Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

A DTA–EGA STUDY OF THE CHEMICAL ISOLATION OF Fe_3C, AMORPHOUS CARBON, AND GRAPHITE FROM STEEL AND CAST IRON*

G. KRAPF, J. L. LUTZ, L. M. MELNICK, and W. R. BANDI
U. S. Steel Corporation, Applied Research Laboratory, Monroeville, Pennsylvania 15146 (U. S. A.)

(Received February 11th, 1972)

ABSTRACT

Data for the combustion of Fe_3C, amorphous carbon, and graphite in a specially designed DTA–EGA apparatus are presented. The peak temperatures for combustion and CO_2 evolution are determined.

The EGA peak temperature is shown to be reproducible within 10 °C irrespective of the reagents used for the isolation of Fe_3C or amorphous carbon, and within 25 °C for isolated graphite.

In general, the DTA–EGA results show that previous claims for isolation of Fe_3C, amorphous carbon, and graphite have been correct. Different amounts of Fe_3C are isolated by various chemical treatments, which explains the contradictions in the literature.

INTRODUCTION

For many years, workers have been attempting to quantitatively isolate cementite (Fe_3C) from steels by chemical and electrochemical methods. Even though the compound is chemically unstable at room temperatures and has been reported to be pyrophoric[1–3], some iron carbide has been isolated by dissolution of the iron matrix in an electrolytic cell with different electrolytes, by chemical displacement of the iron, and by chemical dissolution of the iron with reagents such as acids and iodine.

Old steel-analysis procedures[4] list treatment of the steel with copper potassium chloride solution as a method of dissolving the iron and concentrating the carbon from the steel in the insoluble portion. The quantitative recovery of the carbon and carbides was considered to be questionable[5], but Fe_3C has been identified in the residues by X-ray diffraction.

Koch and his co-workers have done a great amount of experimental work in developing the electrolytic isolation of metal carbides and other compounds from steel. Most of this work has been summarized in an excellent book[6] that describes

---

*Presented before the Third Annual Meeting of the North American Thermal Analysis Society in Waco, Texas, on February 7–8, 1972.

the use of electrolytic isolation procedures. Koch and many others[2,7–10] stated that the isolation of Fe_3C is not always quantitative and that the carbide is most often contaminated with amorphous carbon.

Smerko and Flinchbaugh[11] are among many workers who have shown that some Fe_3C can be isolated by the Rooney method[12], in which the matrix is dissolved by treatment with a solution of iodine and methyl alcohol. It has been generally realized that only part of the carbide is isolated and that the residue also contains amorphous carbon. Substitution of bromine for the iodine leads to a nearly complete conversion of Fe_3C to amorphous carbon[13].

Ron *et al.*[14] proved by Mössbauer spectroscopy that Fe_3C could be isolated by dissolving the matrix in sulfuric acid; the chemical results obtained for the analysis of the isolated material showed that elemental carbon also was present. Dubrovina and co-workers[15] showed that some elemental carbon remained after the treatment of an isolated residue with $HF–HNO_3$.

Gurry *et al.*[1] claimed to be able to isolate nearly pure Fe_3C by using an electrolyte of CdI_2 with a purified inert gas flowing through a specially designed electrolytic cell. They filtered the isolated carbide in the absence of air and stored the isolated residue in a vacuum. Upon exposure of the residue to air the evolution of heat was detected, presumably due to oxidation of Fe_3C. Therefore, these workers postulated that the initial decomposition of Fe_3C in air coats the outside of the particle with amorphous carbon and an oxide of iron. They further theorized that this coating prevented complete decomposition of the remaining Fe_3C. This surface oxidation would explain why it is almost impossible to isolate pure Fe_3C and also why it is possible to isolate some contaminated Fe_3C by most of the isolation procedures except those using an initial attack with a strong oxidizing agent.

For the past seven years, metal carbides in steel have been determined by applying differential thermal analysis–evolved gas analysis (DTA–EGA) to the chemically and electrochemically isolated residues[16–22]. In many DTA–EGA curves, two or more characteristic combustion peaks have been observed, along with the corresponding number of EGA peaks for the evolution of CO_2, when the isolated residue was programmed heated in an oxygen atmosphere. On the basis of microchemical analysis of the residue and diffraction data obtained on the residue or the original sample, it was assumed that one CO_2 evolution peak (at about 380°C) was due to the oxidation of Fe_3C and another CO_2 evolution peak (at about 480°C) resulted from the combustion of amorphous carbon. However, recently it has become necessary to develop more proof of this assumption. To show that the DTA–EGA responses for Fe_3C, amorphous carbon, and graphitic carbon are different, and that these responses can be used to determine the concentration of these constituents in an isolated residue, we conducted a number of experiments with specially selected samples. These samples were subjected to a number of chemical treatments designed to isolate or dissolve one or more of the carbon phases in the isolated residue. X-ray diffraction and chemical microanalyses were also performed to aid in understanding the thermal response. This paper presents some of the results of this work.

EXPERIMENTAL

Isolations

Isolation of Fe_3C by use of copper potassium chloride solution. — For the isolation of Fe_3C and Fe_3C plus graphite, copper potassium chloride solution (125 ml) containing $CuCl_2 \cdot 2KCl \cdot 2H_2O$ (25 g) was added to a 250-ml Erlenmeyer flask containing a steel or cast iron sample (0.5 g). Argon was bubbled through the solution while dissolution was in progress and the solution was filtered under argon on a 47-mm, 50-mμ VMP Millipore organic membrane using a Millipore Model XX1004700 filtering apparatus. The residue was washed with water and then with methanol and dried in a desiccator in an atmosphere of argon containing a small amount of air.

Isolation of Fe_3C by use of iodine–methanol. — For the isolation of Fe_3C in iodine solution, iodine (5 g) was added to an Erlenmeyer flask containing absolute methanol (100 ml). The mixture was stoppered and shaken to dissolve the iodine. A preweighed sample (~5 g) of 1–2-mm-thick steel sheet was added to the flask, the flask was purged with argon, stoppered, and shaken at room temperature for 2–3 h. The steel sheet was removed, placed in a small beaker containing methanol, and agitated ultrasonically to remove adhering particles. The remaining sample was dried and weighed to determine how much had dissolved. The iodine solution and the alcohol rinse were filtered under argon through a 47-mm, 200-mμ Gelman Alpha 8 organic membrane mounted in the previously mentioned Millipore filtering apparatus. The membrane and residue were washed with methanol and dried in a desiccator under an atmosphere of argon containing a small amount of oxygen.

Isolation of amorphous carbon with bromine–methyl acetate. — For the isolation of amorphous carbon, an apparatus similar to the one described by Smerko and Flinchbaugh[11] was used. The sample (1 g) was transferred to the clean, dry flask, and after attachment of the condenser, methyl acetate (15 ml) and bromine (5 ml) were added through the top of the condenser. Dissolution was accomplished in 1–2 h by heating the sample so that a slight refluxing occurred. The solution was filtered in an argon atmosphere through a 47-mm, 200-mμ, Gelman Alpha 8 membrane mounted in the Millipore filtering apparatus. Because the filtering membrane appeared to gain weight and because the top membrane appeared to gain more weight than a membrane placed immediately under it in the filter apparatus, no attempts were made to preweigh the Gelman membrane. The residue was washed with methyl acetate until free of bromine color and then washed five times with methyl alcohol. While still moist with alcohol the residue and membrane were transferred to a desiccator and dried under argon.

Electrolytic isolation of Fe_3C and graphite. — Isolation of Fe_3C plus other carbon constituents of steel or cast iron was accomplished by using the procedure, electrolytic cell, and filtering technique which the authors had previously used for the isolation of intermetallic phases[20]. With each electrolyte and each type of steel, a current-potential curve similar to those shown by Koch[6] was plotted. The voltage was then set so that the isolation of Fe_3C could be accomplished. Isolations were conducted with 1% ammonium sulfate–1% citric acid and with 10% sodium citrate–2% potassium bromide solutions.

Isolation of graphite by treatment with 3:2 HNO_3. — To isolate graphite or nearly pure graphite from cast iron samples, the sample (0.5 g) was heated with 3:2 HNO_3 (50 ml) until no further action was observed. The solution was then diluted to 200 ml with water and filtered in the same manner as in the copper potassium chloride method.

Isolation of carbon compounds with 10% HCl. — To isolate carbon compounds with 10% hydrochloric acid, the sample (1–4 g) was transferred to a 500-ml Erlenmeyer flask containing 10% by volume hydrochloric acid (250 ml). The solution was purged with argon and sealed with a relief valve (Bunsen valve) attached to a stopper. The samples were then heated to 40°C in a water bath until dissolution of the matrix was complete. Filtering and desiccation were the same as described in the copper potassium chloride method.

Treatment of electrolytically isolated residues with HF–HNO_3. — To separate graphite and amorphous carbon from other carbides, a portion of the residue which was electrolytically isolated with 1% ammonium sulfate–1% citric acid was then heated with HNO_3 (5 ml), water (5 ml), a few drops of HF, and ammonium persulfate (1 g) (HF–HNO_3 will completely dissolve most stable carbides). The solution was diluted to 25 ml and filtered on a Millipore Model XX102500 filtering apparatus containing a 25-mm, 50-mμ VMP Millipore organic filtering membrane.

Determination of DTA–EGA data

Fe_3C. — To establish the DTA–EGA data for Fe_3C, three samples of iron–carbon alloy (containing only traces of other metals and nonmetals), which had been heat-treated to precipitate large carbide particles, were used as a source of Fe_3C. In addition, National Bureau of Standards (NBS) Standard Reference Materials (SRM) No. 493, which contains 14% spheroidized cementite in ferrite, was also used. Fe_3C was identified in the samples by both X-ray and electron diffraction.

M_3C in highly alloyed steel. — To determine whether M_3C could be isolated from a complex alloy steel, and to determine the nature of the DTA–EGA peaks for M_3C, isolation of carbides from a 10Ni–2Cr–1Mo–8Co–0.2C steel was attempted. To precipitate M_3C, the hot-rolled ½-in. plate was austenitized at 815°C for 1 h and water-quenched. The plate was then aged at 205°C for 5 h.

Graphite. — To determine the DTA–EGA temperature responses for the combustion of graphite, NBS SRM No. 82b was used. This standard is certified to contain 2.37% graphite, which is insoluble when the remainder of the carbon is dissolved in 3:2 HNO_3.

Fe_3C+graphite+amorphous carbon+other carbides. — An alloy cast iron sample was used as a source of a complex carbon mixture containing both forms of elemental carbon and several different carbides. Attempts were made to identify the DTA–EGA peaks for Fe_3C, graphite, and amorphous carbon in isolated residues which also contained other carbides.

Instrumental

All the DTA–EGA results were obtained with a modified R. L. Stone Model $12BC_2$ instrument[18,20,21]. A specially constructed sample compartment, having a very small gas volume which facilitates the use of a very slow gas flow rate (3 ml O_2/min), was used for this work. Details of this sample compartment have been published previously[21]. The EGA of CO_2 from the combustion of carbides was accomplished by amplifying and recording the change in thermal conductivity of the evolved gas. A Gow-Mac Model 9999 power supply was used with a Gow-Mac Model Tr111A constant-temperature thermal conductivity cell and a 1 mV recorder. Details on this have been previously described[21]. The following instrumental parameters were used.

DTA. — Heating rate, approx. 10°C/min; temperature reproducibility, ±5°C; DTA sensitivity, 15 μV/in. = 0.33°C/in.; thermocouples, platinel; atmosphere, dynamic oxygen at 3 ml/min; DTA sample pans, 6 mm round flat platinum with an approx. capacity of 3 mg of residue, Al_2O_3 was used in the reference pan.

EGA. — Sensitivity, based on 0.25 in.^{2} as detectable above the base line, was 5 μg carbon as CO_2 (which is equivalent to 0.001% TiC in 3 mg of residue from 1 g of steel). Lag time of the EGA peak behind the DTA peak was 6–8 min (60–80°C).

Resolution of EGA responses

Although the temperature for the peak combustion of individual carbides in a mixture is usually reproducible and detectable, the rate of combustion may be such that the decomposition of one carbide is not complete before the programmed rise in temperature has caused the ignition of another carbide. Therefore there will be considerable overlap of the two EGA peaks. To resolve the individual EGA responses, a duPont 310 Curve Resolver was employed[21]. By knowing some of the peak temperatures for metal carbides, by being able to observe certain peaks in the EGA response, and by using the diffraction and microchemical results, a resolution of the overall EGA response is obtained which often reveals the presence of a carbide which could not otherwise be detected. Therefore, quantitative determinations of minor amounts of stable carbides are possible even in the presence of large amounts of amorphous carbon or cementite.

Examination of steel and isolated residues by diffraction methods

Many of the isolated residues were examined by standard X-ray diffraction procedures. Replica electron diffraction techniques were also used for *in situ* identification of certain compounds in the steel.

Chemical analysis of isolated residues

When the determination of the concentration of one or more metallic elements was useful for the identification of compounds in the separated residue, the analysis of the residue for these elements was performed by conventional chemical and microchemical procedures.

RESULTS AND DISCUSSION

Fig. 1 is the DTA–EGA response recorded for the combustion of 0.27 mg of impure Fe_3C residue isolated by treatment of a 4.4% carbon alloy with iodine–methanol. This iron–carbon alloy had been heat-treated and water-quenched so that, based on theoretical considerations and on X-ray and chemical observations, nearly all the carbon in the alloy and the major portion of the iron were combined as the iron carbide. Therefore, the predominate phase (60%) in the sample was Fe_3C and the remainder was ferrite. By treatment of a sheet of this sample with iodine and methanol at room temperature, 4/5 of the sample was dissolved. The undissolved material was identified by X-ray diffraction as Fe_3C. The residue contained 90% iron and less than 10% carbon by EGA analyses (Fe_3C contains 6.7% carbon). It therefore appears that 2/3 of the Fe_3C was dissolved.

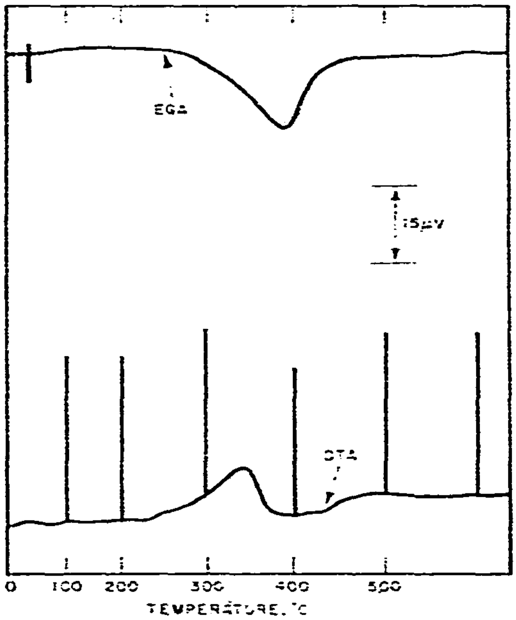


Fig. 1. DTA–EGA response for the combustion of impure Fe_3C residue isolated from Fe–C alloy with iodine–methanol.

Fig. 2 shows the DTA–EGA response for 1.92 mg of residue containing Fe_3C which was isolated from the same 4.4% carbon alloy by treatment with copper potassium chloride solution. This residue is not pure Fe_3C; FeOOH was identified in the material by X-ray diffraction. The change in the DTA slope at 270°C and the small endotherm at 300°C may be caused by the presence of FeOOH. The residue contains 11% carbon, which is too high for a pure Fe_3C, and 80% iron, which is too low for pure Fe_3C. The EGA response shows CO_2 being evolved up to 630°C, whereas Fig. 1 shows no further evolution of CO_2 beyond 480°C. The peak evolution of CO_2 is at 380–390°C.

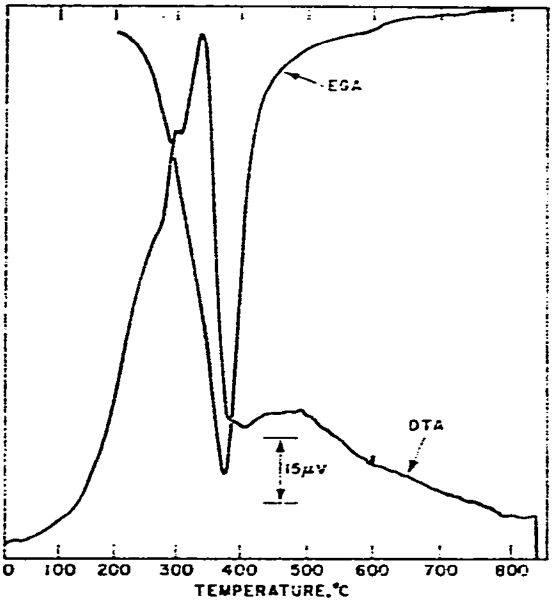


Fig. 2. DTA–EGA response for Fe_3C residue isolated from Fe–C alloy with copper potassium chloride solution.

Fig. 3 shows the DTA–EGA response for a residue isolated from an 0.97% carbon steel which had been used previously for X-ray diffraction studies of Fe_3C. The carbon content and heat treatment of this steel were specified so that all carbon would be combined as Fe_3C. Although the EGA results showed that 0.93% carbon

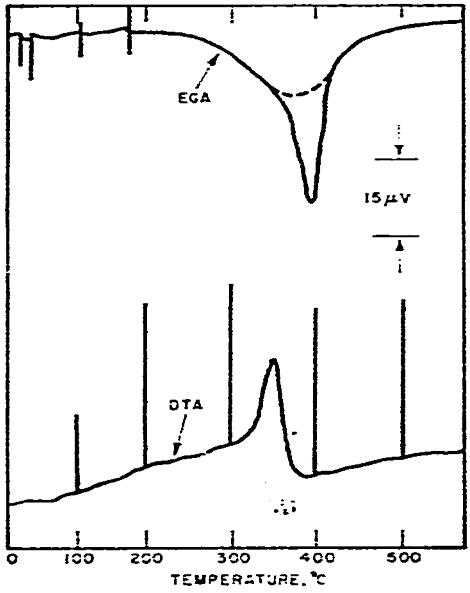
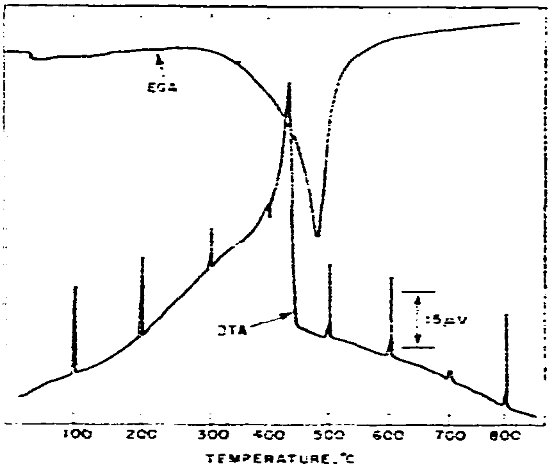


Fig. 3. DTA–EGA response for the residue isolated from a carbon alloy with copper potassium chloride solution.

was recovered in a residue from this steel by treatment with copper potassium chloride solution, only 50% of the residue was iron. The shape of the EGA curve definitely suggests two CO_2 evolution peaks, one a rounded peak at 375°C and the other a sharp peak at 395°C. It appears that the CO_2 was evolved from Fe_3C and from carbon remaining in close proximity to Fe_3C. The combustion of this carbon may be catalyzed by iron oxides and/or traces of copper so that the amorphous carbon does not burn over the usual temperature range. It is interesting to note that the measurement of the area of EGA peaks at approximately 380°C is a better estimation of the Fe_3C concentration than analysis of the isolated residue for iron.

Treatment of NBS SRM No. 493 (14% cementite in ferrite) with copper potassium chloride solution yielded a residue that had an EGA response very similar to that shown in Fig. 3; the iron content of the residue was only 35%. Shaking a solid piece of this standard with iodine-methanol for time intervals from 3 to 12 h failed to yield a pure Fe_3C phase. A residue which appeared to be finely divided iron powder was obtained. The DTA-EGA response for this material appeared to be the same as that obtained by burning powdered steel in the instrument, and X-ray diffraction examination showed iron and Fe_3C to be present. We do not know why the iodine treatment was not successful, but it may be that a preferential attack took place around the grain boundaries.

All the above results show that Fe_3C or partially decomposed Fe_3C burns between 250 and 500°C with peak evolution of CO_2 occuring at 370–395°C. These results are in agreement with the observations made by Koch and Keller[2], who used a more conventional carbon combustion apparatus to determine that combustion of coarse particles of Fe_3C began at 200°C and was complete at 600°C. The residue that they examined was 7% carbon and 92% iron, and Fe_3C was identified by X-ray diffraction.



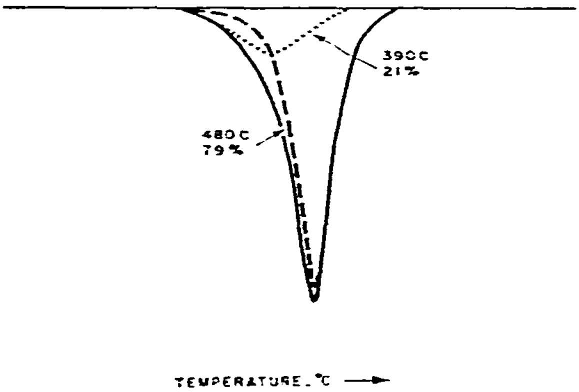


Fig. 4. DTA–EGA response for a residue isolated from an iron–carbon alloy with bromine–methyl acetate.

Fig. 5. Resolution of the EGA response shown in Fig. 4.

Yakovlev and co-workers[8] have stated that the amorphous carbon in an isolated residue is completely burned at 600 °C and that the graphite burns at 900 °C. Other workers[13] have stated that treatment of a steel with bromine in an organic solvent will result in formation of large amounts of amorphous carbon. Fig. 4 shows the DTA–EGA results for a residue isolated from an iron–carbon alloy (4.4% C) with bromine–methyl acetate. Most of the residue yielded a combustion peak at 430 °C, with the peak evolution of CO_2 occurring at 480 °C and complete evolution by 630 °C. This is 100 °C higher than shown in Fig. 1. However, Fig. 4 indicates that more than one carbon-containing compound was present. Fig. 5 is the resolution of the EGA response in Fig. 4 and shows that a CO_2 evolution occured at 380 °C, which indicates that Fe_3C is present. The Fe_3C did not completely dissolve in bromine–methyl acetate because large particles were present and the particles were coated with amorphous carbon which prevented further attack on the particles by the bromine[1]. No Fe_3C pattern was found by X-ray diffraction even though more than half the weight of the residue was Fe_3C, as shown by EGA resolution and analysis for Fe_2O_3. The results in Figs. 1–5 show that there is no binding rule about dissolution of Fe_3C. The time allowed for dissolution and the size of the carbide particles appear to affect the amount of Fe_3C that is dissolved.

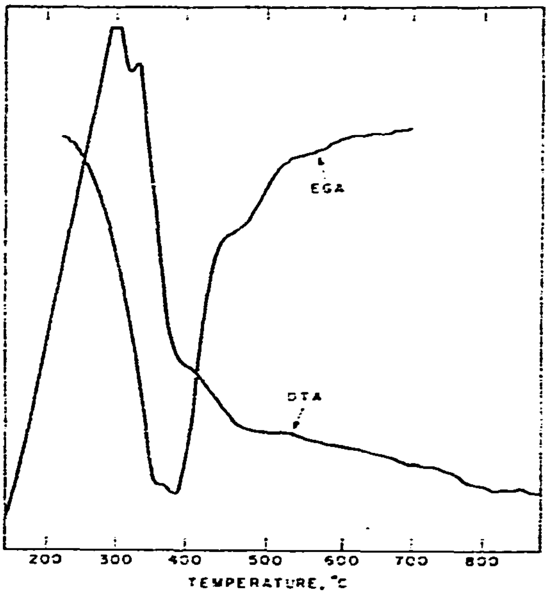


Fig. 6. DTA–EGA response for the residue electrolytically isolated from a high-alloy steel.

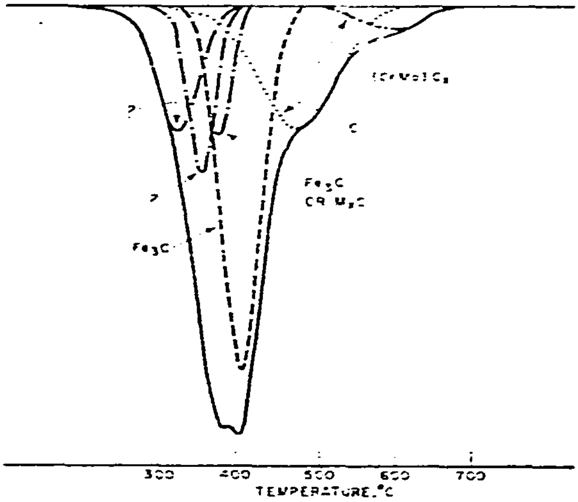


Fig. 7. Resolution of the EGA response shown in Fig. 6.

Fig. 6 is the DTA–EGA recording for the residue isolated from a highly alloyed steel by dissolving the matrix electrolytically in 1% ammonium sulfate–1% citric acid. The two major EGA CO_2 peaks (Fig. 7) are the amorphous carbon peak at 460 °C and the M_3C peak at 390 °C. There is also a small peak at 370 °C which may be due to an M_3C of composition different from the other M_3C. The residue contained 12% carbon, 60% iron, 11% molybdenum, and 7% chromium. The only compound that could be identified by X-ray diffraction was Fe_3C. To prove that the 390°C peak resulted from the combustion of Fe_3C, a portion of the isolated residue was heated to 390°C, then cooled and again examined by X-ray diffraction. An indefinite pattern believed to be a mixture of oxides could not be identified, but the Fe_3C pattern disappeared, which indicated that peak combustion of the M_3C (Fe_3C) probably occurred at 300–330°C and the corresponding CO_2 evolution occurred at 370–390°C.

The DTA–EGA response for Texas lamp black, which is amorphous carbon, was recorded and showed a single peak (DTA at 610°C and EGA at 670°C) at a temperature higher than that ascribed to amorphous carbon in this work.

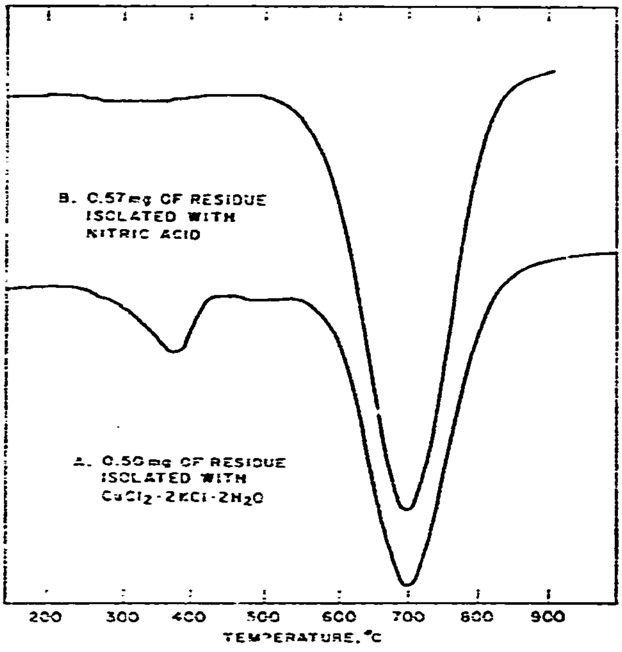
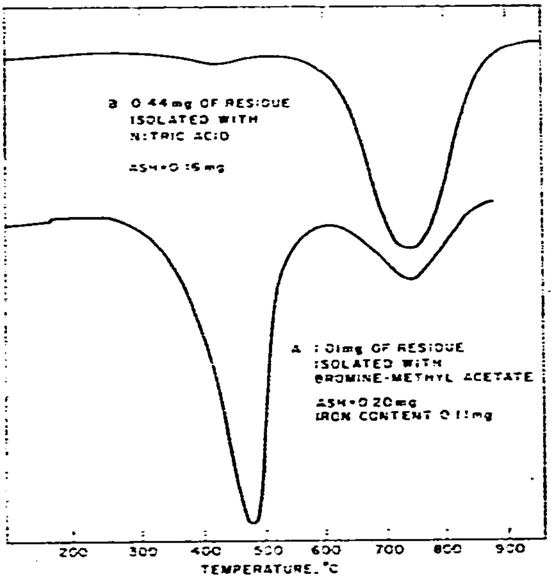


Fig. 8. EGA responses for the residues isolated from the NBS cast-iron standard No. 82b. A, treatment of the residue with copper potassium chloride solution. B, treatment of the residue with nitric acid.

Because another form of elemental carbon (graphite) is present in cast irons, we wished to determine whether DTA–EGA would also show a distinct temperature for this form of carbon and whether it could be distinguished from Fe_3C or amorphous carbon. Fig. 8 is a comparison of the EGA CO_2 recordings for residues isolated from NBS SRM No. 82b cast iron by treatment with (*A*) copper potassium chloride solution, and (B) nitric acid. The peak in Fig. 8A at 380°C has been previously shown to be associated with Fe_3C, whereas the peak at 700–730°C is believed to be associated with the combustion of graphite. We have assumed that the 700°C peak is due to graphite because the isolation method used here has been used for at least 50 years as a procedure for isolating and determining graphite in cast iron, an X-ray diffraction pattern for graphite was identified, and the DTA exotherm for naturally occurring graphites from various sources is in the range 620–820°C[23]. More than 2/3 of the weight inserted in the DTA–EGA apparatus for the recording of Figures 8A and 8B was evolved as CO_2, indicating that as much as 80% of the sample in Fig. 8B was carbon.



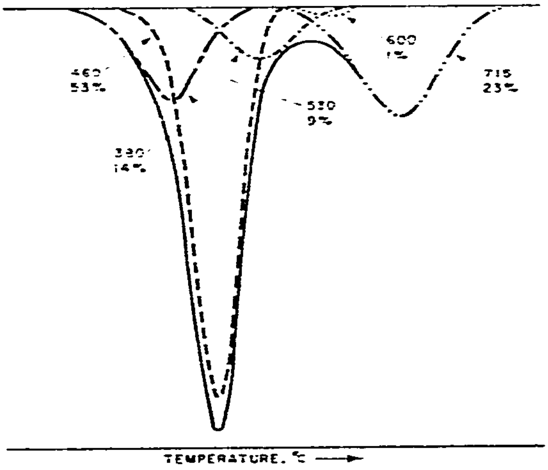


Fig. 9. EGA responses for the residues isolated from an alloy cast iron. A, treatment of the residue with bromine–methyl acetate. B, treatment of the residue with nitric acid.

Fig. 10. Resolution of the EGA response shown in Fig. 9A.

Fig. 9 is a comparison of the EGA CO_2 recordings for residues isolated from a highly alloyed cast iron by treatment with (A) bromine-methyl acetate, and (B) nitric acid. The figure indicates that both forms of elemental carbon (graphite and amorphous) are easily distinguishable. After the DTA–EGA analyses, less than 20% of the sample weight of residue isolated by bromine–methyl acetate remained in the sample pan. This indicated that the residue was nearly 90% carbon; analysis of the remaining ash showed 0.11 mg of Fe which, as Fe_2O_3, accounted for most of the weight remaining in the pan after the DTA–EGA analysis. Examination of the EGA response in Fig. 9A with the duPont Curve Resolver shows (Fig. 10) that some Fe_3C was not dissolved in bromine–methyl acetate. The iron equivalent of the amount of CO_2 evolved at 380°C fits the microchemical iron value obtained for the isolated residue. This is further proof that the 380°C EGA peak is the result of the combustion of Fe_3C.

The large area of the 460°C peak in Fig. 10 relative to the area of the graphite peak at 710°C shows that much of the Fe_3C is converted to amorphous carbon by bromine-methyl acetate. This is in agreement with the literature, which says that bromine-methyl acetate treatment produces amorphous carbon[13], and tends to support the evidence that the peak CO_2 evolution at 460–480°C is the result of the combustion of amorphous carbon.

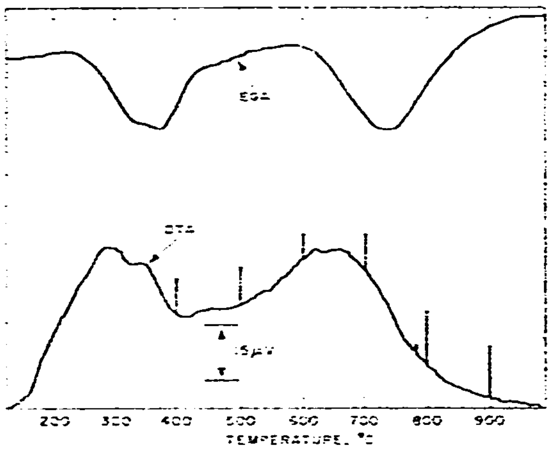


Fig. 11. DTA-EGA response for the residue (2.16 mg) electrolytically isolated from an alloy cast iron.

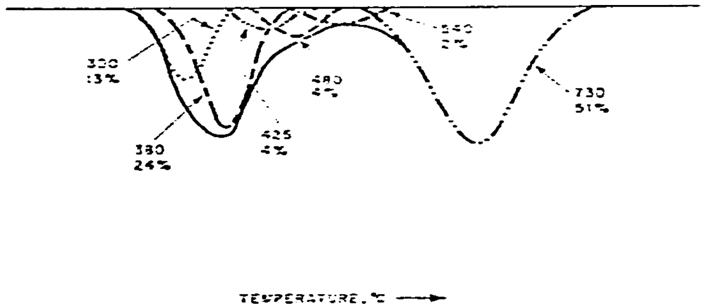


Fig. 12. Resolution of the EGA response shown in Fig. 11.

Fig. 11 shows the DTA-EGA response for a residue electrolytically isolated from an alloy cast iron in 10% sodium citrate and 2% potassium chloride[6]. The two major responses shown in Fig. 12 (resolution of EGA response in Fig. 11) are due to graphite and Fe_3C, and this is in agreement with the findings of Koch[6] who isolated Fe_3C in a similar manner. However, the peak area for CO_2 evolved from Fe_3C is smaller than the peak area for graphite. From knowledge of the carbon and graphite contents of the sample, this indicates that the isolation of the Fe_3C was poor. Fig. 13 shows the DTA-EGA response obtained from a residue isolated from the same material by using copper potassium chloride solution; a predominant peak for Fe_3C at 380°C is shown.

Much less Fe_3C is isolated by use of hydrochloric acid than by either the electrolytic or copper potassium chloride methods. This is shown by the DTA-EGA

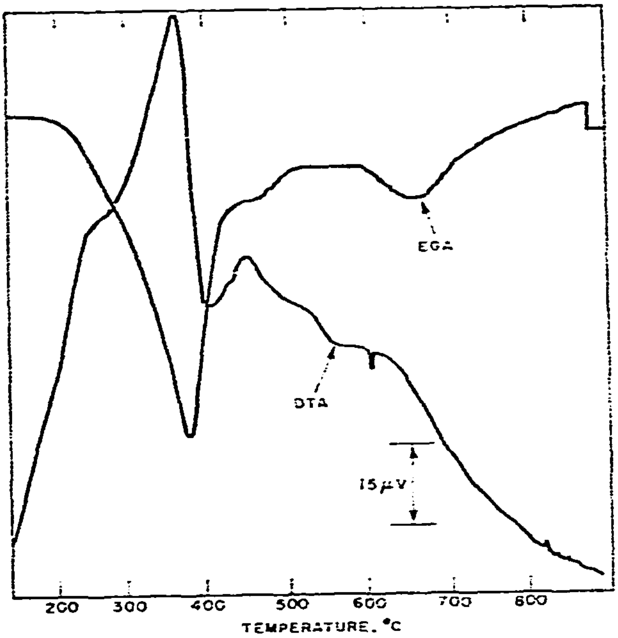
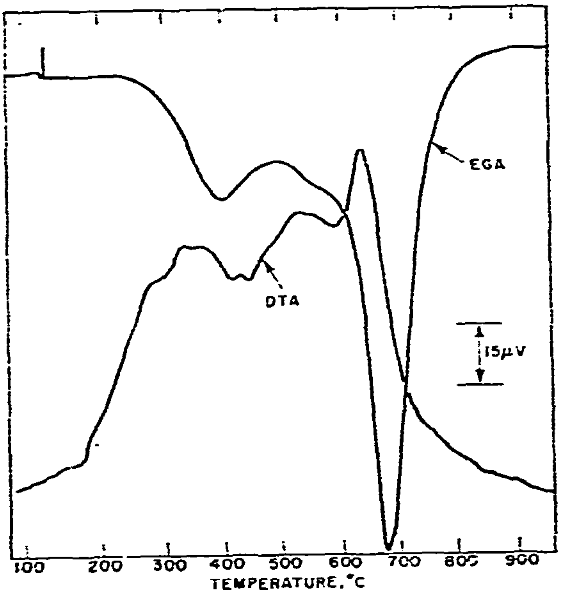


Fig. 13. DTA–EGA response for the residue (1.82 mg) isolated from an alloy cast iron using copper potassium chloride solution.



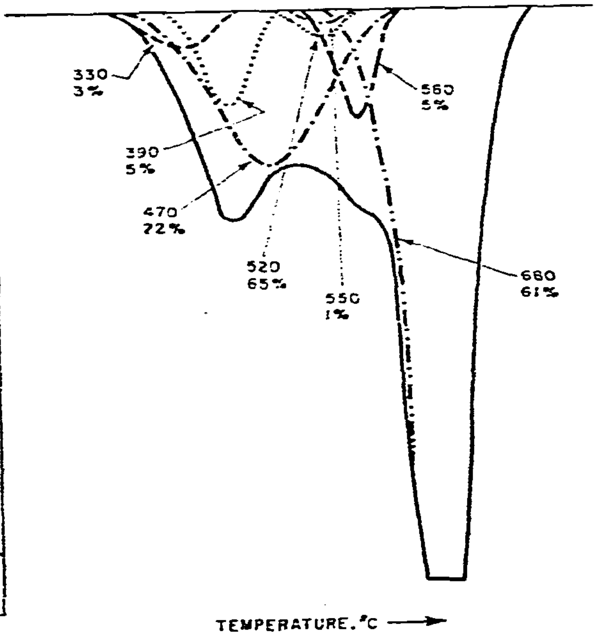


Fig. 14. DTA–EGA response for the residue (1.98 mg) isolated from an alloy cast iron using 10% hydrochloric acid.

Fig. 15. Resolution of the EGA response shown in Fig. 14.

response in Fig. 14, and the resolution of the response (Fig. 15) in which 61, 22, and 5% of the CO_2 evolved are due to graphite, amorphous carbon, and Fe_3C, respectively. Figs. 14 and 15 reveal small amounts of other stable carbides which are probably quantitatively isolated in hydrochloric acid and which form a much greater percentage of this residue than of other residues partly because more Fe_3C was dissolved. In

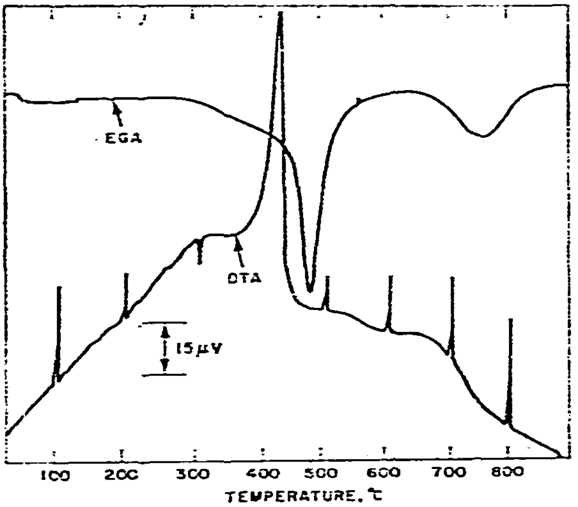


Fig. 16. DTA–EGA response for the residue electrolytically isolated from the high-alloy cast iron and treated with HF–HNO_3.

TABLE I

SUMMARY OF EGA PEAK TEMPERATURES FOR DTA COMBUSTION OF Fe_3C, AMORPHOUS CARBON, AND GRAPHITE ISOLATED BY VARIOUS CHEMICAL AND ELECTROCHEMICAL PROCEDURES

Isolation procedure	*Sample type*	*EGA peak temperature (°C)*		
		Fe_3C or M_3C	*Amorphous carbon*	*Graphite*
I_2–CH_3OH	Fe–C alloy	390		
$CuCl_2(KCl)_2 \cdot 2H_2O$	Fe–C alloy	380		
$CuCl_2(KCl)_2 \cdot 2H_2O$	Cast iron	380		710
$CuCl_2(KCl)_2 \cdot 2H_2O$	Alloy cast iron	380		670
Br_2–Methyl acetate	Fe–C alloy	380	480	
Br_2–Methyl acetate	Alloy cast iron	380	460	715
3:2 HNO_3	Alloy cast iron			730
3:2 HNO_3	Cast iron			710
Electrolytic, 1% ammonium sulfate–1% citric acid	10Ni–2Cr–1Mo–8Co–0.2C Steel	390 370	460	
Electrolytic, 1% ammonium sulfate–1% citric acid then treated with HF–HNO_3	Alloy cast iron		480	730
Electrolytic, 10% sodium citrate 2% potassium chloride	Alloy cast iron	380	480	730
10% HCl	Alloy cast iron	390	470	680

spite of many literature statements about the instability of Fe_3C, the results show that some Fe_3C can be identified by DTA–EGA residues isolated in acid. This agrees with a recent publication[14] which showed by Mössbauer spectroscopy that some Fe_3C was isolated in residues which were exposed to sulfuric acid.

As a final experiment, a residue was electrolytically isolated from the high-alloy cast iron material by using 1% ammonium sulfate–1% citric acid electrolyte. The residue was than treated with HF–HNO_3, which is known to dissolve most carbides and to leave an amorphous carbon residue[8]. Fig. 16 shows that the main EGA response peaks were at 480°C (amorphous carbon) and at 730°C (graphite).

Table I summarizes the EGA results obtained for Fe_3C, amorphous carbon, and graphite by using eight different extraction procedures and four different types of iron–carbon samples. It appears that the Fe_3C and amorphous carbon EGA peaks can be reproduced within 10°C, whereas the graphite EGA peak can be reproduced within 25°C.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of P. A. Stoll who directed the X-ray and electron diffraction examination of the isolated residues.

REFERENCES

1 R. W. Gurry, J. Christakos, and C. D. Stricker, *Trans. A.S.M.*, 50 (1958) 105.
2 W. Koch and H. Keller, *Arch. Eisenheuttenw.*, 34 (1963) 435.
3 E. Houdremont, P. Klinger, and G. Blaschezyk, *Arch. Eisenheuttenw.*, 15 (1941) 257.
4 G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, *Chemical Analysis of Iron and Steel*, John Wiley & Sons, New York, 1931, pp. 179–80.
5 C. M. Johnson, *Chemical Analysis of Special Steels*, 4th edn., John Wiley & Sons, New York, 1930, p. 257.
6 W. Koch, *Metallkundliche Analyse*, Verlag Statileisen Mbh, Düsseldorf and Verlag Chemie, 6 Mbh, Weinheim Bergstr., 1965.
7 N. M. Popova, *Carbide Analysis of Steel*, Oborongiz., 1956, p. 78.
8 P. X. Yakovlev, E. F. Yakovleva, and A. I. Orzhekhovskaya, *Zavod. Lab.*, 35 (1969) 904.
9 K. Segawa, *Trans. Iron Steel Inst. Jap.*, 7 (1967) 163.
10 K. Narita, A. Miyamoto, and H. Matsumoto, *Tetsu to Hagane*, 57 (1971) 68.
11 G. Smerko and D. A. Flinchbaugh, *J. Metals*, (1968) 43.
12 T. E. Rooney, *J. Iron Steel Inst. Special Rep. No. 25*, (1939) 141.
13 H. F. Beeghley, *Anal. Chem.*, 24 (1952) 1713.
14 M. Ron, H. Shechter, and S. Niedzwiedz, *J. Appl. Phys.*, 39 (1968) 65.
15 I. M. Dubnovina, D. N. Zharkova, and E. F. Yakovleva, *Zavod. Lab.*, 34 (1968) 917.
16 W. R. Bandi, H. S. Karp, W. A. Straub, and L. M. Melnick, *Talanta*, 11 (1964) 1327.
17 W. R. Bandi, W. A. Straub, H. S. Karp, and L. M. Melnick, *ASTM Spec. Tech. Publ. No. 393*, ASTM, Philadelphia, Pennsylvania, 1966.
18 H. S. Karp, W. R. Bandi, and L. M. Melnick, *Talanta*, 13 (1966) 1679.
19 H. S. Karp, E. G. Buyok, W. R. Bandi, and L. M. Melnick, *Mater. Res. Bull.*, (1967) 311.
20 W. R. Bandi, J. L. Lutz, and L. M. Melnick, *J. Iron Steel Inst.*, (1969) 348.
21 W. R. Bandi, E. G. Buyok, G. Krapf, and L. M. Melnick, in R. W. Schwenker and P. D. Garn (Eds.), *Thermal Analysis, 2*, Academic Press, Inc., New York, 1969, pp. 1363–76.
22 Y. Riquier and A. Vilain, *Metallurgie*, 8 (1968) 107.
23 D. J. Swaine, in R. W. Schwenker and P. D. Garn (Eds.), *Thermal Analyses, 2*, Academic Press, Inc., New York, 1969.