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Wire Injection of Metallurgical Powders into Molten Metal

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The metals industry is expanding its use of powders contained in cored wire. Wire is being applied in iron and steelworks, in foundries and, to a lesser degree, in the non-ferrous field.

The principal use of cored wire is in the steel industry for calcium treatment and micro-alloying. Steelmakers are striving to improve methods in order to meet stringent specifications and improved quality assurance.

The tightening of environmental standards in industry has focused attention on wire injection as a technique that eliminates the handling hazards associated with powder.

Introduction

Major developments in steelmaking techniques have taken place in the past decade. One of the most significant changes has been the introduction of the ladle furnace, which has improved the control and direction of steelmaking operations.

The principal steelmaking unit, whether electric or oxygen blown, has been adapted for the efficient rapid melting of scrap and the conversion of liquid iron, while refining, alloying, and temperature adjustment are primarily carried out in the ladle furnace.

This secondary refining has resulted in the growth of cored-wire injection, which is an automated method of introducing metallurgical powders into molten metal.

Principles of Cored-wire Injection

Cored wire is manufactured by encapsulating graded powders in steel sheaths and packaging the wires in variable-sized coils. The coils are produced in sizes from 100 to 3000 kg, and wire diameters range from 3,0 to 18,0 mm. The smaller wires are favoured for use in moulds and tundishes, and for the small ladles in foundries.

Injection of the wires is carried out at either the ladle furnace or the ladle station by the use of specially designed machines (Figure 1). These feeders are equipped with pinch rolls and with intermediate guides and supports designed to feed a range of wire sizes. Pressure is exerted by pneumatic or hydraulic cylinders. The pinch rolls are driven and, for 13 mm wires, the motor sizes would be 10 to 15 kW. The total length of wire is measured for each batch and automatically shut off at the end of the predetermined injected length. The machine can be preset for speed rate and final length, and the total control incorporated into a furnace computer.

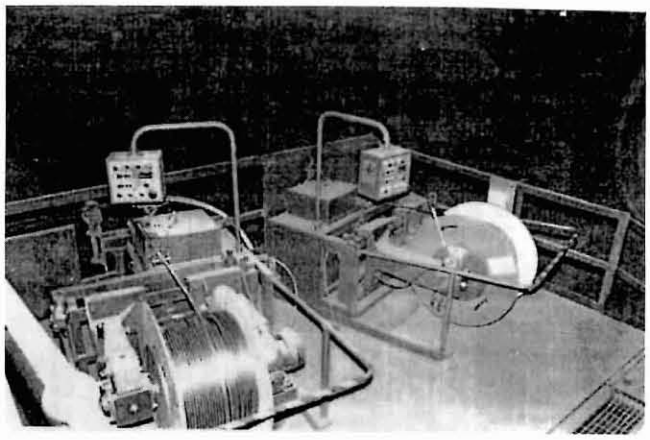

FIGURE 1. An injection machine

The machine can be equipped for driven or stationary coils, while the coils can be positioned on the furnace floor or below floor level (Figure 2).

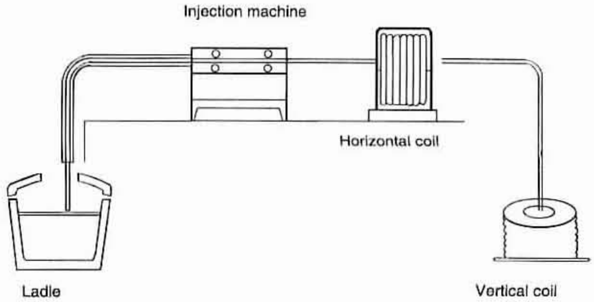

FIGURE 2. General layout of the injection machine

Feed rates of up to 300 m/min can be achieved. On occasion it is necessary to install a telescopic guide tube in order to facilitate clearance of the ladle and minimize the distance from the slag surface of the ladle.

Many stations have been installed to operate with remote and computerized control. The simplicity of the design is a factor in the low capital-investment costs.

Injection stations have also been designed with the capability of feeding up to eight different cored wires, including ferromanganese, silicon, niobium, titanium, boron, and carbon. Aluminium wire can also be injected with similar machines.

The principal impetus for cored-wire injection was the increased use of calcium and its alloys in continuous casting, although it is now applied for many other purposes.

Wire Applications

Calcium Treatment

A range of calcium alloys, including calcium silicide, calcium silicon barium, and, to lesser degree, calcium-metal-based powder are used for inclusion modification, deoxidation, and desulphurization in steels. The use of calcium is particularly successful with aluminium-killed fine-grained steels, in which the calcium combines with the solid alumina inclusions (melting point 2000°C), which are liquid at casting temperatures. The reactions are as follows:

$$Ca(l) \rightarrow Ca(g)$$

$$Ca(g) \rightarrow [Ca]$$

$$[Ca] + [O] \rightarrow CaO$$

$$[Ca] + [S] \rightarrow CaS$$

$$Ca + (x + 1/3)\ Al_2O_3 \rightarrow CaO\ x\ Al_2O_3 + 2/3\ (Al).$$

The solid alumina inclusions are converted to liquid calcium aluminates. These inclusions tend to agglomerate and float to the surface during inert gas stirring.

In order to achieve the maximum benefit from calcium injection it is necessary to operate in a standard mode, which involves neutral or base linings, aluminium deoxidation (O_2 in solution <50 p.p.m.), low oxide minimal slag volume, inert gas stirring and stream protection during casting.

The use of cored wired for calcium treatment has virtually superseded powder injection owing to the enhanced control, greater calcium recovery, operational consistency, and flexibility and simplicity of the combined operation[1].

The yield of calcium in cored wired is more consistent and higher than with powder injection. Typical results are shown in Table I, in which a comparison is also made with the calcium mixes that are used in low-silicon steels[2]. It is noteworthy that yields in excess of 20 per cent have been achieved. The yield increases with higher carbon and silicon contents while, for maximum benefit, it is desirable to maintain low sulphur contents (<40 p.p.m.). It is important to regulate the injection rate when calcium metal is used in order to avoid spontaneous vaporization. It is one of the key advantages of calcium silicide in that its relatively lower vapour pressure results in higher recoveries. It is usually recommended that operating rates of 0,1 kg of calcium per ton of hot metal per minute should not be exceeded.

TABLE I
Ca ADDITION AND RECOVERY

Steel grade	Type of Ca wire	Amount kg/t	Recovery %
Al-killed	CaSi + CaFe	0,13 + 0,33	23 13
	CaFe	0,50	13
	Ca mix	0,70	9
Al/Si-killed	CaSi	0,20	25
Rimming substitute	CaSi	0,10	0
	CaFe	0,10	0

The avoidance of nozzle blocking during sequence continuous casting is a major objective of calcium treatment. Faulring *et al.*[3] demonstrated that castability improved when the calcium/aluminium ratio was carefully controlled. During casting the nozzles rapidly became blocked with solid alumina inclusions until the addition of calcium modified the inclusions into liquid calcium aluminates. Further investigations have shown that the calcium/oxygen ratio is a superior indicator of castability[4]. In high-sulphur steels, the nozzle blocking can be caused by the formation of solid calcium sulphide, although this effect can be minimized if the aluminium content is reduced.

Calcium treatment also enhances the physical characteristics of the steel, and the machinability of both aluminium- and silicon-killed steels is improved, as shown in Figure 3 for carbide tool life[5]. The abrasive silica and alumina inclusions are converted to calcium and aluminosilicates, which soften to provide a protective barrier during machining.

The transverse ductility and impact strength of high-strength low-alloy steels can also be increased by the use of calcium. By globularization of the inclusion, the steels become more isotropic, this being enhanced with lower sulphur (<50 p.p.m.) and oxygen contents[6] (Figure 4).

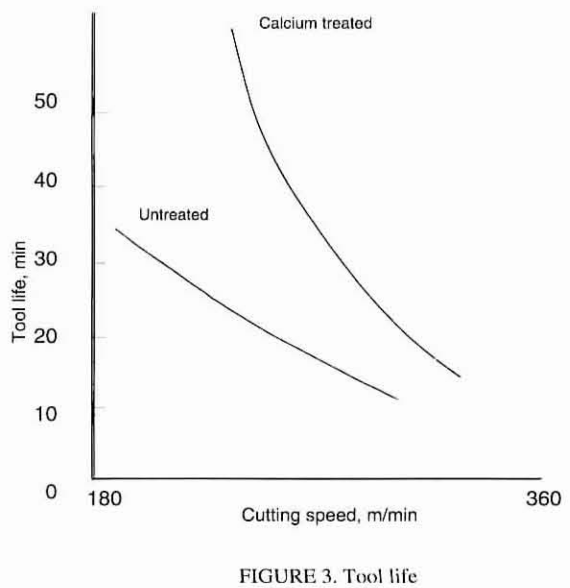

FIGURE 3. Tool life

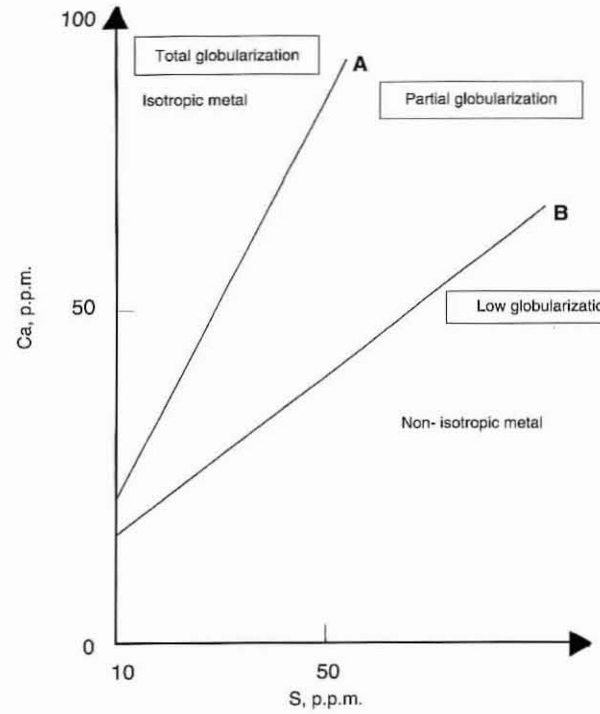

FIGURE 4. Effect of calcium and sulphur on inclusion morphology

The performance of pipeline steels in sour-gas environments can be affected by hydrogen-induced cracking. This is aggravated by the presence of elongated inclusions of manganese sulphide. Calcium improves the resistance of these steels to hydrogen cracking by globularizing inclusions and reducing the tendency of manganese sulphide to accumulate at critical grain boundaries.

To achieve this modified sulphide shape control, it is beneficial to aim for a cleaner steel with oxygen contents of less than 15 p.p.m. and sulphur contents of less than 30 p.p.m.

Enhancement of Steel Chemistry

The utilization of cored wire as a medium for the introduction of steel-ladle additions has proved to be immensely beneficial. Improved alloy yields are achieved by injecting the wire deep into the bath while being virtually unaffected by the presence of high-oxide slags. Of greater significance for total quality control is the consistency and reproducibility of the alloy recovery. The trimming technique is generally carried out on steel qualities that have narrow specification limits. Little refining has been attempted with cored wire although, under controlled conditions, the method can be used to attain a certain degree of desulphurization[5], as shown in Figure 5.

The normal procedure for trimming is to add the bulk of the alloys to the ladle during tapping and, after stirring, analysis, and temperature checks, the cored wire is automatically injected to reach the desired specification. It should be stressed that not all heats require analysis adjustment. A reduction in the overall alloying tests can be achieved if the lower range of the specification is aimed for and wire alloying is used only when the concentration of an element is less than the minimum required. Clearly, this method can significantly reduce the out-of-specification heats.

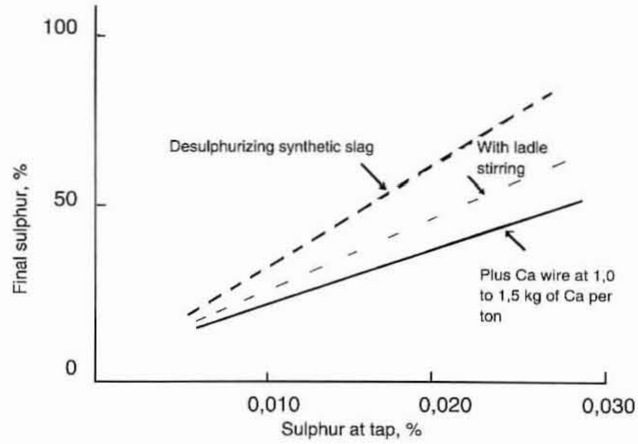

FIGURE 5. Ladle desulphurizing of aluminium-killed steel

The alloy yields obtained with wire trimming are shown in Table II.

TABLE II
YIELD OF VARIOUS ALLOYS

Element/alloy	Yield, %
Carbon	95 – 100
Sulphur	90 – 95
Ferroboron	90 – 98
Ferromanganese	90 – 100
Ferrotitanium	90 – 98
Ferroniobium	90 – 98
Ferrosilicon	95 – 100
Ferrovanadium	90 – 98
Aluminium	80 – 90

The benefit of optimum scheduling of the steel plant and rolling mill is a significant factor in the use of these techniques. A growing number of operators have adapted their ladle furnace practice, including Rautaruukki[7], who have confirmed the increased control (Table III). A further example of improved quality control is shown in Figure 6, in which the recoveries of ferroniobium are compared[8].

Another factor in the use of cored wire is the speed of dissolution of alloy powders. Ferro-alloy additions have been classified[9] as follows.

Class I alloys are those in which the melting point is below the solidification temperature of steel (1500 to 1520°C). The alloys are therefore absorbed by a melting process. Class I alloys include ferromanganese, silicomanganese, ferrochromium, ferrosilicon, and aluminium. Exothermic alloys such as ferrosilicon will have accelerated melting characteristics.

Class II alloys are those in which the melting point is above the solidification range of steel. These include ferrovanadium, ferrotungsten, and ferromolybdenum. Many of these alloys can also exhibit exothermic characteristics, which assist in dissolution. It has been demonstrated that Class II alloys can require extended periods to dissolve in liquid steel. This dissolution time can be reduced by increased stirring and reduced particle size of the alloy.

TABLE III
ANALYTICAL RESULTS FOR WIRE TRIMMING

Element	Composition range, %	Standard deviation, %	
		Trimmed heats	All trimming heats
C	0,10 – 0,30	0,005	0,007
Si	0,25 – 0,45	0,010	0,015
Mn	0,90 – 1,55	0,019	0,023
Al	0,015 – 0,045	0,005	0,007
Nb	0,015 – 0,045	0,0015	0,002
Yields: C 100% Mn 95 – 100% Nb 95% Si 100% Al 80 – 85%			

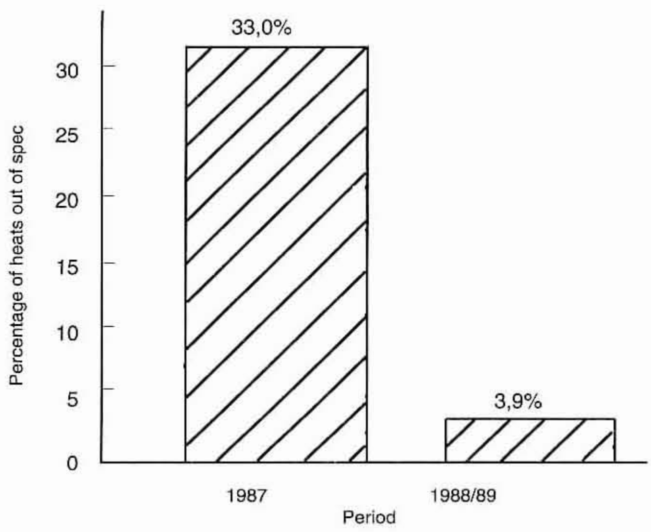

FIGURE 6. Improvement in specifications from the use of wire

Therefore, the utilization of fine powders in cored wire, combined with directional controlled stirring, makes it possible to accelerate the dissolution of the alloy and produce a homogeneous melt in a shorter time.

A particular application of wire injection is ferroboron, which is used to increase hardenability in steels and also improves certain categories of high-strength low-alloy steels. Precise and minute quantities of ferroboron are required because excessive quantities can cause hot shortness. The normal boron range is 0,0005 to 0,005 per cent. The boron is susceptible to oxidation and, therefore, the steel is carefully deoxidized with aluminium (approximately 0,03 per cent minimum). The nitrogen content is also carefully controlled to maintain levels around 60 p.p.m. Ferrotitanium is then added to the ladle, and combines with surplus nitrogen to achieve a Ti/N ratio of approximately 4,0. The magnitude of this addition is based on the level of nitrogen in the steel. A dilute form of ferroboron wire (normally 18 per cent boron) is injected to produce a residual level of 20 p.p.m. The wire method is rapidly superseding the use of boron–titanium alloys.

The stringent health regulations being introduced have been instrumental in creating another outlet for cored wire. Noxious fumes can be minimized by the encapsulation of materials such as selenium and tellurium in cored wire. The recoveries of these alloying materials are also greater than by the orthodox techniques. Lead shot is commonly used as a steel additive to improve machinability. Unfortunately, the toxicity of lead fume makes it a health hazard, and there are limited possibilities for the disposal of steel dusts containing lead. Because of the low boiling point of lead (1560 °C), it is necessary to adopt special procedures. The use of bismuth is being investigated as a ladle addition in order to produce a substitute for lead in free-cutting steel alloys[10]. Bismuth has previously been used for this purpose to a limited extent, but further consideration of its incorporation in cored wire is being given priority.

Aluminium rod is frequently used as a ladle addition. Similar techniques to those for cored wire can be applied, with the aluminium coils injected at the wire station by the same machines. A serious limitation of aluminium ingots is the wide variation in the final aluminium content, with yields that can range from 30 to 70 per cent. Aluminium rod produces improved consistency (Figure 7), and recovery levels with yields of 80 to 90 per cent are achieved regularly[11]. A further advantage of the controlled injection of aluminium wire is that nitrogen pick-up can be reduced if the bulk of the aluminium is added in wire form after tapping.

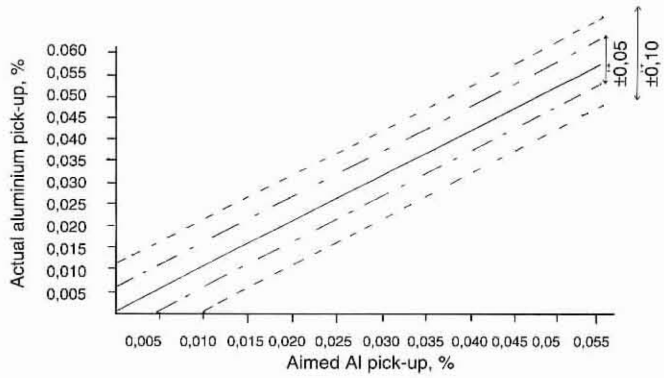

FIGURE 7. Aluminium control using wire injection

Iron Desulphurization

Currently, both calcium carbide and mixtures of carbide and magnesium are being used in cored wire to desulphurize iron. Calcium carbide wire is injected into cupola iron to reduce the sulphur content from 0,12 to 0,01 per cent. At least 6 to 8 kg of carbide per ton of hot-metal carbide is consumed, and the effectiveness depends on the degree of stirring. This mode of desulphurization results in significant temperature losses. The impetus for the use of wire is the improved environmental aspects, with reduced fume and slag. The lower slag volume is beneficial because disposal can be a problem.

In steelworks there has been a tendency to use magnesium-rich wires to desulphurize hot metal in the transfer ladle. Magnesium has a low boiling point (1107°C), and can react violently if the injection rates are not strictly controlled. The relative efficiencies of various reagents are shown in Table IV, in which the efficiency of magnesium is demonstrated[12]. A key aspect for maximum benefit is to ensure that there is a high mass of magnesium vapour in the bubbles without creating splashing conditions. In this respect, it is prudent that the magnesium injection rate be maintained between 5 and 10 kg per minute. Trials at Sollac[13] were carried out with 78 per cent magnesium and 22 per cent calcium carbide in a 9 mm cored wire. The wire was injected in a 200 t ladle at speeds of up to 175 m/min, equating to 8,75 kg of magnesium per minute. A summary of the results is given in Figure 8, which shows that significant desulphurization can be achieved with 0,2 to 0,5 kg of magnesium per ton of hot metal.

TABLE IV
COMPARISON OF MOST COMMONLY USED DESULPHURIZATION INJECTION AGENTS

Desulphurization agent	Relative consumption of desulphurization agent for same desulphurization*
Magnesium granules	1,00
Mg in lime–mag	0,77
Calcium carbide	9,50
Soda ash	14,80
Lime	22,00

*These are average values at about 1350°C

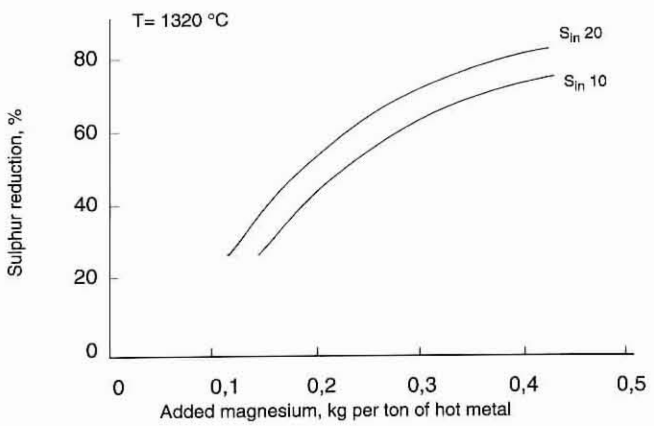

FIGURE 8. Results achieved at Sollac

Desulphurization with cored wire is also in operation at Hoogovens[14]. A vertically driven injection machine feeds wire through a telescopic guide tube into a 100 t hot metal ladle. After deslagging, wire is injected for around 6 minutes, the quantity of wire being based on the initial sulphur content. The ladle is further deslagged before the steelmaking vessel is charged. The composition of the powder is 35 per cent magnesium, 45 per cent calcium carbide, and the balance is a lime aluminate slag. Effective desulphurization was also achieved with the following average results:

Initial sulphur	0,022 per cent
Final sulphur	0,009 per cent
Hot-metal temperature	1313°C
Magnesium consumption	0,52 kg per ton of hot metal.

Hoogovens concluded that wire desulphurization could be incorporated into the operations to treat hot metal on a selective basis in order to meet its wide steel-quality programme without major capital expenditure, and avoiding the necessity of treating all liquid iron.

Both companies continued to add soda ash to their torpedoes as a standard practice during the magnesium treatment of iron in the transfer ladle.

Post-alloying in Tundishes

Calcium modification in the tundish had a moderate degree of success when cored wire was introduced initially. Little further development took place until recent attempts to introduce alloys into the tundish. The role of the tundish as a continuous reactor is now being re-assessed. The introduction of tundish dams, stirring devices, and plasma and induction heating confirm the gradual progress in adapting the tundish for purposes other than solely as a transfer vessel between ladle and caster. The next logical stage of post-alloying is now being studied[15], and Schade *et al.* have suggested a Class III alloy, which are those used in powder form combined with exothermic materials in order to accelerate dissolution. Individual ferro-alloys (ferromolybdenum, ferroniobium, and ferrochromium) were mixed and concentrated with quantities of silicon into a cored wire. This experimental work demonstrated that the exothermic nature of the alloys improved the solution characteristics compared with those of orthodox ferro-alloys in cored wire.

It was suggested that intermetallic compounds were formed, which modified the assimilation from a dissolution process to a melting process. If this technique proves to be practical, steel chemistry could be modified within the ladle. Smaller batches of steel of various specifications could be produced, with the possibility of reducing stock values and providing increased flexibility.

Foundry Applications

Spheroidal graphite (nodular) iron

The foundry industry has adopted a wide range of methods to produce spheroidal graphite (SG) iron. A greater proportion of SG iron is produced with magnesium and blends of magnesium ferrosilicon than with any other material. No single process has established pre-eminence in this field, although the intensification of environmental regulations may be the stimulus for future standardization with cored wire.

The systems currently in use are categorized as follows[16].

(1) *Tundish cover.* A specially designed lid is placed over the ladle, and metal is poured through the tundish onto the magnesium alloy. This has the advantage of minimizing temperature loss and reducing the ingress of air.

(2) *Sandwich.* A master alloy is placed in a recess in the ladle and covered with small pieces of steel. This delays and lengthens reaction times and improves recovery.

(3) *Flotret, Sigmat, Imconod.* These systems utilize a closed refractory-lined channel with a reaction chamber

in the middle. The reaction is fairly quiet, and magnesium yields can be high.

(4) *Plunger.* Enriched magnesium alloys are placed in a plunging bell and lowered to the ladle bottom. There is considerable flare, and the system can be labour-intensive.

(5) *Inmold.* The magnesium alloys are positioned inside the mould, usually part of the gating system. Fading is minimized but the yield can be affected.

(6) *Fischer converter.* Inexpensive magnesium is placed in the reaction chamber and the vessel is rotated to allow contact. The recovery can be erratic.

(7) *Cored wire.* Cored wire contains a range of magnesium contents, 5 to 60 per cent combined with either ferrosilicon or filler materials (carbon, iron, etc.). Depending on the end-product, the powder can also contain significant quantities of rare earths, calcium, bismuth, etc.

The magnesium content is dictated by the ladle size, available ladle freeboard, and process time. Many foundries utilize the facilities previously occupied by the plunging systems. Others have designed an injection stage so that the operation can be fully automatic, thus reducing labour costs and improving productivity.

The efficiency of the magnesium wire follows the same basic principles as other systems in that the major factors are temperature, sulphur content, and time. The range of magnesium residual required depends on the end-product, and on the ladle holding time, as magnesium tends to fade. It has been established that, for ladles of a nominal 20 t capacity, a 40 per cent magnesium-rich wire can be injected at speeds of 100 m/min.

Inoculation

Small quantities of ferrosilicon alloys are added to liquid flake graphite iron in order to reduce chill and promote graphite formation, reduce fine graphite, and produce a uniform structure.

In SG irons, the alloy addition also reduces chill, and encourages the formation of spherical nodules by increasing the number of nuclei in the melt. Unfortunately, this phenomenon is affected by fading, and therefore the inoculant must be injected as late as possible before solidification. This can be achieved by mould or stream additions. Powder dispensers are usually favoured, although powder sizing is critical and the dispenser must be capable of consistent feeding at variable pouring rates. Fading can be minimized by controlling the inoculant composition; for example, cerium in the ferrosilicon can reduce fading in SG iron.

Sulphur is a major factor, and must be controlled above 0,05 per cent for good inoculation in grey iron and SG iron, with superior results being obtained at 0,09 per cent.

All inoculants contain a quantity of aluminium and calcium. There are a wide range of inoculants, with the most common containing barium or zirconium. Manganese can reduce the melting range of an inoculant, which would be an advantage in low-temperature castings. Titanium is useful with grey cast iron containing excess nitrogen.

Strontium is used in grey cast iron for controlling the number of cells, but should not be used with SG iron if calcium and rare earths are present. These elements prevent strontium acting as an inoculant.

Calcium is used in magnesium ferrosilicon alloys to control the reactivity of magnesium during treatment, and rare earths counteract the negative effects of tramp elements in SG iron.

Bismuth has a positive effect by increasing the nodule count in ductile iron. Graphite can be blended with other inoculants for use in grey cast iron. The 75 per cent ferrosilicon inoculating grade is used with ductile iron, and enhances the inoculant effect of magnesium and rare earths.

Cored wire is now being used regularly for inoculation, and is ideally suited for Autopour systems. Cerium ferrosilicon wires have been introduced into foundries in which difficulties have been encountered with chill formation[17]. These wires are introduced into the launder as near the throat as possible in order to effect an increased residence time (Figure 9). The inoculant is added at the rate of 0,1 per cent, which has resulted in direct cost savings and a reduction in scrap due to inclusions.

This post-inoculation technique is efficient because the wire is fed accurately at a late stage in the process and adapts readily to automation. The wire can also be used for the post-inoculation of SG cast iron.

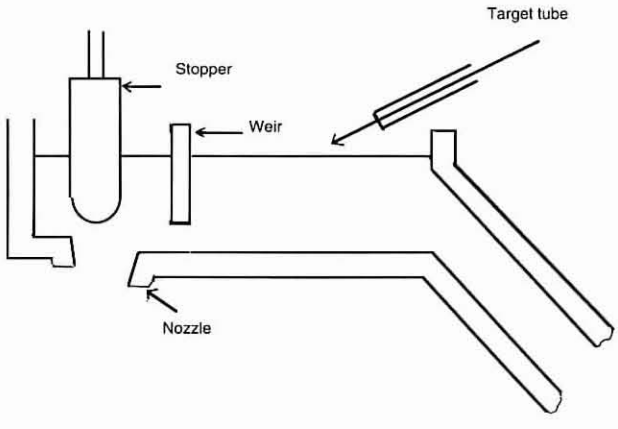

FIGURE 9. Basic launder arrangement for Autopour (in cross-section)

Future Development

Although most of the cored wire produced is used in the steel industry, in which a steel sheath is desirable, there is also a demand for copper- and aluminium-based wires. For example, copper phosphide powder is used in wires for copper refining.

Wire is an ideal medium for handling and storing, and is also a cost-effective means of disposal of high-value toxic dusts. Fine materials (less than 2 mm) can be difficult to recycle for a variety of reasons; for example, agglomerated fines can decrepitate when being processed and create additional pollution hazards. The possibility of recycling dusts in wire and injecting them into molten metallic baths or chemical liquids can be feasible for high-value metals and ferro-alloys.

The growing demand in the steel industry for cleaner and higher-quality alloys will result in the further downstream treatment of ferro-alloys in order to reduce the concentration of undesirable residual elements. Powder injection will be a part of this secondary treatment of alloys after primary smelting.

Another significant feature of wire in the metals industry is the ability to feed various mixtures of elements and alloys into a molten bath, thus achieving maximum benefit without laborious intermediate stages. Wire has also been used to encapsulate an oxide mixed with a reductant in order to achieve either cost savings or environmental benefits (e.g. lead oxide and aluminium).

Further cost reductions in wire manufacture are expected, since coil masses are becoming larger and wire diameters are increasing. At present, the optimum wire diameter is 13 mm, but diameters of 18 mm are being considered for use in larger ladles.

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