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VISCOUS CHARACTERISTICS OF SYNTHETIC MOLD POWDER FOR HIGH SPEED CONTINUOUS CASTING

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Synopsis : Effects of F, Li_2O, Al_2O_3, B_2O_3, MgO, Na_2O contents and basicity on the viscosity and crystallization temperature of synthetic mold powders have been investigated by using rotating viscometer. Viscosity-temperature relationship of the melts could be expressed as an Arrhenius type equation. The addition of alkali metal oxides and fluorides reduced both the activiation energy for viscous flow and crystallization temperature. Al_2O_3 and B_2O_3 enhanced activation energy and lowered crystallization temperature. As a whole, the less viscous mold powder shows lower crystallization temperature. And this crystallization behavior has also been discussed by using metallography and X-ray diffraction analyses.

Keywords : mold flux(or mold powder), lubrication, viscosity, crystallization temperature, high speed continuous casting.

1. Introduction

Recently, casting speed has been increased to improve productivity and to save energy in continuous casting process[1]. In high speed continuous casting, one of the most serious problems in mold is the sticking type break-out caused by insufficient lubrication between solidified steel shell and mold. This is mainly due to the shortage of mold powder consumption. Generally, mold powder consumption varies with the change in casting speed, mold oscillation conditions and properties of mold powder. Among the properties of mold powder, viscosity and crystallization temperature are the key factors that control the mold powder consumption. These viscosity and crystallization temperature are controlled by the chemical compositions of mold powder. In case of Nippon Kokan, mold powder with optimum viscosity, softening temperature and crystallization temperature by adding Li_2O has been used for high speed continuous casting[1]. Also, it was reported that special additives such as BaO, MgO and B_2O_3 are effective in lowering freezing temperature and also in preventing crystallization of slag[2].

This study has been carried out to investigate systematically the effects of various chemical compositions of mold powder on these two important factors, viscosity and crystallization temperature.

2. Experiments

2.1 Mold powder composition

The compositions of experimental mold powders were varied as F(0 to 12 wt%), Li_2O (0 to 10 wt%), Al_2O_3(0 to 15 wt%), B_2O_3(0 to 15 wt%), MgO(0 to 13 wt%), Na_2O(0 to 15wt%) and V-ratio(0.7 to 1.2). And the desired composition was adjusted by adding determined amount of reagents such as $CaCO_3$, SiO_2, MgO, Al_2O_3, Li_2CO_3, B_2O_3, CaF_2, LiF and NaF to the base material wollastonite. The compositions of 35 mold powders after having been premelted at 1300 ℃ are given in Table 1.

2.2 Measurement of viscosity and cystallization temperature

Viscosities are measured with a rotating viscometer. As viscosity value of tested mold powder is very low it is necessary to obtain higher shear rate between rotor and cup to measure stable viscosity at high temperature. So in this experiment, the rotor and cup system which has as low ratio of the radii($\delta = 1.18$) as possible(Fig.1) is selected. After holding at 1400 ℃ for 15 min. to eliminate the thermal gradient in the melt, viscosities were measured continuously with constant cooling rate. The measurement is ended when the viscosity increases infinitely or reaches the upper limit of measuring range.

Crystallization temperature has been defined as the temperature at which the viscosity increases suddenly.

Table 1. Chemical composition of experimental mold powder(slag state).

(wt%)

Sample	SiO_2	CaO	MgO	Al_2O_3	Na_2O	F	Li_2O	B_2O_3	Fe_2O_3	V-ratio*
1	38.4	35.3	5.4	6.0	11.2	0.0	3.3	0.0	0.6	0.9
2	37.0	34.1	5.3	6.0	11.1	2.8	3.3	0.0	0.5	0.9
3	35.2	32.8	5.4	5.7	11.2	6.1	3.2	0.0	0.5	0.9
4	33.9	31.1	5.6	5.6	11.3	8.7	3.2	0.0	0.6	0.9
5	32.7	29.2	5.7	5.7	11.0	12.0	3.1	0.0	0.6	0.9
6	36.1	32.2	5.3	5.7	11.2	9.1	0.0	0.0	0.4	0.9
7	35.1	31.3	5.3	5.7	11.1	9.0	2.1	0.0	0.4	0.9
8	33.6	30.6	5.2	5.7	11.1	9.0	4.3	0.0	0.6	0.9
9	32.3	30.0	5.3	5.7	11.1	8.9	6.3	0.0	0.5	0.9
10	30.1	28.1	5.3	5.7	11.1	9.0	10.4	0.0	0.5	0.9
11	37.1	33.4	5.3	0.7	11.0	9.0	3.2	0.0	0.4	0.9
12	34.1	31.1	5.3	5.7	11.2	9.1	3.2	0.0	0.4	0.9
13	32.7	29.9	5.3	8.3	11.2	9.0	3.2	0.0	0.4	0.9
14	30.5	28.0	5.3	12.2	11.3	9.1	3.2	0.0	0.3	0.9
15	28.9	26.7	5.4	15.3	11.2	9.0	3.2	0.0	0.3	0.9
16	34.0	30.1	5.6	5.5	11.2	9.3	3.3	0.0	0.4	0.9
17	32.4	29.4	5.6	5.6	11.2	9.2	3.2	3.0	0.4	0.9
18	30.8	28.2	5.6	5.5	11.1	9.2	3.2	6.0	0.5	0.9
19	28.6	26.5	5.6	5.5	11.0	9.1	3.2	9.9	0.8	0.9
20	26.2	24.2	5.6	5.5	11.0	9.1	3.2	14.8	0.5	0.9
21	38.6	26.4	5.6	5.5	11.1	9.2	3.2	0.0	0.4	0.7
22	36.0	28.7	5.6	5.5	11.3	9.2	3.2	0.0	0.4	0.8
23	31.9	32.6	5.6	5.6	11.4	9.2	3.2	0.0	0.4	1.0
24	29.7	34.1	5.8	5.7	11.7	9.3	3.3	0.0	0.5	1.1
25	28.3	34.7	6.0	6.0	12.0	9.3	3.3	0.0	0.5	1.2
26	36.7	33.0	0.5	5.6	11.4	9.2	3.2	0.0	0.4	0.9
27	35.3	31.8	3.1	5.6	11.3	9.2	3.3	0.0	0.4	0.9
28	33.4	30.4	6.2	5.6	11.3	9.3	3.3	0.0	0.6	0.9
29	31.8	29.1	9.4	5.6	11.3	9.2	3.3	0.0	0.5	0.9
30	30.2	27.6	12.6	5.5	11.1	9.2	3.2	0.0	0.6	0.9
31	40.1	35.5	5.7	5.5	0.2	9.1	3.2	0.0	0.5	0.9
32	38.5	33.6	5.6	5.6	3.8	9.2	3.2	0.0	0.6	0.9
33	36.0	32.5	5.7	5.6	7.3	9.2	3.2	0.0	0.5	0.9
34	33.4	30.4	6.2	5.6	11.3	9.3	3.3	0.0	0.6	0.9
35	32.0	29.0	5.7	5.6	14.9	9.2	3.2	0.0	0.4	0.9

* V-ratio=(CaOwt% / SiO_2wt%)

Table 2. The viscosities, activation energies and crystallization temperatures(Tc) of experimental mold powders.

Sample	Viscosity(poise)			A. Energy(kJ/mol)		Tc(℃)
	1300℃	1200℃	1100℃	T > Tc	T < Tc	
1	2.85	8.67	-	216.9		1191.6
2	2.00	4.83	12.63	165.4		1097
3	0.84	1.74	3.84	139.8	295.1	1030.7
4	0.76	1.53	3.24	132.9		1002.4
5	0.41	0.80	11.68	128.5	340.9	947.2
6	1.32	3.04	7.14	153.1		1016.6
7	0.77	1.65	3.84	145.8	405.2	1044.9
8	0.78	1.49	2.83	118.1	210.6	1011.9
9	0.55	0.96	1.82	108.0		959.8
10	0.22	0.42	0.82	120.7		927.0
11	0.52	1.03	1.84	117.9	249.0	
12	0.65	1.28	2.68	128.0	334.9	1049.7
13	0.57	1.27	2.99	150.2		1007.1
14	1.02	2.23	5.37	150.4		977
15	1.20	2.72	6.62	154.8		978.8
16	1.07	2.09	4.25	126.9		1039.9
17	0.72	1.42	2.45	117.6		900
18	0.45	0.85	1.72	123.1	209.5	930.2
19	0.33	0.73	1.40	130.1	282.9	842.2
20	0.24	0.49	1.17	137.2		
21	1.21	2.44	5.40	136.3		967.4
22	0.95	1.90	3.94	130.7		964.3
23	0.57	1.16	2.58	135.5		978.4
24	0.45	0.87	1.63	120.1		969
25	0.39	0.78	1.73	134.2		954.8
26	0.98	1.95	4.33	133.9		1025.7
27	1.02	1.67	2.90	97.3	230.1	1043
28	0.63	1.22	2.59	127.7	340.4	992.6
29	0.49	0.95	1.97	129.4		942.2
30	0.60	1.10	2.13	118.1	239.4	1030.5
31	1.67	3.29	7.67	143.0		1016.2
32	0.81	1.90	4.78	162.4		1030.5
33	0.55	1.22	2.96	152.1		1028.9
34	0.63	1.22	2.59	127.7	340.4	969.0
35	0.52	1.06	2.46	136.5		920

3. Results and discussion

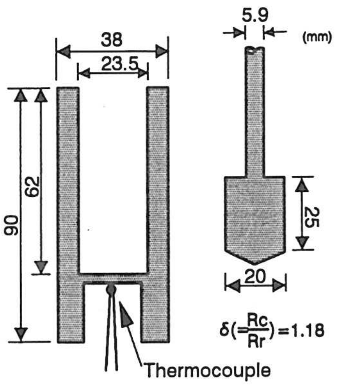
3.1 Viscosity

The dependency of viscosity(η) on temperature could be approximated by Arrhenius's relationship as :

$$\eta = A \exp(E\eta/RT) \qquad (1)$$

where, A : frequency factor
$E\eta$: activation energy for viscous flow
R : gas constant
T : absolute temperature.

The relation between log viscosity versus reciprocal absolute temperature for the Li_2O series mold powders, as an example, is shown in Fig.2. Linear tendency is observed. Activation energies for viscous flow are calculated from the slopes of these lines. There are two types of rheological behavior of melts around crystallization temperature. One ("type A" in Fig.2) is that viscosity increases infinitely at its



(a) Graphite cup (b) Graphite rotor

Fig. 1. Sensor for viscosity measurement.

crystallization temperature, the other ("type B" in Fig.2) is that viscosity increases greatly(about 3-12 times) at crystallization temperature and increases again keeping a certain slope as the temperature decreases further. These phenomena will be discussed in 3.2. The viscosities, activation energies, and crystallization temperatures of all experimental mold powders are given in Table 2.

The addition of fluoride reduces viscosity very effectively. As the radius of F^- (1.31 Å) is similar to that of O^{2-} (1.38 Å) in tetrahedrally bonded Si-O network structure[3], F^- can easily replace the divalent oxygen ion resulting in break-down of the Si-O network. Adding over 10 wt% of Al_2O_3 increases viscosity remarkably. Generally, Al_2O_3 in $(SiO_4)^{4-}$ network is classified as intermediate because it would either join the continuous network or only occupy the holes between the $(SiO_4)^{4-}$ tetrahedra according to its surrounding conditions. The Al^{3+} substitutes for a Si^{4+}, i.e. an $(AlO_4)^{5-}$ tetrahedron can be formed which joins in the network formed by the $(SiO_4)^{4-}$ tetrahedra, provided that an additional cation is available and can be located in a hole nearby to preserve electrical neutrality. The schematic representation of this solution mechanism is shown in Fig.3[4]. In this study, as the melt has available metal ions (Na_2O : 11 mol%, Li_2O : 7 mol%) sufficiently, the Al_2O_3 readily joins in network forming and consequently raises viscosity. Increase in V-ratio up to 1.1 decreases the viscosity but further increase shows no effects. Addition of B_2O_3 up to 10wt% reduces viscosity as shown in Fig.4. Li_2O and Na_2O lower the viscosity effectively when they are added up to around 10wt%. MgO also shows that it reduces viscosity when it is added up to 9 wt% but further addition raises viscosity on the contrary. Addition of monovalent ions in the form of an oxide such as Na_2O, Li_2O has been known to disrupt the continuity of $(SiO_4)^{4-}$ tetrahedra structure as each pair of monovalent metal ions introduced make one of the link in the $(SiO_4)^{4-}$ network be broken and produce two non-bridging oxygen ions[5]. This mechanism can be represented schematically by following reaction.

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + (\mathrm{M_2O}) \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O^-}(\mathrm{M^+}) + (\mathrm{M^+})\mathrm{O^-}-\overset{|}{\underset{|}{\mathrm{Si}}}- \qquad (2)$$

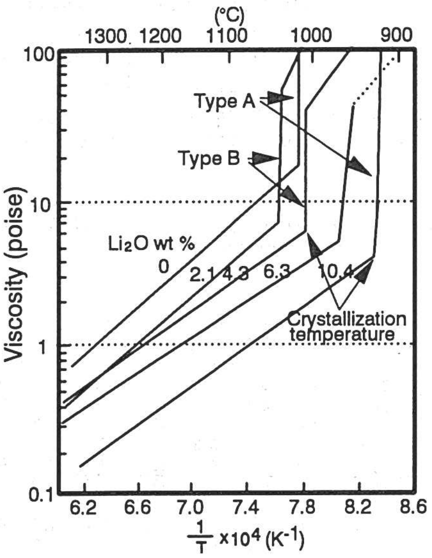


Fig. 2. Viscosity as a function of temperature for the mold powders, Li_2O series.

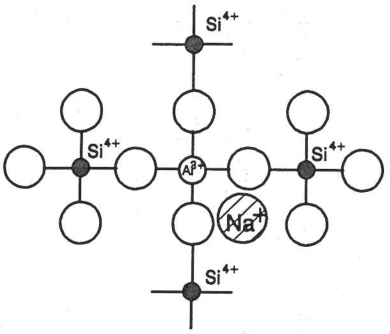


Fig. 3. Schematic representation of Al_2O_3 in a silica net work[4].

As temperature gradient exists between solidified steel shell and mold, the viscosity of infiltrated mold slag film is also dependent on this temperature gradient. Therefore, to get a uniform lubrication lower activation energy and crystallization temperature are desirable. Activation energies for viscous flow in high temperature(T>Tc) and low temperature(T<Tc) were in the range of 92-217 KJ/mol and 211-405 KJ/mol, respectively. The effects of various chemical compositions on the activation energies are shown in Fig.5.

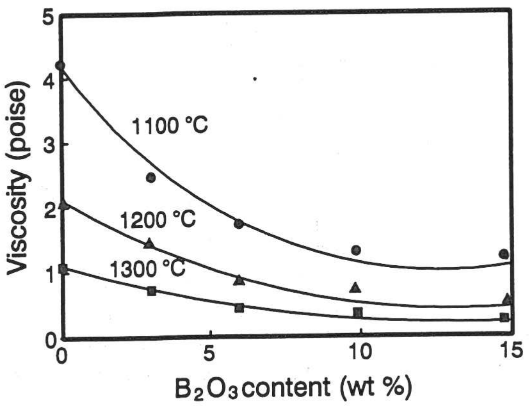


Fig. 4. Effect of B_2O_3 content on the viscosity of mold powder at various temperatures.

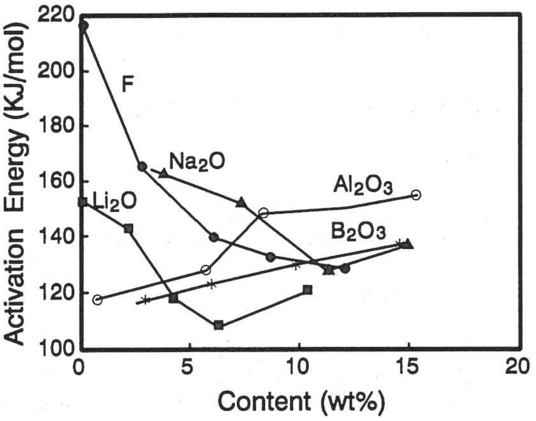


Fig. 5. Effect of various chemical composition content on the activation energy at T>Tc.

Fluoride lowers activation energy very effectively whereas Al_2O_3 and B_2O_3 raise it. This result means that F acts as a very strong network modifier and Al_2O_3 and B_2O_3 act as network former. The reason why the addition of B_2O_3 reduces viscosity in spite of increasing activation energy is thought that it decreases the frequency factor A in Eq.(1) effectively. The frequency factor is mainly dependent on the activation energy but it seems to have a relation with melt temperature. The addition of B_2O_3 reduces melting point remarkably, consequently the superheating is so high that it gives more holes available in liquid state structure resulting in lower viscosity. Li_2O and Na_2O reduce activation energy when they are added up to 6 and 10 wt%, respectively and further addition raises it on the contrary. It is thought that alkali metal oxides could act as modifier within a certain amount but with further addition they could not act as network modifier any longer but as intermediate as shown in Fig.3.

3.2 Crystallization temperature

The phenomena of a sudden increase in viscosity at critical temperature during viscosity measurement in cooling down have been discussed by many authors as the names of "break point", "crystallization temperature" and "solidification temperature"[6-9]. And there has been a little difference in meaning between them. As mentioned in 3.1 there are two types of this point (Fig.2). To examine thease behaviors, metallographic and X-ray diffraction analyses are carried out on the quenched samples. Mold powder No.22 and 27 were selected for tests because they have showed typical behaviors of type A and type B, respectively. The quenching temperatures and results of X-ray diffraction analyses at each temperature are shown in Fig.6. The main crystal phases are identified as cuspidine($3CaO\cdot 2SiO_2\cdot CaF_2$). Number 22 shows that crystals precipitated just after the crystallization temperature(or might be at the same time). But No.27 shows that the crystal precipitation occurs progressively after the crystallization temperature. Also, its crystallization temperature determined from the viscosity measurement(1043 ℃) is different from the first crystal idendified temperature(around 1020 ℃). From these results, it can be said that the crystallization behavior can be classified into two types i.e. whether it occurs suddenly at the same time with the crystallization temperature or occurs progressively after the crystallization temperature. The existence of these two types of crystallization behavior could be thought to have a relation with solidification range and crystallization tendency. Strictly speaking the crystallization temperature discussed so far should be defined as rather a solidification beginning temperature(liquidus line) than a crystallization temperature. This fact is confirmed by the results that both low basicity mold powder(V-ratio=0.7, sample No.21) and high B_2O_3 contained mold powder(B_2O_3=9.9 wt%, sample No.19) have shown pronounced crystallization temperature without precipitated crystal.

The effects of F, Al_2O_3 and B_2O_3 contents on crystallization temperature are shown in Fig.7. F and B_2O_3 lower crystallization temperature effectively and Al_2O_3 also decreases it slightly. The effects of Li_2O, MgO and Na_2O contents on crystallization temperature are shown in Fig.8. Li_2O and Na_2O reduce it. MgO also decreases the crystallization temperature when added up to 9 wt% but further addition increases it. The role of these fluoride and alkali metal oxides in reducing the crystallization temperature are understood as these components have the ability to reduce the solidification temperature. The effect of slag basicity on

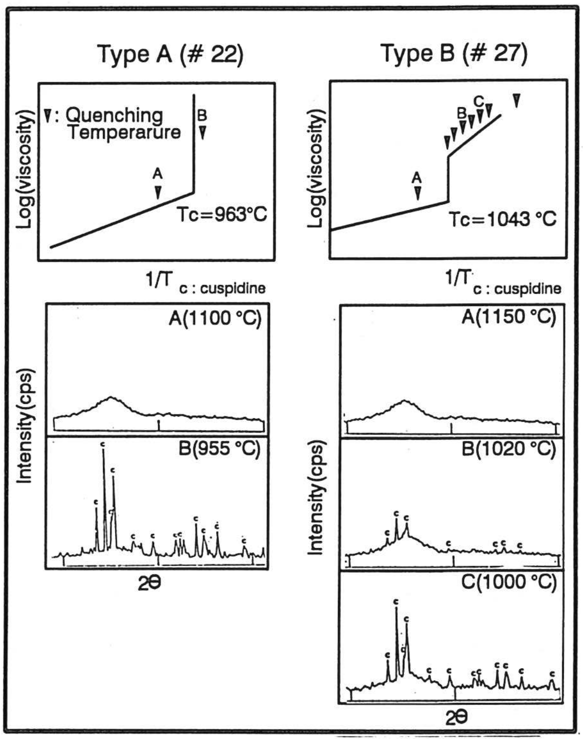


Fig. 6. X-ray diffraction analyses for the two types mold powder quenched at various temperature.

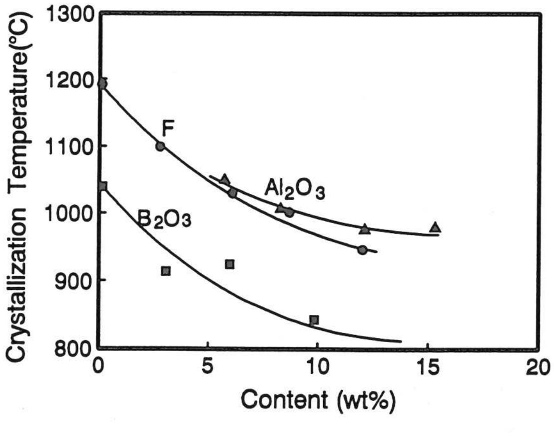


Fig. 7. Effect of F, Al_2O_3 and B_2O_3 content on the crystallization temperature.

the crystallization temperature is shown in Fig.9. As an interesting result, the crystallization temperature shows no relation with the slag basicity. Generally, the tendency of a melt to precipitate crystalline phase is known to be promoted with lower viscosity and higher basicity because of the short range order structure[8]. But in this study the basicity does not show any relation with crystallization temperature. Moreover, the less viscous mold powder shows lower crystallization temperature. The reason of can be explained as follows.

(1) The crystallization temperature does not mean the crystallization tendency or intensity. It exists near the solidification beginning temperature.

(2) Network modifiers such as fluoride, alkali metal oxides and B_2O_3 can play a role in lowering the solidification temperature(liquidus line) when it is added to a basic CaO-SiO_2 system. Of course, these additives reduce the viscosity effectively.

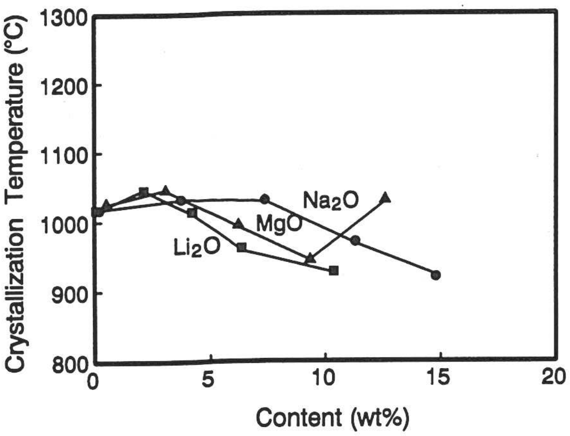


Fig. 8. Effect of Li_2O, MgO and Na_2O content on the crystallization temperature.

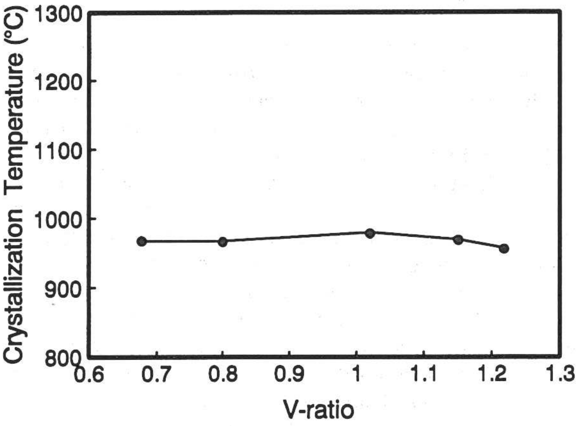


Fig. 9. Effect of basicity on the crystallization temperature.

3.3 Regression analyses

Linear least squares regression analyses have been carried out on the several chemical composition variables to predict the viscosity and crystallization temperature. The method of regression analysis for viscosity prediction is similar to those of other authors[10-11]. The results are obtained as :

$$\mathrm{Log}(\eta) = \log A + B / T \tag{3}$$

$$\log A = -2.307-0.046[XSiO_2]-0.07[XCaO]-0.041[XMgO]-0.185[XAl_2O_3]+0.035[XCaF_2]-0.095[XB_2O_3]$$

$$B = 6807.2+70.68[XSiO_2]+32.58[XCaO]+312.65[XAl_2O_3]-34.77[XNa_2O]-176.1[XCaF_2]-167.4[XLi_2O]+59.7[XB_2O_3]$$

$$Tc = 1241.6-2.15[XMgO]-1.41[XAl_2O_3]-4.49[XNa_2O]-8.55[XCaF_2]-6.41[XLi_2O]-15.28[XB_2O_3] \tag{4}$$

where, η : viscosity(Pa· s)
Tc : crystallization temperature(℃)
X : mole %
T : absolute temperature.

With aids of these prediction equations, it is possible to design a mold powder which satisfies the desired viscosity and crystallization temperature.

4. Conclusions

Viscosity and crystallization temperature of mold powder have been measured with the change of F, Al_2O_3, B_2O_3, Li_2O, MgO, Na_2O contents and V-ratio. Viscosity-temperature relationship shows Arrhenius type behavior. The addition of fluoride and alkali metal oxide reduces the activation energies for viscous flow effectively but B_2O_3 and Al_2O_3 raise them. There are two types of crystallization behaviors of melts, i.e. whether it occurs at the same time with the crystallization temperature or occurs progressively after the crystallization temperature. And the crystallization temperature obtained from the point at which viscosity increases greatly and suddenly during cooling seems to be rather a solidification beginning temperature than a crystallization temperature. F, Li_2O and B_2O_3

reduce crystallization temperature effectively. The viscosity and crystallization temperature can be predicted from chemical compositions by simple regression equations. Finally, from the results of this study a mold powder for high speed continuous casting has been developed which has optimum viscosity, crystallization temperature and lower F content by adding small amount of Li_2O and B_2O_3 to the basic mold powder system.

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