measurement; Section 5: insoluble residue extraction.

The boron contents were measured by ICP-5000 Inductively Coupled Plasma.

2.2 Extraction of borides

The sedimentary layer(Section 5 in Fig. 1) of ingot A was machined into fine chips and dissolved in 250 mL of methanol containing 10 g of iodine and 25 g of tartaric acid[7]. The insoluble residue was filtered off, rinsed, dried and collected for further SEM, EDX and X-ray diffraction analysis.

2.3 Resistivity measurement

Section 3, 4 taken from ingots A and F were extruded into rods with 9.5 mm diameter by hot-extruder after heated for 2 h at 400 ℃, and then were drawn into wires with 2.28 mm diameter for the resistivity measurements.

The electrical resistivity was detected in accordance with IEC468 specification.

3 RESULTS

3.1 Morphology and compositions of borides

The actual boron contents at different parts of ingot A are shown in Table 2. The results indicate that boron is enriched at the bottom of ingot A. It is known that pure boron is lighter than aluminum melts, so it can be confirmed that there are some borides with higher density accumulated at the bottom of ingot A during the 2 h settling process.

Table 2 Distribution of boron in ingot A (mass fraction, %)

Nominal content	Measured content		
	Top	Middle	Bottom
0.06	0.019	0.022	0.16

Microstructure examinations are conducted in ingots A and F respectively. The results show that both ingots present the same morphology except the bottom of ingot A. Their morphology is characterized by α-Al matrix phase and Fe-Al phase at grain boundaries (Fig. 2). However, at the bottom of ingot A, three phases with different contours are observed except for α-Al matrix (Fig. 3), respectively in the forms of hexagonal shape, lath, and fine clusters aggregated with very small particles. The SEM morphology of the three phases in the extractive residue is shown in Fig. 4, in agreement with Fig. 3. The chemical compositions of the three typical phases are detected with EDX as shown in Figs. 5~ 7. The hexagonal-shaped

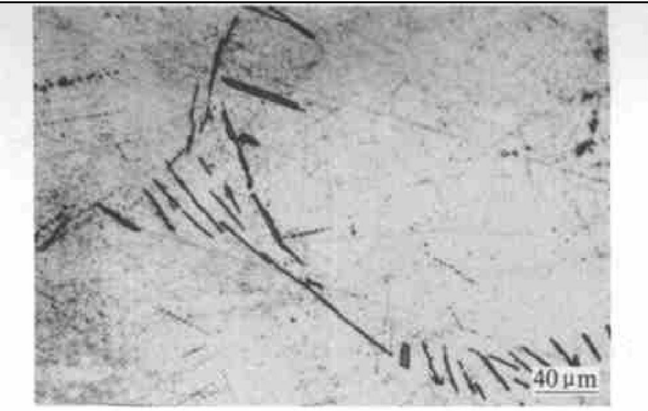

Fig. 2 Morphology of bottom of ingot F (boron-free)

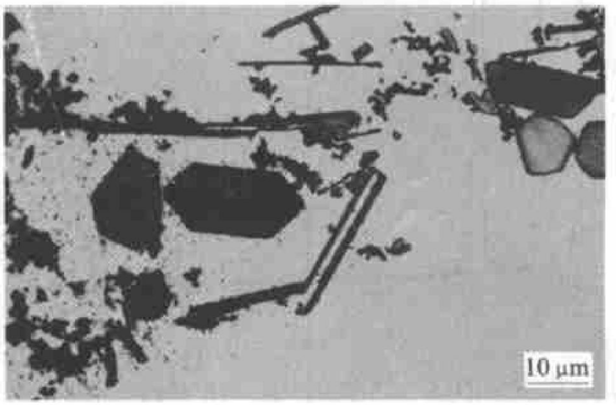

Fig. 3 Morphology of bottom of ingot A (boron-added)

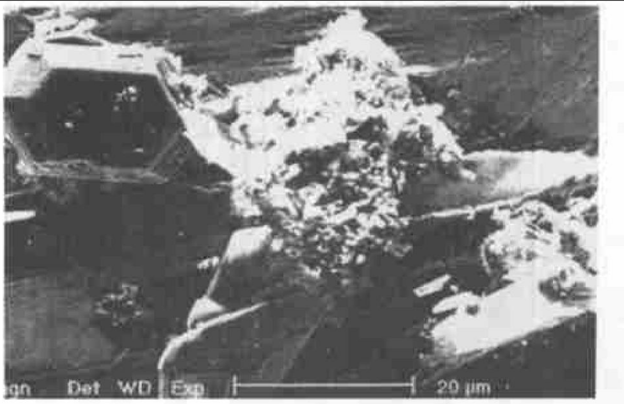

Fig. 4 SEM image of insoluble residue at bottom of ingot A

Table 3 Resistivity of settling ingots

Position	Resistivity/ ($10^{-8}\ \Omega\cdot m$)		Decrease of ingot A than F in Resistivity	
	Ingot F	Ingot A	Absolute value/ ($10^{-8}\ \Omega\cdot m$)	Relativity value/ %
Top	2.805 9	2.748 1	0.057 8	100
Bottom	2.805 8	2.755 8	0.050 0	86.2

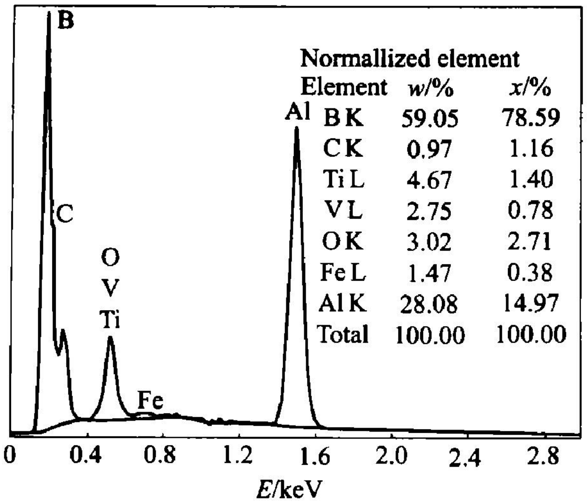

Fig. 5 EDX analysis for hexagonal-shaped phase

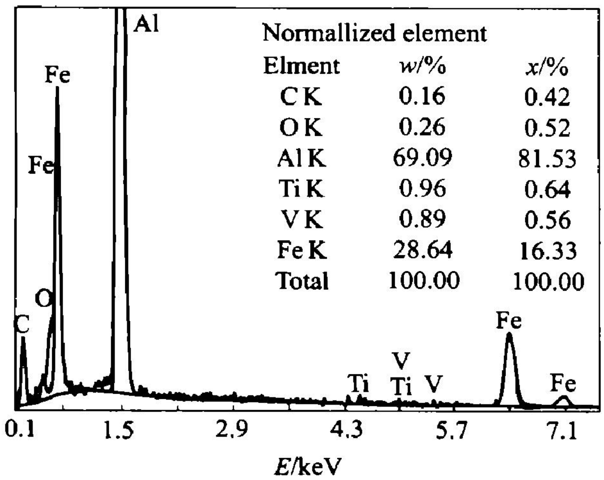

Fig. 6 EDX analysis for lath-shaped phase

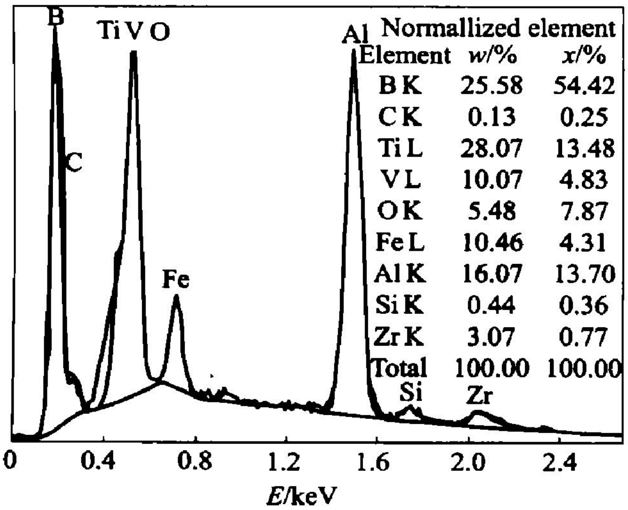

Fig. 7 EDX analysis for phase in cluster form comprising fine particles

phase contains 78.59% B, 14.97% Al and 2.56% (mole fraction) transition elements. The lath-form phase contains 81.53% Al, 16.33% Fe (mole fraction), and a small amount of other trace elements. The cluster compound contains 54.42% B, 13.70% Al and 23.39% (mole fraction) transition elements Ti, V, Zr and Fe, much more than that in the original aluminum shown in Table 1. Neither Cr nor Mn is found in the extractive residues.

The X-ray diffraction analysis identifies three phases AlB_2, $FeAl_3$ and TiB_2 in the residues (Fig. 8). There are also some unknown phases.

3.2 Resistivity measurement

The resistivity is measured for ingots A and F respectively, and the results are displayed in Table 3. The results are marked by two features: first, ingot A, both its top and bottom parts, present lower resistivity values than that of ingot F; second, the top and the bottom of ingot F manifest the same resistivity values, but for ingot A, the resistivity value of its bottom is slightly higher than that of its top. This fact and the microstructure examination mentioned above indicate that boron can improve the electrical conductivity of aluminum by combining with harmful transition elements Ti, V, Zr etc. After boron is added in the aluminum melts, some transition element impurities diffuse out of the solute state to form insoluble borides, so ingot A presents lower resistivity values than that of ingot F. With the insoluble borides settling down to the bottom, the top of ingot A presents a lower resistivity due to the removal of the transition elements, and the bottom display a slightly higher resistivity value because of the existence of transition elements in the precipitate form. The data in Table 3 also indicate that the conversion of some transition metal impurities from solid solution state to the boride precipitates form leads to a decrease in electrical resistivity, and this decrease constitutes 86.2% of that can be achieved by complete removal of transition element impurities from aluminum melts.

Element Fe is also found in the two kinds of borides, however it is believed that Fe has little effect on the electrical conductivity of aluminum. Since the content of Fe in the commercial aluminum (shown in Table 1) is much more than its maximum solubility (0.04%), it often presents in $FeAl_3$ form in commercial aluminum. It is just converted from one precipitate

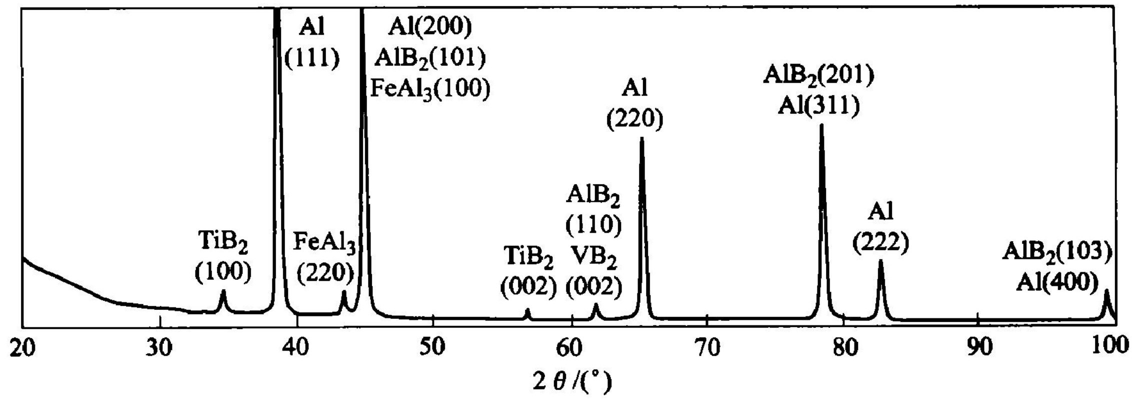

Fig. 8 X-ray diffraction analysis for insoluble residue in ingot A

($FeAl_3$) to another one (the boride of Fe) after boron is added in the aluminum melts and the contribution from solute is negligible.

4 DISCUSSION

4.1 Phases in ingot A

The lath-shaped phase is also found in ingot F after etched deeply with an iodine-methanol solution (shown in Fig. 9). Its composition as determined with EDX is almost the same as that of the lath phase in the residues of ingot A. So the phase in lath form in the residue can be determined as $FeAl_3$.

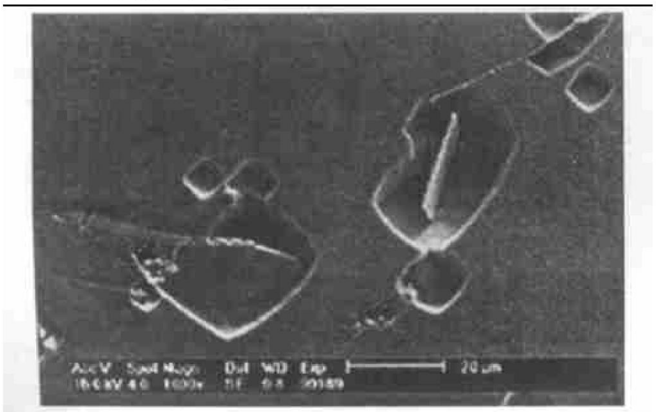

Fig. 9 SEM image of bottom of ingot F etched deeply in iodine-methanol

Cibula et al[8] reported that the AlB_2 phase is often in hexagonal shape in Al-B master alloy. According to the results of EDX, X-ray diffraction analysis (Figs. 5 and 8), and the characteristics of AlB_2, the hexagonal phase at the bottom of ingot A (Figs. 3 and 4) can be deduced to be AlB_2.

As to the phase in the cluster form containing relatively more transition elements and boron, it is believed to be the boride formed after boron is added.

4.2 Action mechanism of boron

As is known, the maximum solubility of boron in aluminum is 0.022%[9]. After more boron is added into aluminum melts, part of boron is dissolved in the aluminum melts in solution state and the surplus part of boron remains in AlB_2 bulk form in aluminum melts.

The dissolved boron can combine with transition elements Ti, V, Zr, Fe in the aluminum melt to produce the borides. Due to the low concentrations of transition elements and their homogeneous distribution, these boride particles are very fine. Since they have higher density, they can agglutinate and settle at the bottom of the ingot. Finally, they appear in the form of clusters of very fine particles.

The EDX examination show that there are also more transition elements Ti, V, and Fe in the hexagonal-shaped phase than that in the matrix. It is reported that some transition metals diborides are isomorphous with aluminum boride (AlB_2) and have very similar lattice constants. Cornish[10], B~ckerud[11], Klang[12], Morimumi and coworkers[13] have observed a complex (Al, Ti) B_2 phase. Marcantonio and Mondolfo[14] have analyzed the chemical composition of complex boride extracted from aluminum and found that aluminum and titanium substitute for one another in the structure. Setzer and Boone[2] made an analysis of the precipitate in commercial aluminum-boron system using EDX and indicated a complex phase (Ti, V) B_2. Careful X-ray measurements[8, 10, 12, 14] have shown that the AlB_2 and TiB_2 crystals are isomorphous. According to these results, it is supposed that the AlB_2 can probably form a continuous range of solid solution of (Al, Ti, V, Fe) B_2 in aluminum melts. It is also considered that the conversion of aluminum borides to the transition elements borides is an incomplete reaction and the aluminum borides nucleate only at the surface[3]. In comparison with the phase in the cluster form, no Zr is found in the continuous range of solid solution of boride.

5 CONCLUSIONS

1) Two kinds of borides are formed after Al-B master alloy is added. One boride is in cluster form, containing 54.42% B, 13.70% Al, 23.39% (mole fraction) transition elements (including Ti, V, Zr and Fe). Another one has hexagonal shape and contains mainly 78.59% B, 14.97% Al and 2.56% (mole fraction) transition elements.

2) Boron improves the electrical conductivity of commercial aluminum significantly by combining with the trace amounts of transition elements Ti, V, and Zr to form insoluble borides. Neither Cr nor Mn is found in the two kinds of insoluble borides.

3) The detrimental effects on the electrical conductivity of aluminum from the transition elements in precipitate form become much smaller than that in the solid solution state. For the Al-0.06% B system, the conversion of some transition metal impurities from solid solution state to the boride precipitates form leads to a decrease in electrical resistivity, and this decrease constitutes 86.2% of that can be achieved by complete removal of transition element impurities from aluminum melts.

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