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3,666,439

**METHOD OF DECARBURIZING ALLOY STEELS**  
Sundaresan Ramachandran, Natrona Heights, Pa., as-  
signor to Allegheny Ludlum Industries, Inc., Pitts-  
burgh, Pa.

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7 Claims

A control method for decarburizing alloy steels such as stainless steel initiated with a reduced flow of diluent gas such as argon. The composition of the effluent gases issuing from the decarburization vessel are monitored to provide an indication of the undesirable oxidation of certain metallic values within the bath being decarburized, such as chromium. The method includes maximizing the flow and thus, the conversion of oxidizer to carbon monoxide and minimizing the flow of the diluent gas in order to promote economy of operation. The concept contemplates increase in the flow of diluent gas upon the observance of excessive oxidation of metallics to promote the maximum oxidation in the carbon within the bath.

## BACKGROUND OF THE INVENTION

This invention relates to the process control of molten alloy steel decarburization wherein a mixture of oxidizing gas and diluent gas is used to decarburize the molten alloy steel. The object of the process control in the decarburization of these molten alloy steels, such as stainless steels, is to preserve certain metallic values within the bath, such as chromium. The unnecessary loss of such values increases the cost of the decarburization process. The process control method discussed herein generally relates to the decarburization of alloy steels and stainless steels using a mixture of argon and oxygen as suggested in the U.S. Pats. Nos. 3,300,865 and 3,046,107 as well as the method for dynamically controlling decarburization of steel disclosed in my Pat. No. 3,594,155, issued July 20, 1971. In Pat. No. 3,300,865, the minimization of metallic oxidation of certain desired metallic values in the bath is disclosed as accomplished by the utilization of a gas mixture of oxygen and a diluent such as nitrogen or argon. The U.S. Pat. No. 3,046,107 discloses, in addition to the foregoing, the continuous variation of the concentration of argon in the input gas to the decarburization vehicle. This patent further discloses the decarburization control or method to be based on thermodynamic consideration in which the metal to be decarburized must have a known composition and be at a known temperature. This patent assumes that the decarburization process will be in control and the appropriate concentrations of decarburization gas, i.e., oxygen and diluent, can be predicted in advance. No attempt is made in this control method to up-date or respond to any changes in the process as it continues. The method disclosed in this patent necessarily leads to the loss of some metallic values such as chromium and to excessive use of diluent, e.g., argon, over the control period as well as the inefficient utilization of the oxidizer supplied. In the aforesaid Pat. No. 3,594,155, it is suggested that a more responsive control method may be effected by maintaining a continuous balance between the oxidizer input and the carbon removal rate. The invention disclosed in this application describes a specific method and technique for effecting this dynamic control of the decarburization process.

The method described herein requires only a determination of the composition and flow rate of the input gases. These input gases are conventionally high-purity

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gases of known chemical analysis. Thus, simple flow rate measurements of the input gas such as argon and oxygen streams are all that are necessary and these may be accomplished by using commercially available gas-flow metering equipment.

The method disclosed herein further requires analysis, such as by sampling, of the off-gases to determine the specific contents of the various components such as argon, oxygen, carbon monoxide, carbon dioxide, etc.

## SUMMARY OF THE INVENTION

A method of initiating and continuing dynamically balanced decarburization of molten metals such as an alloy steel in a vessel wherein gaseous oxidizing material with a gaseous diluent is introduced into the vessel at controlled rates to react with the carbon contained within the molten metal by which the carbon is removed therefrom at a measured rate, including the steps of: introducing a nominal flow of diluent gas into the vessel, preferably by submerged blowing, allowing the flow to stabilize, introducing a nominal flow of oxidizing material into the vessel, allowing the reaction to stabilize, measuring the composition of the effluent gas exiting the vessel, measuring the flow rate of the input gases to determine the rate of carbon removal from said steel, measuring the oxidizer conversion efficiency for said flow rate, alternately increasing oxidizer flow rate in predetermined amounts, and measuring oxidizer conversion efficiency to maximize the oxidizer flow rate at a conversion efficiency above a predetermined value. Preferred embodiments include the steps of alternately reducing the diluent gas flow rate in predetermined amounts and measuring gas conversion flow rate after the oxidizer flow rate has been maximized, thereby minimizing the diluent gas flow rate so long as the conversion gas efficiency remains above the predetermined desirable value. It is also desirable to include control functions for the situation wherein the oxidizer conversion efficiency falls below the predetermined values, which are steps of increasing the diluent gas flow rate a predetermined amount for the given oxidizer flow rate, reducing the partial pressure of the carbon oxidizer medium, promoting the removal of carbon from the bath, thereby establishing the decarburization process at an efficiency such that the desirable metallic values are not oxidized from the bath.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred practice, the invention is used in the decarburization of alloy steels to avoid appreciable losses of metallic values such as chromium. The procedure for blowing oxidizers such as oxygen into these alloy steels as they are decarburized must be responsive to the variations that occur in any given heat. It is a further objective of this invention to initiate the carbon oxidizer reaction without undue oxidation of metallics. It is to be noted that the initiation of this reaction will entail the use of less than optimum gas mixtures. Upon the initiation of the carbon-oxygen reaction, the total flow of the injected gases, i.e., oxidizer and diluent, as well as the concentration of the oxidizer may be increased to the optimum value. The method hereby provided achieves this optimum value, i.e., a selected efficiency, without the appreciable loss of these metallic values. The method may be practiced at atmospheric and subatmospheric, e.g., vacuum, pressure conditions.

Measuring apparatus necessary to provide the control of the reaction is not complex. The only requirements are for the measurement of the flow rate of the injected gases and for sampling the off-gases from the reaction. It is desirable that the off-gases are sampled from a location

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within the vessel so that there is less chance of sampling entrained air within the vessel.

The decarburization process is started with a small flow of diluent gas such as argon of commercial purity or a mixture of oxidizer and diluent gas such as argon and oxygen, the mixture generally containing between 5-10% of oxygen. In the installations where the gases are supplied from a tuyere already submerged in the bath in which there is a small flow of gas trickling through the tuyere to keep it from plugging, the diluent gas flow is increased to a small predetermined value. In the instances where gases are supplied to the vessel through a submersible lance, the gas flow is started and then the lance is submerged into the bath. After a small but predetermined time sufficient for the diluent gas to flush the decarburizing vessel, the oxygen flow in the input gas is increased by a small amount to begin the decarburization reaction. The amount is empirically determined to all several (i.e., 4 or more) of these increase steps prior to reaching the maximum flow rate. The amount of the increase may be lessened when approaching the predetermined maximum efficiency so that an overshoot situation may be avoided. The off-gas composition is monitored continuously at short time intervals (20 to 30 seconds). Concurrent with the off-gas composition monitoring, the oxygen conversion efficiency is calculated from the composition of the off-gas and the flow rate of the input gases as is taught in my Pat. No. 3,594,155 previously mentioned. So long as the predetermined maximum efficiency has not been reached, the oxidizer flow is continually increased in this step-wise manner, allowing 20-30 seconds between each for stabilizing of the system and measurement of the off-gases. In conjunction with the oxygen conversion efficiency calculations, the rate of carbon drop for the decarburization process is also calculated.

Upon calculation of the rate of carbon drop, a calculation is further made to determine the current carbon level within the bath, a value which is compared with the specified end point carbon level desired to be reached in the process. These calculations are also disclosed in my Pat. No. 3,594,155, previously referred to. It will be apparent to those skilled in the art that if the carbon level in the bath is as low as or lower than the specified end point level, the process will be terminated. Whenever the carbon level is greater than that desired for the end point, the process will be continued. Concurrent with the gas conversion efficiency calculation performed at intervals as described above, the assessment is made as to whether the conversion efficiency is greater than, equal to, or less than 100%. If the efficiency is greater than or equal to 100%, the decarburization is proceeding satisfactorily, i.e., all of the oxygen being introduced to the system is being converted either to carbon dioxide, carbon monoxide, and all of the oxygen is being devoted to the decarburization of the steel and not to the reduction in the other metallic values within the bath, such as the formation of chromium oxide, etc., so long as the efficiency continues to be above this predetermined level.

One object of the process is to maximize the amount of oxidizer flow. The amount of oxidizer flow is increased in the small empirically determined amounts as previously mentioned with concurrent measurements of off-gas compositions and calculations of oxygen conversion efficiency. The increasing of flow rate and the computation of conversion efficiency are alternately continued until the amount of oxygen or oxidizer being flowed into the system is at the supply maximum or the oxygen conversion efficiency reaches the minimum preselected value.

Upon the maximization of the amount of oxidizer flow, so long as the decarburization process is continuing with an efficiency value above the predetermined minimum, the next step is to minimize the diluent gas flow. The effect of this is to reduce the cost associated with

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the diluent gas which is unnecessary to the process. The reduction in diluent gas, e.g., argon, is effected in a similar manner to that of the increase of oxygen, i.e., alternately reducing flow rate while monitoring off-gas composition and the input-gas flow rates and computing the oxygen conversion efficiency of the process. If, in the measurements, the calculations reveal that the supposed maximum oxygen flow is less than the actual oxygen flow determined from the measurements, then errors are indicated in the system which must be resolved to insure accuracy of the measurements and minimization of loss of metallic values.

In the instance that the oxidizer conversion efficiency is less than 100%, those familiar with the art will recognize that metallic oxidation is occurring. It may be advantageous in the decarburization process to allow some metallic oxidation. In such cases, the gas conversion efficiency may be a value less than 100% but above that value which would indicate the maximum metallic oxidations to be permitted. In that event, so long as the process is continuing with a gas conversion efficiency above this minimal value, the process is considered under control. In those instances where the actual efficiency is less than the desired or predetermined efficiency, it is necessary to reduce the oxygen flow to a value equal to that of the existing oxygen flow multiplied by the actual efficiency of the operation and that value divided by the desired efficiency. This calculation will provide a value for oxygen input to establish a gas conversion efficiency consistent with the minimum predetermined value. At this point it is desirable to increase the diluent flow rate a predetermined amount. Those familiar with the art will recognize that this addition of diluent gas, so long as it is not a carbon-containing gas such as carbon monoxide, will promote the decarburization process. This is true because the increased diluent gas serves to lower the partial pressure for carbon monoxide within the process and thus lower the end point carbon value that may be reached in the decarburization process.

Once the series of steps discussed above have been followed to achieve an optimized decarburization process, the removal of carbon from the bath is dynamically balanced. At this point, decarburization process is continued by monitoring the off-gas composition and calculating efficiency of the conversion and carbon drop. These procedures are taught in my Pat. No. 3,594,155 previously discussed. Further, it should be apparent to those skilled in the art that my invention now makes computerized control of the decarburization process a practicality.

I claim:

1. In the dynamically balanced decarburization of molten steel in a vessel wherein gaseous oxidizing materials with a gaseous diluent is introduced into the vessel at controlled rates to react with carbon contained in the steel to remove said carbon at a measured rate while maintaining oxidizer conversion efficiency above a predetermined value, the improvement comprising initiating said balanced decarburization without appreciable metallic losses by: introducing diluent gas into the vessel flushing the decarburization vessel; introducing gaseous oxidizing material into the vessel to initiate decarburizing reactions; measuring the composition of the effluent gases from the vessel; measuring the flow rate of the input gases to determine the rate of carbon removal from said steel; calculating the oxidizer conversion efficiency from measured flow rate and measured composition of the effluent gases; and progressively increasing oxidizer flow rate while periodically calculating oxidizer conversion efficiency until said oxidizer flow rate is maximized within the limitations of the oxidizer supply system while maintaining oxidizer efficiency above said predetermined value.

2. The method according to claim 1 including upon maximization of said oxidizer flow rate, the steps of

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alternately decreasing said diluent gas flow rate in predetermined amounts and measuring said gas conversion flow rate, so long as said conversion gas efficiency remains above said predetermined value, thereby minimizing said diluent gas flow rate.

3. The method according to claim 1 wherein said conversion efficiency falls to the predetermined value, the step of increasing said diluent gas flow rate relative to the given oxidizer flow rate, thereby reducing the partial pressure of the carbon oxidizer medium promoting the removal of carbon from the bath.

4. The method according to claim 3 wherein introducing said diluent and oxidizer gases is by top blowing.

5. The method according to claim 3 wherein introducing said diluent and oxidizer gases is by submerged blowing.

6. The method according to claim 3 wherein said initial flow of diluent gas contains up to 10% by volume of oxidizing gas.

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7. The method according to claim 6 wherein said decarburization process is carried out under subatmospheric conditions.

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L. DEWAYNE RUTLEDGE, Primary Examiner

G. K. WHITE, Assistant Examiner

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