

## RESPONSE OF COLD BRIQUETTED IRON (CBI) TO HIGH TEMPERATURES TREATMENT

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(Received 01 September 2009; accepted 10 May 2010)

### Abstract

This investigation was carried out to assess the behaviours of Cold Briquetted Iron (CBI) when exposed to increasing temperature changes up to its complete melting. High-temperature behaviours and melting characteristics of CBI were studied. Ground as-received CBI briquette and those heated to temperatures ranging from 500°C to 1000°C were sieved to maximum of 30 microns diameter size and their room-temperature x-ray diffraction (XRD) measured. CBI was found to contain among others,  $\alpha$ -iron, cementite and silica phases. Cementite was found to commence decomposition at 500°C - 600°C and completed by 700°C with conspicuous increase in the concentration of  $\alpha$ -iron phase. Only  $\alpha$ -iron and silica phases were sustained in CBI at temperatures above 700°C. In an inert atmosphere, it was discovered that CBI melted over a temperature range of 1527.3°C to 1536.96°C accompanied by an irrecoverable weight loss of 9.6 wt.% of the starting material. It was concluded that melting CBI would require charging along it appropriate fluxes to take care of the unreduced iron oxide and incorporation into facility for melting CBI an effective deslagging mechanism to remove unavoidable possible voluminous slag that would be formed.

*Keywords:* Cementite; Cold briquetted iron; High temperatures; XRD

### 1. Introduction

In spite of its long time practice, metal casting still remains one of the most versatile

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forming processes for the production of machine components and spares for various machineries. In Nigeria and in many other countries worldwide where production of pig iron is far below their demand or absolutely non-existence, most iron foundries are fast folding up due to the unavailability of this major raw material. Iron scrap which is often used to supplement pig iron in foundry is fast becoming scarce worldwide. This implies that iron foundries have to depend on the importation of pig iron for sustenance. The absolute dependence of foundries on imported pig iron as major raw material has bad economic and industrial implications. This increases the cost of unit cast products and creates a proportional price increase on the finished products of industries that depend on foundry for the supply of replaceable damaged components and spares for their facilities. Therefore, alternative raw materials have to be sourced to replace the scarce pig iron and iron scrap in Nigeria iron foundry.

Incidentally, Midrex process adopted in Delta Steel Company (DSC), Aladja in Nigeria utilizes direct reduced iron (DRI) as the main feedstock during which large quantities of under-size fines (with diameter  $\leq 3$  mm) are generated as bye-product. Like other wastes recovered from some other steelmaking processes and converted into useful products [1-3], this generated bye-product from Midrex DRI is made into briquettes either in cold or hot condition. In cold condition, these generated fines are made into briquettes by using sodium silicate and lime to act as binder and flux respectively. The briquettes which are so formed are called cold briquetted iron (CBI).

Apart from enhancing fines utilization, cold briquetting system has been found to be a very important development in the handling and storage of Midrex DRI [4, 5]. The low specific surface area of these high-density briquettes, about 5 – 6 grams per cubic centimetre, increases their resistance to reoxidation [4-6].

As for DRI, a lot of works have been done on its high-temperature applications [7-15]. For instance, many successes have been reported in the application of DRI in electric arc furnace [7, 8], Blast furnace [9, 10], BOF [11] and foundries [12 – 13]. Hot briquetted iron (HBI) formed from DRI product in hot condition (above 650°C) has also received wide applications in steelmaking processes [14, 15]. However, little is known about CBI. It has been reported that CBI among others, has a high degree of metallization (89 wt %), an average of 3.5% carbon, 0.004% sulphur, and 0.07% phosphorus [16]. These properties make CBI favourable candidate material for application as possible feed charge in iron foundry. Although about twenty five tons of CBI are being produced daily by the DSC, there is no reported useful engineering or industrial application of them yet found. The preliminary investigation reveals that its direct use is very difficult in existing foundry melting facilities. The losses incurred as a result of damages done to furnaces during the melting trials have discouraged many foundries from further trials [16].

In an attempt to solve this problem and enhance its application as foundry feed stock, an insight into chemical changes in CBI as it is exposed to high temperatures during its melting has therefore become

relevant. This information is not yet reported in the literature. Therefore, this investigation is conducted to study the behaviour of CBI at different temperatures for information on possible chemical reactions and changes that may occur during its melting. This will have a great industrial and economic significance. The information generated will provide a database for the design of appropriate processes and material selection for future furnaces meant to melt CBI. The use of CBI as foundry feed stock will also boost the development of iron foundry and greatly reduce the cost of unit cast product.

## 2. Experimental Procedure

Using a jaw crusher, some as-received (untreated) CBI samples were crushed and thereafter, ground to pass through 30 microns sieve aperture of Endecotte Sieve. Some of the ground material was mounted in special flat sample holders and was measured in transmission at room temperature under rotation. The rotating sample was thereafter subjected to a convergent Co K<sub>α</sub> radiation (with a wavelength of 1.7890 Å) in Debye-Scherer geometry focused by means of curved germanium monochromator. With the aid of two-positioned STOE proportional sensitive detector (PSD), the x-ray diffraction (XRD) patterns were recorded by a STOE automatic powder diffractometer [15]. With the use of Rietveld technique [17] the produced patterns were refined (using STOE software) and the measured values, were compared with the calculated data stored in an International Centre for Diffraction Data (ICDD) data bank.

Five separate briquettes (CBI) were heated to 500°C in a Linn Elektro Therm Eurotherm Model LM 31213 heating furnace under normal atmosphere, and soaked at this temperature for about an hour. One of the briquettes was then quenched in cold water and cooled to the ambient temperature. The temperature of the furnace was thereafter raised to 600°C, soaked at this temperature for the same period of time and similarly quenched to ambient temperature. The choice of this temperature range was based on the observation made during the high-temperature trial run which showed that there was no significant phase change in the sample from room temperature (RT) to 500°C. Similar procedure was repeated for the third, fourth and fifth samples at 700°C, 800°C, and 1000°C respectively. Thereafter, powder of each heat-treated sample was similarly prepared and their XRD measured as earlier explained. The XRD pattern obtained in each case was compared with the pattern of the untreated sample.

Another briquette of CBI was heated in Netzsch STA 449 F1 thermobalance flushed continually with helium to ensure oxygen-free atmosphere until the material melted completely. The DTA and TG chart recorded were then analyzed.

## 3. Results and Discussion

The indexed diffraction pattern of as-received CBI is presented in Fig. 1a while the room temperature measurement of water-quenched sample at 500 °C shown in Fig. 1b. Room temperature measurements of XRD pattern of heat-treated samples at 600°C, 700°C, 800°C and 1000°C are also presented

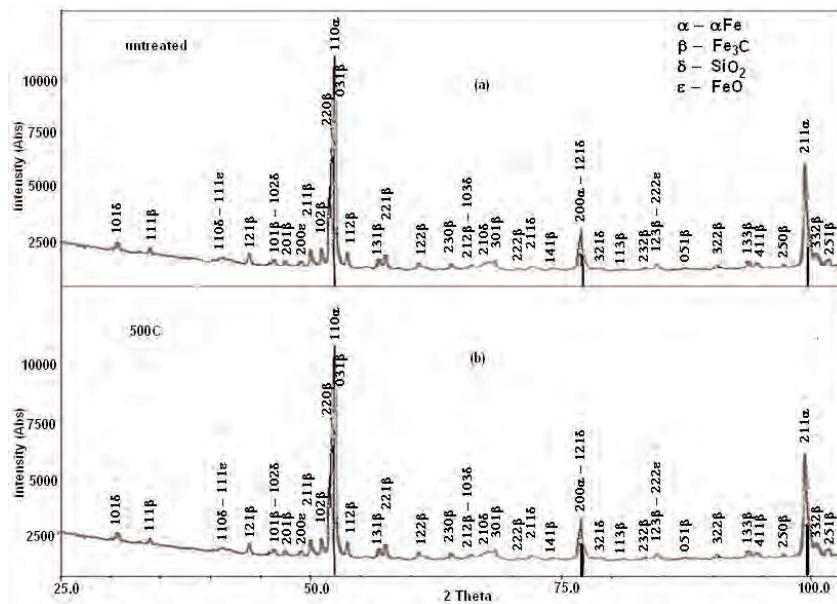


Fig. 1: Indexed XRD pattern of CBI showing constituent phases of:  
 (a) as-received and (b) heat-treated at 500°C

in Figs. 2 - 3. The results of the melting of CBI are summarized in Figs. 4, 5 and 6. Fig. 4 shows the reduction in weight with increasing temperature. The thermograph

showing both the TG and DTA of CBI during the melting and cooling down to the room temperature (RT) in helium atmosphere is presented in Fig. 5.

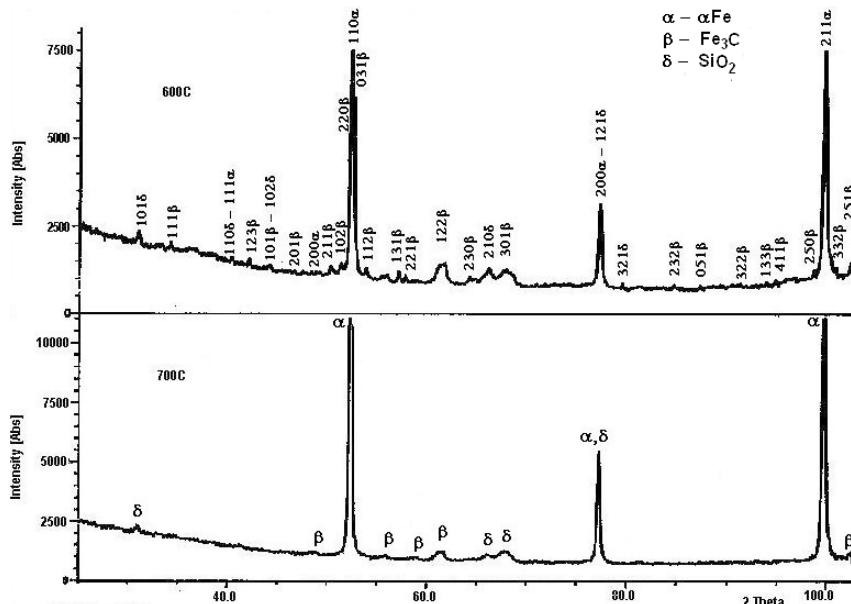
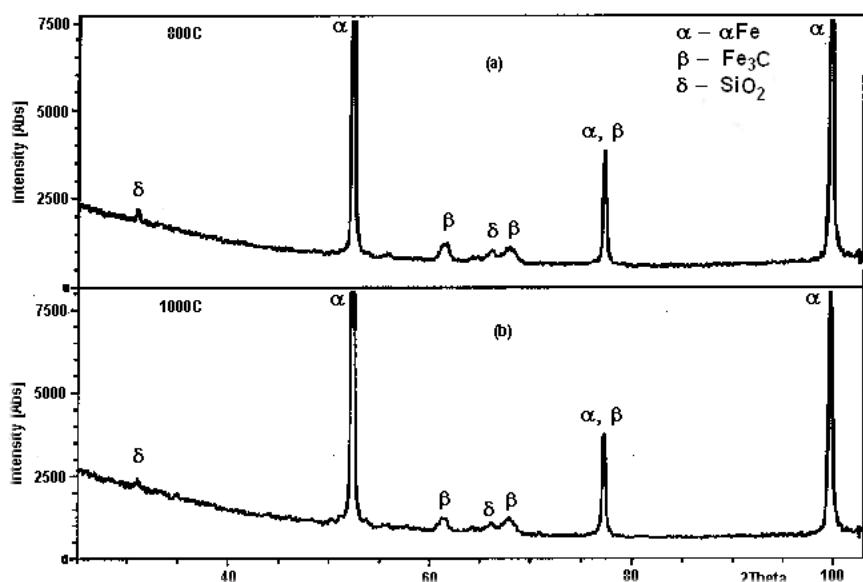


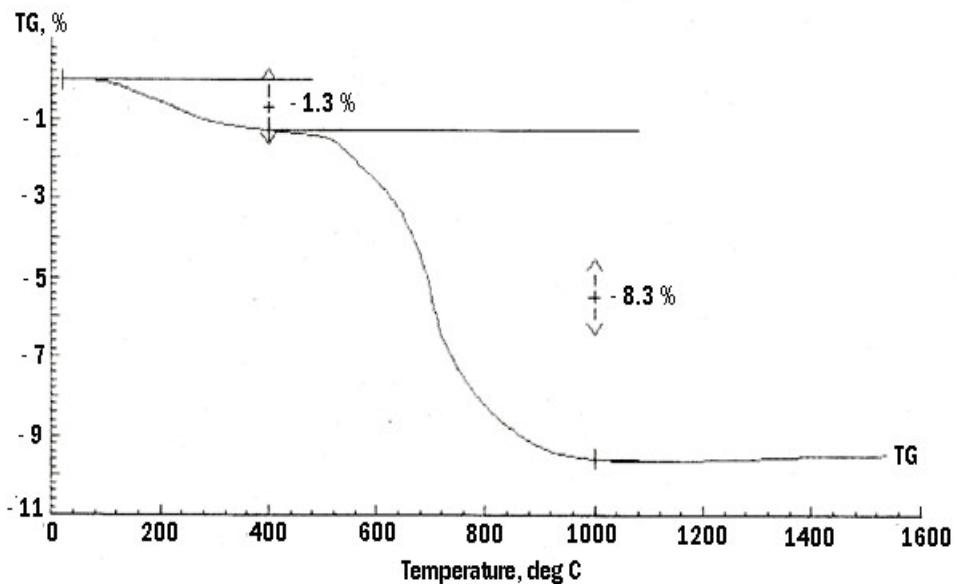
Fig.2: Indexed XRD pattern of CBI measured at room temperature showing constituent phases for heat-treated sample at 600°C and 700°C



*Fig.3: Indexed XRD pattern of CBI measured at room temperature showing constituent phases for heat-treated sample at (a) 800°C and (b) 1000°C*

The room-temperature measurement of XRD pattern of the water-quenched sample at 500 °C when compared with the untreated sample does not show any noticeable difference (Fig. 1). However, the XRD

pattern of the water-quenched sample at 600°C indicates some noticeable changes when compared with the pattern of the untreated sample. It has been reported that on average, CBI among others consists of about



*Fig. 4: Changes in the weight with temperature during melting of CBI*

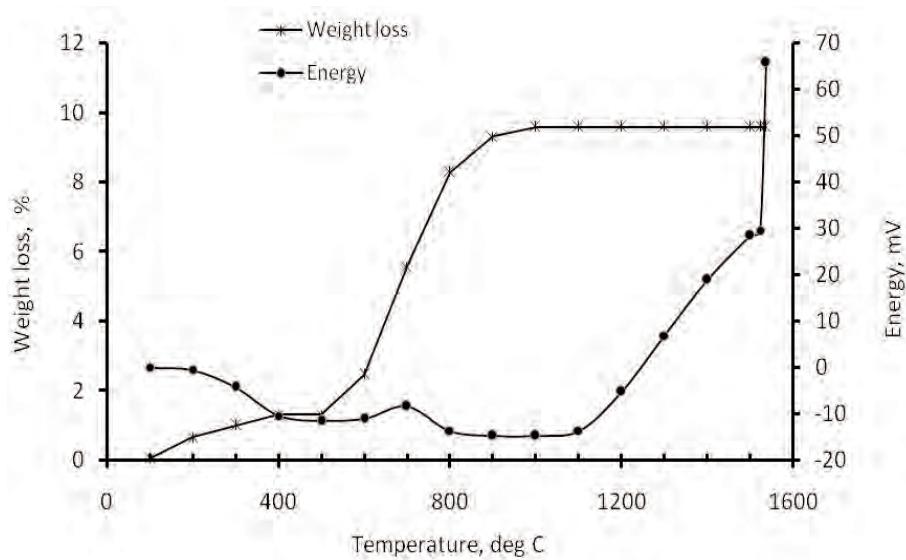


Fig. 5: Weight loss and energy profile of CBI with increasing temperature

67%  $\alpha$ -Fe (ferrite), 23.5%  $\text{Fe}_3\text{C}$  (cementite), 5%  $\text{SiO}_2$  (silica) and 4.5%  $\text{FeO}$  (wustite) [16]. Comparing the thermograph for 600°C to that of 500°C, there is an observed sharp decrease in the intensity of cementite (Fig. 3a). This suggests possible commencement of decomposition of cementite phase in this temperature interval.

CBI among others consists of about 3.5 wt. % carbon (Table 1) [13, 16] which can react with oxygen at this temperature to form products that depend on its availability.

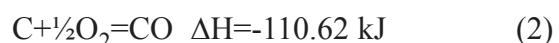
Table 1: Chemical composition of Aladja CBI [1,19]

Component	CBI (wt.%)
Iron (Fe)	78.00 – 85.70
Iron (Fe, metallized)	81.60 – 89.00
Carbon (C)	3.50 – 4.03
Lime ( $\text{CaO}$ )	2.71 – 3.50
Aluminium Oxide ( $\text{Al}_2\text{O}_3$ )	0.70 – 0.72
Silica ( $\text{SiO}_2$ )	3.50 – 4.10
Magnesium Oxide ( $\text{MgO}$ )	0.028 – 0.032
Phosphorous (P)	0.05 – 0.07
Sulphur (S)	0.004 – 0.005
Moisture	2.1

When available in adequate quantity in the vicinity of the reaction, oxygen could combine with available free carbon in the heated CBI to form carbon dioxide according to equation (1):



With limited availability of oxygen, carbon would combine with it to form carbon monoxide through the equation (2):



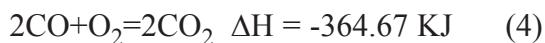
The carbon dioxide formed in reaction (1) might combine with cementite through the reaction:



The observed decrease in the intensity of cementite in the sample at this temperature connotes a decrease in its concentration. This could only be possible if reaction (3) is favoured to move to the right. And for this to take place, the carbon monoxide formed as a result of reactions (2) and (3) has to be removed from the reaction site. This removal

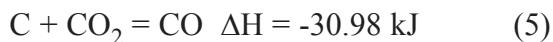
of the formed CO probably could have been achieved through combination or any of these three possible scenarios.

Firstly, when the carbon monoxide formed in the system combined with oxygen present in the vicinity of the reaction to form carbon dioxide by the reaction:



The carbon dioxide produced through reaction (1) and reaction (4) might have combined with cementite to produce  $\alpha$ -Fe as indicated in equation (3). The removal of carbon monoxide and subsequent formation of carbon dioxide in reaction (4) favoured reaction of cementite as indicated in reaction (3). This consequently might have caused the observed decline in the concentration of cementite.

Secondly, removal of carbon monoxide via the carbon deposition reaction (the reverse reaction):



The carbon deposition reaction is most pronounced in the temperature interval of 500°C – 550°C [17, 18]. At such low temperature as 600°C, carbon dioxide is the stable gas phase. Any carbon monoxide present tends to dissociate into carbon dioxide and carbon is deposited as soot. The stability of CO decreases with increasing temperature and increasing pressure [17]. The maximum instability occurs between 600°C and 800°C [17 – 19]. These seem to be in line with the observation under consideration and might have also been a likeable contributing factor to the observed decrease in the cementite concentration.

Thirdly, when the formed CO present in the reaction site was expended in the

reduction of wustite to  $\alpha$ -Fe through reaction (6):



This reaction is feasible at temperatures above 570°C [16, 19, 20], a condition already met in this temperature interval. The reaction also encourages carbon monoxide removal from the reaction site as discussed above. Not only does this facilitate the decomposition of cementite as earlier discussed but also increases the concentration of  $\alpha$ -Fe in the sample.

The XRD pattern of the heat-treated sample quenched at this temperature also confirms the disappearance of wustite phase and lends support to possibility of FeO reacting with available CO as expressed in equation (6). The diffractogram obtained for samples treated at 600°C and 700°C (Fig. 2) shows similar result. Reaction (6) also produces more  $\alpha$ -Fe thereby causing its concentration in the sample to increase. This might have explained the observed strong intensity of  $\alpha$ -Fe phase at these temperatures. The decomposition of wustite to form magnetite and  $\alpha$ -Fe is unlikely in this case since conversion of wustite to magnetite and  $\alpha$ -Fe is only possible at a temperature below 570°C [18, 19, 21] and no trace of magnetite was recorded in any of the measured XRD pattern.

Further heating to 800°C and 1000°C did not produce any noticeable change (Fig.3). From 700°C only  $\alpha$ -Fe and quartz phases remained and these were maintained up to 1000°C (Figs. 3b – 4). The intensities of  $\alpha$ -Fe however, became stronger and sharper indicating an increase in the concentration of this phase.

Since the prominent phases in CBI from temperature of 600°C upward appear to be  $\alpha$ -Fe and silica, the major component of CBI that might have been posing problem to melting of CBI in the existing melting facilities might therefore be attributed largely to the presence of silica (gangue content) and the unreduced iron (wustite). The effect of unreduced iron (wustite) and silica in CBI can be solved by charging along with it suitable fluxes that can reduce the wustite in CBI and absorb the silica into the slag formed during melting. As a result of large volume of slag that is likely to form, an effective deslagging mechanism should be incorporated into the design of such furnace to remove the generated slag regularly from the system.

The profile of melting CBI can distinctly be divided into four temperature zones with respect to changes in weight during the process. The first zone starts from room temperature up to about 400°C (Fig. 4 & 5). Starting from about 80°C up to about 400°C, it is noted that there is a gradual loss in weight in the neighbourhood of about 1.3% of the weight of the starting material. This corresponds to a loss of about 0.004 % per °C. The chemical analysis of CBI shows that it consists among others things, of 2.10% moisture, 0.004 - 0.005% sulphur and 0.05-0.7 phosphorous [16]. This initial loss in weight of CBI may partially be attributed to loss of moisture and gaseous products of any of these elements at these temperatures.

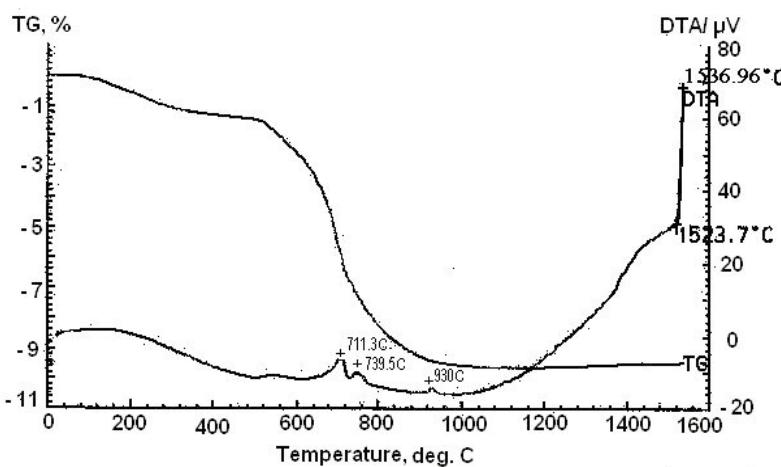
This is followed by an observed stable weight in the temperature interval from 400°C to about 520°C which constitute the second temperature zone. (Fig. 4 & 5). This may probably be an indication of the absence

of any reaction that involves evolution of gaseous products.

The third zone starts from 520°C and ends at about 930°C at which interval there is an observed rapid decrease in the weight of CBI by about 8.3% of the weight of the initial starting material (Fig. 4 & 5). This corresponds to a weight loss of approximately 0.02% per °C rise in temperature. Compared to the first zone, the rate of weight loss in the third zone is approximately five times for every one-degree rise in temperature! The mineralogical analysis of CBI revealed that it consists among others of a total of 23.5 wt % iron carbide [16]. Apart from the reasons already given for the loss in weight in the first zone, the decomposition of iron carbide takes place at about 638°C, which may have partially attributed to the observed loss in weight in this zone.

The fourth zone starts from about 930°C up to the end of melting temperatures, 1536.96°C. There is no observed further change in the weight of the sample (Fig. 4). This may indicate that solid CBI attains chemical stability before its transformation from solid to liquid phase in the temperature interval of approximately 1523.70°C to 1536.96°C.

There is a sudden absorption of energy at three temperatures namely 711.3°C, 739.5°C and 930°C during the heating process (Figs. 6). The reason for the increased energy absorption at 711°C is not very certain. However, the decomposition and reduction of CBI to alpha iron starts between 550°C and 600°C and concludes between 725°C and 750°C, in the neighbourhood of 739°C [18, 20]. For this reason, the energy peak at



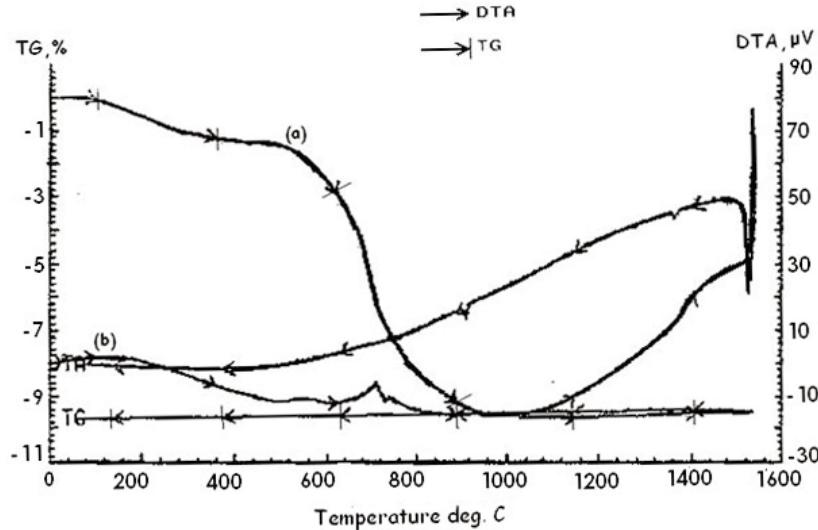
*Fig 6. Thermograph of heated CBI to melting temperature showing weight loss and energy profile*

739.5°C on the TG/DTA chart (Fig. 5) strongly suggests that the cementite in CBI completely dissociates into alpha iron and carbon at this temperature through equation (7).



This finding also supports an earlier report that cementite decomposes at a temperature of 738°C [22, 23]. What actually

happens at 930°C is not very certain. It is however noted that this temperature is close to the tail end of the third temperature zone when constancy of weight is obtained during the heating of CBI. That CBI is non-homogeneous and melts in the range of temperatures of approximately 1523.7°C to about 1536.96°C (Fig. 4 & 5) supports the results of the chemical and mineralogical



*Fig. 7. Thermograph showing changes in: (a) weight and (b) energy profile as CBI is heated, melted and cooled to the room temperature*

analyses, which reveal that the material is not homogeneous [13, 16]. It is further noted that having frozen the molten CBI and cooled back to room temperature, the solidified CBI maintains the earlier weight lost and never recovers the loss (Fig. 7). This suggests that the decrease in weight may have been attributed to formation of gaseous products which must have escaped from the vicinity of the reaction. The thermograph also reveals that about 30 kilojoules of energy is needed to start the melting of a briquette of CBI, which weigh approximately 95g (320 kJ/kg).

#### 4. Conclusion

Heating CBI up to 500°C under a normal atmospheric condition does not bring about any noticeable chemical change. By 700°C there is an observed increase in the concentration of  $\alpha$ -Fe phase and this is attributed to the decomposition of cementite and the reduction of wustite phases. Only  $\alpha$ -Fe and cementite phases remain in CBI at temperatures ranging from 700°C to 1000°C.

Four distinct temperature zones are identified during the melting of CBI. The first corresponds to RT - 400°C which is accompanied by 1.3 wt % loss in the weight of the initial charged CBI; the second zone is 400°C - 520°C during which the weight of CBI remains constant; the third being 520°C - 930°C during which there is a rapid weight loss of 8.3 wt.% of the starting material; while 930°C – 1536.96°C forms the fourth zone at which there is no loss in weight. CBI is non-homogeneous and melts in the temperature range of 1523.7°C to about 1536.96°C. It is inferred that the possible major components of CBI that could have

been posing difficulty to melting CBI in the existing melting facilities might probably be silica (gangue content) and unreduced iron oxide. Therefore furnaces meant to melt CBI should have incorporated into them an effective slag forming system and deslagging mechanism.

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