[Article ID] 1003- 6326(2002)02- 0204- 06

Purification effects of glass flux on A356 melt ①

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[Abstract] In order to remove hydrogen and inclusions from A356 alloy melt, a low melting-point glass flux, JDN-Ⅱ, was developed. The results indicated that JDN-Ⅱ flux has distinct effect of purification and protection on A356 alloy melt. When the dosage of the flux was 3%, the content of hydrogen in A356 melt was only 2.6 mL/kg at 857 ℃ and 0.7 mL/kg even at 750 ℃. In the meantime, the mechanical properties of the alloy increase greatly with the covering of 3% JDN-Ⅱ flux. Compared with no flux, the tensile strength of A356 alloy increases by 9.42% and the elongation increases by 22%. The purification mechanism of JDN-Ⅱ glass flux was discussed too.

[Key words] JDN-Ⅱ flux; A356 alloy; degassing; borate glass with low melting-point

[CLC number] TG146.2+1; TG146.4+5 **[Document code]** A

1 INTRODUCTION

High gas content is an important factor that restricts the improvement of the quality and the increase in quantity of aluminum ingot in aluminum processing industry. The hydrogen content of the aluminum melt is 4.0~ 8.0 mL/kg commonly, and it is still around 1.0~ 2.0 mL/kg after degassing. It is well known that the hydrogen content should be very low for the airplane parts, and that sometimes the content is required no more than 1.0 mL/kg. Furthermore, high quality aluminum foil and aluminum materials used in the electronic industry require the content of hydrogen no more than 0.6 mL/kg[1]. On-line degassing equipments, such as SNIF, MINT, ALPUR, RDU and FI, can improve the degassing effect to a certain extent, but the content of hydrogen in the melt still cannot meet the requirement of low hydrogen content. Moreover, the cost of degassing is enormous, and the pollution is severe[2, 3]. As a result, only reasonable method is adopted to remove hydrogen and inclusions from the aluminum melt, then aluminum alloy of high quality and low cost can be gotten.

In the course of casting and melting of the aluminum alloy, the main source of H and O is damp atmosphere, and the temperature of the melt and the contacting time of the melt with vapor are the key factors which determine the quantity of H and O absorbed by the aluminum melt[4]. Therefore, using fluxes by conering the melt to isolate aluminum melt from atmosphere, through a series of physical and chemical reactions, has an significance of preventing the melt from absorbing gas, removing hydrogen and inclusions and increasing the purity of the melt.

The fluxes used to purify the molten aluminum can be generally divided into five types: cover fluxes, cleaning fluxes, refining fluxes, drossing fluxes and wall-cleaning fluxes[5~ 7]. However, all fluxes above mentioned are mixed salt fluxes and they have no notable effect and cannot be used to purify and protect high-temperature melt. Low melting-point glasses based on removing both hydrogen and inclusions have notable effect of degassing as a green purificant, and they have found their ways into purifying Fe, Cu, Zn and their alloy melts[8~ 12]. However, because active metal elements, such as Al, Mg can replace some components of oxide glasses, there are few reports on research of low melting-point glasses used to purify the aluminum melt. In this paper, a low melting-point borate glass, JDN-Ⅱ flux, on the basis of experiments is reported.

2 EXPERIMENTAL

2.1 Producing of JDN-Ⅱ flux

The main components of JDN-Ⅱ flux are $Na_2B_4O_7$ and some assistant additions. All the required components were kept at 250 ℃ for 6 h to get rid of moisture, then weighed accurately and put into a graphite crucible. After that, the crucible was put into SG2 standard crucible resistance furnace (7.5 kW) with KSW temperature controller. It was kept at 780 ℃ for 10 min, the glass melt was mixed, then the crucible was taken out of the furnace and the melt was quenched in the water. The JDN-Ⅱ flux from the processing above was kept at 150 ℃ for above 3 h before being used.

① **[Foundation item]** Project (G1999064900) supported by the National Key Fundamental Research and Development Program
[Received date] 2001- 07- 13; **[Accepted date]** 2001- 09- 17

2.2 Experimental content

A356 alloy ingot was used in this study. A SG_2 standard crucible resistance furnace (12 kW) with KSW temperature controller was used to melt the alloy. 10 kg A356 alloy was loaded in the furnace and heated to a temperature above the eutectic point after a pretreatment of removing water and oil from the surface of the alloy, then JDN-Ⅱ flux was added. The melt was heated to the pouring temperature and kept for 10 min. After being poured into metal moulds for testing mechanical properties and fluidity respectively, the melt was heated to the prearranged temperature and kept for 10 min, then the hydrogen content of the melt was measured.

The schematic diagram of fluidity mould for A356 melt is shown in Fig. 1. An ELH-ⅢB type hydrogen tester was used to measure the hydrogen content, whose measuring range is 0 ~ 9.9 mL/kg and the resolution is 0.1 mL/kg. The as-cast tensile samples (d12 mm × 60 mm) was measured in WE-60 testing machine. A multi data collection system was used to measure the melting point of the glass flux. A D/max-ⅢA X-ray diffraction instrument was used to determine the microstructure of the glass.

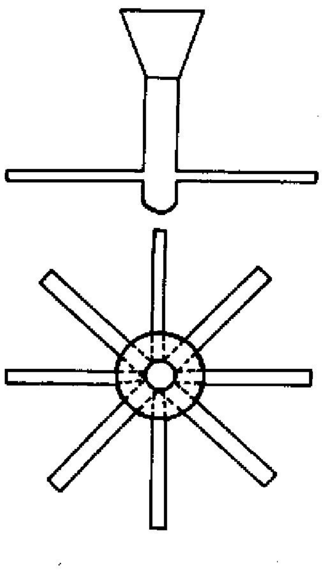

Fig. 1 Schematic diagram of fluidity mould for A356 melt

3 RESULTS

3.1 Noncrystalline characteristic of JDN-Ⅱ flux

Fig. 2 indicates that JDN-Ⅱ has typical noncrystalline structure because there is no obvious solidification flat.

XRD pattern in Fig. 3 indicates that JDN-Ⅱ flux has typical noncrystalline structure because there is no obvious diffraction peak. Fig. 3 also shows that the assistant additions of JDN-Ⅱ flux has entered the structure of the glass molecules.

3.2 Effect of purification of JDN-Ⅱ flux

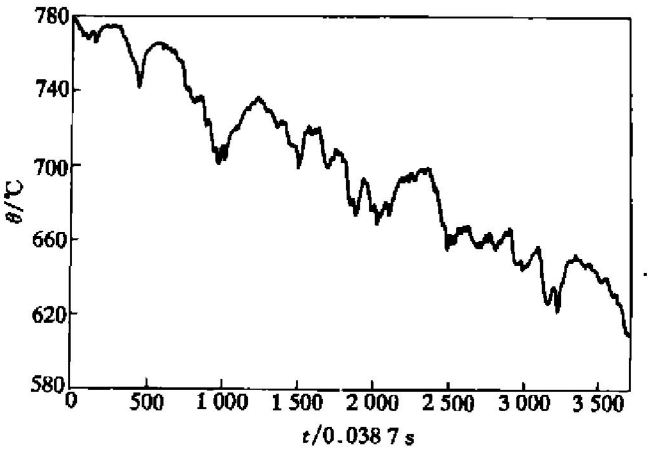

Fig. 2 Cooling curve of JDN-Ⅱ flux

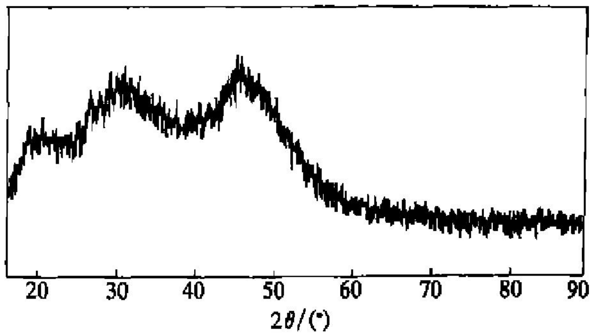

Fig. 3 XRD pattern of JDN-Ⅱ flux

As shown in Fig. 4, when the melt temperature was below 800 ℃, the hydrogen content was above 4.4 mL/kg at 750 ℃ and 3.7 mL/kg at 720 ℃ without flux covering.

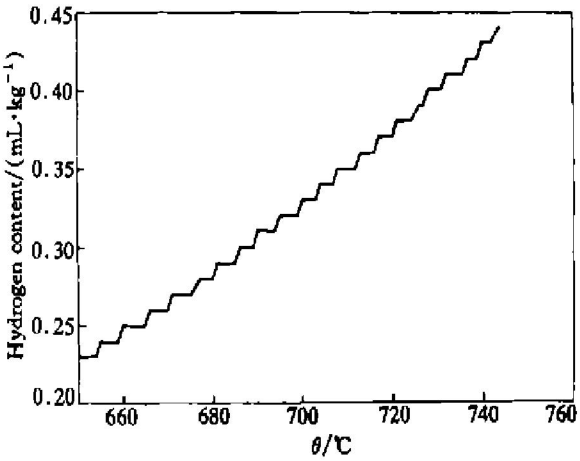

Fig. 4 Hydrogen content of A356 melt without flux below 800 ℃

Fig. 5 indicated that the degassing effect of 2% JDN-Ⅱ flux was not good, for example, hydrogen content was 2.5 mL/kg at 720 ℃ and 2.2 mL/kg at 700 ℃. The hydrogen content had a drop of 1.2 mL/kg, which was decreased by 32.4% in comparison with that no flux covering at the pouring temperature. This fact showed that 2% JDN-Ⅱ flux has not enough effect of protection and purification on

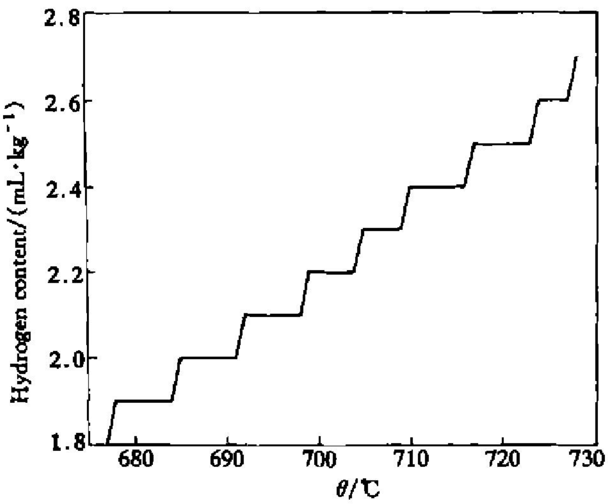

Fig. 5 Hydrogen content of A356 melt with covering of 2% JDN-Ⅱ flux below 800 ℃

the A356 alloy, but is still worked.

Fig. 6 shows that when 3% JDN-Ⅱ flux was used to protect and purify A356 alloy melt, the protecting layer was destroyed because of the improper processing, in the meantime, a great deal of gas was absorbed by the aluminum melt. Therefore, hydrogen content was 7.5 mL/kg at 840 ℃, 4.5 mL/kg at 750 ℃ and 3.8 mL/kg at 720 ℃. The values above mentioned are higher than those shown in Fig. 4 without flux at the same temperature.

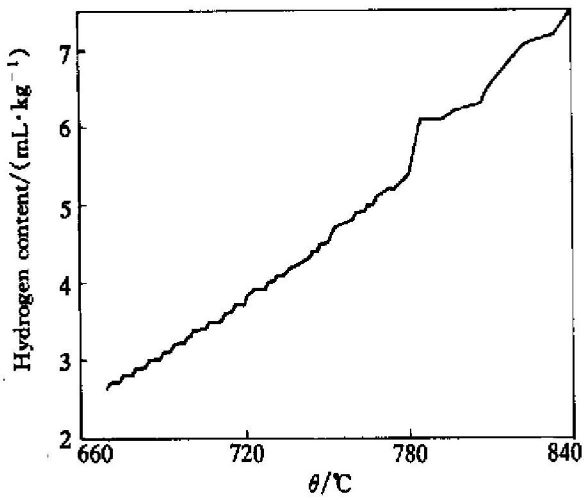

Fig. 6 Hydrogen content of A356 melt with invalid covering of 3% JDN-Ⅱ flux above 800 ℃

Fig. 7 shows that when 3% JDN-Ⅱ flux was used to protect and purify A356 alloy with proper processing, the flux had excellent effect on the melt. As a result, the hydrogen content of the melt was 2.6 mL/kg at 857 ℃, which is much lower than that of 7.5 mL/kg at 840 ℃ shown in Fig. 6. Moreover, the hydrogen content was 0.7 mL/kg at 750 ℃ and 0.5 mL/kg at 720 ℃, while the comparison with those shown in Fig. 4, Fig. 5 and Fig. 6, the values are decreased by 3.2 mL/kg, 2.0 mL/kg and 3.3 mL/kg respectively.

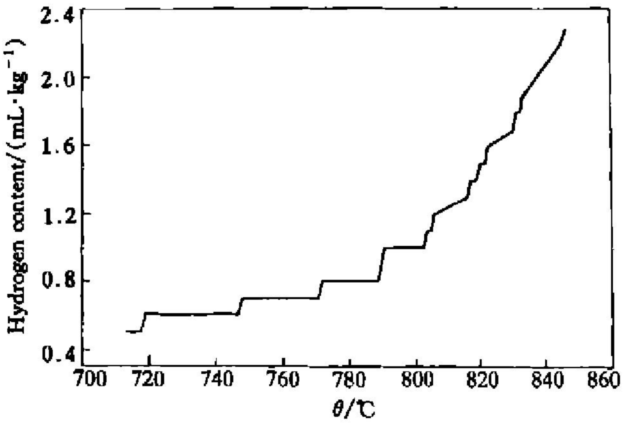

Fig. 7 Hydrogen content of A356 melt with effective covering of 3% JDN-Ⅱ flux above 800 ℃

These results indicate that (1) the use of 3% JDN-Ⅱ flux has excellent effects of protection and purification on A356 alloy; (2) JDN-Ⅱ flux is highly propitious to aluminum melt at high temperature above 800 ℃, so it may fit for the melting of aluminum and aluminum alloys in the reverberating furnace; (3) only with the proper use, can the JDN-Ⅱ flux not only protect the melt effectively, prevent the melt form vapor and oxygen in the air, but also purify the melt with a better effect that the rare earth flux — JDN-Ⅰ [13].

3.3 Effect of JDN-Ⅱ flux on properties of A356 alloy

3.3.1 Mechanical properties

As listed in Table 1, the tensile strength of the alloy is only 145.5 MPa and the elongation is 5% without flux. When 3% JDN-Ⅱ flux was used to cover and purify the melt, the mechanical properties are greatly increased, for example, the tensile strength increases by 9.42%, and the elongation increases by 22% in comparison with the values without flux. In addition, there are no nonmetallic inclusions found in the fracture of the test samples with 3% JDN-Ⅱ flux. Moreover, when 2% JDN-Ⅱ flux was used, the mechanical properties are increased too: the tensile strength increases by 6.39% and the elongation increases by 10%. However, at the same time its effect of purification decreases, and there are inclusions in the fracture of the test samples.

3.3.2 Fluidity

Table 2 shown that the fluidity of the melt, which was purified with 3% JDN-Ⅱ flux, is much higher than those of the melt that was treated with 2% flux and no flux.

4 DISCUSSION

4.1 Structure of JDN-Ⅱ glass flux and speciality of inclusions removal

Table 1 Mechanical properties of A356 alloy under different conditions

Samples	Conditions	Tensile strength / MPa	Elongation / %	Fracture location
1	No flux	145.5	5.0	Inclusions
2	JDN-Ⅱ, 3%	159.2	6.1	No Inclusions
3	JDN-Ⅱ, 2%	154.8	5.5	Inclusions

Boron oxide of glass state is made up of disorder layer structure of B-O plane triangle (Fig. 8) and this B-O plane triangle structure of chains and layers which determines that boron oxide of glass state has low softening temperature, high thermal coefficient of expansion and low chemical stability[14, 15]:

JDN-Ⅱ flux contains tetra-borate. Because of the high content of Na_2O, tetra-borate has a structure of mixed network on B-O plane triangle [BO_3] and containing a high-ration B-O tetrahedron and partial borate. In addition, in negative ion of tetra-borate group, B whose coordination number is 4 is the central atom in the [BO_4] tetrahedron cell, and B whose coordination number is 3 is the central atom in the [BO_3] plane triangle cell. Therefore, there is a complex structure made up of two [BO_3] plane triangle cells and two [BO_4] tetrahedron cells through a connection by the O atom which shares their point of angles (Fig. 9)[16, 17] in tetra-borate group. This structure determines that the glass flux has a higher chemical stability than boron oxide glass.

With regard to borate glass, Al_2O_3 can enter into the network structure of [BO_3] and [BO_4]. Intermediate oxide Al_2O_3 can form intermediate [AlO_4] and enter into the network structure of glass firstly because of the existence of oxygen ion of free state in the structure. When the oxygen ions of free state are insuffcient, Al_2O_3 will be located in octahedron [RO_6] acting as network-modifying ion oxide[18]. Therefore, the structure of JDN-Ⅱ flux can ensure the great ability of glass molecules to absorb the non-metallic oxide in aluminum melt. Intermediate oxide Al_2O_3 acts a special function in the glass that Al^{3+} can enter into the structure to strengthen the stability of the framework, consume the oxygen of free state in glass and enhance the toughness of the liquid glass film. All these can greatly enhance the chemical stability of the glass. Thus, the glass liquid has great ability of absorbing Al_2O_3 in aluminum melt. In addition, the compactness of the liquid film of glass can be increased through absorbing Al_2O_3. Therefore, the oxide inclusions can be removed and the hydrogen content can be decreased in A356 alloy melt.

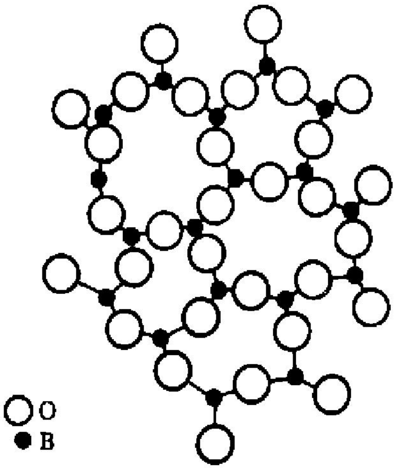

Fig. 8 Random network framework of B_2O_3 glass

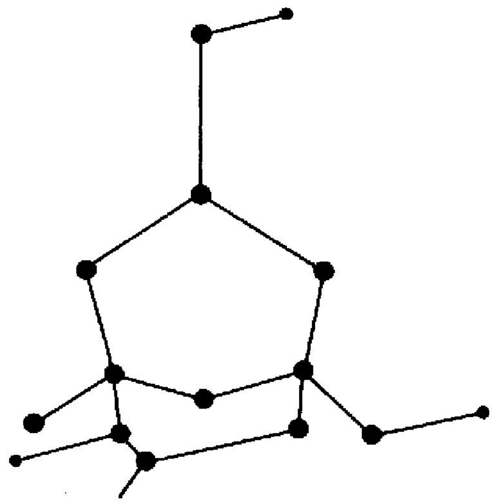

Fig. 9 3-dimensional framework of $[B_4O_7]^{2-}$

4.2 Surface structure and degassing characteristic of JDN-Ⅱ flux

Glass is a kind of noncrystalline material that has long-distance disorder and metastability. The surface of glass has a trend of keeping a low-energy state that is most stable. Thus, a great variety of components

Table 2 Fluidity of A356 alloy under different conditions at 720 ℃ (mm)

Samples	Conditions	Flow passage							
		4.34	3.92	3.44	2.70	2.26	1.82	1.16	1.10
1	No flux	128	128	105	39.5	44	14.5	10.54	8
2	JDN-Ⅱ, 3%	128	128	128	128	123	50.7	26	13
3	JDN-Ⅱ, 2%	128	128	127	87	54	42	24	10

that can decrease the surface energy will be collected in the surface. The surface of glass is a kind of sub-surface that has poriferous surface layer and borate glass has positive temperature coefficient of surface tension. This indicates that more energy will be required when molecules transfer from interior to surface of the melt at high temperature than that at low temperature. Therefore, absorbed gas does not dissolve in the interior of the glass, but dissolve in the surface of the glass. The fact that the ability of absorbing hydrogen of the Pyrex glass increases with the increase of temperature from 400 ℃ to 550 ℃ under the pressure of 1.01×10^5 Pa indicates that the surface layer of glass augments with increasing temperature[19]. JDN-Ⅱ flux has poriferous surface as well, which have larger area and stronger absorbing ability when it is melted and covered on the surface of A356 alloy so that it can remove hydrogen from the melt effectively.

4.3 Effect of galss flux on properties of A356 alloy

When 2% JDN-Ⅱ flux is covered on the melt of A356 alloy, firstly, the flux is not able to protect the melt effectively because of the insufficient amount, which leads to the result that much H and O enter into the melt at high temperature; secondly, the insufficient amount leads to the insufficiency of the oxygen ions of free state so that the hydrogen and oxygen contents are high because only partial Al_2O_3 can enter the network of glass structure and partial hydrogen can be absorbed by the flux.

Compared with no flux or 2% flux added, 3% JDN-Ⅱ flux can protect the A356 melt effectively, reduce crack source in alloy and increase the compactness of the alloy because the sufficient oxygen ions of free state and the poriferous surface can absorb hydrogen and oxide inclusions in the melt so that the mechanical properties of the A356 alloy can be enhanced.

Without flux and with 2% flux, the hydrogen and oxygen contents are high and the viscidity of the alloy is great. However, with 3% JDN-Ⅱ flux, the hydrogen and oxygen contents decrease greatly and the viscidity is small thus the fluidity increases greatly.

4.4 Effect of reaction between flux and aluminum melt on purification of melt

In aluminum melt, reducing reaction is sure to emerge if borate oxide glass is used as flux as follows[16],

$$B_2O_3 + 2Al \rightarrow 2B + Al_2O_3 \quad (1)$$

The structure of boron oxide glass is mainly a network of chains and layers which is made up of B-O plane triangle with low chemical stability, so boron oxide glass is unsuitable as the purificant of some active alloy melts which need high undercooling such as Al melt. The reason is that reaction (1) that exists in the melt produces some heterogeneous crystal nucleus such as B and Al_2O_3 so that the purifying requirement of high undercooling cannot be met.

Fig. 8 and Fig. 9 also show that the structure of JDN-Ⅱ flux, which is more stable, is greatly different with the structure of the common boron oxide glass. Moreover, the network-modifying ion oxide Na_2O can give oxygen ions of free state and make the structure of B-O transform from plane triangle to tetrahedron that enlarges the area of borate and weakens the reducing ability of Al to B so that reaction (1) can be neglected. After the glass absorbs Al_2O_3, the oxygen ions of free state given by Na_2O turn Al_2O_3 into [AlO_4] firstly and make it enter the network to form complex glass system which makes the glass more stable. However, when the content of Al_2O_3 in the melt reaches a certain value, oxygen ions of free state give by Na_2O will be insufficient and cannot turn Al_2O_3 into [AlO_4] totally, so the remaining Al_2O_3 will not enter the network but probably destroy the structure and make the glass unstable[14]. This may be one reason why the effect of adding 2% flux is unsatisfied, that is, the hydrogen and oxide inclusions absorbed by the flux has reached its peak, then the superfluous oxide inclusions will destroy the structure of the glass and make the protection effect of the flux partially disabled.

With the covering of JDN-Ⅱ flux on the surface of the melt, the cracks which appear when the melt refined with common inorganic salt flux under the conditions of high temperature and disturbance in the inner of the melt will not appear in the glass, so the protecting effect is excellent; some part of the flux which contacts with the melt maybe slightly react with the Al and product Al_2O_3, however, the formative oxide with the oxide in the melt can be absorbed by glass molecules and make the glass more stable. In addition, the amount of the oxide absorbed has a certain value; once it reaches this value, the reaction will react leftward. And if enough JDN-Ⅱ flux is used, the effect of reaction between flux and melt is much smaller than the effect of protection and purification of the flux on the melt.

Therefore, if JDN-Ⅱ flux is used to purify A356 alloy, the effect of protection and purification greatly exceeds the negative effect of the reaction between the flux and the Al melt so the requirement of melt purification can be met entirely.

5 CONCLUSIONS

1) JDN-Ⅱ flux is a kind of noncrystalline glass flux with complex structure.

2) JDN-Ⅱ flux has effect of purification and

protection on A356 alloy melt and is especially applicable in the aluminum melt at high temperature.

3) When 3% JDN-Ⅱ flux is used to purify A356 alloy, the hydrogen content is 2.6 mL/kg at 857 ℃ and 0.7 mL/kg at 750 ℃ respectively.

4) JDN-Ⅱ flux can increase the mechanical properties and fluidity of the melt.

5) JDN-Ⅱ flux has a much greater effect of purification on the aluminum melt than that of reaction with the melt.

6) JDN-Ⅱ flux will have a galactic foreground of application if its erosion to crucible can be improved.

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(Edited by HUANG Jin-song)