

Recarburisation Method

Technical Field

A method for recarburising ferro-alloys (such as steel) is disclosed. The method finds particular application in recarburising ferro-alloys in tapping ladles and ladle furnaces that are employed subsequent to both integrated mill steelmaking (that typically comprises a blast furnace and a basic oxygen furnace) and mini-mill steelmaking (that typically comprises an electric arc furnace (EAF)). Whilst the method will primarily be described in the context of recarburising in tapping ladles and ladle furnaces it should be appreciated that it is not limited to such types of recarburising.

Background Art

There are increasing problems with plastics and tyre disposal. Recycling of both plastics and tyres accounts for a small proportion of material recovery, with the bulk still being disposed of either through landfill or burning in incinerators. In landfill neither material degrades readily, and either material may also leach toxic elements to soils and groundwater, whilst conventional burning often generates hazardous emissions such as dioxins and can also increase greenhouse gas emissions.

Worldwide the steel industry is facing pressure to minimise its impact on the environment by improving the efficiency of energy and resource utilisation, and especially to reduce CO₂ emissions.

Waste plastics addition to electric arc furnaces is known. Examples are shown in US 5,554,207 and JP 2004-052002.

WO 2006/024069 to the present applicant also discloses the addition of waste plastics to electric arc furnaces and further discloses the possible use of waste plastics as a recarburiser, but only in the context of an induction furnace and without disclosing how this method may be practiced.

A reference herein to a prior art document is not an admission that the document forms a part of the common general knowledge of a person of ordinary skill in the art in Australia or elsewhere.

Summary of the Disclosure

In a first aspect there is provided a method for recarburising a molten ferro-alloy in a ladle or ladle furnace. The method comprises the step of adding a carbon-containing polymer to the ladle or ladle furnace, wherein the polymer is adapted to function as a recarburiser of the ferro-alloy.

It has not previously been investigated how a carbon-containing polymer could

best function as a recarburiser in the production of a ferro-alloy (i.e. where the polymer is used to substitute traditional recarburisers such as coal, coke and graphite that are in turn used to increase the amount of carbon present in the final ferro-alloy produced). A carbon-containing polymer can be selected and adapted such that it can replace or reduce the use of expensive recarburisers such as anthracite coal and graphite.

In this regard, whilst WO 2006/024069 discloses the potential use of waste plastics as a recarburiser, it does not teach how this may be practised, nor does it disclose how a waste plastic can be used in recarburising ferro-alloys in tapping ladles and ladle furnaces.

When the term "ferro-alloy" is used herein it is intended to include a broad range of iron-carbon alloys (including steels) and other iron-carbon and/or iron-based alloys, including ferrochromium, ferrochromium silicon, ferromanganese, ferrosilicomanganese, ferrosilicon, magnesium ferrosilicon, ferromolybdenum, ferronickel, ferrotitanium, ferrophosphorous, ferrotungsten, ferrovanadium, ferrozirconium etc.

In one form of the method the carbon-containing polymer can be specifically adapted to suit the ladle or ladle furnace prior to being added so that carbon in the polymer preferentially dissolves into the ferro-alloy and does not combust to any substantial or detrimental extent.

For example, one way in which the polymer can best be adapted to function as a recarburiser can comprise the step of optimising the size (e.g. its shape and/or dimension) of polymer to the given ladle or ladle furnace prior to addition thereto. This size optimisation has been observed to promote carbon dissolution and minimise polymer combustion when contacted by the molten ferro-alloy.

In one embodiment the size optimisation can comprise the binding together of polymer layers to form a block. For example, in the case of a polymer comprising waste rubber, layers of tyre tread/wall or conveyor belt can be tied together into a bundle by a suitable ferro-alloy wire.

In the case of ladle addition, the carbon-containing polymer can be added into the ladle prior to the tapping of molten ferro-alloy thereinto.

In the case of ladle furnace addition, the carbon-containing polymer can be added into the furnace with or onto the molten ferro-alloy from the ladle. For example, the carbon-containing polymer may be injected into the ladle furnace (e.g. into an uppermost layer such as a slag layer).

In one form the carbon-containing polymer is a waste plastic or rubber. In this form the waste plastic can comprise polyethylene (e.g. HDPE), and other plastics such as polypropylene, polystyrene, poly butadiene styrene, ABS, etc, as well as difficult to

re-process plastics such as Bakelite, etc. Also, in this form the rubber can be derived from a used tyre or belt. The belt can be a used/discarded rubber conveyor belt.

The addition of a waste plastic or waste rubber into the ladle or ladle furnace provides another effective means of disposal of the waste, which wastes otherwise pose environmental challenges.

Whilst usually the carbon-containing polymer will comprise the atoms C, H and optionally O only, other elements may be present in the polymer (e.g. N, S, P, Si, halogens etc). Where these elements interfere with ferro-alloy production and/or produce contaminants, pollutants, noxious or harmful gases (e.g. hydrogen gas) etc, the carbon-containing polymer can be judiciously selected and judiciously added, and/or certain flux additives can be introduced to the ladle/ladle furnace, to avoid or mitigate the formation of noxious/harmful gases and other detrimental or harmful by-products.

In one form the ferro-alloy produced is a steel or steel alloy.

In one variation of the method, in addition to the carbon-containing polymer, another source of carbon can be added to the ladle or ladle furnace, with the other source of carbon being one or more of coal, coke, carbon char, charcoal and/or graphite.

In one form the ladle or ladle furnace forms part of an electric arc steelmaking process, with the ladle receiving molten ferro-alloy from the electric arc furnace, and with the ladle furnace receiving molten ferro-alloy from the ladle.

In a second aspect there is provided the use of a carbon-containing polymer as a recarburiser of a ferro-alloy in a ladle or ladle furnace.

In the second aspect the carbon-containing polymer can be as defined in the first aspect.

In a third aspect there is provided a method for recarburising a molten ferro-alloy, the method comprising the step of contacting the alloy with a carbon-containing polymer that can function as a recarburiser, whereby the polymer has a format such that, when it contacts the molten ferro-alloy, it promotes dissolution of carbon from the polymer into the molten ferro-alloy.

It has been observed that polymer format (e.g. its shape and/or dimension) can be optimised so that, when it contacts the molten ferro-alloy, a bulk of carbon in the polymer dissolves rather than combusts or gasifies. This, in turn, can enhance the recarburisation function of the polymer.

In the method of the third aspect the polymer format can comprise a unit that is dimensioned so as to minimise its exposed surface area relative to its mass. Further, the dimension of the polymer can be optimised to the given ladle or ladle furnace. This

allows for maximum carbon dissolution to occur, and can minimise combustion or gasification of carbon in the polymer. One or more such units (e.g. one or more 10 kg blocks of waste polymer) can be employed as a recarburiser of a ferro-alloy.

In the method of the third aspect the polymer can be added into the molten alloy, or the molten alloy can be added onto the polymer, or the polymer can be added together with the molten alloy into e.g. a ladle or ladle furnace.

The method of the third aspect can otherwise be as defined in the first aspect.

Brief Description of the Drawings

Notwithstanding other embodiments which may fall within the method for recarburising a ferro-alloy as defined in the Summary, specific embodiments of the method will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 shows an X-ray Diffraction plot for each of a) raw metallurgical coke (as a current recarburiser); and b) raw high density polyethylene (as a waste plastic recarburiser); as described in Example 1;

Figure 2 shows X-ray Diffraction plots for raw high density polyethylene and metallurgical coke; and high density polyethylene and metallurgical coke after combustion; as described in Example 1;

Figure 3 shows a first schematic diagram of a horizontal tube resistance furnace set up for a sessile drop approach, as described in Example 1;

Figure 4 shows plots of carbon pick-up (% carbon content) over time, for two experimental runs as described in Example 2, for a 100% metallurgical coke as well as a mixture of 30% high density polyethylene and 70% metallurgical coke;

Figure 5 shows a schematic diagram of a drop tube furnace, as described in Example 3;

Figure 6 shows a second schematic diagram of a horizontal tube resistance furnace set up for a sessile drop approach, as described in Example 3; and

Figure 7 shows a plot of carbon pick-up (% carbon content) over time, for an experimental run as described in Example 3, for a 100% metallurgical coke as well as a mixture of 30% Bakelite and 70% metallurgical coke;

Figure 8 shows a schematic diagram of an electric arc process for the production of a ferroalloy such as steel;

Figure 9 shows a schematic detail of an electric arc furnace being tapped into a ladle;

Figure 10 shows a schematic detail of the ladle of Figure 9;

Figures 11A and 11B respectively show side and top perspective views of a

bundle of tyre tread suitable for addition to a tapping ladle; and

Figures 12A to 12C respectively plot the pick-up (in % per 10kg sample) of plastic (waste rubber) and standard carbon recarburiser:

Fig 12A - in a transfer ladle;

Fig 12B - in a ladle furnace; and

Fig 12C - standardised data.

Detailed Description of Specific Embodiments

It was postulated that a carbon-containing polymer (e.g. a waste plastic or a waste rubber) could be introduced into ferro-alloy (e.g. steel) production to function as a recarburiser (i.e. to “trim” carbon content in the alloy) in stages occurring subsequent to basic ferro-alloy formation (e.g. subsequent to steel formation in a blast furnace and basic oxygen furnace, or subsequent to steel formation in an EAF furnace). In this regard, it was postulated that the carbon-containing polymer can function as a recarburiser in either or both of the transfer ladle and the ladle metallurgy furnace.

Currently worldwide, there are two major process routes for steelmaking: the “Integrated Mill” route, which produces iron from ore and coke and then converts the iron into steel, and the “Mini-Mill” route, which produces steel from scrap steel. The major differences between the two routes are the type of furnaces used to produce steel. However, common to both processes are the transferring of the molten steel into ladles, the trimming of the steel temperature and composition in the ladles using a Ladle Metallurgy Furnace (LMF), and the casting of the steel (e.g. using a Continuous Casting Machine (CCM)).

An integrated mill produces high-carbon molten iron in a blast furnace charged with iron ore, coke, fluxes and fed with a hot air blast. The iron from the blast furnace is transferred in its molten state to one or more Basic Oxygen Furnaces (BOFs). Oxygen is used to remove most of the carbon to convert the iron into low-carbon steel. Up to 25% of the BOF charge can be solid scrap heavy steel. Steel trimming for carbon content is then subsequently performed.

A mini-mill uses one or more Electric Arc Furnaces (EAFs) to melt solid scrap steel, which can consist of heavy scrap, light scrap, and pig iron (from blast furnaces). Oxygen is used to remove carbon and other impurities from the molten steel, such as silicon, aluminium and manganese, which react with the oxygen to form silicon oxide (SiO_2) aluminium oxide (Al_2O_3) and manganese oxide (MnO). A large amount of iron also reacts with the injected oxygen to form iron oxide (FeO or Fe_2O_3). Calcium oxide (CaO) and magnesium oxide (MgO) are added to the furnace in order to build a slag layer on top of the steel. This slag layer traps the various oxides of impurities that

have been burnt out of the steel, along with a percentage of iron oxide, and protects the refractory material that lines the furnace from chemical attack by the impurity oxides, and also lowers the heat loss from the arcs to the furnace roof and sidewalls.

Once the composition and the temperature of the steel are correct, the electric furnace is tapped. This involves transferring the steel from the furnace to a ladle, where the steel can be moved in its molten state to the LMF. A schematic of the EAF production process is shown in Figure 5. Figure 6 shows a detail of the steel being tapped into a ladle, and Figure 7 shows a detail of the ladle in which a first stage of steel trimming can take place.

During tapping, carbon ('recarburiser') in a relatively pure form (typically metallurgical grade carbon) is added to the steel (known as 'recarburisation') to bring it into a desired specification. The metallurgical grade carbon is granulated and forms a comparatively expensive part of the process. Various ferro-alloys are also added to the steel to enhance the physical properties of the metal. Thus, investigations were conducted into alternative carbon substitutes not heretofore considered as suitable.

Examples

Non-limiting examples of methods for producing a ferro-alloy will now be provided. Examples 1, 2 and 3 provide laboratory derived experimental data that supports that the carbon in a carbon-containing polymer (waste plastic) is able to dissolve into molten metal and thus function as a recarburiser. Example 4 provides actual on-site trial data for a carbon-containing polymer (waste rubber) as a recarburiser in a transfer ladle and in a ladle furnace.

The methodology of Examples 1 to 3 involves the removal of volatile matter (VM) prior to testing for carbon dissolution, whereas the method of Example 4 (being an on-site trial) involves no such prior removal. Thus, the data of Examples 1 to 3 is not directly comparable with the data of Example 4.

It should also be noted that the type and quality of metallurgical coke that was employed varied between Examples 1 and 2 and Example 3, and it was this variation that was noted to contribute to different outcomes on the carbon dissolution into liquid steel. Thus, a direct comparison does not apply between the results of Examples 1 and 2 and Example 3.

It was further noted that experimentation into the effects of the coke characteristics, and also the waste plastic characteristics, could be performed, whereby those characteristics could be optimised to enhance the carbon dissolution into liquid steel.

Example 1 - Carbon Dissolution/Recarburisation of Waste Plastics

Experiments were conducted to investigate the dissolution of carbon from a mixture of 30% HDPE and 70% metallurgical coke into liquid steel at 1550°C to check for suitability for use in ladles and ladle furnaces. The experiments provided data representing sample characterization, including proximate analyses and X-ray patterns, as well as the details and results of carbon dissolution experiments.

Sample Characterization

Carbonaceous residues of waste plastics and metallurgical coke mixtures to be used for a carbon dissolution study were prepared by combustion in a drop tube furnace (DTF). The collected residues from the DTF were found to contain a level of volatile matter. Therefore, these residues were further devolatilised using a horizontal tube furnace (HF) – Figure 3. Raw samples and their carbonaceous residues collected from the drop tube furnace and the horizontal tube furnace respectively were analysed for percentages of fixed carbon, ash, volatile matter (VM) and moisture, and their structures were characterized using X-Ray diffraction.

Proximate Analysis

The proximate analysis data of samples was obtained and is shown in Table 1. For the reference material - metallurgical coke (Met Coke) - the fixed carbon content of raw samples and samples after combustion in the drop tube furnace and the horizontal tube furnace was almost constant at 64.5%. It was therefore understood that the combustion of Met Coke in the drop tube furnace and the horizontal tube furnace did not change its carbon content under the experimental conditions. When Met Coke was mixed with plastics, the fixed carbon content increased after combustion in the drop tube furnace and the horizontal tube furnace, whereas volatile matter decreased significantly.

Table 1 - Proximate Analysis of HDPE and Met Coke samples

Samples		Proximate Analysis			
		%Moisture	%Ash	%VM	%Fixed Carbon
Met Coke	Raw	1.30	31.80	2.40	64.50
	After DTF	1.30	33.50	0.70	64.50
	After HF	0.60	33.70	0.90	64.80
	Raw	0.70	22.60	36.00	40.70

30% HDPE+ 70% Met Coke	After DTF	1.20	28.10	6.00	64.70
	After HF	1.00	29.60	1.40	68.00

X-Ray Diffraction

X-ray diffraction patterns of carbonaceous residues from HDPE and coke mixtures were obtained using a Siemens D5000 X-ray diffractometer. Raw Met Coke and raw plastics were firstly analysed, followed by their mixtures. Then, their residues after combustion in the drop tube furnace and further devolatilisation in the horizontal tube furnace were characterised. Metallurgical coke was considered as the reference coke, and all X-ray patterns of the mixtures were compared with it. X-ray patterns for all the carbonaceous samples are shown in Figures 1 and 2. From these Figures, it was clear that the raw mixtures show high intensity peaks of hydrocarbons (plastics). After combustion in the drop tube furnace and the horizontal tube furnace, the X-ray pattern of the residue samples still shows a hydrocarbon peak of plastics having a low intensity. This indicated that the plastics would be suitable for use as a recarburiser.

Example 2 - Experimental Details for Waste Plastics Dissolution

Carbon dissolution from 100% metallurgical coke and the mixture of 30% HDPE and 70% metallurgical coke was investigated using the sessile drop technique. Firstly, material to be investigated was ground and sieved to obtain particles of size less than 1 mm and then combusted in the drop tube furnace at 1200°C in 80% nitrogen and 20% oxygen atmosphere. The residue collected from the drop tube furnace was found to contain high volatile matter content. Thus, it was devolatilised again in the horizontal tube furnace at 1200°C in an argon atmosphere for 15 minutes. The collected residue was again ground into powder using a grinding machine and then used for the carbon dissolution experiment.

To make the substrate, approximately 1.6 g of residue sample was used. The residue was compacted in a steel die under 7 KN load applied using a hydraulic press. The substrate obtained from the die had a top surface area of 3.14 cm². The substrate was placed on a graphite sample holder, and then approximately 0.5 g of electrolytic pure iron (99.98% Fe) was placed on the centre of the substrate. The carbon dissolution experiment was run under an inert argon atmosphere at 1550 °C. The sessile drop assembly was firstly put in the cold zone of the horizontal tube furnace where the temperature was approximately 1200°C to protect the sample holder from thermal

shock and to allow volatile matter from the substrate to escape. After approximately 15 minutes it was pushed into the hot zone where the temperature was 1550°C. The time generator started counting once the metal melted and formed a liquid drop. The sample was quenched after 1, 2, 4, 8, 15, 20, 30 and 60 minutes. During the experiment, the reaction inside the furnace was observed using a CCD camera. After the sessile drop experiment, the carbon content contained in the droplet was measured using a carbon-sulphur LECO analyser (model CS 230). The horizontal tube furnace schematic is presented in Figure 3.

Experimental Results

Carbon pick-up from carbonaceous substrates by liquid iron was obtained and is shown in Figure 4. It was clearly observed that carbon pick-up by the iron which reacted with the 30% HDPE + 70% Met Coke substrate was higher than the iron which reacted with metallurgical coke.

Example 3 Carbon Dissolution using Bakelite/Coke blend

Material Selection and Preparation

In this example electrolytic pure iron (99.98 wt% Fe) was employed. The carbonaceous materials investigated include pure metallurgical coke, and blends of coke with Bakelite. Bakelite (Phenol Formaldehyde) is a high cross-linking thermosetting material, produced by condensation polymerization of phenol and formaldehyde. Bakelite consists of C, H and O atoms. The chemical composition depends on the relative phenol to formaldehyde ratio used (1:1 or 1:2). However, CaCO₃ is commonly added into commercially grade bakelite as a filler.

To prepare the samples, Bakelite and coke were blended in a ratio of 30% and 70% respectively. The mixture was crushed in a jaw crusher, was sieved to a size of less than 1 mm, and was then mixed homogeneously in a ball mill. The mixture was fed into a drop tube furnace (DTF) at the rate of 0.52 g/min and combusted at 1200°C in an atmosphere of 20% O₂ and 80% N₂. A schematic diagram of the drop tube furnace is shown in Figure 5.

Carbonaceous residues were analysed for proximate analysis and ash analysis. The proximate analysis values of all residual chars are shown in Table 2, and include the fixed carbon, ash, volatile matter and sulphur contents. The chemical composition of ash in the residue samples was also analyzed and is reported in Table 3.

Table 2 Proximate analysis

Composition (wt%)	Coke	Bakelite/Coke
Fixed Carbon	75.5	68.1

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Volatiles	2.1	3.4
Ash	22.4	28.5
Sulphur	0.3	0.25

Table 3 Ash composition

Ash Composition (wt %)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	P ₂ O ₅	TiO ₂	MgO	K ₂ O	Na ₂ O	SO ₃	Mn ₃ O ₄
Coke	61.10	32.10	1.60	0.71	0.68	1.00	0.17	0.29	0.19	0.13	0.05
Bakelite/Coke	47.30	22.80	2.20	18.30	0.52	0.77	1.70	0.35	0.18	3.50	0.13

Carbon Dissolution

Carbon dissolution experiments were carried out using the sessile drop method. The sessile drop method was employed to study carbon transfer into liquid iron, as well as interfacial phenomena during wetting of graphite/Fe and coke/Fe. To make a substrate, approximately 1.6 g of the powder residue collected from the DTF was put in a die and compacted by applying 75 KN of force using a hydraulic press. The substrate, with a top surface area of 3.14 cm², was placed on a graphite sample holder.

Approximately 0.5 g of electrolytic pure iron (99.98% Fe) was placed on the centre of the substrate. This assembly was first placed at the cold zone of a horizontal tube furnace where the temperature was 1200°C and sealed while Ar gas flowed through the furnace at the rate of 1.0 L/min. After approximately 15 minutes, the assembly was inserted into the hot zone where the temperature was 1550°C. The reaction time was noted to start when the metal completely melted and formed the droplet. Samples were quenched after 1, 2, 4, 8, 15, 20, 30, 60 and 180 minutes by sliding the assembly into the cold zone thus terminating the reactions occurring on the metal/carbon interface. The schematic of the horizontal tube furnace is presented in Figure 6.

After the experiment, the carbon content of the metal droplet was measured using a Carbon-Sulphur analyzer (LECO CS 230). Metal/carbon interface and the reaction products were investigated using a Scanning Electron Microscope (SEM Hitachi 3400X) coupled with Energy dispersive Spectroscopy (EDS).

Results

Carbon pick up from Bakelite/Coke blend by liquid iron as compared to coke were plotted with time and are shown in Fig. 7. The data was tabulated and is presented in Table 4.

Table 4 Carbon pick up from Bakelite/Coke blend with time compared to coke

Time(min)	%Carbon picked up	
	Coke	Bakelite/Coke
1	0.07812	0.1323
2	0.08280	0.1265
4	0.08333	0.1362
8	0.06800	0.1318
15	0.08702	0.1469
20	0.10690	0.1405
30	0.07326	0.1719
60	0.10170	0.1927
180	0.26540	0.34840

Example 4 - Recarburisation in EAF Ladle and EAF Ladle Furnace using Waste Plastic and Waste Tyres

Experimental trials were conducted in an EAF steel production process to investigate the use of polymer material as a recarburiser in steelmaking operations. The aim of the trials was to replace a percentage of the relatively expensive recarburising material (metallurgical grade carbon costing at around \$650/tonne) in current use with waste polymer (obtainable at significantly lesser cost). It was thus understood that replacement of the carbon material would have benefits in terms of cost but also environmental impact.

The first polymer trialled was a high density polyethylene (HDPE) which was observed to contain about 85% bonded carbon and 15% bonded hydrogen compared to the existing recarburiser containing about 95% carbon. The first trial was conducted using virgin plastic rather than recycled material to optimise the conditions and provide feasibility of converting to recycled material.

The majority of trials were conducted with polymer charging into the EAF ladle just prior to tapping, however further trials were also conducted at the ladle furnace. Polymer was added to the ladle while it was in the isle before being moved into the tapping position. 10kg of polymer was weighed out into buckets ready to be added to the ladle. Once the electric arc furnace sample was taken, the amount of recarburiser required was taken from a recipe. Polymer was then added to the ladle (10kg) and the volatiles were allowed to burn off, leaving a residue high in carbon. Normal (known) recarburiser was optionally added on top of this according to the recipe. The ladle was then moved into the tapping position and tapped.

Trials at the ladle furnace were performed upon arrival where polymer material was added on top of the steel over the porous plug and allowed to dissolve. The data taken for the EAF ladle was initial carbon content, plastic added, recarburiser added,

ladle arrival carbon. The data taken for the ladle furnace was arrival carbon, polymer added, recarburiser added, and ladle furnace departure carbon. This data was compared to normal heats and the Experimental Results are discussed below.

Tyre and belt-derived polymer additives were found to be optimally added as bundles of mats, typically having a weight of around 10kg and an approximate 300x300x300 mm³ volume, as shown in Figures 11A&B. The bundles were added to the ladle by hand. Ferro-alloys were also added in the form of lumps of metal approximately 50mm across, and were batched into hoppers before being gravity-fed into the ladle. These alloys were added midway through the tapping process. A proportion of carbon was optionally added just before the EAF was tapped, or just after the tapping process began.

The bundles of mats were shaped and dimensioned so as to minimise the surface area of the bundle relative to its mass (e.g. an optimum shape may approximate a generally spherically-shaped bundle). This was observed to provide for maximum dissolution into molten metal of the carbon in the polymer, and to minimise the amount of carbon in the polymer bundle that combusted or gasified. It also allowed the molten metal to quickly cover the bundle, thus restricting oxygen flow to the bundle, thereby further reducing combustion and gasification of carbon in the bundle.

The process steps were as follows:

1. The ladle was taken off the pre-heater and placed in the ladle car.
2. The ladle furnace operator inspected the ladle brickwork for possible damage and sanded the slidegate nozzle.
3. The ladle was transferred to the EAF for tapping.
4. Prior to being moved under the taphole, carbon additions in the form of 10kg bags of coke were added to the ladle, according to the percentage of carbon in the steel. Where polymer recarburiser was solely being used, this step was omitted. Once the required number of bags had been added, the ladle was moved under the taphole.
5. Aluminium bars (30-80kg) were added to the ladle base to reduce alloy oxidation during tapping. The polymer recarburiser was then placed on top of these bars.
6. The taphole was opened and mats/bundles (Figure 11) of polymer recarburiser were continued to be added to the ladle in 10kg batches, according to the percentage of carbon required in the steel/alloy.
7. Alloying additions, such as ferro-alloys, were added to the ladle once a quarter of the ladle was full.
8. Flux additions were added to the ladle shortly after the alloying additions. Depending on the grade of steel being made, which stipulated the amount of recarburiser to be added to the ladle, some of the carbon additions were also batched into hoppers, prior to

gravity-feeding into the molten alloy in the ladle. It was noted that polymer recarburiser could be added during tapping of the furnace and also at the ladle furnace.

Experimental Results

Trials were conducted during a so-called "ES35 Green Shift" and were compared to normal recarburiser uptake results that usually occurred during the ES35 Green Shift. The results of % carbon picked-up are plotted Figure 12A. These results indicate an acceptable level of carbon pick-up from the use of polymer recarburiser. The carbon values were all taken from Celox measurements (for consistency) and were compared to arrival LF samples. The results for the column labeled "PLASTIC" are for 20kg of plastic and the remainder comprising normal recarburiser. The chart shows pickup per 10kg of material added. Figure 12A shows that plastic as a recarburiser is less efficient by weight than pure recarburiser, however this difference was in part attributed to the difference in percentage of bonded carbon in the two materials (i.e. less carbon in the plastic). Similar trends were observed in Ladle Furnace trial as shown in Figure 12B.

To estimate the contribution of the different components in the mixture, the weight of plastic was multiplied by 0.85 and the recarburiser by 0.95, assuming that all bonded carbon was dissolved into the steel. The result of this calculation was plotted and is shown in Figure 12C. There was only a slight increase in the disparity between the "PLASTIC" and "RECARB".

From this analysis it was noted that the particular form of the metallurgical grade carbon recarburiser resulted in a more efficient uptake than that arising from the form of polymer recarburiser. The difference was attributed to carbon losses from gaseous emissions (i.e. in the form of CO/CO₂) whereby a portion of the polymer combusted upon contact with the molten alloy.

From this, the format (e.g. shape and dimension) of the polymer was optimised to ameliorate and minimise such combustion. In this regard, reducing the amount of surface area of polymer recarburiser whilst increasing its mass, in each addition, was to be further optimised.

In general, the experiments demonstrated that waste plastics and waste rubber can provide an effective alternative to coke and graphite for the recarburisation of ferro-alloys. Thus, an effective means for using and consuming the vast quantities of waste plastics and rubbers in society is provided.

Whilst a number of specific embodiments have been described, it should be appreciated that the method can be embodied in many other forms.

For example, whilst specific waste plastics and waste rubbers have been

described, it will be appreciated that the carbon-containing polymer may come from a wide variety of sources including (but not limited to) waste polymer from white goods, waste carpet (especially underlay), automotive scrap residue, textiles, building waste material and other forms of industrial and domestic waste. Sources that currently represent a disposal or environmental issue are preferred.

In the claims which follow, as well as in the preceding description, the word "comprising" (and its grammatical variants "comprise" and "comprises") is used in an inclusive sense and not an exclusive or "consisting only of" sense, whereby further features can be associated with the features as recited.

Claims

1. A method for recarburising a molten ferro-alloy in a ladle or ladle furnace, the method comprising the step of adding a carbon-containing polymer to the ladle or furnace, wherein the polymer is adapted to function as a recarburiser of the ferro-alloy.

2. A method as claimed in claim 1 wherein the format of the carbon-containing polymer is adapted such that it promotes dissolution of carbon from the polymer into the molten ferro-alloy.

3. A method as claimed in claim 2 wherein the adaptation of the polymer format that enables it to function as a recarburiser comprises the step of optimising the shape and configuration of the polymer to be added to the ladle or ladle furnace prior to charging.

4. A method as claimed in any one of the preceding claims wherein the carbon-containing polymer comprises polymer layers bound together to form a block.

5. A method as claimed in any one of the preceding claims wherein:

- for a ladle, the carbon-containing polymer is added into the ladle prior to the tapping of molten ferro-alloy thereinto;
- for a ladle furnace, the carbon-containing polymer is added into the furnace with or onto the molten ferro-alloy from the ladle.

6. A method as claimed in any one of the preceding claims wherein the carbon-containing polymer is a waste plastic or rubber.

7. A method as claimed in any one of the preceding claims wherein the rubber is from a used tyre or belt.

8. A method as claimed in any one of the preceding claims wherein the ferro-alloy produced is steel or steel alloy.

9. A method as claimed in any one of the preceding claims wherein, in addition to the carbon-containing polymer, another source of carbon is added into the ladle or ladle furnace, with the other source of carbon being one or more of coal, coke, carbon char, charcoal and/or graphite.

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10. A method as claimed in any one of the preceding claims wherein the ladle or ladle furnace forms part of an electric arc steelmaking process.

11. Use of a carbon-containing polymer as a recarburiser of a ferro-alloy in a ladle or ladle furnace.

12. Use as claimed in claim 11 wherein the carbon-containing polymer is as defined in any one of claims 2 to 4, 6 or 7.

13. A method for recarburising a molten ferro-alloy, the method comprising the step of contacting the alloy with a carbon-containing polymer that can function as a recarburiser, whereby the polymer has a format which, when it contacts the molten ferro-alloy, promotes dissolution of carbon from the polymer into the molten ferro-alloy.

14. A method as claimed in claim 13 wherein the polymer format comprises a unit that is dimensioned so as to minimise its exposed surface area relative to its mass.

15. A method as claimed in claim 14 wherein the dimension of the polymer is optimised to the given ladle or ladle furnace.