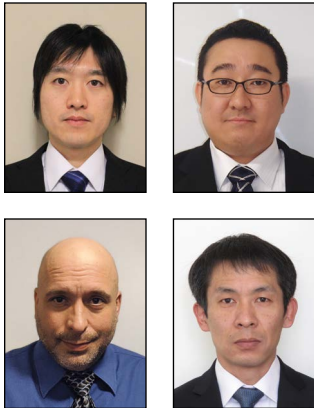


Crystallization Behavior Evaluations of Mold Powder by Differential Thermal Analysis



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In the continuous casting process, it has been known that a mold powder with a high crystallization temperature is effective in preventing surface cracks on the steel strand. To improve mold powder technology, various samples were evaluated by employing differential thermal analysis (DTA). Quenched glass samples were heated until melted and then cooled. According to the DTA curves, a supercooling degree was obtained by the difference between liquidus temperature and crystallization temperature. As a result, it was recognized that the consideration of not only the crystallization temperature but also the supercooling degree can be effective in mold powder technology improvement.

One of the roles of mold powder in the continuous casting process is the prevention of strand surface cracking. Mold powder selection is particularly important on crack-sensitive steel grades, including peritectic and medium-carbon grades. High-crystallization-temperature/high-basicity mold powder is a common and effective method to prevent surface cracking due to its softer heat removal.

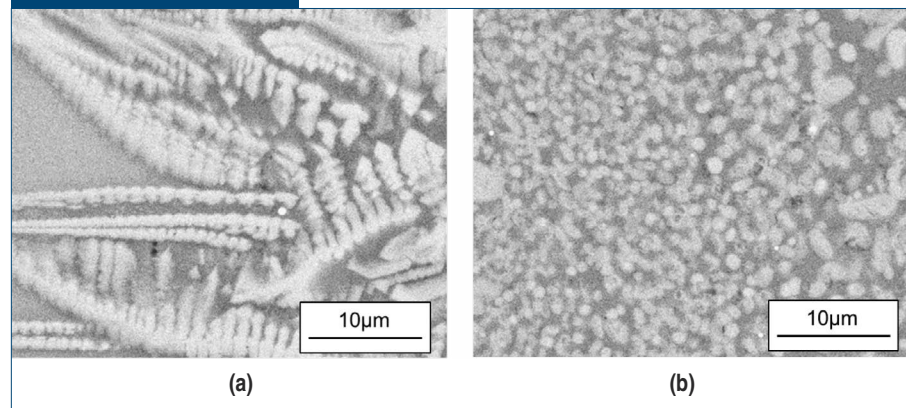
Crystallization of the mold powder can be classified into the following:

- Crystallization from the molten slag.

- Crystallization from the solid glass slag.

The crystallization from the liquid phase is a dendrite-shaped structure, as shown in Fig. 1a. On the other hand, the crystal generated from the solid phase shows a fine-grained structure, as shown in Fig. 1b. In this report, the crystallization types were classified as “crystallization,” which is crystallization from the liquid slag phase in the cooling process, and “recrystallization,” which is crystallization from solid glass phase during the heating process.

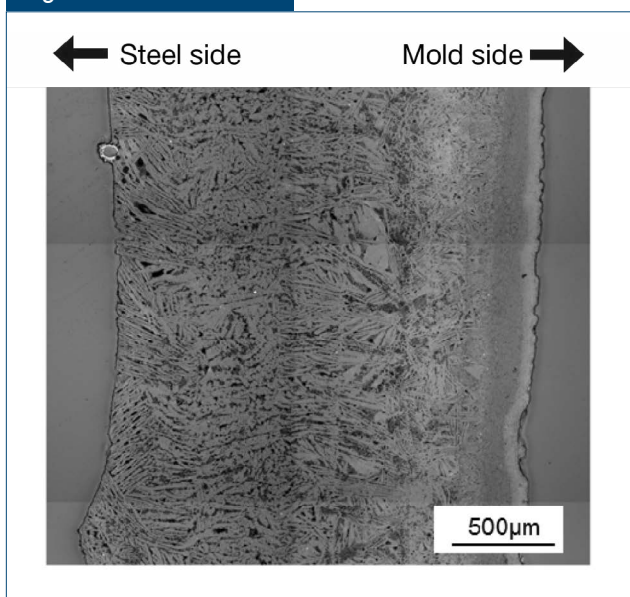
Figure 1



Dendrite-shaped crystal generated from liquid phase (a) and fine-grained crystal generated from solid phase (b).

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Figure 2



Cross-section of slag film sampled from inside the mold.

There were many research studies previously on mold powder crystallization characteristics using the cooling process from molten slag.^{1,2} However, there were few studies on the recrystallization of solid glass during heating.

Fig. 2 shows the cross-section of slag film collected from inside the mold after actual casting. In observation of the slag film, a microcrystal layer was formed on the mold side. It is considered that the fine-grained crystal layer was generated by the following steps:

- Melted slag was solidified by rapidly cooling in the mold.
- Recrystallization of solid glass slag occurred due to transfer of heat from the steel.

Since formation of a recrystallized layer was observed in the slag film from actual casting, it was considered that not only crystallization characteristics but also recrystallization characteristics of the mold powder can contribute to the reduction in heat transfer from the steel. Thus, it is expected that investigating the recrystallization property of mold powder slag while heating should help to develop a mold powder for crack prevention.

Also, a large variation in the crystallization temperature during cooling of the molten slag was detected. The large variation was amplified when a higher cooling rate was used (hard conditions for crystallization). The investigation of crystallization under difficult conditions could be useful for the development of mold powder for peritectic and medium-carbon grades.

This report will present the results of crystallization and recrystallization behavior evaluations of the mold powder by employing differential thermal analysis (DTA).

Experimental Procedure

Experimental Method — Table 1 shows the chemistry range of the 93 different mold powders. To make a solid glass sample, each powder was melted at 1,300°C and kept for 7 minutes, and then it was quenched in water. After drying at 150°C, the slag samples were crushed for the evaluations.

Thermogravimetry (TG)-DTA Measurement Conditions

- Measurement device: TAS-200 from Rigaku Co. Ltd.
- Atmosphere: Argon (80 cc/minute).
- Temperature condition: Sample temperature was increased from room temperature to 1,280°C using a heating rate of 15°C/minute. The sample was kept at 1,280°C for 3 minutes. After that, the sample was cooled to 900°C using a cooling rate of 10°C/minute.
- Sample amount: 200 mg.
- Reference material: Al₂O₃.
- Crucible: 90% Pt-10% Rh, φ5 mm × H 10 mm.

TG-DTA Measurement Result — Fig. 3 shows the TG-DTA result of mold powder A, the chemistry for which is in Table 2.

Fig. 3 shows an endothermic peak was observed at around 490–600°C during heating. The endothermic peak appeared at the glass transition point, which is the temperature at which glass becomes a supercooled liquid when it is heated.³ Because the test sample was in the glass phase from quenching in the water,

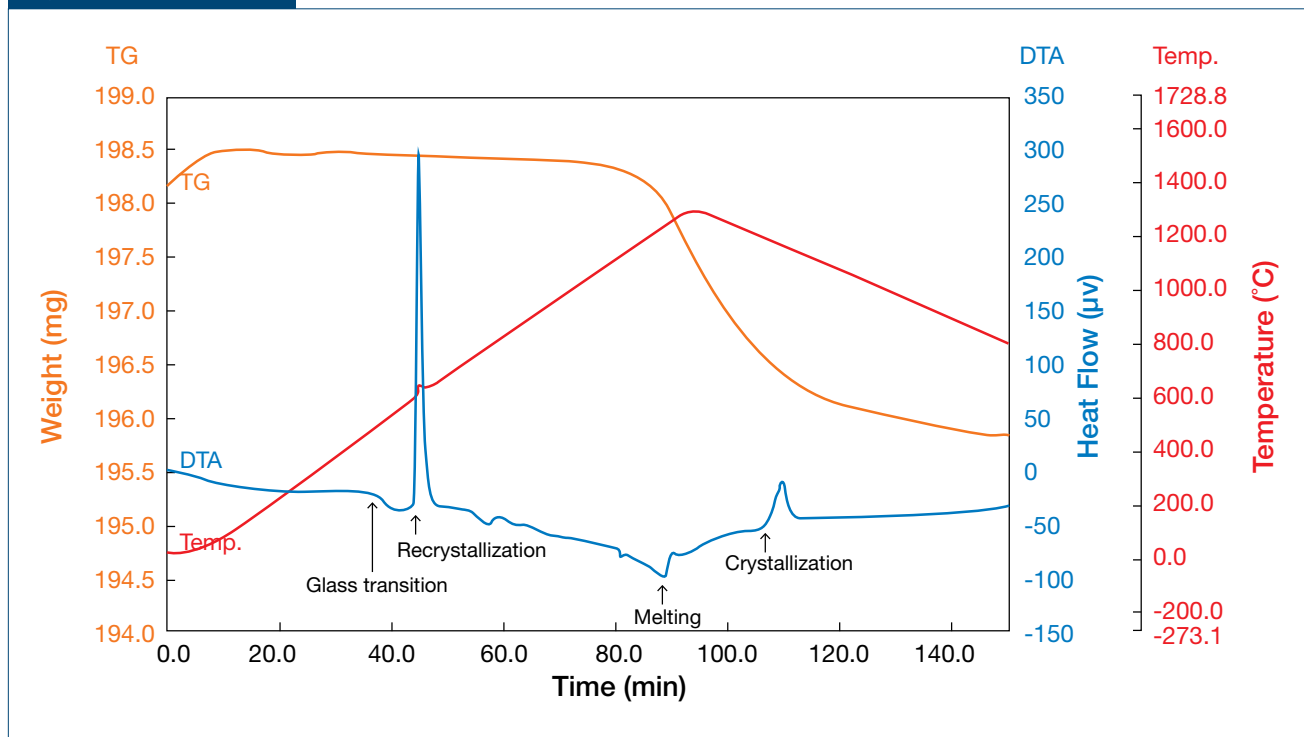
Table 1

Chemical Compositions of Mold Powder Samples (wt.%)		
	Range	Average
SiO ₂	27.60–45.80	36.30
Al ₂ O ₃	2.60–7.80	5.00
CaO	29.80–52.10	39.20
MgO	0.50–7.60	2.20
Na ₂ O	1.10–14.80	7.00
Li ₂ O	0–5.30	2.00
F	2.60–11.20	6.90
CaO/SiO ₂	0.77–1.53	1.08

Table 2

Chemical Composition of Mold Powder A (wt.%)								
	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	Li ₂ O	F	CaO/SiO ₂
Mold powder A	32.80	3.30	43.00	1.50	9.20	0	9.10	1.31

Figure 3



Thermogravimetry-differential thermal analysis (TG-DTA) data of mold powder A.

the endothermic reaction was made from the glass transition.

Then, an exothermic peak appeared from 600 to 650°C in the DTA chart. Fig. 4 shows the sample appearance and x-ray diffraction (XRD) after heating at each temperature for mold powder A. The exothermic reaction was considered to be caused by recrystallization, because the XRD peak intensity increased remarkably from the 600°C to the 650°C sample in Fig. 4. Here, the exothermic peak was defined as recrystallization temperature.

As the temperature was increased further, another endothermic peak caused by the melting of the crystals was shown. In Fig. 4, the shrinkage due to sintering began at 700°C and continued. A large amount of the liquid phase was found at 1,000°C in the sample. The endothermic reaction continued as the temperature increased, and a maximum endothermic peak appeared at 1,226°C. This behavior indicated that all of the previously formed crystals during the heating

process were melted, and this point was defined as the melting temperature.

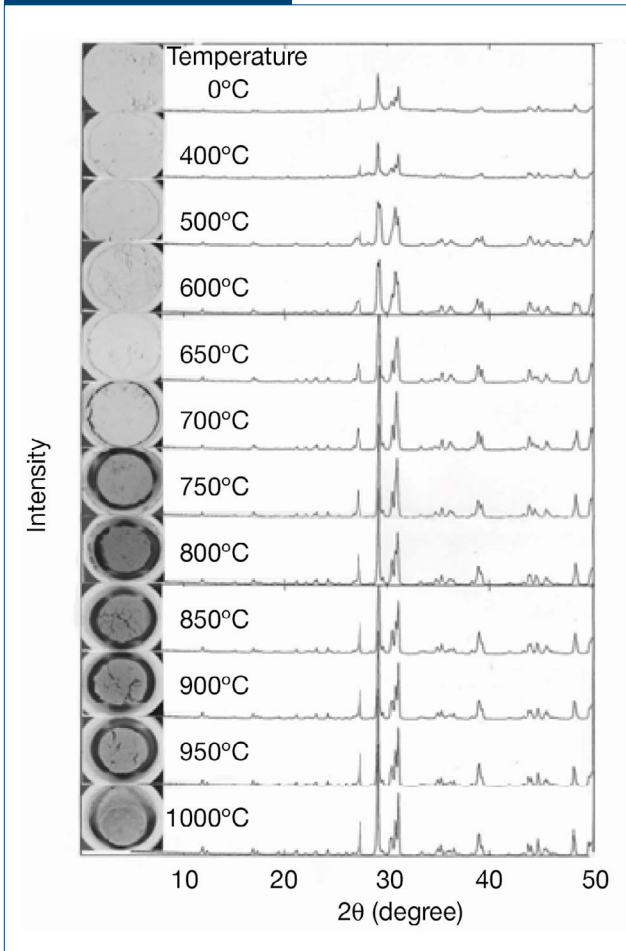
An exothermic peak was observed at 1,167°C during the cooling process. This temperature was defined as the crystallization temperature.

The weight loss began at around 1,150°C and escalated with an increase in temperature. This weight loss is due to the vaporization of low melting point elements including Na, Li and F. Weight loss began between 1,150°C and 1,200°C in all samples, and there is no correlation with the melting temperature.

Recrystallization Temperature and Melting Temperature —

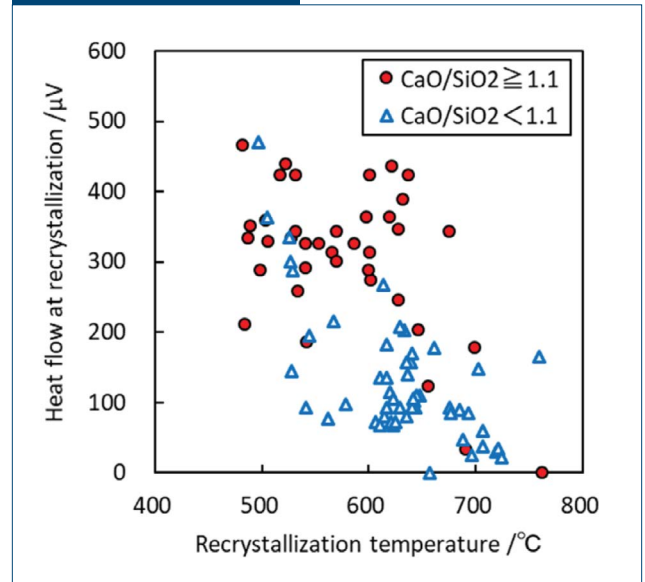
Fig. 5 shows the relationship between the recrystallization temperature and the heat flow at recrystallization on 93 different mold powders. Each data was plotted and separated to two symbols depending on whether its basicity is over or under 1.10. High-basicity mold powder tends to have lower recrystallization temperature and higher exothermic amount at recrystallization as compared with low basicity. High-basicity

Figure 4



Sample appearance and x-ray diffraction (XRD) chart after heating mold powder A.

Figure 5

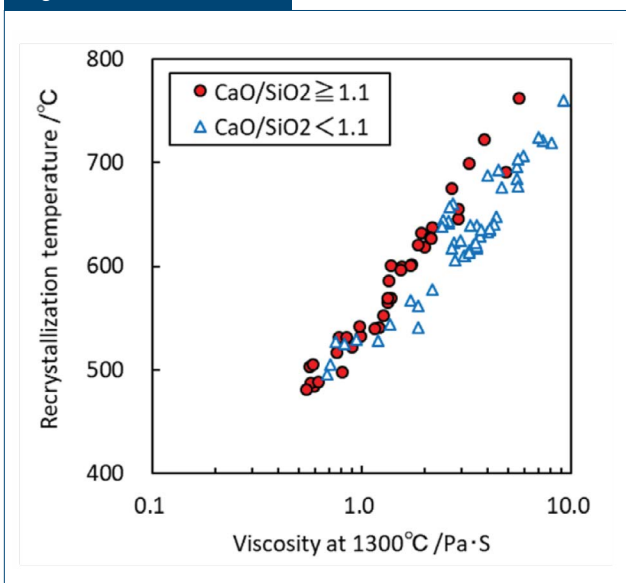


Relation between recrystallization temperature and heat flow.

samples with high crystallization during liquid slag cooling also showed a tendency to have large crystal growth at recrystallization.

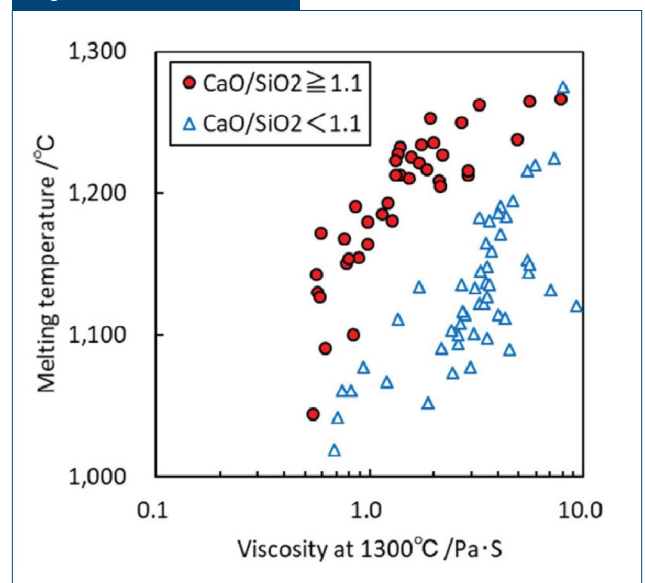
Fig. 6 shows the relationship between the melted slag viscosity at 1,300°C and the recrystallization temperature. There is a high correlation between the slag viscosity and the recrystallization temperature. Higher-basicity mold powder samples have a stronger correlation. A solid glass becomes supercooled liquid when the temperature reaches its glass transition

Figure 6



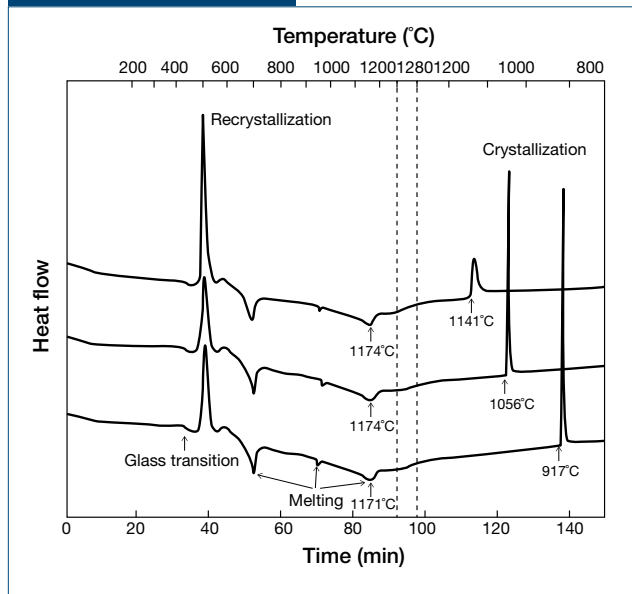
Relation of recrystallization temperature to viscosity.

Figure 7



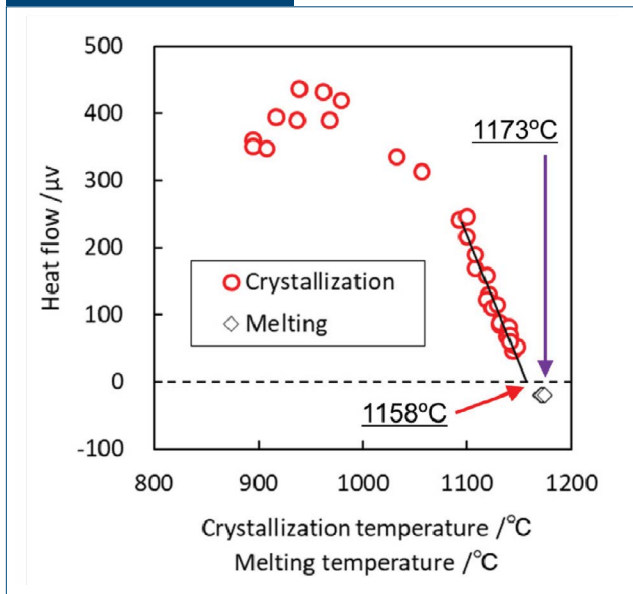
Relation of melting temperature to viscosity.

Figure 8



Measurement examples of mold powder B.

Figure 9



Relation between crystallization temperature and heat flow from 30 samples of mold powder B.

Table 3

Chemical Composition of Mold Powder B (wt.%)								
	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	Li ₂ O	F	CaO/SiO ₂
Mold powder B	29.60	3.20	44.10	0.50	7.90	3.50	10.90	1.49

temperature. Elements in the mold powder slag can move in the supercooled liquid and it can be regarded as liquid, which has infinite viscosity.⁵ The correlation between the slag viscosity and the recrystallization temperature is because the elements in low slag viscosity at 1,300°C can easily move and align to form crystals.

Fig. 7 shows the relationship between the melted slag viscosity at 1,300°C and melting temperature. Both higher basicity and higher viscosity mold powders tend to have high melting temperature. These results suggested that more flux content in mold powder slag for lower viscosity decreased its melting temperature.

Crystallization Temperature — Mold powder B shown in Table 3 was measured 30 times to evaluate reproducibility of the results. The results from the DTA curve during the heating process were reproducible. The temperature differences of the glass transition temperature, recrystallization temperature and melting temperature were within the range of 6°C. However, less reproducibility was found in the DTA curve of the temperature in the cooling process. There were large differences in the crystallization temperature, up to 250°C. There was a large variation in the amount of

exothermicity during cooling. As shown in the DTA chart in Fig. 8, typically the exothermic content was low when the crystallization temperature was high, and exothermic amount was high when the crystallization temperature was low.

Fig. 9 shows both the relationship between the crystallization temperature and the exothermic quantity (heat flow), and the relationship between the melting temperature and the endothermic quantity (heat flow).

When the crystallization temperature was greater than 950°C, the exothermic amount reduced with increasing crystallization temperature with good correlation. The sample, which measured a lower crystallization temperature and higher exothermic amount, showed high crystal growth after the test.

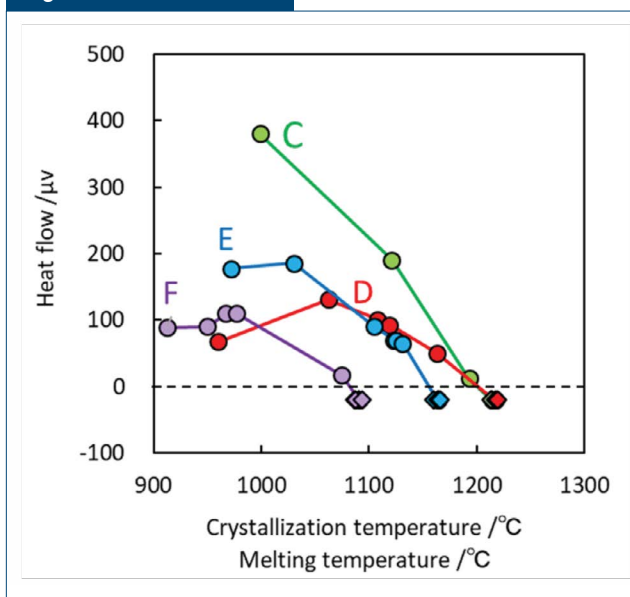
Crystallization during cooling from the molten slag occurred in the supercooled state, which was below the liquidus temperature. Crystallization from a supercooled liquid is a phenomenon in which a decrease in free energy accompanying crystallization acts as a driving force. It occurs as the process of crystal nucleation followed by crystal growth from the nucleus.⁵ Therefore, crystallization does not occur unless there is nucleation in the process of cooling the molten slag.

Table 4

Chemical Composition of Mold Powders C, D, E and F (wt.%)

	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	Li ₂ O	F	CaO/SiO ₂
Mold powder C	32.50	3.90	43.60	1.10	7.40	1.50	9.10	1.34
Mold powder D	34.70	6.20	42.20	1.00	8.90	0	6.10	1.22
Mold powder E	30.10	4.90	40.40	3.10	7.80	1.80	10.90	1.34
Mold powder F	28.10	5.80	38.30	2.50	10.90	3.10	10.70	1.36

Figure 10



Relation between crystallization temperature and heat flow of mold powders C, D, E and F.

The reason for the large variation in the crystallization test during cooling is that both the cooling rate (10°C/minute) was too fast and the sample amount (200 mg) was too small for nucleation to occur. It is considered that slowing the cooling rate, increasing the sample amount and adding agitation to molten slag could increase nucleation. The supercooling becomes smaller and the crystallization temperature approaches the liquidus temperature.

The reason why the calorific value increases as the crystallization temperature decreases is that the larger the supercooling, the larger the difference between the free energy of the supercooled liquid and the free energy of the crystal.⁵

The liquidus temperature is a temperature at which the free energy of the supercooled liquid is equal to the free energy of the crystal. This temperature is where the calorific value becomes zero by a linear function of the crystallization temperature and the calorific value, as seen in Fig. 9. In the case of mold powder B, 20 plots of crystallization temperature over

1,090°C showed a high correlation between the crystallization temperature and the heat flow. The crystallization temperature of B where the linear equation at heat flow goes to zero was 1,158°C. The average melting temperature of powder B was 1,173°C, which was found using the endpoint of the endothermic during heating. There was a 15°C difference between the crystallization temperature and the melting temperature. In this study, a heating rate of 15°C/minute was used, and the cooling rate was 10°C/minute. It is assumed that the difference between the crystallization temperature and the melting temperature will be closer when these rates are decreased.

Supercooled Tendency — The slope of the relationship between the crystallization temperature and the heat flow of additional four medium-carbon steel mold powders other than mold powder B were investigated. Their chemistries are listed in Table 4. Fig. 10 shows the results.

Crystallization temperature of mold powders C, D, E and F were measured several times, and there was variation observed in each sample just as with mold powder B. There was a difference in the slope of regression line between the different mold powder samples.

The steeper the slope of regression line, the larger the heat flow is by small supercooling. In other words, a mold powder that has a steeper slope will tend to crystallize more. The mold powder sample F has a high probability of having a crystallization temperature less than 1,000°C. This suggests that mold powder F has characteristics that lead to supercooling instead of crystallizing.

Crystallization in the slag film is needed to gain softer heat removal in the mold for prevention of cracking on peritectic and medium-carbon steel grade casting. A suitable mold powder for peritectic and medium-carbon steel grades has a short time range of supercooling, fast crystallization rate and has a larger exothermic content at crystallization when it is below the liquidus temperature. Conversely, a mold powder such as sample F, which tends to be supercooled easily, is not suitable for the grades due to lower nucleation/crystallization.

The crystallization properties of mold powders can be evaluated by measuring the crystallization temperature in conditions where supercooling is likely using the methods in this study. This will help determine if a mold powder is suitable for peritectic and medium-carbon steel grades.

Conclusions

An evaluation of crystallization properties of 93 mold powders was conducted by measuring recrystallization temperature, melting temperature and crystallization temperature. This was performed by heating from solid glass to molten slag, and cooling from melted slag to solid using DTA.

A good correlation between the recrystallization temperature and the viscosity when heating from solid glass was found. Lower-viscosity mold powders had lower recrystallization temperatures. Mold powders with higher CaO/SiO₂ were more likely to show both higher recrystallization (on heating solid) and higher crystallization (on cooling liquid).

When using a fast cooling rate on several samples, the crystallization when cooling from glass melt was quite variable. Crystals were not grown enough at temperature near the liquidus, which means low

supercooling. Crystals were also more easily grown at temperatures with more supercooling. There was a correlation between a degree of supercooling and exothermic amount. A mold powder with a low degree of supercooling and a high exothermic amount during crystallization is desired for prevention of cracks on the steel during casting.

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This paper was presented at AISTech 2019 — The Iron & Steel Technology Conference and Exposition, Pittsburgh, Pa., USA, and published in the Conference Proceedings.

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At AISTech 2019, two of AIST's young professionals, Karim Alshurafa of SMS group Inc. and Lauren Keating of Songer Services Inc., had the opportunity to interview prominent AIST members. These oral histories are scheduled for release in 2020:

- Dale Heinz, ArcelorMittal Burns Harbor. Interviewed by Karim Alshurafa.
- Sara Hornby, Global Strategic Solutions Inc. Interviewed by Lauren Keating.
- Harriet Dutka, SANGRAF International. Interviewed by Lauren Keating.
- Michael Stelbisky, Tallman Technologies Inc. Interviewed by Karim Alshurafa.

The following oral histories are also available on the webpage:

- David Matlock, Colorado School of Mines. Interviewed by Ginny Judge, Colorado School of Mines.
- Ted Lyon, Hatch Associates Consultants Inc. Interviewed by Jennifer Emling, AIST.
- Joe Poveromo, RMI Global Consulting. Interviewed by Amanda Blyth, AIST.
- Charlie Totten (deceased), T&M Equipment. Interviewed by Kurt Edwards, AIST.
- Harry Paxton, Carnegie Mellon University. Interviewed by Michele Lawrie-Munro, AIME.

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