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LIME-BASED SLAGFORMERS, REFINING & ALLOYING POWDERS, CASTING MOLD FLUXES IN IRON AND STEEL INDUSTRY

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中 文 摘 要

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利用喷枪和多孔塞进行惰性气体搅拌同时向钢包喷粉，生产潜力大、灵活性高、投资少，已经成为最实用的钢包冶金方法。据统计世界上几乎100%转炉钢厂和35%电炉车间均安装了喷粉设备。

本文简单总结了吹气和喷粉技术的决窍和设备方面最新成就。

吹气和喷粉过程动力学：熔体的搅拌方式对钢包内的流体动力学特征影响很大。图1比较了气体搅拌、机械搅拌和复合搅拌的效果。可见，气体搅拌提供了良好的渣—金和气—金传质条件。

在钢包冶金中，高杂质时渣相传质可能成为速度控制环节；而钢包处理后期的低杂质时金属相传质可能成为速度控制环节。文中计算了气体搅拌时气体流动速度与混合时间的关系（图2），从而得到提高流体循环速度的因素：气流速度高，压力低，熔池深度大，钢包直径和体积小。（图3）是1600℃钢水中Kolmogoroff涡流尺寸与搅拌强度和气流量的关系。可见，要获得10μm以下的涡流尺寸，搅拌强度要大于10^5W/t。钢包冶金中通常的涡流尺寸为40－50μm。

喷吹实践和设备发展：现代化喷粉站，每种粉剂都有单独的分配器，由PLC控制。另设喷枪进行气体搅拌。把两种粉剂分配器的软管相接并仔细调整气体压力就可以喷吹两种粉剂。完成顶渣制备、增碳、氧化、脱硫、夹杂物改善和分离等各种操作，操作程序为：惰性气体洗涤—焦炭—石灰—CaSi—石灰—惰性气体清洗。

用喷吹冶金进行铁水予处理：在过去的五年里日本就已广泛地应用喷吹冶金进行铁水予处理，进行炉外脱硅脱磷和脱硫。目前，铁水的炉外脱硫已经成为现代钢铁厂的基本冶炼过程。而喷吹石灰粉剂技术在提高脱硫效率降低硫含量方面显示了特别的优越性。图5为联合喷吹Mg－CaC_2和Mg－CaO时脱硫率及镁回收率与镁消耗量的关系。

钢水的脱硫：根据质量平衡导出了瞬时和永久性接触同时存在时渣的脱硫效率（$\Delta S/S_0$）。公式列出了脱硫速度（d[S]/dt）公式。图6和图7是喷粉和顶渣精炼两种情况下脱硫速度常数和实测硫的分配比。图8为喷吹CaO／CaF_2时脱硫的瞬时效率。

钢水中的添加钙：采用喂线技术和喷粉技术向钢水加钙各有优缺点，具体选哪种方法，取决于下列条件：钢质量生产计划，现有的钢包冶金设施和熔炼量的大小。

ON PNEUMATIC LADLE METALLURGY - KINETIC´S AND DEVELOPMENTS IN INJECTION TECHNOLOGY

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1. INTRODUCTION

Ladle metallurgy has become an indispensible part of steelmaking. Especially in combination with contineous casting. Also in refining and alloying of non-ferrous metals, ferroalloys and aluminium have ladle metallurgy processes been applied.

Along with the development of ladle metallurgy for production of ultra clean steels and for improving the efficiency and thereby the process economy the demands on all added materials have gradually increased. Every process step should be carried out quickly and without disturbing side reactions, pick up of H, O or N or heat losses. All consumables should thus have an optimum composition and particle size, be completly dry and not cause any environmental problems.

Inert gas stirring by lance and porous plug together with powder injection have become the most utilized ladle metallurgy processes. It is due to the great metallurgical potentials, the high flexibility and also due to the low investment cost. According to Wakayama /1/ nearly every second BOF shop and nearly 35% of the EAF shops have powder injection equipment today. The massive introduction of pretreatment of hot metal by lance injection in Japan in the 1980´s have also shown the ability of powder injection for real heavy duty usage.

The aim of this paper is to briefly review some areas of development of both know how and equipment in the field of gas and powder injection and the relation of that to added materials composition and size.

2. KINETIC CONSIDERATIONS IN GAS AND POWDER INJECTION

A large number of industrial and scientific papers have been published on gas and powder injection during the last 10 years in specialised conferencies /2,3/. "The Shenyang symposium on injection metallurgy and secondary refining of steel" in 1984 also included several such presentations.

Gas stirred melts can be characterised as systems with high surface turbulence, moderate melt circulation and low bottom turbulence and melt velocities. Inductive stirring on the other hand gives a more homogeneous flow with similar turbulence throughout the melt and with high melt velocities at the surface and at the bottom. This is illustrated in Fig. 1 /4,5/ together with combined stirring.

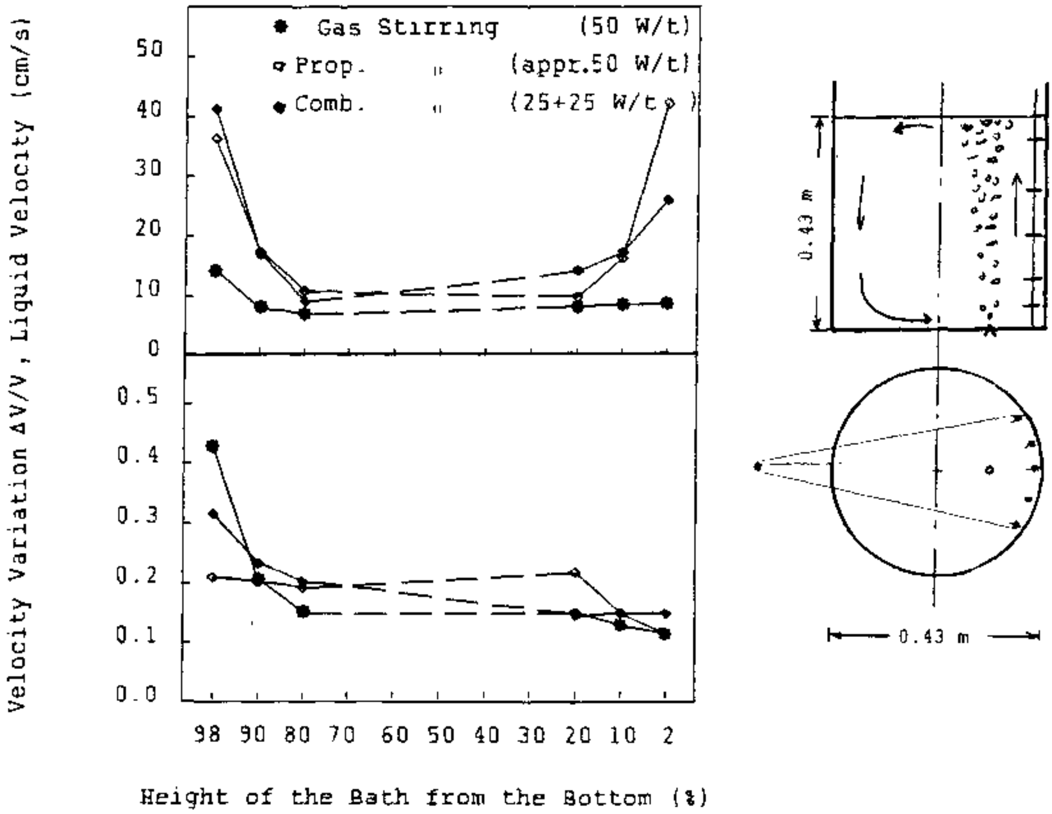

Fig. 1. Hot film annemometer measurements at the center line of a cylindric water model with a set of propellers simulating the inductive stirring.

Each data point in Fig. 1. shows the average of 150 measurements and the stirring power from the propeller stirring is defined such that it is equal to that of gas stirring when the mixing time is equal.

The turbulent surface by gas stirring provides very good conditions for slag/metal or gas(vacuum) /metal mass transfer. The mechanical stirring and inductive stirring with high bottom velocity and a relatively high bulk turbulence is suitable for dissolution of heavy scrap or alloys and extensive deoxidation. The calm surface by inductive stirring also provides suitable conditions for arc heating with short arc´s.

A combined stirring may create a comprehensive pattern without weak parts. It also allows a great flexibility by alternating from pure gas stirring to inductive stirring in the latter part of the treatment.

In ladle metallurgy systems a large number of part reactions,connected in series, take place. The slowest reaction control the total rate of reaction. Slag transport can be rate controlling at high impurity concentrations while metal phase transport can be rate controlling in the end of the treatment at low impurity levels.

In refining and alloying the following transport mechanism s are considered the most important /6,7/.

a) Bulk metal circulation flow rate.

b) Turbulent transfer to, or from, reaction boundary.

c) Diffusional transfer in micro areas.

The circulation flow rate can sometimes be rate controlling in powder injection. Especially in torpedos where secondary volumes are formed in the long vessel.

In a gas stirred ladle the mixing time , t_m, for 95% homogenisation, is a convinient concept. The circulation flow rate is directly proportional to the mixing time such that

$$t_m = 3 \cdot t_c \qquad (1)$$

where t_c is the circulation time.

According to Sano and Mori /8/ the stirring power in gas injection can be expressed,

$$\dot{\mathcal{E}} = \dot{V}_{GM} \cdot \rho_L \cdot g \cdot H_0 \qquad (2)$$

where $\dot{V}_{GM}$ is the gas flow rate at melt temperature and at a logaritmic mean pressure P_M, ρ_L the melt density, g gravitional constant and H_0 the melt depth. The mean pressure is defined,

$$P_M = P_1 - P_2 / \ln P_1/P_2 \qquad (3)$$

where $P_1 = P_2 + \rho_L \cdot g \cdot H_0$ and P_2 the atmospheric pressure.

A useful relation between the stirring power and mixing time based on a circulation model which agreed well with several measurement was also presented,

$$t_m = 100 \ ((D^2/H_0)^2/\dot{\mathcal{E}})^{0.337} \qquad (4)$$

Murthy and Szekely have also published a similar more general relation which also include an efficiency factor, η, of the power input,

$$t_m = ((80/\eta^{1/3})L^2/\dot{\mathcal{E}})^{1/3} \qquad (5)$$

By equating (4) and (5) the efficiency factor for gas stirring was found to be approximately 50%.

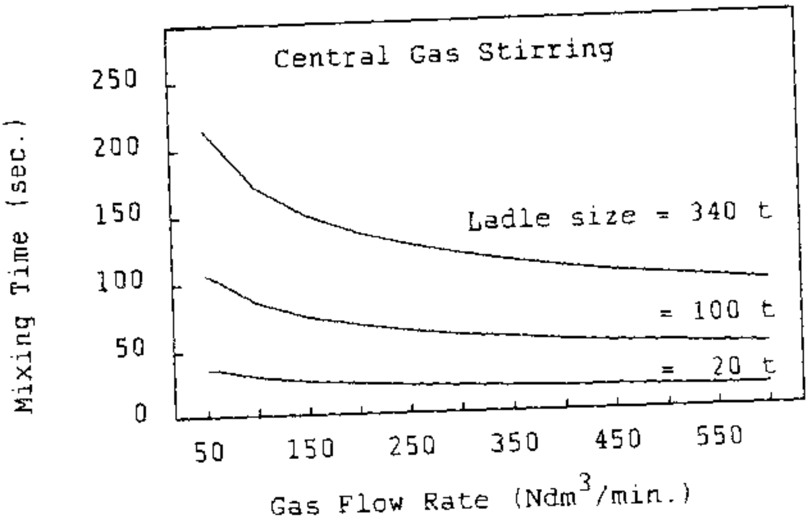

Fig. 2. Mixing times versus normal gas flow rates in ladles of 340, 100 and 20 tonnes and an assumed $D/H_0 = 1$.

Mixing times according to eqs (2), (3) and (4) are given in Fig. 2. At normal gas flow rates for gas rinsing the mixing time is around 2 minutes for 340 tonnes heat size, 1 minute for 100 tonnes heat size and below 30 seconds for 20 tonnes. The mixing time increases rapidly at very low gas flow rates. The corresponding circulation flow rate is for instance 170 tonnes/minute at 50 Ndm^3/minute gas flow rate and 340 tonnes/minute at 400 Ndm^3/minute in a 100 tonnes ladle.

From the eqs (1) - (5) it can be concluded that high circulation flow rate can be created by,

a) High gas flow rates.

b) Low atmospheric pressure.

c) High bath depth and small ladle diameter.

d) Small ladle size.

The turbulent mass transfer to or from dispersed solid particles, in the reaction zone, will depend on eddies in the immediate vicinity which are of the same size or smaller than the particles. Eddies larger than the particles will only move the particles /10/.

Emperical equation as below,

$$Sh = k_m \, d_p / D = K_1 + K_2 \cdot Re_p^{1/2} \cdot Sc^{1/3} \qquad (6)$$

can be adequate for the mass transfer. Re_p is the particle Reynold number ($d_p \cdot u_p/D$), Sc is the Schmidt number ν/D and K_1 respectively K_2 are constants which can have numbers equal to 0-2 and 0.6-1.1 respectively.

The smaller particle size and the higher relative velocity , u_p, the higher mass transfer rate.

Asai /11/ however quoted low temperature experiments /12/ which showed an optimum particle size at around 40-50 um. At both lower and higher particle diameters were the mass transfer rate lower.

The smallest efficient particle size can be found by comparison with Kolmogoroff´s isotropic eddy size.

$$\lambda = (\nu^3/\dot{\varepsilon})^{1/4} \qquad (7)$$

which show the size of the small eddies in a turbulent fluid.

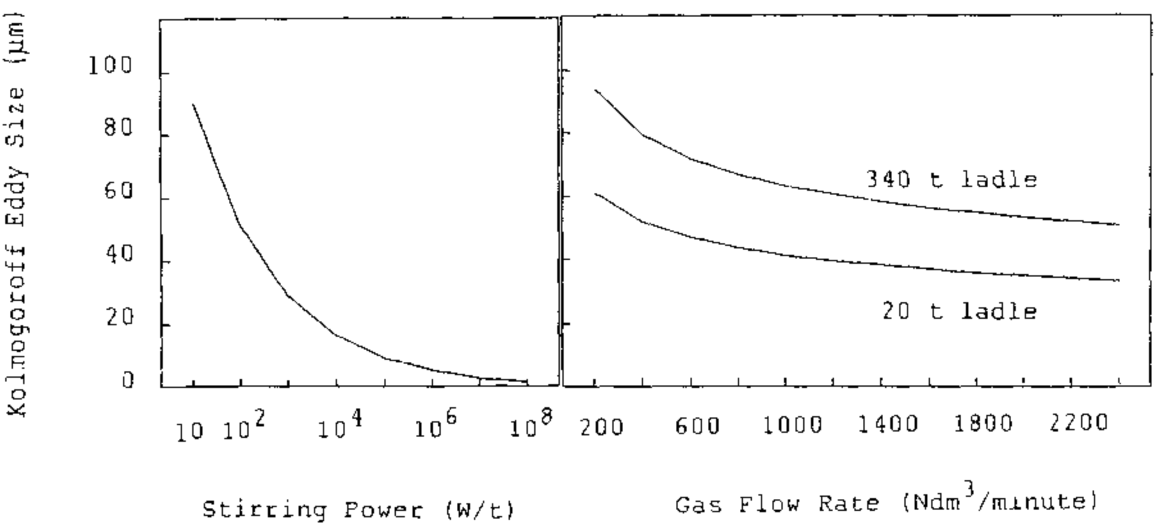

Fig. 3. Kolmogoroff´s eddy size versus stirring power and gas flow rate in liquid steel at 1600°C.

In Fig. 3. it can be seen that to obtain eddy sizes below for example 10 µm, stirring power larger than 10^5 W/tonne is necessary. Under normal gas and powder injection conditions in ladle metallurgy the eddy size is in the range of 40-50 µm.

For particles in stagnant melt conditions, boundary film diffusion with the particle radius as film thickness and the particle surface area as reaction area, takes place. This is a much slower process and correspond to,

$$Sh = 2 \qquad (8)$$

in eqn. (6) above.

When the particles which are injected becomes liquid the mass transfer increases and it may be described by Higbie's surface renewel theory,

$$k_m = 2(D/\pi \cdot t)^{1/2} \qquad (9)$$

where t is the contact time for the particle between each surface renewel,

$$t = d_p/u_p \qquad (10)$$

When a solid layer is formed on the surface through which diffusion must happen, the mass transfer becomes slow and the powder efficiency low. Such a rate eqn is described by Emi and Iida /6/.

3. DEVELOPMENT OF INJECTION PRACTISE AND EQUIPMENT

The recent development concerning injection technology was reviewed by Carlsson and Berg /13/ recently.

A modern injection station consist of one dispenser for each type of powder. The dispensers are controlled by a PLC and sequens injection of all the powders can be carried out automatically without lifting the lance. Gas stirring with a separate lance is also included in the sequence. Simultaneous injection of two powders can also be carried out by careful pressure regulation and connection of the two powder dispenser hoses near the lance.

By sequence injection with inert gas flushing-coke-lime-CaSi-lime-inert gas rinsing an efficient treatment including top slag preparation, recarburisation, deoxidation, desulphurisation, inclusion modification as well as inclusion separation by the powder injection and gas rinsing can be carried out within a 15 minute cycle.

Injection of a CaO/CaSi mixture or simultaneous injection of CaO and CaSi have also shown to be efficient ways to reduce the N-pick up during extensive desulphurisation and Ca treatment. A 50/50 mixture reduces the N-pick up with about 50% compared with injection of CaSi only.

Desulphurisation of hot metal by simultaneous injection of for instance Mg and CaO is a very flexible process by which the most economic mixture can be used in each case with consideration of hot metal temperature and starting respectively final sulphur concentrations.

Contineous change of the dispenser outlet nozzle diameter is another development which is under testing together with MEFOS in Sweden. By such arrangement can the powder flow rate be reduced during a desulphurisation course to improve the powder efficiency at low sulphur concentration.

A very interesting development in the field of injection technology is the use of very fine powders. There are many different conditions which can decide the most appropriate powder size range,.

a) Availability and price of the powder.

b) The behavior of the powder in the injection. equipment.

c) The influence on lance clogging.

d) Reaction mechanism´s in the liquid metal.

e) Environmental problems (dusting).

f) Absorption of humidity.

Dens phase flow in opposit to dilute phase flow has been utilized in pneumatic conveying of fine powders for many years. Such powders, as cement and flying ash can be conveyed smoothly at low gas velocities, 5-10 m/s, and thus at high solid loading ratios (kg powder/kg gas). Dens phase is not clearly defined but it is usually considered above a solid loading ratio of 25.

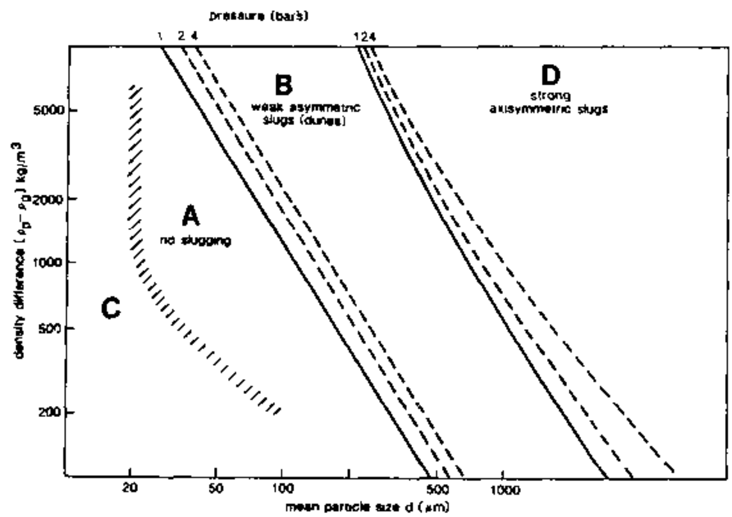

Fig. 4. Dixon´s slugging diagram for pneumatic conveying in a 2 inch pipe /14/.

Group A powders often have good air retention proporties and can be conveyed smoothly in dens phase. B and D can also be conveyed in dens phase but as slugs which makes the flow uneven and not suitable for injection in melts. Materials in group C are to fine and are likely to be cohesive.

Optimum powder mean size is 0.002-0.1 mm according to Fig. 4. depending on particle density but more important the air retention proporties.

Another important aspect is the powders tendency of arch formation in the dispenser under pressure. This is avoided by using free flowing powders usually obtained by a restricted amount of fines. This can not easily be quantified instead practical tests of the powder must be carried out.

The positiv influence of fine powders and high solid loadings on lance clogging have clearly been shown /15-17/. Irons /16/ suggest a model of uncoupled or coupled powder gas behavior which are promoting bubbling respectively jetting discharge outside the nozzle. The optimum mean particle size according to above model, agrees well with what was suggested in Fig. 4 group A materials.

The contact between the melt and the injected particles can depend on the discharge regime e.i. bubbling or jetting. Bubbling requires larger particles size for penetration than jetting. According to Hara /18/ and Narita /19/ is the critical particle size for trapping during injection of fine $CaCo_3$ (-0.1 mm) based mixtures <2 µm I injection alloying of liquid aluminium /20/ on the other hand was the critical particle size found to be around 20 µm.

The use of dens phase injection with low gas flow rate will increase the mixing time and thus decrease the melt circulation flow rate. If the gas consumption during injection of 120 kg powder/minute can be decreased from 1200 to 600 Ndm^3/minute the circulation flow rate is lowered from about 830 to 650 tonnes/minute, equal to 20% and the Kolmogoroff´s eddy size is increased from about 60 to 70 µm.

4. INJECTION FOR HOT METAL PRETREATMENT

Complete pretreatment of hot metal has been extensively applied in Japan during the last 5 years. It has been regarded as a major cost saving methode in integrated steel works. Today the major tonnage of hot metal from the large steel producers is pretreated. The hot metal is afterwards decarburised in combined-or top and bottom blowing converters with a low amount of slag.

The hot metal pretreatment in Japan considered of desiliconisation in the blast furnace runners, and after tapping when necessary, to <0.15% Si followed by simultaneous dephosphorisation and desulphurisation by lance injection of lime and iron ore based powders in the torpedo or ladle. The main benefits of pretreatment in Japan are considered to be,