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Core temperature measurement in carbothermal reduction processes

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ABSTRACT

An accurate temperature measurement of the core in carbothermal reduction processes, such as boron and silicon carbide manufacturing processes, is not only important from product quality viewpoint but also quite a challenging task. The core temperature in these processes ranges 2200 to 3000 K. In this study, a device has been designed to measure the core temperature. Much attention has been paid towards the accuracy of measured temperatures as this is missing in all previous studies which are mostly 7–8 decades old. The effect of relative emissivity of the target material on temperature has been studied carefully. The effect of purging gas flow rate in the measuring device on measured temperature has also been quantified along with the effect of measuring block thickness which is in contact with the core (electrode). It is found that relative emissivity of the target material and measuring block thickness has pronounced effect on temperature measurement.

1. Introduction

Measurement of high temperature in any manufacturing process is a challenging task. Accuracy has always been a problem in measuring the high temperature especially above 1600 K. There are many high temperature processes where one can not measure the temperature directly. One of such processes is the boron carbide manufacturing process which is similar to the Acheson (silicon carbide (SiC) manufacturing) process [1]. This process is almost a century old and it is still the only process which is used for the mass production of boron carbide at commercial scale [2].

Boron and silicon carbide manufacturing processes are known as carbothermal reduction processes. The furnaces which are used to carry out these processes are essentially heat resistance furnaces. These furnaces have been successfully commercialized for boron and silicon carbide production because of their remarkable features such as, high thermal efficiency and high-density product yield relative to other existing processes. These furnaces, are generally rectangular in shapes. The precursor materials for carbothermal reduction are the intimate mixture of the metal oxide and petroleum coke [2]. Either fine sized granular coke vein or electric arc-furnace grade graphite is buried in the center of the precursor material along the length of the furnace which acts as the resistor core. The precursor material is heated by applying a potential difference across the heating resistor. Due to the applied voltage across the electrode, the precursor material gets heated up and once the reaction temperature is reached the raw materials react to form metal carbide. The reaction is highly endothermic and consumes high energy. The main controlling mechanism is heat transfer through a poorly conductive raw material and once this is properly accounted the reaction proceeds very fast [3,4]. Because of the reaction, a cylindrical product ingot is formed around the heating element, which grows with the extent of reaction. During firing the temperature at the core is reached up to 2800 K. The byproduct, i.e., carbon monoxide which is evolved during the reaction diffuses out through the precursor material and is burnt at the top of the furnace and the gaseous products are driven away. Commercial furnaces are fired for around 35–50 h (in case of SiC and about 20–30 h in case of boron carbide) and after sufficient cooling the sidewalls are removed to get the product, which will be a mass of sharp brilliant crystals.

Temperature plays an important role in the whole processes. Continuing efforts have been made to understand the temperature profile in the various parts of the furnace, especially the electrode (core) temperature. An accurate measurement of core temperature is essential as it can be used to control the process and thus the quality of the product. Temperature measurements at various locations, especially of the electrode (heating element), which is the core of the furnace, is of critical importance because, carbide formation takes place only in a specific range of temperatures. Operating the furnace above this temperature range will lead to the decomposition of the formed product and if the operating temperature

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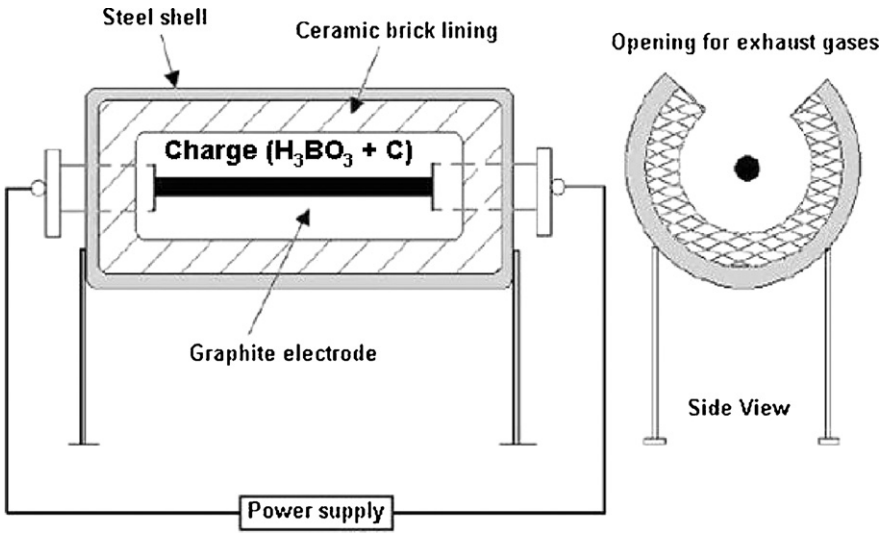

Fig. 1. Schematic of experimental furnace for the production of boron carbide.

is lower, then the extent of reaction is affected. Measurement of the core temperature reported in the literature [5–8] are very old (almost 75 years old) and vary quite significantly from each other [9] except the recent measurement made by Nagamori et al. [1]. Most of these measurements were made using the same technique which was established more than a century ago by Gillett [7]. Previous investigators [5–8] have used a thick bottom (between 5 and 19 mm) type co-axial graphite tube to measure the core temperature. Suction was applied to the outer tube to remove the thick smoke/fumes, particles from the inner tube so that they should not interfere in pyrometer readings during the temperature measurement. It is also reported that tube was getting oxidized by out side flames coming out from the furnace during the measurements. With all these arrangements and taking various precautions to avoid oxidation of the tubes and fumes entering in the tube, etc make this design unsuitable for industrial purpose on regular basis. More details can be found elsewhere [5,6]. None of previous investigators had studied the accuracy of their measured temperature. None of them also mentioned about the emissivity value which they have used during their core temperature measurements. As such they all have done commendable work in high temperature measurement but the accuracy in measurement is lacking in all the previous investigations and that is the reason their core temperature measurement differ significantly to each other (maximum temperature between 1900 and 2800 K) [9].

It should be noted that all the core temperature measurements in the previous studies were made on the Acheson process. No attempt has been made to measure the core temperature for boron carbide (B_4C) manufacturing process. It may be due to more hazardous and high temperature conditions involved in B_4C process than SiC process. The current study is focused on core temperature measurement in B_4C manufacturing process and the same would be applicable to any other similar process.

Therefore, in this article we present a more accurate way to measure the core temperature which is not only independent of the bottom thickness of the tube but also independent of any suction of fumes. It is also shown that the emissivity of the target or source affects the temperature measurement significantly. A temperature-emissivity graph for the carbothermal reduction processes has been presented in this study. A new technique and robust design, to measure the core temperature, has been proposed. The effect of gas purging/flow on the measured temperature has also been investigated. The effect of block thickness (graphite layer) at the bottom, which is in contact with electrode, on the core temperature has been investigated properly.

2. Process description

In order to simulate the boron carbide manufacturing process at laboratory scale, a cylindrical resistor furnace was fabricated as shown in Fig. 1. The reaction chamber dimensions of the furnace were 400 mm long and 450 mm in diameter which resembles to pilot scale boron carbide furnace. The outer part of the furnace is made of stainless steel, which is lined with high temperature magnesite bricks from inside. The carbon electrodes equipped with electric connections protrude into the furnace space through this lining. A characteristic part of B_4C furnace is the resistor core (made of graphite) that connects the current-conducting electrodes and serves for the conversion of electric power into heat energy. This heat energy passes to the surrounding charge (boric acid ($H_3{\cdot}BO_3$) or B_2O_3 and petroleum coke), which is around the resistor core. During the firing, core temperature reaches up to 2800 K. This causes the chemical reaction to occur, which forms B_4C, in the surrounding mixture. Firing is done for about 3–6 h and after cooling, the side and bottom walls are removed to get the product. The overall reaction of B_4C formation can be represented by the following reaction.

$$4H_3{\cdot}BO_3 + 7C = B_4C + 6CO + 6H_2O \quad (I)$$

The CO produced during the process is burnt at the top of the charge, which is open to atmosphere. The product mass is broken to recover the fused B_4C chunk and powder. More details about the process can be found in Ref. [10].

3. Measurement principle

From the above discussion, it is obvious to measure the core temperature in this process is an arduous task. As the involved temperature may reach up to 2800 K, one of the possible ways to measure the temperature is by using pyrometer which would be able to measure such a high temperature (no thermocouple would be able to measure such a high temperature). Without going much into details of the suitability of pyrometer (for which appropriate literature can be referred [11–17]), a two colour pyrometer has been used in the current study. A brief description of the working principle of it is given below.

Radiation pyrometer uses the concept of measuring the energy emitted from the surface of the target to measure its temperature from a distance. Planck's law relates the energy radiated from a body at a particular wavelength 'λ_i' to its temperature 'T'. The radiation intensity 'W_{λ_i} (W m^{-2})' coming from a surface can be related to its emissivity 'ε' and the absolute temperature 'T' of the body as

$$W_{\lambda_i} = \frac{C_1}{\lambda_i^5}\varepsilon_{\lambda_i}[e^{C_2/\lambda_i T} - 1]^{-1} \quad (1)$$

where, 'C_1' and 'C_2' are the radiation constants [18]. The characteristic spectrum of the radiation emitted from any object, depends on the objects temperature including its surroundings absolute temperature especially in gas/fuel fired furnaces. 'ε', the emissivity of the target (fraction of the energy emitted by the target as compared to the blackbody at the same temperature and wavelength), is not only a strong function of temperature and wavelength but also the properties of the target such as shape, oxidation and surface finish [11,16,17]. Other factors, which affect energy, received by the pyrometer from the target, are radiation from other sources, loss in radiation due to dirt, smoke, dust, and/or atmospheric absorption. For the temperature evaluation, a relation between the measured ratio temperature 'T_R' and the true temperature 'T' can be written as (from Planck's law [11]).

$$T_R = \left(\frac{1}{T} + \frac{\ln(\frac{\varepsilon_1}{\varepsilon_2})}{C_2(\lambda_2^{-1} - \lambda_1^{-1})}\right)^{-1} \quad (2)$$

This equation shows that the measured ratio temperature 'T_R' will be equal to the true target temperature 'T' approximately if the surface emissivities are equal, $\varepsilon_1 = \varepsilon_2$ (i.e. considering the grey body), at both the wavelength λ_1 and λ_2. The deviation between the true and the measured temperature will depend on the λ_1 and λ_2 and the emissivity ratio of the surface at these wavelengths. If the two wavelengths chosen are very close to each other then the emissivity in these narrow wavelengths can be assumed to be the same. Choosing the wavelength below 2 μm further reduces the errors [15]. In this way the ratio of two intensities (say, W_{λ_1} and W_{λ_2} see Eq. (1)) can be made a function of temperature only. This technique of temperature measurement is known as the ratio technique. This technique also minimizes/eliminates the errors caused by the obstructions in view field. Any parameter such as the target size, which affects the amount of energy in each band by an equal percentage, has no effect on the temperature measurement. However, not all the forms of sight obstructions will attenuate the energy equally [13,14,16,17]. For example when the particle in the sight path has the same size as one of the wavelengths, the ratio will become unbalanced. To account for this unbalance a relative emissivity, that is, the ratio of the emissivity of shorter wavelength band to the emissivity of longer wavelength band is used. This ratio is popularly known as relative emissivity or slope. This value of relative emissivity has to be determined by experiments. Hence experiments were conducted to determine the relative emissivity. This is discussed in detail below.

In brief, two colour radiation pyrometer also known as ratio radiation pyrometer measures the radiation energy at two different wavelength bands. That is, the intensity of radiation from a body is compared at two distinct wavelength bands. In the current study M90R-2 two colour pyrometer (supplied by Mikron Infrared, Inc., New Jersey, USA) has been used to measure the core temperature. The spectral band for the M90R-2 is 0.9–1.06 μm. This pyrometer has a focus from 0.5 m to infinity and has a built in filter to protect the eyes when viewing a bright, high temperature target. Pyrometer has a field of view for measurement 180:1 which requires that the minimum target size should be about 2 mm. The accuracy of the instrument is ±0.7% of the reading and temperature resolution is 1 degree and the response time is 0.5 s. It has LCD indicator and can be connected to a computer/data logger to store the desired values.

4. Core temperature measurement device

To measure the temperature of the core of a furnace, which is surrounded by reacting charge, is a challenging task. Before making any device, attention should be paid on the view field that should be free from dust, all kinds of intervening particles like smoke, fumes and absorbing and scattering gases. Therefore, after a few unsuccessful designs of the tube to view the core, a final design was adopted which works satisfactorily. This arrangement is shown in Fig. 2. Graphite tube of 16.5 mm outer diameter, wall thickness 3 mm and tube length 450 mm was used as a sighting tube. This sighting tube was inserted into the furnace through one of the furnace insertion pockets right up to the electrode as shown in Fig. 3, before charging the raw materials.

The hot end of this tube, i.e., the end towards the electrode, was press fit into a blind hole of a rectangular graphite block. The block dimension was 55 mm × 55 mm × 20 mm with an internal hole of 5 mm and having provisions for holding the sighting and the exhaust tubes. A small groove was cut along its length for positioning it on the electrode, and this graphite block acted as a pseudo target. In order to avoid the materials related difficulties in measuring the temperature, the material of the electrode and the block was kept same. In order to have a clear view field during the temperature measurement, ultra high purity (UHP) nitrogen gas was purged

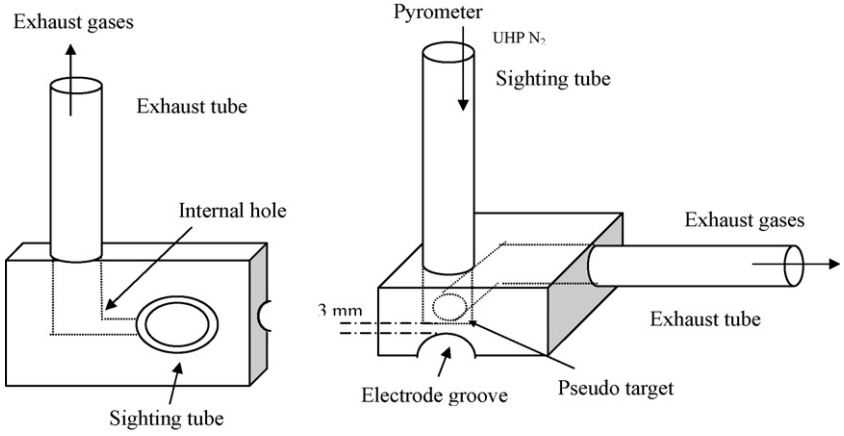

Fig. 2. Schematic of core temperature measurement device.

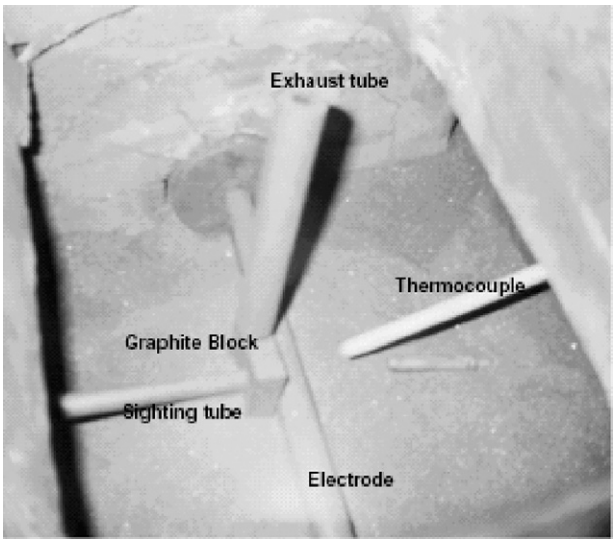

Fig. 3. Photograph of temperature measuring device in the furnace.

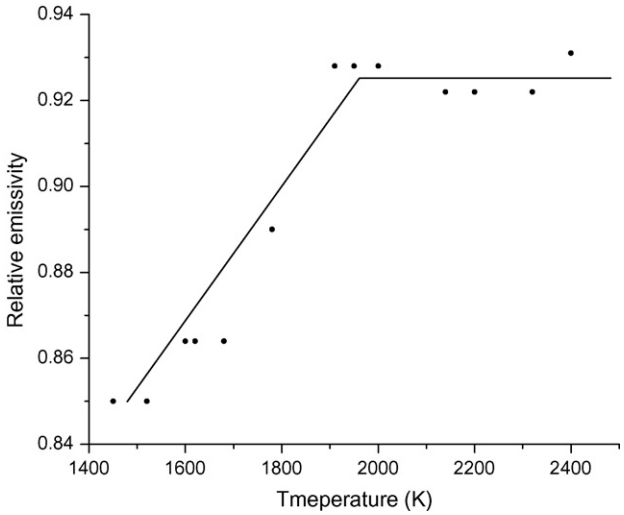

Fig. 4. Variation in relative emissivity of graphite electrode with temperature.

continuously from a recrystallized alumina tube through out the experiment. This tube was of 3.5 mm diameter and 180 mm long and was inserted into the sighting tube from the pyrometer end to achieve a good purging of the gases. This tube emits a gas jet which carries all the gases from the sighting tube to the furnace exhaust through an exhaust tube. A graphite tube of 7 mm inner diameter and wall thickness of 10 mm was used as an exhaust tube. An internal hole in the graphite block was providing the desired connection between the sighting and exhaust tubes. The exhaust tube was also press fit on to the block. The graphite layer (block) thickness between the blind hole and electrode was 3 mm. As the temperature of interest was more than 1200 K, temperature gradient across the 3 mm thick graphite layer was neglected.

5. Determination of relative emissivity and calibration

There is no published data available on the change in relative emissivity of the graphite with temperature, in particular for the carbothermal reduction processes. In order to quantify the relation between the settings of relative emissivity values and the temperature indicated by the instrument, temperatures were recorded for series of relative emissivity settings. With a change of 0.001 in relative emissivity there is about 3.1 K change in the recorded temperature at constant source temperature (±10 K above 2100 K). Reported change by the manufacturer of the instrument is 3.0 K per 0.001 changes in the relative emissivity which is close to our measurement. Because we had a little fluctuation in our constant temperature (±10 K above 2100 K) as discussed above, therefore, we have taken the manufacturer's value as standard. This means, if the relative emissivity is changed by 0.01 (say from 0.85 to 0.86) there is a change of 30 K in the temperature. Therefore, it is absolutely necessary to know the correct value of the relative emissivity before measuring the correct temperature of the target. Hence, it was decided to determine experimentally the relative emissivity of the target, which is graphite in our case, with respect to the temperature.

In order to determine the relative emissivity of the graphite surface, calibrated C type thermocouple (W–5%Re and W-26%Re) was used. To determine the correct relative emissivity for the target, a few separate experiments were carried out in which, temperature measurement were made by both pyrometer and C type thermocouple simultaneously and separately. In one set of experiments, the calibrated C type thermocouple was inserted into the furnace, through the sighting tube, and pyrometer was also focused on to the target simultaneously through the same tube. The temperature indicated by thermocouple was measured and the relative emissivity setting of the pyrometer was adjusted to read the same temperature. In another set of experiments only the pyrometer was first focused on to the target with an approximate relative emissivity setting and once the temperature indicated by the pyrometer became constant (i.e. not changing with time), calibrated C type thermocouple was inserted through the sighting tube, removing the pyrometer. Output from the C type thermocouple was measured and the thermocouple was removed from the sighting tube and then the pyrometer was replaced to its earlier position and the relative emissivity was varied to get the same temperature, as read by the thermocouple. The entire exercise was done almost at a constant temperature (±10 K). Both the techniques, using C type thermocouple continuously and intermittently, gave almost the same results. The later technique has a drawback that it can not be used when source temperature is not constant. Fig. 4 shows the plot of relative emissivity determined as a function of temperature. It can be seen from Fig. 4 that the relative emissivity of the target increases from 0.85 ± 0.003 at 1453 K to 0.928 ± 0.003 at 1900 K. Also, one can notice from this figure that at temperature higher than 1900 K the relative emissivity does not vary much and a constant value of 0.925 may be considered between the temperature ranges of 1900 to 2400 K. The relative emissivity for temperatures more than 2400 K could not be measured due to the limitation of C-type thermocouple which can be used to measure the maximum temperature up to 2450 K. However, looking at the nature of the curve in Fig. 4, one may expect a constant value of relative emissivity beyond 2400 K. Therefore, relative emissivity value 0.925 was used to measure the temperature higher than 2400 K. Similar trend between emissivity and temperature has been found by other investigators [17] however, direct numerical comparison between the two sets of data is not possible because of different sample surface finish and measurement technique.

A typical core temperature measurement curve, using pyrometer, with time during an experiment is shown in Fig. 5. As the relative emissivity value was set constant (0.925) from beginning of the experiment, therefore, temperature measured below 1900 K (Fig. 5) may not be considered as the true temperature because the emissivity changes almost linearly between 1400 and 1900 K, as shown in Fig. 4. After 1900 K it is constant (0.925) as discussed

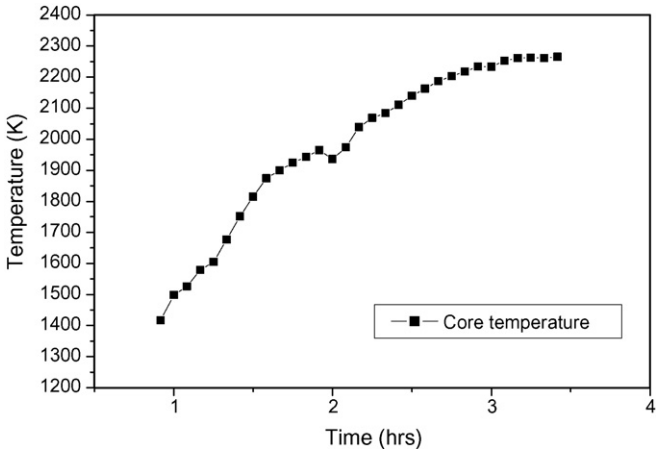

Fig. 5. Core temperature variation with time during an experiment.

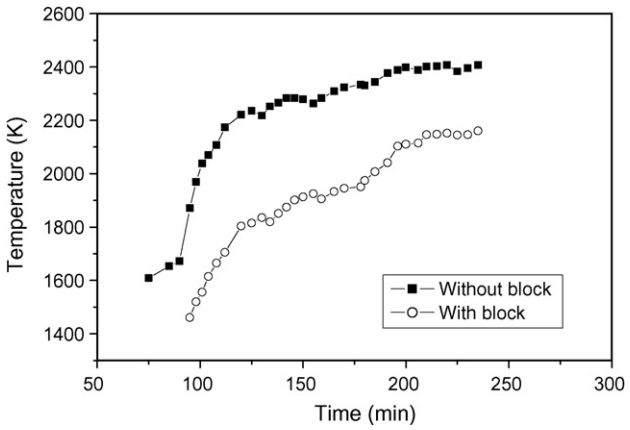

Fig. 6. Core temperature measurement with and without graphite layer.

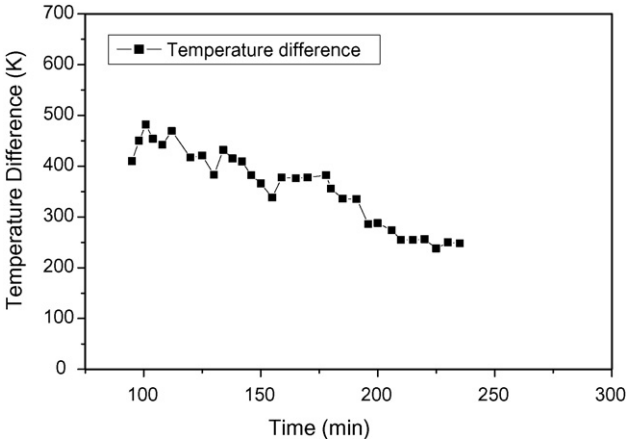

Fig. 7. Difference in core temperature measurement with and without graphite layer.

before. However, the correction in temperature can be made, based on Fig. 4, when the temperatures are lower than 1900 K. In the present case, temperatures below 1900 K would be slightly lower than what are they shown in Fig. 5.

6. Effect of graphite layer on temperature measurement

The authors of this paper have developed a mathematical model for the same process in terms of heat and mass transfer. Results of this would be published in a separate paper. During the computer simulation it was found that the experimental core temperature results are not matching well with the theory. As we could not find any serious problems with our mathematical formulation, attention was paid towards the experimental procedures/measurements to find the probable causes. As it was mentioned before that in measuring the core temperature the effect of block thickness (3 mm graphite layer) was assumed negligible. Therefore, it was decided to measure the core temperature with a through hole instead of blind hole, i.e., pyrometer should be focused directly on to the core. This means there is no 3 mm graphite layer between the blind hole and the electrode. Therefore, two separate experiments were performed under the identical experimental conditions, one with a block having blind hole and another with a block having a through hole (i.e. no 3 mm thick graphite layer between the electrode and graphite block). We kept the heating cycle and initial composition of the charge constant for both the experiments along with the other parameters such as flow rate of purging gas. The measured temperature profiles are given in Fig. 6.

From Fig. 6 it is obvious that there is a significant difference in the measured core temperature using graphite layer and without graphite layer. The temperature measured without graphite layer is always higher than with layer. In case of without graphite layer, pyrometer is able to read the first temperature in about 30–40 min before than with the layer. All the measured temperatures in Fig. 6 are based at constant relative emissivity value (0.925) and the same correction may be needed in the temperatures which are lower than 1900 K as discussed above in Fig. 5. As such, we are interested in the temperature difference between the two methods and this difference is not going to affect by the emissivity change as it would be applicable to both data. Fig. 7 shows the plot of temperature difference obtained by two methods against time. It is seen from this figure that temperature difference varies between 450 and 235 K with time. This variation is more or less linear with time up to about 200 min. The temperature difference, when the core temperature was almost constant in both the methods (between 207 and 240 min), is about 235 to 255 K. This difference can be attributed to the thickness of the graphite layer. Once we had obtained the correct temperature (i.e., without layer) there was a good match between the theoretical and experimental core temperature. This also shows a good example that how a mathematical model could be used to get insight of the process and to improve the process.

7. Effect of air flow

After knowing the correct relative emissivity of the graphite electrode in our process, it was thought that we should quantify the effect of purging gas flow rate on the temperature measurement. This was done when the core temperature had reached a constant value (±10 K). Relative emissivity value of the pyrometer was set to 0.925 between the temperature ranges 1900 to 2400 K as it was found constant in this range as discussed before. The core temperature became constant, in this particular case at 2284 K, at 5 lpm gas flow rate (UHP nitrogen) through the rotameter. The flow range of the rotameter was 0 to 20 lpm. At each flow rate, the temperature indicated on the pyrometer was recorded once a steady value was reached. Gas flow rate was increased in steps and it was found that as the gas flow rate is increased, temperature decreases. However, the decrease in temperature was not significant. The effect of gas flow rate on the core temperature measurement is shown in Fig. 8. From this figure it is clear that when the gas flow rate is zero the measured temperature is 2287 K and when the gas flow rate is maximum, i.e., 20 lpm the temperature is 2264 K. This figure shows

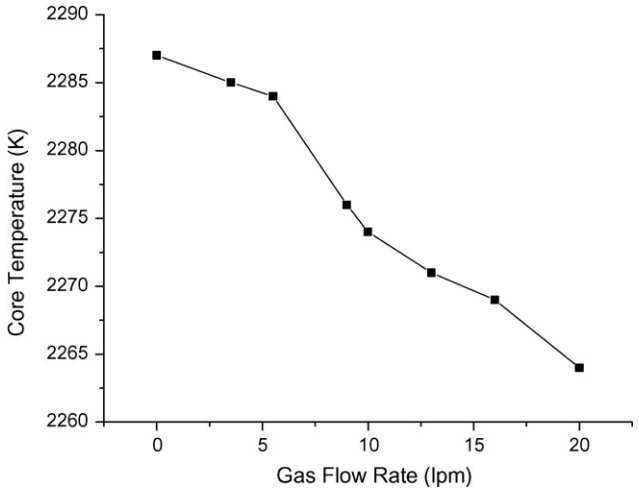

Fig. 8. Effect of purging gas flow rate on core temperature measurement.

almost a linear variation in the temperature with respect to the gas flow. In the present case the gas flow in all experiments was maintained 5 lpm. Therefore, the error in temperature estimation would be about 3 K, i.e., temperature measured in presence of gas flow (at 5 lpm) is 3 K lower than the temperature measured without gas flow.

8. Conclusions

An accurate core temperature measurement device has been developed for carbothermal reduction processes considering boron carbide manufacturing process as a typical example in a hot model study. A relative emissivity vs. temperature graph for graphite core (electrode) has been developed in order to find the correct relative emissivity value at a particular temperature. It is found that relative emissivity value is almost constant ($\varepsilon = 0.925$) when the core temperature is in between 1900 and 2400 K. Though relative emissivity value could not be measured beyond 2400 K due to the limitation of thermocouple, however, we believe that it may be considered constant even at higher temperature. Relative emissivity value increases linearly from 0.85 to 0.92 when temperature is increased from 1400 to 1900 K. The effect of purging gas flow rate (0–20 lpm) on the core temperature measurement is negligible. However, the effect of graphite layer thickness on the core temperature measurement is very significant. The temperature measurement device is very simple and robust and can be used in industries on regular basis.

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