

CHARACTERIZATION AND ANALYSIS ON THE HEMISPHERICAL POINT TEMPERATURE UNCERTAINTY PROBLEM OF MOLD FLUX WITH VOLATILES

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Abstract

In hemisphere point temperature (T_{hp}) measurement of continuous casting mold flux, the evaporation of volatiles under high temperature will have a strong impact on the results. Based on the comprehensive analysis of hemisphere point method and its influencing factors, the corresponding volatile-containing mold flux and non-volatile mold flux were selected to get T_{hp} with different heating rates. Combined with the T_{hp} measurement and TG-DSC results, the effect of relevant factors during measuring process were analysed and the way to characterize and evaluate the effects were suggested. Furthermore, an improved method of mold flux melting point test was put forward. The results showed that for non-volatile mold flux, the temperature hysteresis had a greater effect than heat transfer delay and fractional melting. As for the mold flux with volatile, the effect of evaporation was greater than other factors. Traditional hemisphere-point method is no longer suitable for the volatile mold flux. In order to get through this problem, improved methods were proposed. One is measuring T_{hp} traditional way, correcting the composition at the T_{hp} , and corresponding T_{hp} with the corrected composition. Another is taking the initial composition, revising the hemispherical point temperature T_{hp} , and matching the revised T_{hp} with the initial composition.

Keywords: Mold flux with volatile; Hemispherical point temperature; Measurement uncertainty; Influencing factors; Characterization and analysis

1. Introduction

Continuous casting has completely replaced mold casting and became the dominant production technology in the crude steel making process [1]. In 2020, 96.9% of world crude steel was produced through continuous casting [2]. As a functional material for smoothly continuous casting product and higher billet quality, mold flux plays a key role. The function of mold flux includes: 1) adiabatic insulation to reduce heat loss from the molten steel; 2) air insulation to protect molten steel from secondary oxidation; 3) absorption and dissolution of non-metallic inclusions; 4) improvement of lubrication between billet and mold wall; and 5) control of heat transfer for better solidification structure [1, 3]. To achieve these points, sodium oxides, potassium oxides, and fluorides are used extensively in the mold flux in order to adjust the properties, which includes melting point, viscosity, crystallization properties, and surface tension [4]. The melting point and viscosity of the mold flux are the most critical properties in

performance control of mold flux. It will directly determine the smoothness of the continuous casting process, the quality of continuous casting billet, and the technical and economic indicators. The physical and chemical properties of mold flux are related to its chemical composition and raw material. At present, the fluxes for continuous casting are fluorine containing mold flux in most cases. The fluoride is added in the form of CaF_2 [5].

During the measurement of mold flux properties (physical properties such as melt melting point, crystallization property, density, viscosity, thermal conductivity, surface tension, and chemical properties such as activity, ability to adsorb inclusions), the samples have to suffer heating and high temperature keeping for a long time [1, 3, 5]. At first, the composition of the sample is generally determined according to the setting one. Second, the mold flux is prepared in chemically pure material or pre-melted materials, and the composition of the mold flux is considered stable and unchanging until measurement process end. That means the composition of the mold

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flux does not change during the heating and high temperature keeping in whole process by default. Third, the sample is briquetted, heated, melted, and held at measurement temperature for hours to get these properties data [6-9]. If there are volatile components in the mold flux, it will evaporate inevitably or reacts to evaporates (refer as evaporated for brief below). The evaporation will lead to changes in composition of mold flux. And as a result, it makes the properties of the mold flux change accordingly. The measured property will no longer correspond to the initial mold flux composition, this phenomenon referred to as "measurement uncertainty" to flux with volatile components. The higher the temperature and the longer the holding time of high temperature, the more significant this effect will be [10-21].

According to the relevant results, the evaporation of the mold flux with fluorine, potassium oxides and sodium oxides can reach more than 50% of its total fluoride amount during heating process. And the effect of evaporation on the results of property measurement cannot be ignored. K. Shimizu [11], N. N. Viswanathan [12], and E. Brandaleze [13] found that the volatiles of mold flux during the warming process were NaF, KF, NaAlF₄, SiF₄, AlF₃, CaF₂, AlOF, BF₃, etc. A. I. Zaitsev [14], T. Watanabe [15], and S. Gu [16] found that in the low temperature section the mold flux volatiles were mainly NaF and KF. In the high temperature section, the mold fluxes the evaporation was dominated by SiF₄ and AlF₃. L. Zhu [17] found that the main volatiles were NaF when the crystallization properties of the mold flux were determined by the double wire method. When the environment filled with SiF₄ gas, the evaporation of SiF₄ could not inhibit in the mold flux, and the evaporation of fluoride would reduce the crystallization rate of the mold flux. K. C. Mills and Z. Wang [18, 19] found that in the continuous casting production plant, the collected waste gas and examined component mainly contained: NaF, KF, SiF₄, AlF₃, NaAlF₄, CaF₂, AlOF, BF₃, etc. The evaporation rate was related to temperature and composition, the lower the CaO content and the higher the Na₂O content is, the higher the fluoride evaporation rate will be [20, 21].

The melting point of mold flux can be determined by hemisphere-point method, differential thermal analysis method, and hot wire method (temperature of crystallization point). Among these methods, hemisphere-point method is the most commonly used. For the sake of unity and brief, hemisphere-point temperature (T_{hp}) will be used in the following content. For hemisphere-point method measurement, it is generally believed that the results are affected by heat transfer hysteresis, fractional melting and inter-particle reaction of mold flux. Heat transfer hysteresis is a common problem in experiments that require

heating up, especially at high heating rate. During the measurement process, the heating module keeps heating up. The temperature showed on controller is higher than the temperature of sample. Taking melting point measurements as an example, when the sample temperature reaches melting point, the sample start to melt. Meanwhile, the temperature keeps rising, and this will lead a phenomenon that the measured temperature is higher than the actual melting point [22]. And it means that because of heat transfer hysteresis, the actual T_{hp} is lower than the measured temperature of thermocouple. The faster the heating rate is, the higher the measured T_{hp} will be. The fractional melting refers to the fact that some components will melt ahead during the heating process [23]. This phenomenon will lead to a failure of the other materials melting in time. When these unmelting materials starts to fusion, the temperature keeps growing, and the time is delayed. So, this leads to T_{hp} becoming higher than the actual value. The more the fractional melting develops, the higher the measured T_{hp} will be. The inter-particle reaction has an influence on rate and extent of reaction. It can be affected by heating rate. The higher the heating rate is, the faster the reaction rate will be, and the less the reaction continues [24, 25]. So, when the heating rate approaches the zero, the mold flux at T_{hp} would be in a condition that to react completely and slowly. It would lead to the T_{hp} becoming higher than the one at low heating rate. In the process of T_{hp} measurement, mold flux is often prepared with different materials. The particle size and compaction degree of these materials will also lead to a difference in measurement results [26]. Increasing the heating rate can restrain the development of fractional melting to some extent. And the measured T_{hp} decreases correspondingly. In the current T_{hp} measurement, the above effects can be controlled to some extent by sample preparation (particle size under 75 μm) and heating rate limit (not more than 15 $^{\circ}\text{C}\cdot\text{min}^{-1}$ in relevant standard).

If the quantity of evaporation is large, it will lead to a large deviation of measurement result [27]. It is more reasonable to correspond the evaporation mold flux composition with the measured result, rather than the initial mold flux composition. The evaporation of fluoride, potassium oxides, and sodium oxides (which can reduce the T_{hp}) will lead to the increase of T_{hp} . The slower the heating rate, the more evaporation would occur, and the higher T_{hp} would be. Increasing the heating rate is beneficial for reducing the evaporation loss, and reducing the measured value of T_{hp} further.

In summary of these factors, different factors have different effects on melting point measurement, and the following table describes the impact.

The measured value of mold flux T_{hp} will ultimately depend on the combined effect of above

Table 1. Chemical composition of magnesite

Factors	Effect on T_{hp} (heating rate rise from $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ - $25\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$)	Reference
Fractional melting	Decrease	[23]
Heat transfer hysteresis	Increase	[22]
Interparticle reaction	Decrease	[24,25]
Particle size	Increase	[26]
Evaporation of fluoride	Decrease	[27]

factors. The above results are also applicable to melting point measurement by hot wire method and differential thermal analysis (DTA).

Up to now, there is no effective resolution to the measurement uncertainty of fluxes with volatiles. This paper will take the melting point measurement as an example, analyze the "uncertainty" to clarify the effect of various factors and mechanism, obtain more reasonable property parameters of mold flux with volatile components, and provide support to develop suitable property measurement methods for mold flux or other melts.

2. Experiment Method

2.1. General description

Continuous casting fluoride-contain mold fluxes with typical compositions were considered, and non-fluoride mold flux were designed based on it. In order to describe the influence of different factors on the melting point of mold flux, several heating rates were carried out to measure the T_{hp} of mold flux with the melting point measurement apparatus (MTLQ-RD-1600, China). In order to describe the degree of evaporation, TGA was performed using a comprehensive thermal analyzer (SETSYS Evolution, SETARAM, France) to determine the evaporation of fluorides.

2.2. Sample preparation

According to the fluoride content of typical mold flux, a representative mold flux composition was determined. First, all the materials were maintained at $200\text{ }^{\circ}\text{C}$ for 6 h to remove free water. Then, they were ground and passed through a $75\text{ }\mu\text{m}$ sieve. The mold fluxes were prepared and placed in a drying oven at $120\text{ }^{\circ}\text{C}$ for more than 2 h, and all the components of the experimental mold fluxes were prepared using pure chemical agents supplied by Tianjin Tianli Chemical Reagent Co. Ltd., China.

Table 2. The composition of experiment mold flux

Mold flux	Mass/%					
	CaO	SiO ₂	Al ₂ O ₃	CaF ₂	Na ₂ O	MgO
1#(Fluoride-containing)	28.18	31.32	7.00	20.00	7.50	6.00
2#(None-fluoride)	38.86	43.2	9.66	-	-	8.28

*Note: The composition difference between none-fluoride mold flux and fluoride-containing mold flux is the volatile content (CaF₂ and Na₂O).

2.3. T_{hp} Measurement in different heating rates

A hemispherical melting-point measurement apparatus was used to measure the melting temperature of the mold fluxes. The mold flux samples were fabricated into a cylinder ($\Phi 1\text{ mm} \times 3\text{ mm}$) with absolute ethyl alcohol. The cylindrical samples were heated on a corundum gasket at a rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ - $25\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The temperature at which the height of the cylinder became half of its original value was automatically recorded by a computer. The variation in height is shown in Fig. 1. Three measurements were carried out for each sample, and the melting temperature was considered as the average of these measurements if they were similar.

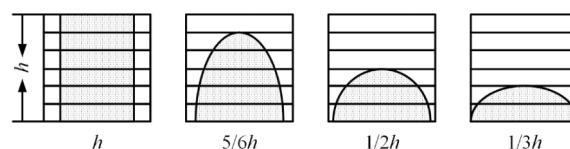


Figure 1. Schematic of melting point measurement by hemispherical method

2.4. TG measurement in different heating rates and samples

TG was performed using a comprehensive thermal analyzer (SETSYS Evolution, SETARAM, France) to determine the evaporation of fluorides. Samples (10 mg each) were heated in a Pt crucible from 50 to $1400\text{ }^{\circ}\text{C}$ at a rate of 5 - $25\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under an argon flow rate of $50\text{ ml}\cdot\text{min}^{-1}$. The heating rate was the same as melting point determination.

At temperatures over $800\text{ }^{\circ}\text{C}$ the weight loss was considered as the result of the evaporation of volatiles other reactions, such as free water and bound water evaporation, occurred at lower temperatures.

3. Results and Discussion

3.1. T_{hp} and TG Results of different kinds of mold flux

The T_{hp} of mold fluxes was measured at different



heating rates and the trends are shown in Figure 2. Figure 3 shows the weight-loss results of non-fluoride mold flux and fluoride-containing mold flux. It can be seen clearly that the non-fluoride mold flux had no evaporation phenomenon occurred from 800 °C to 1400 °C. The heating rate of 5 °C·min⁻¹ was used in TG measurement.

For the none-fluoride mold flux, it can be seen that with the heating rate increasing, the T_{hp} value also increased. The amplification of T_{hp} reached 30.7 °C approximately when the heating rate increased from 5 °C·min⁻¹ to 25 °C·min⁻¹. And for the fluoride-containing mold flux, the T_{hp} of the mold flux decreased with the increase in heating rate. The value of T_{hp} decreased by 42.3 °C when the heating rate increased from 5 °C·min⁻¹ to 25 °C·min⁻¹.

For none-fluoride mold flux curve, there was no effect of evaporation. So, the measurement result was influenced by the comprehensive effect of fractional

melting, heat transfer hysteresis, interparticle reaction and others. It can be seen that the measured T_{hp} increased with the heating rate. Among these factors, heat transfer hysteresis would cause the measured temperature to get higher than the actual melting point, while the fractional melting influence was, on the other side, seen with heating rate increasing.

At the same time, fractional melting would be more notable with the heating rates decrease. This means that if only the fractional melting was considered, T_{hp} was supposed to reach its maximum at heating rate approaching zero. However, this phenomenon cannot be seen in this figure. So, the trend of both curves showed that the effect of heat transfer hysteresis was greater than that of fractional melting, or the effect of fractional melting was limited.

This was the result of the combined effects of factors in none-fluoride mold flux and evaporation for the fluoride-containing slag curve. The fractional melting and evaporation would lead to the decrease of the measured value at the hemisphere-point with the

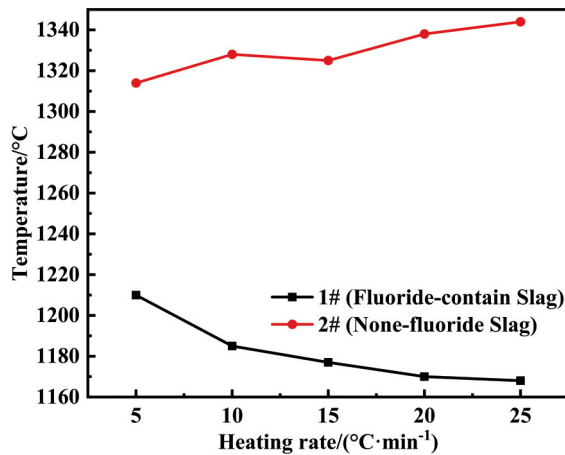


Figure 2. Relation between T_{hp} and heating rate

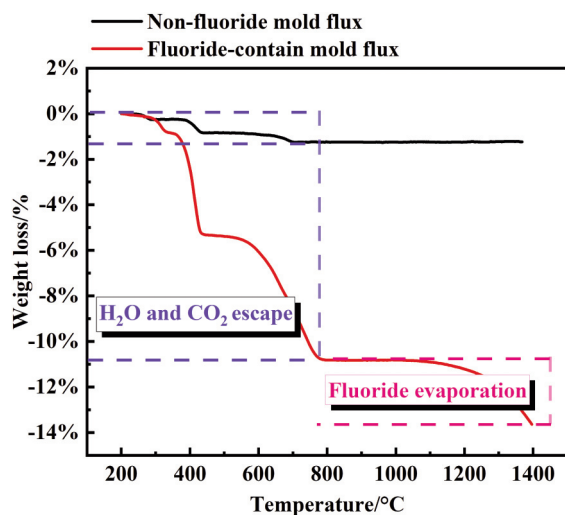


Figure 3. The TG curve of non-fluoride and fluoride-containing mold fluxes at 5 °C·min⁻¹

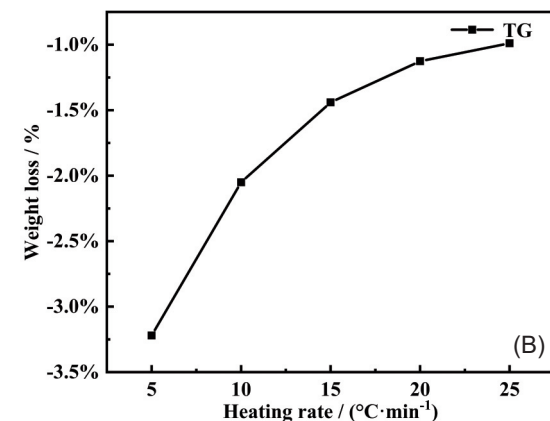
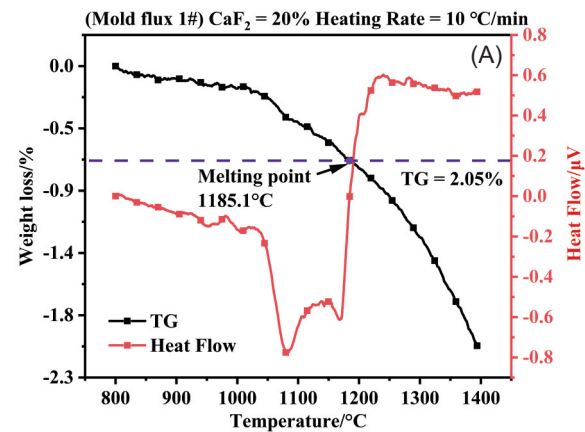


Figure 4. TG-DSC results and the effect of heating rate (A) TG results of fluoride-contain mold flux in 10 °C/min; (B) Relationship between TG and heating rate of fluoride contain mold flux in 5 °C·min⁻¹ to 25 °C·min⁻¹



increase of the heating rate. Meanwhile, the effect of heat transfer hysteresis was opposite. Therefore, it can be inferred that the effects of fractional melting and evaporation on the mold flux with volatile were greater than the heat transfer hysteresis. Combining the clarification about heat transfer hysteresis and fractional melting above, it can be concluded that the effect of evaporation was much greater than that of heat transfer hysteresis.

Under the conditions of the T_{hp} measurement, the TG measurements results are shown in Figure 4. Corresponding to the T_{hp} , the weight loss (evaporation loss rate) of the mold flux was reduced from 3.46% to 1.14%. The weight loss was considered to be mainly fluoride evaporation [28, 29]. So, convert the weight loss into fluoride in mold flux, the evaporation rate can reach 4.15%-12.6% of the total dosage of fluoride. The evaporation effect of fluoride on the hemisphere-point of mold flux cannot be negligible. It can also support the results that the effect of evaporation to T_{hp} is greater than that of other factors.

3.2. Discussion on the measurement of various factors influence on T_{hp}

As mentioned above, the combination of these factors creates the phenomenon between hemisphere-points and heating rate. The samples were prepared with same material. It can be seen that the factors (particle size, degree of compaction, hysteresis effect of heating rate, fractional melting, etc.) were all the same. In this situation, the results of the evaporation mold flux measurements can be seen in Figure 5.

It can be seen from Figure 5 that the difference between two curves was the effect of increasing heating rate on evaporation inhibition. In other words, the area between the red curve and black curve was

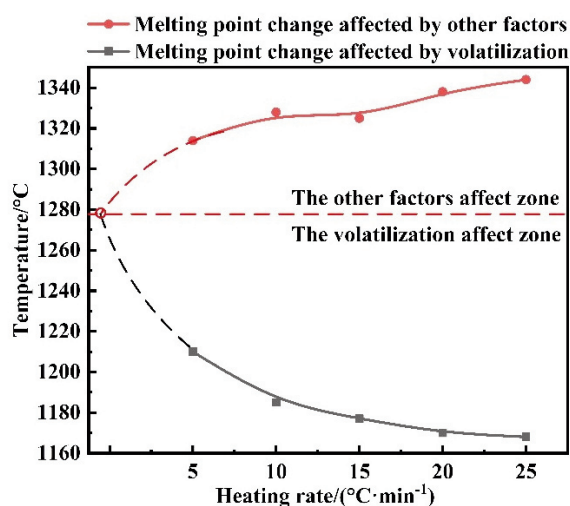


Figure 5. The characterization of different influencing factors

the zone of evaporation effect. The larger the distance between the two curves, the more significant the inhibition of evaporation.

Taking heating rate $25\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ as an example, it can be seen that the heat transfer hysteresis caused by the heating rate increased the measured T_{hp} approximately $34\text{ }^{\circ}\text{C}$. The increase of the heating rate to suppress evaporation phenomenon could lead to the T_{hp} decrease for approximately $72\text{ }^{\circ}\text{C}$ of fluoride-containing mold flux. Under the effect of comprehensive factors, the measured value of mold flux T_{hp} was reduced to $1168\text{ }^{\circ}\text{C}$. Using this T_{hp} as a benchmark, the effect of evaporation on measured T_{hp} would be 6.2% and the effect of other factors would be 2.9%. In other words, for the fluoride-containing mold flux listed in Table 2, the effect of evaporation would be much greater than heat hysteresis and fractional melting. The faster the heating rate, the smaller the fluoride evaporation and the lower the measured T_{hp} .

For the zero point in Figure 5, the extrapolation of the measured results, when the heating rate was infinitesimally small (tends to zero), the effect of other factors tended to be zero too. For non-volatile mold fluxes, the T_{hp} value close to zero was the measured one after the full development of fractional melting. If the limited effect of fractional melting was considered, this value was close to the T_{hp} of non-fluoride mold flux "true value". As for volatile mold flux, both evaporation and fractional melting were fully developed at this time and the volatile evaporated completely. The mold flux already showed the characteristics of the non-volatile one. The measured mold flux T_{hp} would be close to the one without volatiles. This T_{hp} value would be significantly higher than the volatilized mold flux.

It is proved that the "uncertainty" was inevitable when the traditional measurement method was used for volatile mold flux T_{hp} test.

3.3. Solutions to the "uncertainty" problem

The "uncertainty" of volatile mold fluxes in the T_{hp} measurement process occurred mainly due to evaporation. It induced changes in mold flux composition and led to the distortion of the results ultimately. So, there are three methods can be selected to obtain the "true value" (closer to the value of the actual mold flux T_{hp}):

(1) Using a high-pressure seal to suppress evaporation when measuring the T_{hp} of mold flux. Obviously, the apparatus is difficult to set up and the operation needs more accuracy. The process of experiments needs to be rigorous which could make the process become complicated and inconvenient for experimenters.

(2) Measuring the composition changes due to

evaporation of volatiles. Then, associate the T_{hp} temperature with the real-time components. During the T_{hp} measurement process, the composition is no longer the initial preparation one [23, 27-31]. Fig.6 shows the results of T_{hp} measurement, TG measurement, and roasting test for the same atmosphere and heating rate. For the mold flux 1#, the measured T_{hp} of 1161.6 °C corresponded to the weight loss of 3.08%. If the volatile weight loss mechanism is known, it can be deduced that the composition of the mold flux at this point corresponded to the T_{hp} of 1161.6 °C. This meant that 1161.6 °C was the T_{hp} of this new composition of mold flux instead of the original prepared one [23, 27]. The composition at 1161.6 °C is shown in Table 3 [27] according to the TG result and combining with the roasting test result.

Table 3. The composition correction of the mold flux 1

Mold flux 1#	Mass/%					
	CaO	SiO ₂	Al ₂ O ₃	CaF ₂	Na ₂ O	MgO
Initial composition	28.18	31.32	7.00	20.00	7.50	6.00
Corrected composition	29.86	31.85	7.07	17.83	7.28	6.11

According to Table 3, the T_{hp} can be matched with the composition. It means that the composition changed into another one when the sample started melting. This method was discussed in one of previous research [27-33].

(3) Correction of measured T_{hp} . It is known that the effect of evaporation affected the measured T_{hp} . The measured value can be revised to obtain the T_{hp} of the initial mold flux corresponding to the initial mold flux composition. It can be seen from the black curve in Fig.3, when the heating rate was over 25 °C·min⁻¹, the trend flattened out. It means that the evaporation was significantly inhibited. It is unnecessary to modify the effects of evaporation. But when the heating rate got lower, a significant effect of evaporation occurred during this process. The lower the heating rate was, the more obvious the effect of evaporation was. And at this heating rate, it was necessary to modify the measured results. Therefore,

on the basis of Fig.3, the red curve can be parallelly moved down to get Fig.7. The top region (backslashes were filled in) showed the effect factors for T_{hp} without fluoride. For the fluoride-contain mold flux, T_{hp} was shown in curve 2. The bottom region (slashes were filled in) was the fluoride influenced area. Curve 3 in Fig.7 is the correction result of T_{hp} considering the effect of evaporation. If all of the factors are taken into account, the "true value" line can be obtained with the corresponding value of curve 1 subtracted from this basis. Taking the results of a 25 °C·min⁻¹ heating rate as an example again, the measured T_{hp} was 1168 °C. It can be seen from the curve 2 that the evaporation had little impact on the results of T_{hp} test. And it can be considered that the evaporation was inhibited. However, the high level of heating rate could make more effect by the heat transfer and other factors. At this time, the measured value of T_{hp} was 1168 °C, and the true value needed to decrease for 60 °C due to the other factors. Thus, the "true value" of the initial T_{hp} was 1108 °C. According to the standard of mold flux T_{hp} measurement, the heating rate was 15 °C·min⁻¹. The result based on the effect of evaporation of mold flux was 1148 °C. The T_{hp} caused by other factors corresponding to red curve was 40 °C. The "truth value" of the hemisphere point of the mold flux was 1108 °C.

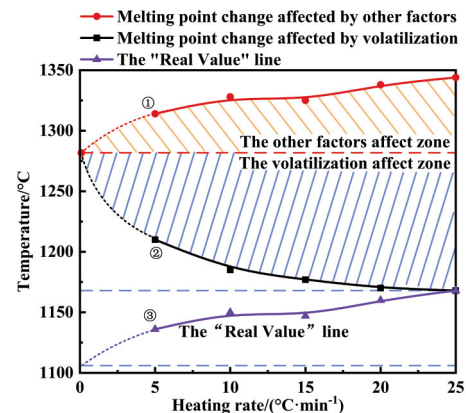


Figure 7. The correction of the T_{hp} by the combination of different factors

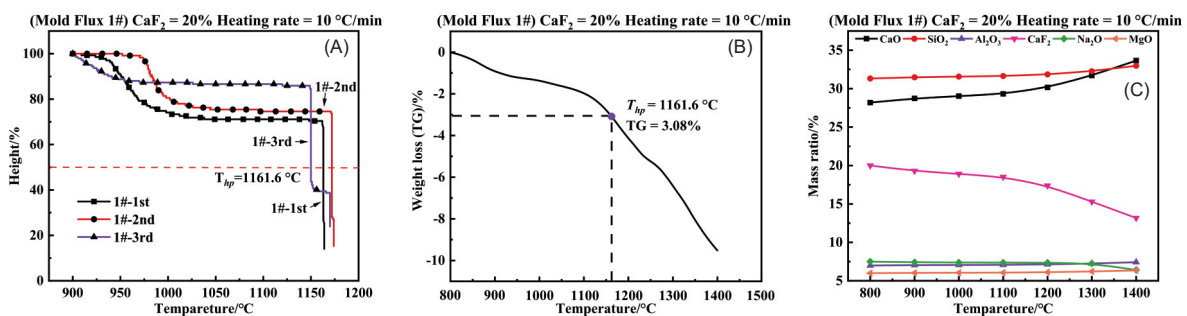


Figure 6. T_{hp} measurement and TG curve required by method two; (A) The height changes during the T_{hp} measurement; (B) Weight loss during the heating process; (C) Composition changes during roasting test result

4. Conclusion

(1) For non-volatile mold flux, the temperature hysteresis had a great effect. It was shown that with the increase of heating rate, the measured value of T_{hp} increased. The effect of fractional melting was limited. For the mold flux with volatiles, the effect of evaporation was much greater than other factors, which showed that the measured value of T_{hp} decreased with the increase of the heating rate.

(2) The effect of factors without evaporation was characterized by the measured T_{hp} difference of non-volatile mold flux with heating rate under the similar raw material conditions. After that, it was combined with T_{hp} of volatile mold flux. The difference between them can be used to characterize the effect of inhibition of evaporation on the measurement results of mold flux.

(3) Increasing the heating rate of hemispherical point measurement can effectively inhibit evaporation. When the heating rate was above 25 °C·min⁻¹, the effect of evaporation was basically unchanged.

(4) A method to obtain the "true value" of volatile mold flux was proposed. The T_{hp} could be measured by conventional methods. One was to match the T_{hp} temperature with the composition of mold flux at this temperature. Another was to modify the measurement results to the initial mold flux composition. Both of the methods can be used to obtain the T_{hp} closer to the "true value".

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Authors contributions

Z. Wang performed the data analyses and wrote the manuscript. M.-M. Ren and J.-X. Zhao helped preform the analysis with constructive discussions. Z.-K. Zhang, H. Wang and A.-L. Hu performed the experiment. J.-X. Zhao and Y.-R. Cui provided the financial support.

Data availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflict of Interest

The authors declare no conflict of interest.

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KARAKTERIZACIJA I ANALIZA PROBLEMA NESIGURNOSTI TEMPERATURE HEMISFERNE TAČKE LIVNOG PRAHA SA ISPARLJIVIM SASTOJCIMA

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Apstrakt

Prilikom merenja temperature hemisferne tačke (T_{hp}) livnog praha za kontinualno livenje, isparavanje sastojaka praha na visokim temperaturama imaće jak uticaj na rezultate. Na osnovu sveobuhvatne analize metode hemisferne tačke i njenih faktora uticaja, odabrani su prahovi sa isparljivim i neisparljivim sastojcima, kako bi se dobila T_{hp} prilikom različitih brzina zagrevanja. Kombinacija merenja T_{hp} i rezultata TG-DSC analize je korišćena za analiziranje uticaja relevantnih faktora, kao i za karakterizaciju i evaluaciju efekata. Pored toga, predložena je i poboljšana metoda ispitivanja tačke topljenja livnog praha. Rezultati su pokazali da je kod livnog praha sa neisparljivim materijama, temperaturni histerezis imao veći uticaj od zakasnelog prenosa toplote i parcijalnog topljenja. Kada je isparljivi livni prah u pitanju, efekat isparavanja je imao veći uticaj od ostalih faktora. Tradicionalna metoda hemisferne tačke više nije prikladna za ispitivanje livnog praha sa isparljivim materijama. Da bi se prevazišao ovaj problem, predložene su poboljšane metode. Prva predstavlja merenje T_{hp} na tradicionalan način, zatim ispravljanje sastava na T_{hp} i nakon toga usklađivanje inicijalnih vrednosti sa ispravljenim. Druga metoda predlaže uzimanje početnog sastava, vršenje revizije temperature hemisferne tačke T_{hp} i usklađivanje revidirane T_{hp} sa početnim sastavom.

Ključne reči: Livni prah sa isparljivim materijama; Temperatura hemisferne tačke; Nesigurnost merenja; Faktori uticaja; Karakterizacija i analiza

