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IMPROVEMENT OF MELTING CHARACTERISTICS FOR CONTINUOUS CASTING MOLD FLUX

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Synopsis: Melting characteristics of mold flux have been investigated by using thermal analysis. Sintering property could be evaluated quantitatively by measuring shrinking behaviour of the flux on heating using Thermo-mechanical analysis(TMA). Initial sintering was recognized as a liquid phase sintering reaction caused by glassy materials or low melting point materials such as alkali oxides and fluorides. The initial sintering property was improved by preheat treatment at the proper temperature, which raw materials changed into inactive complex compounds or crystalline.

Then, an improved flux with a better thermal insulation and a homogeneous melting property has been developed.

Key words: mold flux, melting characteristic, sintering, thermal analysis, thermal shrinkage, preheat treatment

1. Introduction

In the continuous casting of steel, casting mold fluxes have a significant role to realize sound casting operations and to obtain high quality products without surface and internal defects. The performances of mold flux are dependent upon melting characteristics of flux and properties of slag formed on melting in contact with the molten steel. Although the properties of slag have been studied well, little is known about the melting characteristics of mold flux.

The mold flux added to the molten steel surface forms a layered structure (molten slag layer, sintered layer and original flux layer). The melting characteristics of flux are seemed to be affected by the degree of sintered layer (thickness and density) produced in the process of fusion [1]. It has been known that carbonaceous particles prevent sintering and control the melting rate of the mold flux [2]. However, in the case of using for an interstitial free steel, for example, added carbon contents are sometimes subject to limitation. Therefore, It is important to study constituent materials to control sintering, besides carbonaceous particles.

This paper describes the knowledge of sintering phenomena investigated by using thermal analysises, and the results of improvement for melting characteristics of mold flux.

2. Evaluation of sintering using thermal analysis

Sintering is defined as a phenomenum of forming a coherent bonded mass by heating powders below the melting temperature. As a volume of powder is decreased by sintering, its shrinking behaviour on heating was investigated by using Thermo-mechanical Analysis (TMA) in order to evaluate sintering characteristics of mold flux. In addition,the thermal analysises as TG, DTA, high temperature X-ray diffraction and high temperature microscopic observation were carried out to relate TMA traces with the sintering phenomena.

A typical mold flux for low carbon alumi-killed steel slab casting, shown in Table 1, was used in this investigation. It consists of wollastenite and prefused glassy calcium silicate as base materials, and the oxides and fluorides such as Na_2CO_3, $CaCO_3$, $MgCO_3$, Li_2CO_3, NaF, CaF_2, Al_2O_3 as melting agent or composition adjusting agent. And carbonblack and coke are added as melting adjusting agent.

TMA experimental apparatus is shown in Fig.1. The powder specimen was put into the alumina cell in a bulk density of 1.0 to 1.2 g/cm^3 and in thickness of about 2.5 mm, and kept in touch with a quartz detecting bar of 3 mm in diameter on loading of 2 g as a compression mode. In TG-DTA, the sample and the reference material(α-alumina) were placed in alumina cell set up the thermocouples. Both measurements were conducted in air using constant heating rate of 20 K·min^{-1}.

Table 1 Chemical Composition of Test Flux (wt%)

CaO	Al_2O_3	SiO_2	Na_2O	Li_2O	MgO	F	F.C	CaO/SiO_2
32.0	4.0	34.5	14.0	1.2	4.0	9.5	3.0	0.93

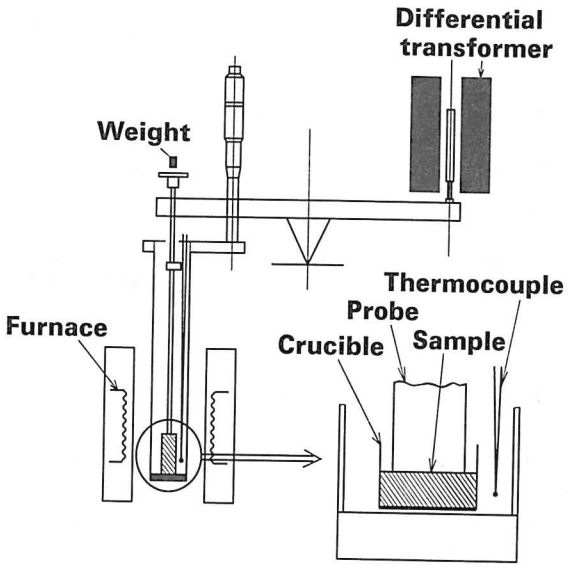

Fig.1 Schematic diagram of TMA apparatus

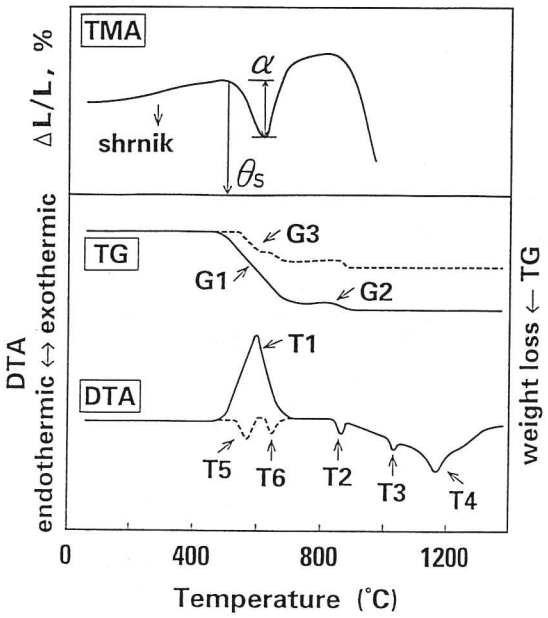

Fig.2 An example of thermal analysis for mold flux

An example of results in TMA, TG and DTA measurement is shown in Fig.2. This figure indicates the following behavior of flux. In TMA, initial shrinkage can be observed at 400-500℃ and following greater shrinkage at about 800℃. This pattern of TMA trace is a typical one for conventional mold fluxes. Here, in order to evaluate measurring results, starting temperature of initial shrinkage(θ s) and initial shrinkage ratio(α) are defined, as shown in Fig.2. In TG-DTA, several thermal events are appeared which are equivalent to the previous findings [3]. Carbon oxidation cause the weight-loss(G1) and the exotherm(T1) at about 500-600℃. The peaks of the weight-loss(G2,G3) and endothermic(T2,T5) indicate thermal decompositoin reaction of carbonates at around 550℃ and 850℃. The peak of endothermic(T6) without weight changes is seemed a melting reaction of low melting point material. These peaks such as G3, T5, and T6 are appeared only in flux without carbon. The peaks of endothermic(T3 and T4) at about 1050℃ and 1150℃ show the melting of materials.

In High temperature X-ray analysis, measurements were performed at about 100℃ intervals in temperature from 400 to 1000℃. The phases present in the specimens were identified by X-ray analysis using monochromatic CuKα radiation. The crystalline phases were identified using the JCPDS index. Figure 3 shows the relative intensities of X-ray diffraction patterns of each crystalline material identified by the high temperature X-ray

analysis. According to this figure, the kinds and quantities of crystalline phases change to decrease Na_2CO_3, SiO_2, $CaCO_3$, $CaO \cdot SiO_2$, and to form $Na_2Ca_2(SiO_2)_3$, involving similar phases unidentified, as newly crystalline phase and increasing above 400℃ [4],[5].Contents of formed liquidus, which are calculated as a reduction of total intensities of crystalline phases, are shown in Fig.4. This figure shows that the original glassy base material crystallizes at 500℃ and liquid phase begins to be formed at above 500℃. This findings for fusion were recognized by using high temperature microscope,also. The high temperature microscopic observations were carried out in air or argon atmosphere using heating rate of 10-100 $K \cdot min^{-1}$. From the observations, fusing state could be seen on the surface of a few grains at 450-500℃, and with elevating temperature, the liquidus was increased to form the fused mass.

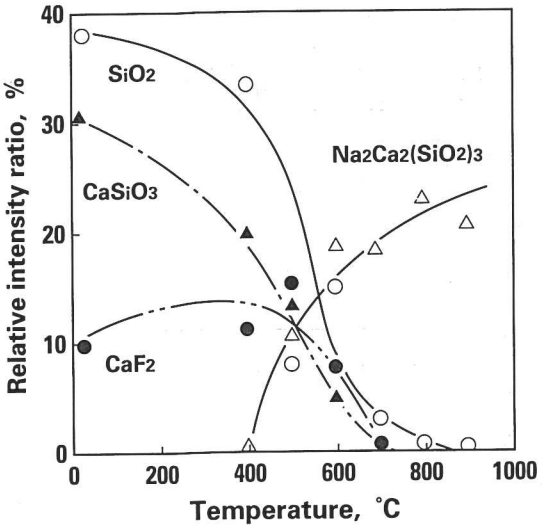

Fig.3 Phase transition on heating in mold flux

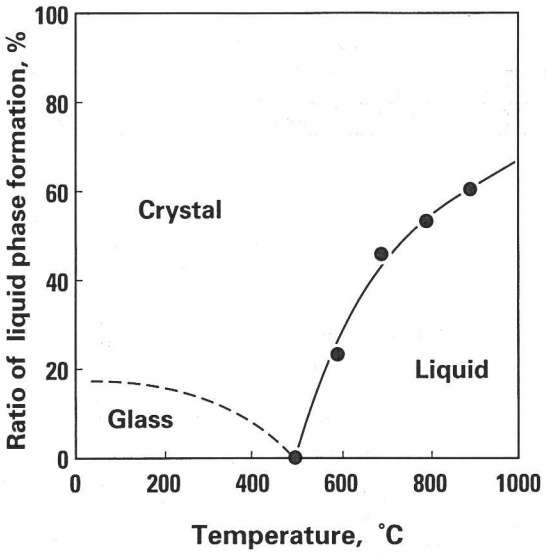

Fig.4 State of liquid phase formation

From the above investigating results, it can be considered that the shrinkage appeared in TMA trace at about 450℃ is caused by rearrangement with melting of low melting point materials. It is guessed to be a liquid phase sintering reaction which is progressed with increasing temperature. Thus TMA measurements are assumed to represent the sintering behaviour of the mold flux. Then, in the following investigation, the TMA method was used for evaluation of sintering property.

It is well known that added free carbon prevent the sintering reaction. The effect of free carbon on sintering was evaluated by using samples with different types and contents of added carbon. Measurements were carried out in nitrogen atmosphere to keep the carbon contain. The results, shown in Fig.5, indicate that the finer and the more carbonaceous particles are added, the lower shrinkage ratio is obtained, which agrees with the findings of other experiments [2].

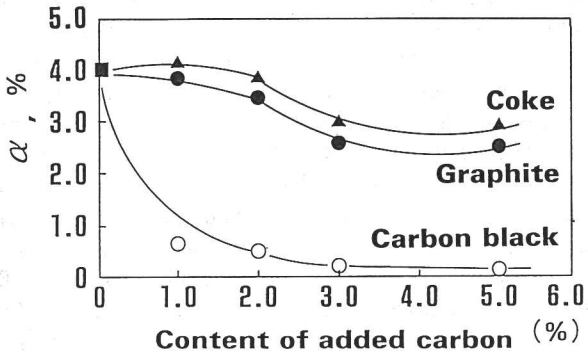

Fig.5 Effect of carbon addition on TMA results

Influence of constituent materials on sintering property was estimated using samples without free carbon to exclude the effects of added carbon. Figure 6 shows the TMA traces of examined each material itself. In alkali carbonates such as Na_2CO_3, Li_2CO_3, K_2CO_3 and glassy silicate(SiO_2-CaO-Na_2O-MgO-F), the comparatively large shrinkage pattern can be observed at a low temperature of 350-700℃. Then, estimated fluxes in TMA were prepared with blending additional material into the base

flux which consists of stable materials without sintering at such low temperature. Figure 7 shows the results illustrated the effects of initial shrinking temperature(θs) or initial shrinkage ratio(α) against the contents of added materials. From this figure, it is appeared that addition of alkali oxides or fluorides to the base flux lead to decrease the initial sintering temperature and increase the initial sintering ratio [6]. The addition of glassy material results in increasing the initial shrinkage ratio with a slag reaction at a temperature of Tg point(glass transfer point).

Although NaF is a stable material by itself, when $CaCO_3$ is coexsistance, Na_2CO_3 with low melting temperature of 300-500℃ is produced. Then NaF decrease the initial sintering temperature and increase the initial sintering ratio of the flux. It is therefore important to consider the reactions of materials in order to controll the sintering perfectly.

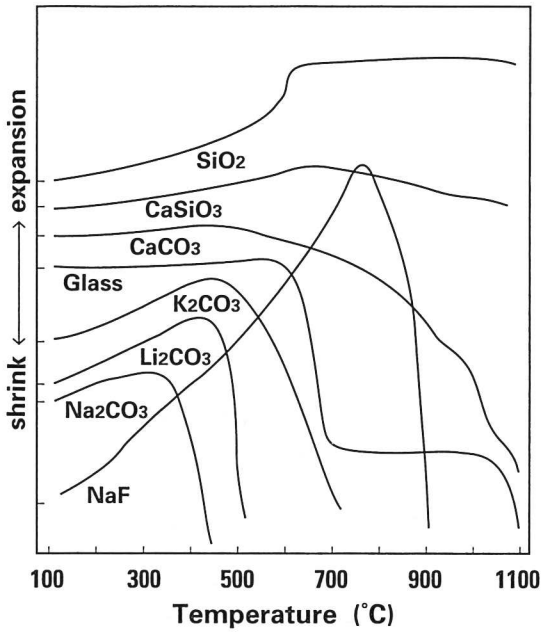

Fig.6 TMA traces of each materials

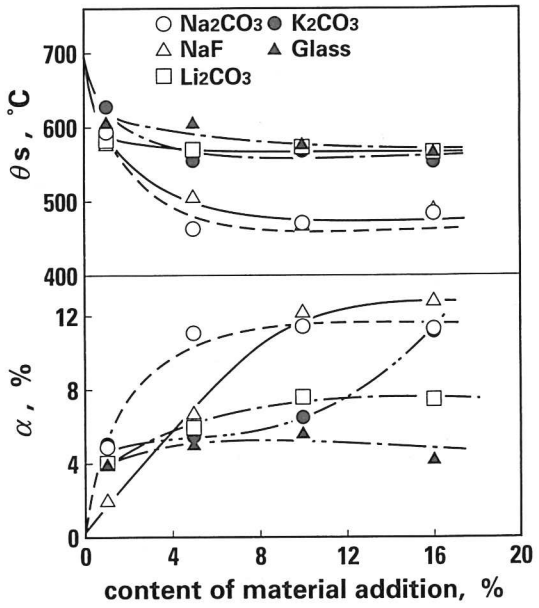

Fig.7 Effect of material addition on TMA results

3. Improvement on sintering property of mold flux

It has been observed that phase structures of the mold flux are changed by heating. Then, effect of the preheating conditions on properties of the mold flux was investigated by thermal analysis (TMA, DTA, high temperature X-ray diffraction) and powder property examination. In these experiments, the test fluxes were mixed and heated at intended temperature. Then after cooled in air, if necessarily,they were powdered into a particle size less than 250μ and examined.

Sintering properties examined by TMA and bulk density are plotted in Fig. 8 against preheat temperature. The initial shrinkage temperature(θs) is increased above 500℃, but decreased in the vicinity of the melting point. In the fluxes preheated from 700℃ to 900℃, the ratio of initial shrinkage(α) is negligible. However, in the samples heated near the melting temperature, the great shrinkage is appeared. Bulk density affecting heat conductivity of the mold flux is decreased with increasing of preheat temperature above 500 ℃, minimized at 700-800℃, and increased again above 800℃.

In microscopic observations, many micro-pores produced by the thermal decomposition of $CaCO_3$, Na_2CO_3, and $MgCO_3$ were observed in the flux preheated at the temperature which the bulk density was low. With higher the pretreating temperature, liquidus was seen on the surface of particles and pores were disappeared. Therefore, the bulk density of flux is increased with proceeding the sintering reaction.

The results in DTA and X-ray analysis, shown in Fig.9, indicate the following facts. In the fluxes preheated up to about 600℃, a liquid phase is formed above 550℃ and finaly

melted at about 1100℃. When preheated temperature is above 700℃, the liquidus forming temperature is increased, the fluxes preheated above 900℃ melts only at final melting point. In the case that fluxes are preheated above 1200℃, glassy phase was recognized by findings of Tg point and crystallizing point on heating.

According to these results, it can be considered that preheat treated flux within the range of proper temperature(in this case, applicable range is 700-900℃) has a homogeneous melting property with low bulk density.

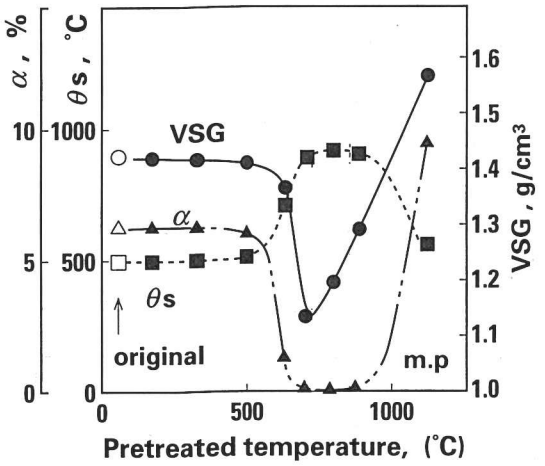

Fig.8 Influence of preheated temperature on characteristics of mold flux

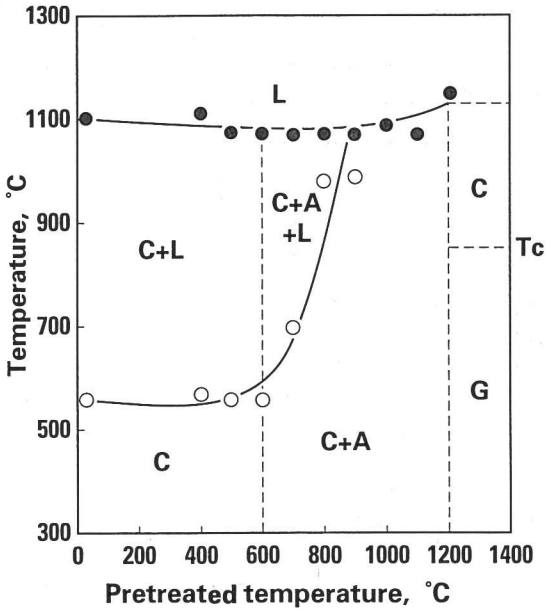

Fig.9 Phase transition diagram for preheat treated flux
C:crystal, A:amorphous,
G:glass, L:liquid,
Tc:crystallizing temperature

For the pretreated base material heated from 800 to 900℃, the influences of added materials on sintering property were examined as well as for the raw materials. The results are shown in Fig.10. The initial shrinkage temperature(θ s) was decreased with increasing the addition of alkali carbonate, but shrinkage rate(α) was maintained in a small degree, which is different from the results in the case of raw materials shown in Fig.7. This can be considered that the preheated base material forms an inactive complex compounds to restrain the reaction with the additional materials such as alkali oxides, fluorides and glass. This result indicate that it may be possible to improve the sintering property of the mold flux by means of preheating only base materials.

Melting characteristics of the improved flux using preheated base material were evaluated by investigations in laboratory and in actual casting. Fluxes used for these investigations, shown in Table 2, have similar composition and properties excepting for bulk density and TMA results.

Table 2 Chemical composition and physical property of developed mold flux

	Chemical Composition (wt%)								
	CaO	Al_2O_3	SiO_2	Na_2O	MgO	F	CO_2	F.C	CaO/SiO_2
Developed	31.0	3.5	42.0	13.0	6.0	5.0	1.0	2.0	0.74
Conventional	30.0	3.5	40.0	12.5	5.8	4.8	4.0	2.0	0.75

Type	V.S.G g/cm³	Viscosity at 1300 ℃ (poise)	Solidifying Temperature (℃)	TMA	
				θ s (℃)	α (%)
powder	1.2	2.25	1048	765	0
powder	1.6	2.24	1049	510	6.5

In the laboratory examination, the sample flux was layered in the magnesia crusible and heated only from the bottom side. Then the temperature distribution was measured with the thermocouples placed in the flux layer. An example of temperature profiles in the vertical section in steady state is shown in Fig.11. In the developed(less sintered) flux, a temperature is lower near the surface, higher at the bottom compared with that of conventional(much sintered) flux. This profile indicates that the developed flux has a low thermal diffusivity which is a feature of good themal insulation [7].

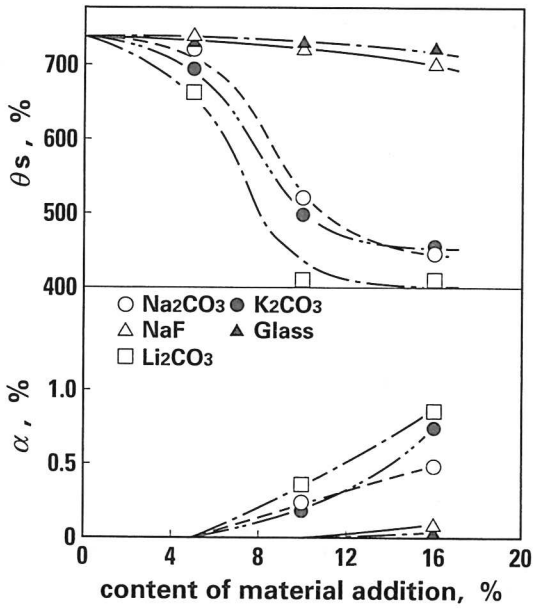

Fig.10 Effect of material addition on TMA results for preheated base material

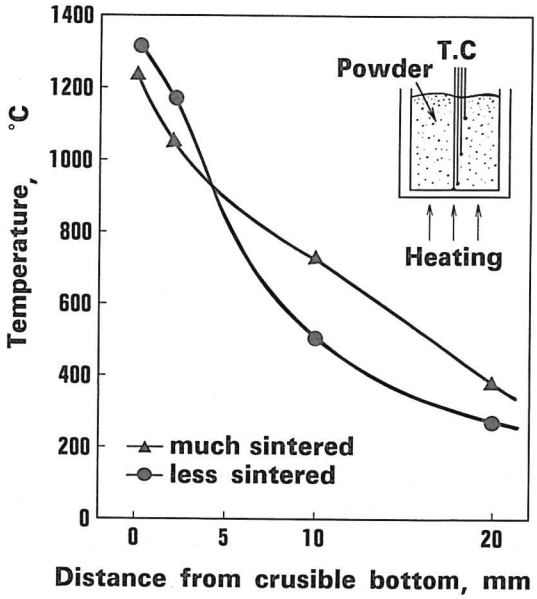

Fig.11 Influence of sintering on temperature distribution of flux layer

As an evaluation in the actual casting, observation of the melting performances in the mold and quality of products were investigated in slab and billet castings.In the developed flux, heavy slag-rim was hardly seen during casting and clean products were obtained, because of success of preventing stirring in the mold which resulted in producing internal defects.

4. Conclusion

The following results were obtained in this study.

① Sintering reaction could be measured quantitatively and estimated by TMA.
② Initial sintering at 400-600℃ produces heavy slag-rim preventing homogeneous melting.
③ Initial sintering is caused by low temperature slag reaction with alkari carbonates, oxides, fluorides, and glassy materials.
④ Preheat treatment for base materials was effective to prevent the initial sintering reaction occured at low temperature. This could be considered that raw materials are changed into inactive complex.
⑤ Newly developed flux used preheated base material has been applied to actual casting, succeeded to obtain the good performance and high quality product.

5. Refference

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