

SHINAGAWA TECHNICAL REPORT

モールドパウダーの熔融性状評価方法の 開発と形状の影響

Development of New Mold Powder Melting Test
and Investigation on the Effects of the Product
Physical Form

伊 藤 純 哉
Junya ITO

山 崎 聡
Satoshi YAMASAKI



報文／REPORT

モールドパウダーの溶融性状評価方法の開発と形状の影響

Development of New Mold Powder Melting Test and Investigation on the Effects of the Product Physical Form

伊 藤 純 哉^{*1} 山 崎 聡^{*2}
Junya Ito Satoshi YAMASAKI

要 旨

鋼の連続 casting に適用されるモールドパウダーは溶鋼から加熱されて溶融し消費される。モールドパウダーは水冷モールド内において溶鋼からの加熱と冷却を同時に受けることから、溶融特性が適合しない場合はモールド壁面にスラグベアと呼ばれる焼結から半溶融状態の塊が固着し、操業や鋼品質に悪影響を及ぼす。その判定のために新たに実機状況を模擬したスラグベア評価方法を開発し、生成挙動におよぼすモールドパウダー形状の調査を行った。結果、粉末形状と内部に気孔を持つ中空スプレー顆粒は低い生成能を示したが、内部に気孔を持たない攪拌凝集顆粒は生成量と生成速度が明確に大きくなった。

Abstract

The mold powder used in continuous casting of the steel is melted by heat provided from the molten steel. At the same time there is a counteracting cooling effect from the water-cooled mold. If the mold powder melting behavior is inappropriate, excessive formation of “slag roping” can occur. This can adversely affect the operation stability as well as the steel quality. In order to facilitate development of improved mold powders, a new evaluation test method for predicting slag roping, which simulates the actual condition, has been developed. This new test has then been successfully used to determine the influence of mold powder physical form on the tendency to form rope. The results showed that the fine powder type and hollow spray dried granules type showed lower formation tendency, while agglomerated granules (without a porous core) showed a much greater tendency to exhibit excessive roping.

1. 緒言

鋼の連続 casting 用モールドパウダーはモールド内で溶鋼上に添加され、溶鋼から熱を受けて溶融し、モールドと凝固シエルの間に流入して消費される。そのプロセスにおいて、①溶鋼の再酸化防止、②溶鋼表面の保温作用、③溶鋼中から浮上してきた脱酸生成物等の吸収、④モールドと凝固シエルの潤滑作用、⑤凝固シエルからモールドへの抜熱制御の役割を果たし、連続 casting の操業安定性と鋼の品質向

1. Introduction

Mold powder for continuous casting of steel is added onto the molten steel surface in the mold, and melts by absorbing heat from the molten steel. The molten mold powder slag is then consumed by flowing into the gap between the mold wall and the solidified steel shell. In the process, mold powder performs the following functions: 1) Protection of the molten steel surface from oxidation, 2) Thermal insulation of the surface of the molten steel,

^{*1} 技術研究所 第3研究部 第2研究室 室長 Chief Manager, Mold Powder R&D Sec., Research Dept. No.3, Research Center

^{*2} 技術研究所 第3研究部 第2研究室 Mold Powder R&D Sec., Research Dept. No.3, Research Center

上に大きく貢献する。

したがって、粉末形状もしくは顆粒形状のモールドパウダーが加熱され、熔融スラグ層を形成する段階は重要であり、適正に保たれることにより安定操業が達成される。しかしながら、熔融挙動が悪化し熔融遅延や粗大な塊などが生成した場合は、保温性の低下、熔融スラグ層厚みの不足などが発生し、操業ならびに鋼品質の悪化を引き起こす^{1,2)}。特に、溶鋼表面からモールドパウダー層にかけてモールド銅板に付着したスラグベアと呼ばれる粗大な塊が発生し、悪影響を及ぼすことが知られている。Fig.1にスラグベア断面外観写真と各部分の名称を示す³⁾。スラグベアは地域や製鉄所間でも異なる名称で呼ばれる場合が多く、他にスラグリム、スラグロープ(ノロヒモ)、スラグリング、スラグブリッジ等と呼称されている。スラグベアという日本固有の名称は過去に日本国内モールドパウダーメーカーの技術者が命名したとの記録もある⁴⁾。本報告中では便宜的にスラグベアで統一するが、“ベア”に対応する明確な英単語が存在しないことから、英語表記と図表中は“Slag Roping”とする。スラグベアはいろいろな名称が存在しているが、いずれもモールド壁に生成した「焼結部分や半熔融部分」、および熔融後に凝固したスラグ部分「スラグリム」を合わせたものを指している点は共通である。

モールドパウダーは水冷モールド内の狭い範囲で冷却と加熱に曝され、加えてモールドオシレーションや湯面変動など、ダイナミックな要素も加わることから生成挙動が複

3) Absorption of non-metallic inclusions that floats to the surface of the molten steel, 4) Lubrication between the mold and the solidified shell, 5) Heat removal control between the mold and steel shell. In these ways, the mold powder greatly contributes to the operational stability and the improvement of steel quality.

Regardless of its form, either fine powder or granule, stable operation can only be achieved when a proper molten slag layer is formed. If the slag layer is insufficient, it could cause severe operational issues and/or poor steel quality due to lack of lubrication, poor thermal insulation, etc.^{1,2)}. One prime example of this is the excessive formation of roping at the steel meniscus, which is a common problem that adversely affects the casting operation. Fig. 1 shows the photograph and schematic of the cross section of a slag roping sample and identifies each part³⁾. Slag roping can be referred to by different names. For example, slag rim, slag ring, slag bridge, slag bear, etc.⁴⁾. In this report, “slag roping” is used for convenience. Although slag roping has various names, all refer to a combination of a “sintering part”, “partially melted part”, and “slag rim”. The slag rim is the solidified slag against the mold wall after fully melting.

Mold powder is exposed to a complex dynamic in which both cooling and heating occurs in a narrow space in the mold. At the same time, mold oscillation

Development of new mold powder melting test and investigation on the effects of the product physical form

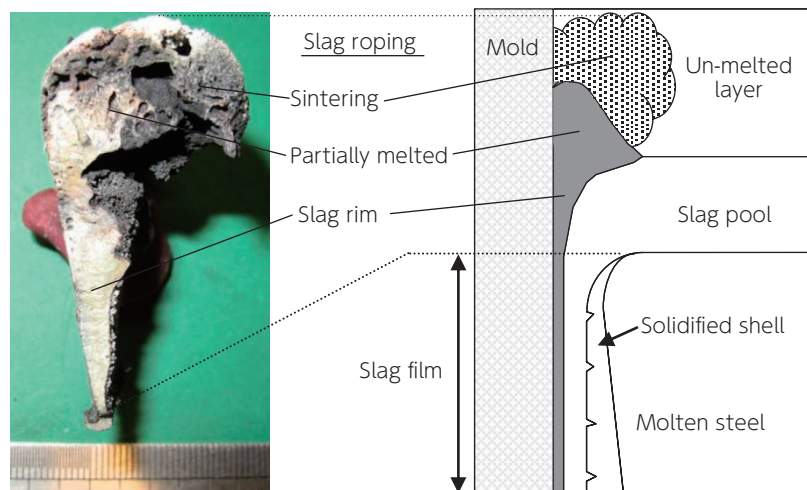


Fig. 1 Slag roping sample.³⁾

雑であり、実験によって再現することが難しい。したがって、認証されたスラグベア生成挙動の評価方法は存在せず、技術報告例も解明において十分とは言えない^{3,5,6)}。また、スラグベアにおよぼすモールドパウダー形状の影響は明確に解明されておらず、業界内においても齟齬が少ない。そこで、本検討では、スラグベアの評価方法を新たに開発し実用化させ、さらに、その評価方法を用いてモールドパウダー形状の影響を調査した。

2. スラグベアについて

2.1 スラグベアの発生メカニズム

スラグベア生成挙動について簡潔に説明する。モールドパウダーの溶融過程は、例えばFig.2に示すように凝集顆粒の溶融進行が中野らによって調査され報告されている²⁾。すなわち、第Ⅰ段階では粉体層の温度が上昇、第Ⅱ段階はカーボンの燃焼および原料基材同士の部分的な接触による焼結反応の開始、第Ⅲ段階は脱炭および焼結反応のさらなる進行、第Ⅳ段階は基材は脱炭状態となり、溶融パウダー粒子の凝集体が進む。この溶融過程、特に第ⅡからⅣ段階において、モールド銅板への接触、追加モールドパウダーとの接触、湯面変動などにより急冷却を受けると、十分に熱量を保持していない液相部分が固化、またはその固化し

and mold level fluctuations occur. This makes it difficult to simulate the conditions in the laboratory because these variable effects occur simultaneously. Thus, there was no previously available reliable method for evaluating and predicting the slag roping generation behavior^{3,5,6)}. Consequently, actual casting operation has been relied on to determine whether the powder is behaving properly without roping. A far from ideal situation. In addition, the influence of the morphology of the mold powder (powder vs. granular, etc.) on the slag roping had not been clarified, with no consensus in the steel making industry. In this study, a new test method to evaluate slag roping was developed and it has then been used to compare the effect of mold powder morphology on this phenomenon. Fine powders and different kinds of granules were investigated using this new evaluation tool.

2. Slag Roping

2.1 Mechanism of slag roping formation

An example of the slag rope formation is described for agglomerated (solid) granules in Fig. 2, where the melting progress of the agglomerated granules has been investigated and reported by Nakano et al.²⁾. In the first step of melting, the temperature of

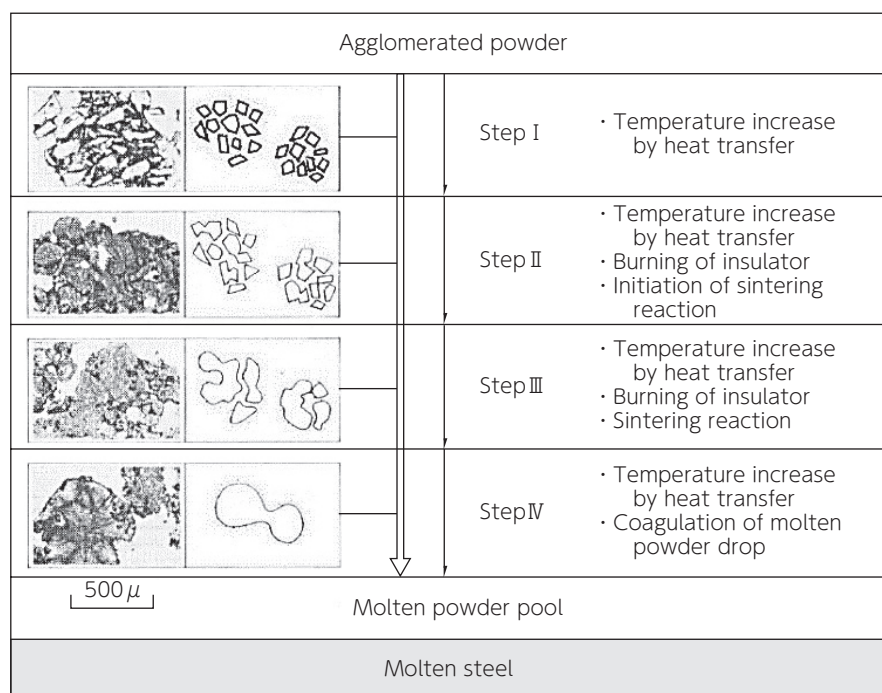


Fig. 2 Schematic model of melting process of agglomerated granules mold powder.²⁾

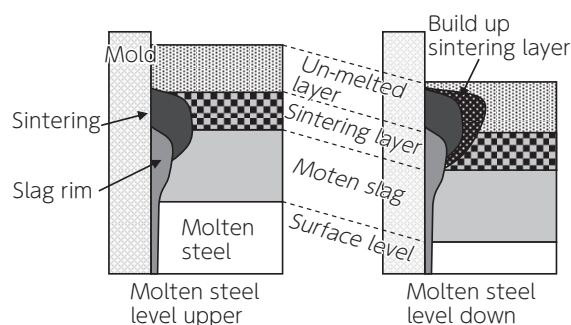


Fig. 3 Influence of mold level fluctuation on slag roping build up.

た液相部分が未熔融原料同士を融着させて焼結塊を生成させる。これがモールド近傍で発生し、モールド壁に固着した部分がスラグベアとなる。

モールド内の溶鋼流動もスラグベア生成に影響をおよぼす。Fig.3に湯面変動によるスラグベア成長イメージを示す。浸漬ノズルのデザインや溶鋼湯面制御が不適合な casting においてはモールド湯面レベル変動が大きくなり、溶鋼湯面下降時にはスラグベアの溶鋼側表面に未熔融層や焼結層が接触して成長しやすい。

さらに、高Al鋼や高Ti鋼など溶鋼成分によりモールドパウダーの組成や凝固温度などの特性が大きく変化する場合はスラグリム部の生成が大きくなる⁶⁾。

また、金属発熱を有するスタートパウダーと本体パウダーの混合時において、金属の酸化反応が抑制されて成分が不均一化し、スラグベア生成する場合もある。

2. 2 鑄造におよぼすスラグベアの影響と対策

スラグベアは、モールド銅板と鑄片間隙への熔融スラグの流入を阻害し、潤滑不足や不均一なスラグ流入を発生させ、拘束性ブレイクアウトや鑄片表面品質の悪化を引き起こす^{1,2)}。さらに、スラグベア自体が鑄片に取り込まれた場合、その部分は局所的に抜熱抵抗として作用するため凝固シェル厚みが不足し、穴あき性ブレイクアウトを発生させる⁷⁾。また、スラグベア除去作業による操業性や鑄片割れなどの品質悪化も懸念される²⁾。

スラグベアの低減には、カーボン原料の増量、熔融温度区間の短縮や凝固温度の低下などが一般的に適用される^{3,5)}。しかしながら、薄スラブやビレットなどの高速鑄造や高合金鋼種の鑄造においては未だ課題となっている場合が少なくない。

the un-melted mold powder layer increases. In the second step the carbon starts to burn off and the result is that the other raw materials (calcium silicates and fluxes) start to sinter. Next, in step three further decarburization occurs and the sintering reactions are further developed. In the fourth step, we see complete decarburization of the raw materials and the formation of a homogeneous liquid slag. In this melting process, particularly from the steps II to IV, the liquid phase portion can resolidify if there is insufficient heat in the system. Critical factors include heat removal rate into the mold, the amount and timing of fresh mold powder additions, as well as mold level fluctuation. The mixture of the solidified part along with semi melted and fully melted phases can form chunks. In this case, the portion in contact with the mold wall becomes slag roping.

Molten steel flow in the mold also affects to the slag roping formation. Fig. 3 illustrates development of slag roping growth caused by fluctuating molten steel surface. When the mold level fluctuation becomes severe it may result in a mixing of un-melted layer and/or sintered layer causing unwanted agglomerates to form. Severe mold level fluctuation can be caused by incompatible Submerged Entry Nozzle (SEN) design for the casting, or SEN clogging. If this occurs when the steel level is dropping, a significant growth of roping will occur.

Certain chemical components such as Al or Ti in the steel can interact with the mold slag and greatly change the slag properties during casting, including composition and solidification temperature changes during casting. This may also significantly increase the tendency to form slag roping⁶⁾.

There is also a specific case where the slag roping is generated during the transition from the exothermic starter powder to the running mold powder. This can be from an inhomogeneous condition caused by the oxidation reaction of the metal.

2. 2 Effect of slag roping on casting and countermeasures

Slag roping can block the inflow of molten slag into the gap between the mold wall and the solidified steel shell. This can potentially result in insufficient lubrication and lead to a sticking type of breakout. It can also cause uneven slag inflow and decreased strand surface quality^{1,2)}. In addition, when the slag roping itself is entrapped into the cast strand, the

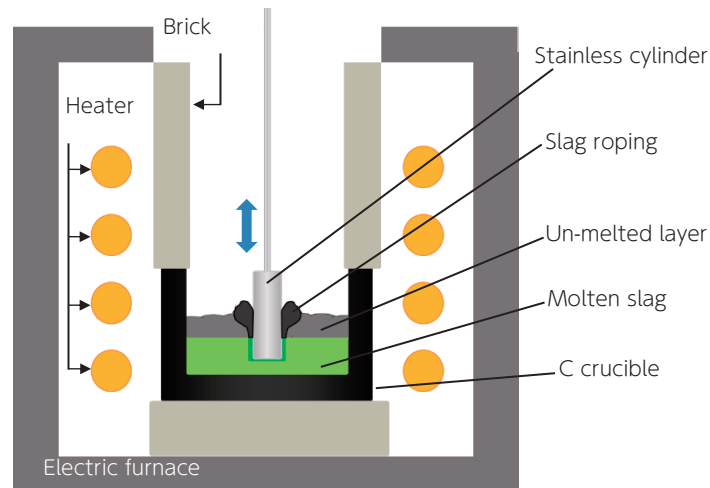


Fig. 4 Schematic image of slag roping simulator.

3. 実験

3. 1 実験方法

Fig.4に開発したスラグベア評価装置の概略図を示す。内部に冷却水路を有する直径25mm, 高さ60mmのステンレスブロックを箱型電気炉内においてカーボンつぼ(内径70mm×深さ55mm)内に作成した20mm厚の1330℃溶融スラグに10mm浸漬させる。ステンレスブロックは昇降装置で±4mmストローク, 198cpmの条件で上下動を付与させた。冷却水量は $600\text{ml}\cdot\text{min}^{-1}$ とした。すなわち, ステンレスブロックは水冷モールドを模擬している。ステンレスブロックが降下し溶融スラグ浴に10mm浸漬したと同時に未溶融モールドパウダーサンプル100gをカーボンつぼ上部より添加し, 1分間および2分間保持したのち, ステンレスパイプとその周囲に生成したスラグベアを同時に炉内より引き上げて空冷した。生成したスラグベアの重量測定およびノギスによる厚み測定を行った。厚みはステンレスブロック接触面から外周の最も厚い部分で測定を行い, 円周方向45°毎の間隔で1サンプルにつき8点測定し平均値とした。同様の試験を3回行い, その平均値を評価に用いた。さらに, 1分間保持のスラグベアサンプルをエポキシ樹脂に鋳込み, 切断および断面研磨後に光学顕微鏡およびSEM写真により組織観察を行った。

3. 2 試験サンプル

現在, 市販されているモールドパウダーは粉末形状の他に, 発塵抑制による作業環境改善を主目的としたスプレー

rope acts to reduce the thickness of the solidified shell and reduces heat removal which can result in a slag entrapment breakout⁷⁾. Steel quality defects such as strand surface cracking and/or operational problems due to slag roping removal are also of concern²⁾.

The simple ways to reduce slag roping, such as increase the addition of carbon raw materials, shorten the temperature range of melting, or decrease the solidification temperature^{3,5)}. However, there are still many problems in high-speed thin slab and billet casting, and on high-alloy steel grades casting.

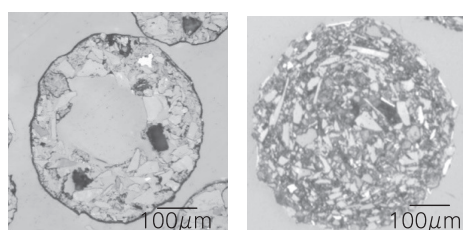
3. Experiment

3. 1 Newly developed experimental method

Fig. 4 shows a schematic of the newly developed slag roping evaluation test. A water-cooled stainless-steel cylinder (diameter 25 mm, height of 60 mm) is submerged into 1330 °C molten slag (20 mm thickness). This is contained in a carbon crucible (inner diameter 70 mm × depth 55 mm) in a box-type electric furnace with SiC heater. The stainless cylinder was oscillated ±4 mm stroke and 198 cpm by a motor. The cooled water flow rate was set at a constant $600\text{ml}\cdot\text{min}^{-1}$. Thus, the stainless-steel cylinder simulates a water-cooled mold as used in continuous casting. The stainless cylinder was submerged 10 mm into the molten mold powder slag bath. At the same time, 100 g of

Table 1 Chemical composition and properties in test samples

Shpe sample	Fine powder	Spray dried granules	Agglomerated granules
Chemical composition / mass%			
SiO ₂		32	
Al ₂ O ₃		4	
CaO		30	
MgO		3	
Na ₂ O		12	
F		8	
Total carbon		3	
CaO / SiO ₂	0.94		
Bulk density / g·cm ⁻³	0.8	0.9	1.1
Angle of repose / degree	60	29	37



Spray dried granules Agglomerated granules

Fig. 5 Cross section of each granule examples.

造粒法によるスプレー顆粒, 攪拌造粒法による凝集顆粒(中実)および押出成形法による柱状顆粒が実用化されている。Table 1に本検討に用いた各サンプルの組成, 形状および諸特性を示した。形状の影響を調査する本検討において, 粉末形状, スプレー顆粒および凝集顆粒をサンプルとして採用した。化学組成は主に低炭鋼種などに使用されている一般的な製品範囲における一例を採用した。各サンプルの化学組成および使用原料種はほぼ同等とし評価結果に影響を及ぼさないようにした。粉末形状は原料をハイスピードミキサーで混合し作成した。また, スプレー顆粒は原料混合粉末を水に溶かしてスラリーを作成し, スプレー噴霧造粒法によって, 凝集顆粒は原料混練時にバインダー水を添加する攪拌造粒法によってそれぞれ製造した。

Fig.5に各顆粒の断面顕微鏡写真を示す。スプレー顆粒は内部に気孔を持った中空形状となるが, 攪拌造粒には気孔はほぼ存在しなかった。

un-melted mold powder was added from the top of the carbon crucible and held for 1 minute and 2 minutes. The stainless cylinder and the slag roping generated around it were simultaneously pulled up from the inside of the furnace and cooled to room temperature. Weight and thickness of the slag roping were measured for each test. The thickness was measured at the thickest position of the outer periphery from the stainless steel cylinder contact surface, and the average value was measured at 8 points per sample at intervals of every 45° in the circumferential direction. Each test was performed in triplicate, and the mean values were used for evaluation. In addition, a slag roping sample kept for 1 min was cast into the epoxy resin, and structure observations were performed by optical microscopy and SEM photography after cutting cross sectionally and polishing.

3. 2 Test samples

From a technical viewpoint, fine mold powder works very well. However, this type of mold powder can be very dusty and so for environmental reasons, granulated types have gained popularity. Now granulated types constitute the majority of the market. Spherical spray dried granules (hollow spheres) made by spray drying, agglomerated granules (solid) made by the stirring granulation method, and extruded granules (solid) by the extrusion method have been put into practical use. Table 1 shows the composition, shape, and various characteristics of each type used in this study. Fine powder, spray dried granules, and agglomerated granules were used as samples in this study to investigate the effect of morphology. For the chemical composition, a typical example of a product mainly used for low carbon steel grade was selected. The chemical composition and raw materials used for each sample were approximately equivalent to each other so as not to affect the evaluation results. The fine powder had been prepared by mixing raw materials with a high-speed mixer. The spray granules sample had been prepared by creating a homogenous water solid slurry and spray drying. The agglomerated granules was produced by a stirring granulation method in which a binder/water mix was added to blended raw material in a mixing and then drying process.

Fig. 5 shows a cross sectional micrograph of both

3. 3 実験結果

3. 3. 1 スラグベア外観および断面

Fig.6に採取されたスラグベアサンプルの外観写真を示す。サンプルは上部より、焼結層、半熔融層および完全熔融部が付着したスラグフィルム部から構成されていた。粉末形状とスプレー顆粒形状の焼結部分は小さかったが、凝集顆粒は大きなスラグベア生成が認められた。

Fig.7にステンレスブロック浸漬1分後に採取された各スラグベアの断面顕微鏡写真を示す。さらに下段にはSEM

types of granules. Spray dried granules had a hollow sphere shape with pores on the inside. Pores were almost absent in the agglomerated granules.

3. 3 Experimental results

3. 3. 1 Appearance and cross section of slag roping

Fig.6 shows photographs of the slag roping samples taken from the test. It can be seen that the samples consist of a sintered layer, a partially melted layer and a slag film layer which was solidified from what was the fully molten portion in the test.



Fig. 6 Appearance of slag roping samples.

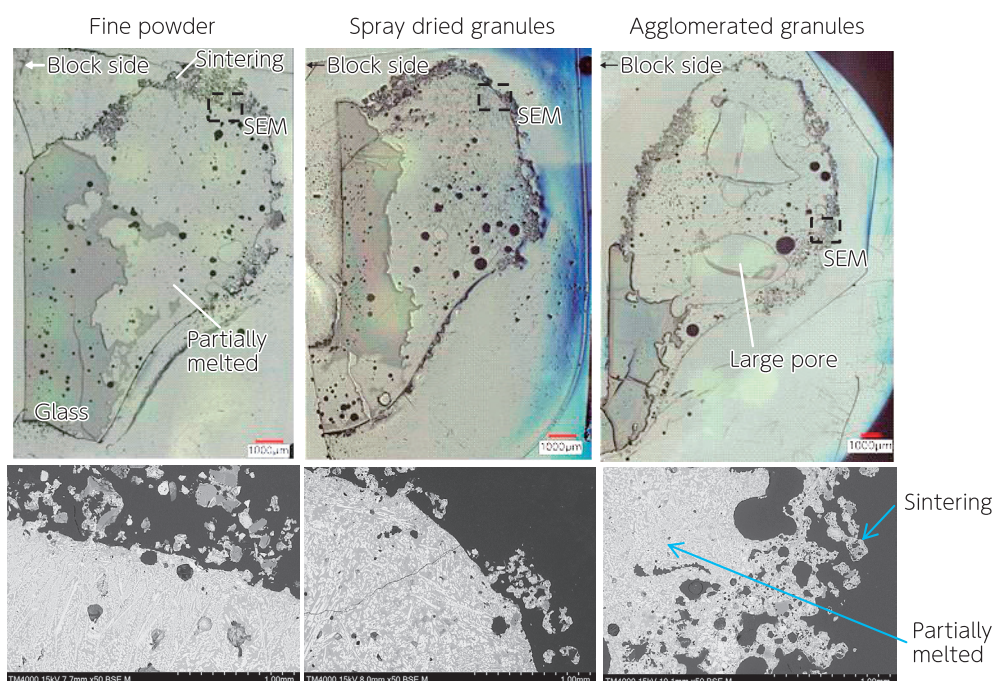


Fig. 7 Upper: Cross section texture of slag roping, Lower: Enlarged part by SEM.

拡大写真を示す。いずれのサンプルもステンレスブロック側にガラス相が認められ、その外側に半溶融層、さらに上部や外側に未溶融原料粒を含む焼結層が形成されていた。焼結層はある程度の原料粒が形状を維持し、半溶融層の外側に付着するように生成していた。半溶融層はSEM拡大写真から、主に針状の結晶粒とその結晶粒界から構成されていた。

粉末形状とスプレー顆粒はほぼ同等の焼結層や半溶融層厚みであった。一方、凝集顆粒はこれらの生成量が大きくなった。さらに、上部方向への大きな成長が認められた。

SEM拡大写真より、粉末形状およびスプレー顆粒は半溶融層と焼結層間に比較的明確に境界が認められたが、凝集顆粒は半溶融部と焼結層間が混在しており、その境界が不明確であった。加えて、半溶融層内部には4000-6000 μm 程度の大きな気孔の生成も認められた。

3. 3. 2 スラグベア生成量

Fig.8にスラグベアサンプルの平均厚み結果 ($n=3$ 平均) を示す。厚み測定結果は最大 $\pm 1\text{mm}$ 以下のバラツキが認められた。スラグベア生成厚みは1分後では粉末形状とスプレー顆粒形状ではほぼ同等であったが、凝集顆粒ではやや厚く生成した。2分後では粉末形状の厚みが薄く、続いてスプレー顆粒、凝集顆粒の順に厚くなった。

Fig.9に平均重量結果 ($n=3$ 平均) を示す。重量測定結果は1分間浸漬で最大 $\pm 5.1\text{g}$ 、2分間浸漬で最大 $\pm 9.4\text{g}$ のバラツキが認められた。粉末形状とスプレー顆粒は概ね同等の成長を示したが、凝集顆粒は重量成長が大きくなる傾向が認められ、特に2分間においては増加量が顕著に大きくなった。

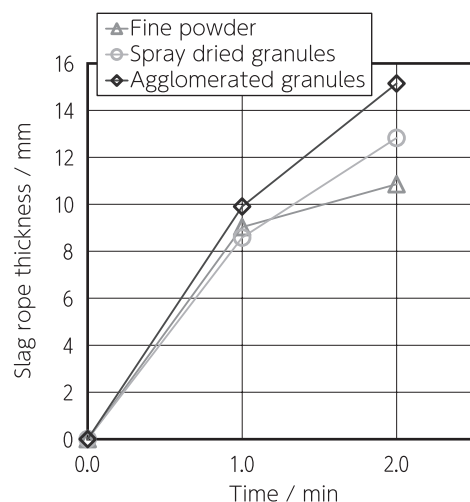


Fig. 8 Slag roping thickness.

Although the sintered parts of fine powder and spray dried granules were small, leading to less tendency to rope, the agglomerated granules showed much more sintering which is expected to lead to a large amount slag roping.

Fig. 7 shows a cross sectional micrograph of each slag roping sample taken 1 minute after stainless steel cylinder had been submerged. Along with this is a SEM photograph showing a magnified view at the bottom of each. In all cases a glass phase was observed on the stainless cylinder side. The partially melted layer was formed outside that, and a further sintered layer containing un-melted raw materials was formed on the top or outside of the samples. The results indicated that the sintered layer was formed with a number of raw materials maintaining their shape, and their were adhered to the outside of the partially melted layer that. It was shown in the SEM photographs that the partially melted layers were mainly composed of needle shaped grains and grain boundaries.

Fine powder and spray dried granules had almost equivalent sintered layer and partially melted layer thickness. On the other hand, the agglomerated granules produced a significantly larger amount of these and a large growth toward to the upper direction was observed.

SEM photographs showed that both the fine powder and the spray dried granules had relatively clear boundaries between the partially melted layer and the sintered layer. However, the agglomerated granules had a mixture between the partially melted layer and the sintered layer and their boundaries were unclear. In addition, pores as large as 4000-6000 μm were observed inside the partially melted layer.

3. 3. 2 Slag roping thickness

Fig. 8 shows the average thickness of the slag roping sample ($n=3$ average). Differences in measured depth were less than maximum $\pm 1\text{mm}$. Slag roping sample thickness was almost equivalent in fine powder and spray dried granules form after 1 min, but it was slightly thicker in agglomerated granules sample. After 2 min, the thickness of the fine powder rope was the least with the spray dried granules slightly more. The agglomerated granules again was the most prone to roping.

Fig. 9 shows the average weight results ($n=3$

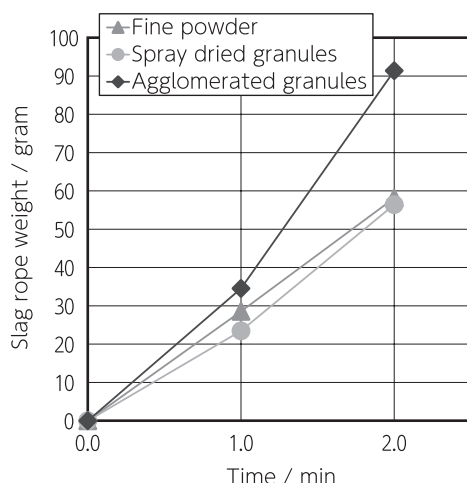


Fig. 9 Slag roping weight.

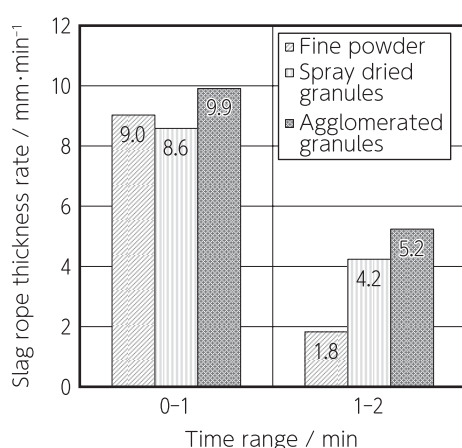


Fig. 10 Slag roping thickness rate.

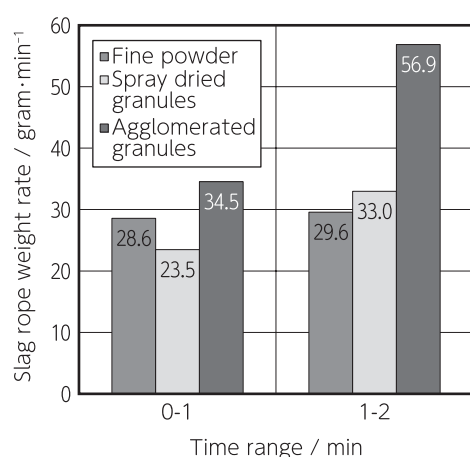


Fig. 11 Slag roping weight rate.

3. 3. 3 スラグベア生成速度

Fig.10にFig.8より求めたスラグベアサンプルの各時間区間における水平厚み方向の平均生成速度を示す (n=3

average). Data showed that maximum ± 5.1 g range for 1 min submerged and maximum ± 9.4 g range for 2 min respectively. The fine powder and the spray dried granules showed generally comparable growth, while agglomerated granules showed a greater tendency to have an increase in weight growth, especially in the 2 min sample where the increase was considerable.

3. 3. 3 Slag roping formation rate

Fig. 10 shows the average formation rate in the horizontal thickness direction in each time section of the slag roping sample calculated from the data shown in Fig. 8 (n=3 average). The formation rate in the thickness direction of slag roping was $9.0 \text{ mm} \cdot \text{min}^{-1}$ to 1 minute after being submerged and dropped to $1.8 \text{ mm} \cdot \text{min}^{-1}$ after 2 minutes, indicating that the growth rate decreased sharply with time. When the fine powder and granules were compared, they were almost equivalent in the 1 min test, but there was a tendency that granule shapes growth is significantly lower after some time.

Similarly, Fig. 11 shows the increase rate of the weight determined from Fig. 9 (n=3 average). The fine powder and the spray dried granule shape were almost the same. The agglomerated granules showed a significantly higher rate of increase from 1 min to 2 min after being submerged.

4. Discussion

4. 1 Slag roping evaluation test.

The slag roping samples obtained by the new slag roping evaluation test could identify the constituent parts, namely the partially sintered part, the partly melted layer, and the slag rim part. These parts are the same as observed in roping samples collected from the actual casting as shown in Fig. 1. Thus, it was recognized that this test method can be used to evaluate the roping tendency and formation rate in the design of mold powders. However, since this test doesn't involve all the effects of actual casting conditions, for example, mold level fluctuation, it is also likely that there may be some cases that will show different results from the actual condition.

4. 2 Effect of mold powder morphology on slag roping formation

1) Roping formation behavior in fine powder and granules

From the results shown in Fig. 8 to Fig. 11, the slag

平均)。スラグベア厚み方向の生成速度は粉末形状では浸漬後から1分間では $9.0\text{mm}\cdot\text{min}^{-1}$ からその後1分間では $1.8\text{mm}\cdot\text{min}^{-1}$ であり、成長速度が急激に低下した。粉末形状と顆粒形状を比較すると、1分まではほぼ同等であったが、顆粒形状のみ時間経過すると成長しやすい傾向が認められた。

Fig.11にFig.9より求めた重量の増加速度を示す($n=3$ 平均)。粉末形状とスプレー顆粒形状はほぼ同等であり、凝集顆粒は浸漬後1分から2分間で高い増加速度を示した。

4. 考察

4.1 スラグベア評価試験について

開発したスラグベア評価試験によって得られたスラグベアサンプルは、Fig.1に示すような実機から採取されたスラグベアに認められる焼結部、半熔融層およびスラグリム部が再現されていた。したがって、大小傾向や生成速度などの評価に適用可能であることが判明した。しかしながら、本試験は湯面変動などの铸造状況の影響全てが網羅できていないため、実機状況と生成挙動が異なることも想定される。

4.2 スラグベア生成におよぼすモールドパウダー形状特性の影響

1) 粉末形状と顆粒形状の生成挙動について

Fig.8からFig.11に示した結果より、粉末形状とスプレー顆粒形状のスラグベア生成重量は同等であったが、スプレー顆粒は粉末形状よりもやや厚み方向に成長しやすいことがわかった。一方、凝集顆粒は生成量や成長速度が粉末形状よりも上昇傾向が明らかであった。粉末形状は粒径が小さく、カーボン原料によってカーボン以外の基材原料が被覆されている状態なので、局所的な先行溶融部分が少なく、比較的にスラグベアが生成しにくいと考えられる。また、Fig.10の結果から、粉末形状は顆粒形状と比較して一定厚み生成後は厚く成長しにくい特徴も認められた。

2) スプレー顆粒と凝集顆粒の生成挙動について

顆粒形状は粉末形状の溶融プロセスに加え、顆粒単位で考えると外部から内部に熱が伝わり溶融するプロセスもある。したがって、Fig.7の凝集顆粒におけるSEM写真結果が示したような顆粒外層部が先に溶融し、内部は未溶融である固液共存状態が発生しやすく、これがスラグベアの成長を促進していると考えられる。

Fig.8からFig.11に示した結果より、スプレー顆粒と凝集

roping weight of the fine powder and the spray dried granules were similar, with the spray dried granules found to be slightly easier to grow in the thickness direction than the fine powder. On the other hand, the agglomerated granules showed a significantly increased tendency to form rope in comparison to the fine powder. Since the fine powder consists of only small particle size raw materials and base materials coated by carbon raw materials, it is seen that only a small area of local premature melting portion develops, and therefore slag roping is less likely to form. Furthermore, from the results shown in Fig. 10, it was also observed that fine powder doesn't tend to grow the roping thicker compared to the granule shapes after the initial period.

2) The difference in slag roping formation behavior between the spray dried granules and the aggregated granules

In the granule mold powder melting, the outer layer part of granule melted first, and the inside of the granule is likely to have a mixture of solid and liquid as shown in SEM photograph in the agglomerated granules of Fig. 7. It is considered that this formation process accelerates the growth of slag roping

From the results shown in Fig. 8 to Fig. 11, it can be concluded that the slag roping is more likely to grow larger in the agglomerated form when compared to the spray dried granules.

Fig. 12 shows schematically the melting progress image of each type of granule. Since spray dried granules have a hollow center, the heating is more consistent which results in smoother melting. Thus, the slag roping formation is believed to be prevented due to the mass changing from liquid and solid quickly. On the other hand, the agglomerated granules, having no pores in the granule, has more time in the solid-liquid mixing state. The center of the granules, being denser, requires more heat to melt. Therefore, it is seen that agglomerated type granules have more tendency to show slag roping behavior when the liquid phase generated was cooled and solidified by direct contact with the additional fresh mold powder and/or in a situation where a large mold level fluctuation occurs.

Both the spray dried granules and the agglomerated granules showed the growth of the slag roping thickness with increases in submerged time in Fig. 8. However, when we look at the weight

顆粒を比較した場合、凝集顆粒の方がスラグベアが大きく成長しやすいと結論づけられる。

Fig.12に各顆粒の熔融進行イメージを示す。スプレー顆粒の特徴として内部に気孔を有することから、外層部が熔融を受けた場合でも内部は空気層であり、熔融が進行すると速やかに完全熔融状態となり粒が消失する。このため固液共存状態となり難く、スラグベア生成が抑制されると考えられる。一方、顆粒内部に気孔を持たない凝集顆粒は固液共存状態で存在する時間が長くなり、湯面変動や追加パウダー投入時の接触によって冷却を受けた時に生成した液相が凝固してスラグベアが助長されると考えられる。

Fig.8ではスプレー顆粒も凝集顆粒も時間経過とともにスラグベア厚みの成長が認められたが、Fig.9ではスプレー顆粒の重量上昇量は粉末形状と同程度となり、厚み挙動と相関がなかった。この理由は、Fig.7の結果から、凝集顆粒は上部方向に半熔融層が成長したことが挙げられる。スプレー顆粒は比較的球形に近く、安息角は 29° であったが、凝集顆粒は比較的角ばった部分も多く存在し、安息角も 37° と拡がり性に劣っていた。この結果より、凝集顆粒はステンレスブロックの上下動を受けてもブロック付近に厚く堆積した状態となり、上部方向に成長したと考えられる。

また、凝集顆粒の半熔融層内部には大きな空隙が生成した。融着の進行が速く、空気層を取り込んだ、またはモールドパウダーの揮発成分が残存したことが要因と考えられるが、今回の実験結果からは明らかにならなかった。

3) 顆粒形状におけるスラグベアの低減方向

上記の評価結果および考察から、顆粒形状におけるスラ

increase amount, the spray dried granules show similar behavior to the fine powder, as seen in Fig. 9. The reason for this is taken from Fig. 7 where it is observed that a partial melting layer of the agglomerated granules had grown toward upper side. The spray dried granules is relatively close to spherical shape, with an angle of repose of 29° . But the agglomerated granules, exhibiting a more angular morphology, (angle of repose was also 37°) which means it has a lower flowability. From this point, it is believed that the agglomerated granules did not flow away from the area of interest so easily and became stuck in the upper area near the stainless cylinder as it moves vertically.

In addition, large pores were observed inside the partially melting layer of the agglomerated granules. The reason has not been clearly identified; however it may be that the air was in the layer during the quick fusion process, and/or the volatile component of the mold powder raw materials created the pores.

3) Reduction of slag roping in granular shape

From the above evaluation of the results and considerations, it is believed that it is important to reduce the time range of mixing between the solid phase and the liquid phase as much as possible to prevent slag roping formation in granular type mold powders. Therefore, it is suggested that ideally smaller particle size, tighter size distribution, larger internal porosity, and spherical shape are all positive attributes for a uniform coverage in the mold.

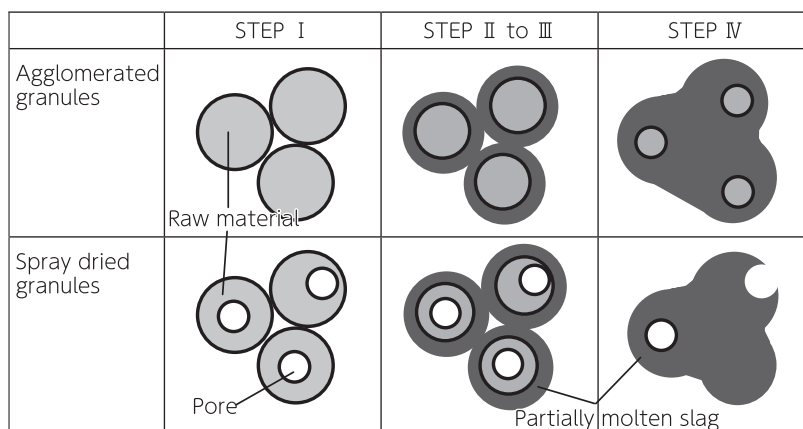


Fig. 12 Melting model comparison in granule mold powders.

グベア生成抑制の方向性は、モールドパウダーの熔融段階において原料の固相と熔融後の液相の共存する状態をできるだけ低減することが肝要である。すなわち、粒径を小さくする、粒度分布を小さくする、内部気孔率を上昇させる、顆粒形状を球形に近づけて均一厚み散布させる方向などが示唆された。

5. まとめ

スラグベアの評価方法を新たに開発し、モールドパウダー形状の影響を調査した結果、以下の事が判明した。

- 1) 水冷のステンレスパイプを用いたスラグベア生成挙動を評価させる方法を確認できた。
- 2) 同一組成において、粉末形状がスラグベア抑制に効果的であった。
- 3) スプレー顆粒のスラグベア生成能は粉末形状よりも厚み方向にやや成長しやすい。
- 4) 凝集顆粒は粉末形状やスプレー顆粒形状と比較してスラグベアの生成や成長が明確に大きかった。
- 5) 顆粒内部に気孔を有するスプレー顆粒はスラグベア低減に有効であり、ほぼ存在しない凝集顆粒は不利であると考えられる。
- 6) 顆粒形状におけるスラグベア生成抑制の方向性は、モールドパウダー未熔融層の固相と熔融後の液相の共存する状態を低減することが肝要である。

5. Summary

A new evaluation test method to predict slag roping has been developed. It has been successfully used to compare roping behavior of fine powders and different types of granules, with the following conclusions.

- 1) A method for evaluating the slag roping formation behavior by using water-cooled stainless cylinder has been developed.
- 2) For a given composition, fine mold powder shape had the least tendency to form rope.
- 3) The spray dried granules showed a slightly higher tendency to form rope and is slightly more likely to grow in the thickness direction than the fine powder shape.
- 4) The agglomerated granules showed a definite greater formation and growth tendency in slag roping compared to the fine powder shape and the spray dried granules shape.
- 5) The reason for the reduced tendency of roping in spray dried compared to agglomerated type lies in the pores in the former versus dense center in the latter causing a longer melting period with agglomerated granules.
- 6) It is especially important to reduce the time that the solid phase and liquid phases coexist to help prevent slag roping in the granule type mold powders.

References

- 1) T. Emi, H. Nakato, K. Suzuki, Y. Iida, T. Ueda: Tetsu-to-Hagane, **60**, 981, (1974).
- 2) T. Nakano, M. Fuji, K. Nagano, S. Mizoguchi, T. Yamamoto, K. Asano: Tetsu-to-Hagane, **67**, 1210, (1981).
- 3) I. Marschall, G. Xia, and N. Kölbl: BHM Berg-und Hüttenmännische Monatshefte, 163, 23, (2018).
- 4) The Iron and Steel Institute of Japan: History of Steel Continuous Casting Japan (1996).
- 5) I. Marschall, H. Harmuth : Proc. of the Scanmet III, Vol 2, p 419-425, (2008).
- 6) I. Marschall, N. Kölbl, H. Harmuth: Material Science & Technology 2010, 1591, (2010).
- 7) Y. Ito, T. Murai, Y. Miki : JFE Giho (Technical Reports in Japanese), No.38, 48, (2016).