

## IDENTIFICATION OF NITRIDE INCLUSIONS IN STEEL USING DIFFERENTIAL THERMAL ANALYSIS AND EVOLVED GAS ANALYSIS

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A preliminary study has been made of the feasibility of applying differential thermal analysis/evolved gas analysis (DTA/EGA) to the identification and estimation of nitrides in residues extracted from iron base alloys. A set of commercially available nitride powders have also been examined.

The results showed that EGA traces are more informative than the DTA observations and, additionally, provide an estimate of the total nitrogen present. Residues from steels often contain elemental carbon and this complicates the interpretation of the DTA and EGA traces. It is generally concluded that the DTA/EGA technique is useful in identifying nitrides but should be ancillary to other techniques such as X-ray diffraction.

In recent years much effort has been given to the identification of non-metallic inclusions in steel since in some cases, these are known to exert important influences on chemical and physical properties. Particular attention has been directed to the quantitative analysis and morphology of carbides, nitrides and sulphides. In general, inclusions may be examined by in situ techniques, using for example the electron probe micro-analyser, or alternatively they may first be extracted from the steel by differential chemical attack and then submitted to a wide range of physical or chemical analytical techniques. The choice of approach depends on the information required. If it is important to determine the character of individual inclusions then clearly in situ techniques are preferable. However, the examination of many inclusions in this way is prohibitively long and for many purposes, it is better to extract the inclusions in bulk from the steel and subsequently examine them as a powdered sample. This paper is concerned with the identification and determination of nitrides present in such bulk extracted residues.

Scholes and White [1] stated that with the exception of aluminium nitride [2], no reliable specific techniques exist for the quantitative determination of individual nitride phases, and more recently [3] the hitherto accepted Beeghly method [2] for aluminium nitride determination has been questioned. In the search for new approaches differential thermal decomposition was considered [1] to have potential and this has been developed [4–7] into a technique involving simultaneous differential thermal analysis and evolved gas analysis, (DTA/EGA) for the examination of carbides, nitrides and sulphides present in residues extracted from steel. White [8] used DTA/EGA to identify the nitrides isolated from two series

of high purity vacuum melted iron base alloys of the type Fe–M–N and Fe–M–N–C, where *M* is the nitride forming element. In this work, the isolated nitride powders were heated in a flowing oxidizing atmosphere and changes in enthalpy were recorded simultaneously with the evolved gas analysis using a mass spectrometer.

The present work has involved a detailed and systematic study of the DTA/EGA technique for quantitatively assessing the presence of nitrides in extracted residues. Using commercially available nitride powders, the thermal decomposition characteristics of relatively pure nitrides have been assessed and the influence of such variables as particle size and mutual interactions when mixtures are treated. The results of this work have been applied to nitrides extracted from alloys described by White [8] and obtained from them.

### Experimental methods and results

#### *Samples*

Two types of nitride samples were used in this investigation *viz.* commercially available powder samples (K & K Laboratories, Inc. of Plainview, New York State, U.S.A.) and nitride residues extracted chemically from special BSC Corporate Laboratories: alloys [8]. These are separately described.

#### *Commercial powder nitride samples*

The ten nitrides are listed in Table 1 together with analytical results, based on X-ray diffraction, chemical analysis and DTA/EGA data.

#### *Nitride residues from ternary (Fe–M–N) and quaternary alloys (Fe–M–N–C)*

The extractions of the nitrides from these alloys were carried out by the Beeghly procedure [2] using a bromine/methyl acetate solvent. The total weights of residue extracted from 9g of alloy varied between about 12mg and 122mg. The residues were examined by X-ray diffraction and the results are summarized in Table 2. The "combined" nitrogen contents of the alloys were determined using a 3g alloy sample weight by the Beeghly procedure [2] and the method described in BS 1121/Part 39, after fuming the extracted residue strongly in concentrated sulphuric acid. The results are given in Table 2.

#### *DTA/EGA apparatus*

The apparatus used is conveniently divided into two sections *viz.* the Du Pont 900 differential thermal analyser fitted with a 1600° cell, and the evolved gas analysis (EGA) unit, which consisted of a Pye Series 104 gas chromatograph fitted with a Pye gas sampling valve. The two units were connected via  $\frac{1}{32}$  in. i.d.

Table 1

Determination of nitrogen in some commercial nitrides (chemical and DTA/EGA procedures) and their X-ray diffraction examination

Nitride	X-ray examination -- compounds identified <sup>1</sup>	N, %			
		Theoretical	Chemical <sup>2</sup>	DTA/EGA <sup>3</sup>	+Δ%
Zirconium	ZrN	13.32 (ZrN)	8.47 8.54	8.11 7.47	— 8.5
Boron	Pattern obtained could not be identified	56.43 (BN)	24.08 24.36	22.00 21.58	— 10.0
Aluminium	AlN	34.18 (AlN)	28.00 28.28	— —	— —
Titanium	TiN	22.63 (TiN)	13.86 15.12	17.46 16.13	+ 15.9
Vanadium	VN <sub>0.9</sub>	19.84 (VN <sub>0.9</sub> )	9.66 10.08	20.76 21.55	+114.4
Niobium	Nb—N—O Nb <sub>2</sub> N (small amount)	11.40 (NbNO)	7.70 7.70	9.27 9.88	+ 24.4
Molybdenum	Mo + γ—Mo <sub>2</sub> N (medium quantity) + δMo <sub>2</sub> N (small amount)	6.80 (Mo <sub>2</sub> N)	3.78 3.92	5.48 5.02	+ 36.4
Tungsten	W	13.22 (WN <sub>2</sub> )	0.28 0.28	0.50 0.32	+ 46.4
Silicon	β-Si <sub>3</sub> N <sub>4</sub> + α-Si <sub>3</sub> N <sub>4</sub> (small amount)	39.98 (Si <sub>3</sub> N <sub>4</sub> )	2.80 3.92	6.88 9.66	+146.1
Chromium	CrN + βCr <sub>2</sub> N (medium amount)	21.22 (CrN)	14.35 14.97	17.13 16.93	+ 16.2

1. Small number of weak unidentified lines observed for most of the materials examined.
2. By method set out in BS 1121/Part 39 using 0.1 g samples.
3. Sample weight in range 1–22 mg for each determination.

$$+ \Delta\% = \frac{100(\% \text{ nitrogen by DTA/EGA} - \% \text{ nitrogen by chemical analysis})}{\% \text{ nitrogen by chemical analysis}}$$

where the % nitrogen values are the average values of the values given in Table 1.

NOTE. The tungsten and molybdenum found in the two samples above may possibly contain some interstitial nitrogen.

(0.8 mm i.d.) stainless steel tubing and Pye stainless steel glass column connector assemblies. One glass column contained Schütze reagent (I<sub>2</sub>O<sub>5</sub>) to oxidize any carbon monoxide formed during combustion which could then be absorbed in a second column containing soda-asbestos. A schematic diagram of the total apparatus is given in Figure 1. As the mode and principle of operation of similar units has been described elsewhere [6, 10] only a brief description will be given

here. The nitride sample was weighed into either a platinum or ceramic liner (in some cases platinum was attacked during the combustion) and a similar depth of Analar grade alumina introduced to the corresponding "reference" liner. The liners were placed in the appropriate cups on top of the thermocouples (Figure 1) and the DTA furnace assembled. Oxygen was then passed at approximately 15 ml/min for approximately 2 hours via the Wösthoff pump through the DTA unit, venting to air at the sampling valve.

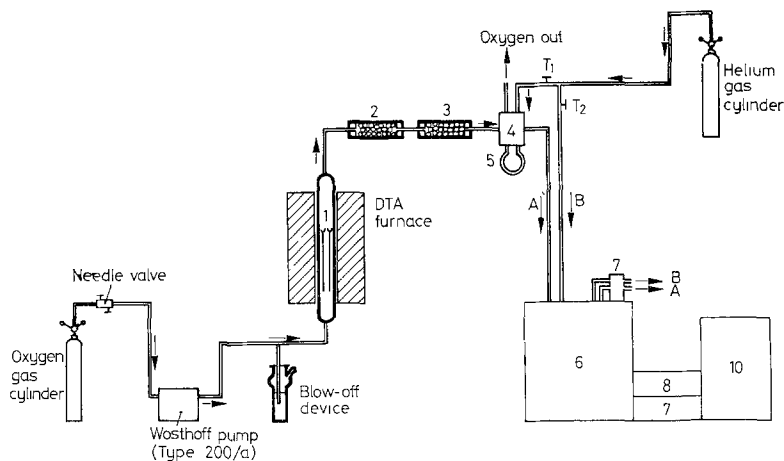


Fig. 1. Schematic diagram of DTA/EGA system: 1. Sample and reference thermocouples with Pt cups and liners; 2. Schütze reagent; 3. Soda asbestos; 4. Sampling valve; 5. Sample loop; 6. Chromatograph oven; 7. Katharometer; 8. Katharometer power supply; 9. Column oven controller; 10. Recorder Foster Cambridge Clarspan P 250 L; A Helium supply for column; B Helium supply for empty column;  $T_1$ ,  $T_2$  Control valves

The chromatograph — one of whose two columns consisted of a coil of copper tubing (length approx 270 cm) containing Linde Molecular Sieve No. 5A (30- to 60-mesh) — was prepared for analysis by adjusting the helium flow through each of the columns to approximately 60 ml/min and ensuring a column temperature of 50°. The katharometer power supply was energized and the automatic timer for the gas sampling valve set to provide a sample of volume 10 ml every 4.35 minutes. Constant low nitrogen peaks were obtained after approximately 2 h purging. The oxygen flowrate through the DTA unit was adjusted to 2 ml/min and the helium flow to 60 ml/min and heating of the DTA chamber was then commenced at 12.1° min. The recorder pen sensitivity for the Y-axis was set at 0.02 mv/in and for the X-axis at 2 mv/in. Heating was continued until the evolution of nitrogen from the nitride sample was complete as observed from the nitrogen peaks on the chromatogram. The temperature on each occasion the gas sampling valve operated was noted from the pen position on the DTA curve. The amount of nitrogen evolved from the DTA sample was determined by first

connecting the nitrogen peak maxima on the chromatogram with straight lines and determining the area enclosed by these lines and the base-line. The weight of nitrogen corresponding to this area was determined from a calibration graph prepared by the procedure described below. The oxidation temperature of the nitride was noted from the exothermic peak position on the DTA curve. The corresponding EGA peak temperature was also noted.

#### *Calibration of EGA section of DTA/EGA apparatus*

The EGA apparatus was calibrated with a commercial sample of aluminium nitride whose purity was 82.3% based on its total nitrogen content relative to the theoretical amount in AlN (Table 1). For a range of weights of aluminium nitride of 2–6 mg a straight line plot of area defined by the nitrogen peak maxima against the actual weights of nitrogen in the samples (assuming 82.3% purity) was obtained using the procedure already described for the DTA/EGA apparatus. It was found that the slope of the calibration curve occasionally varied due to changes in the amount of EGA gas in the chromatograph sampling loop. As this slope was shown to be related to the oxygen peak width on the chromatogram the effect of this variation on the accuracy of the analysis could be eliminated.

#### *Examination of nitride samples by DTA/EGA procedure*

The commercial nitride powders and the nitrides contained in residues extracted from iron base ternary and quaternary alloys were examined (a) to compare the nitrogen contents obtained by DTA/EGA with those by chemical analysis and

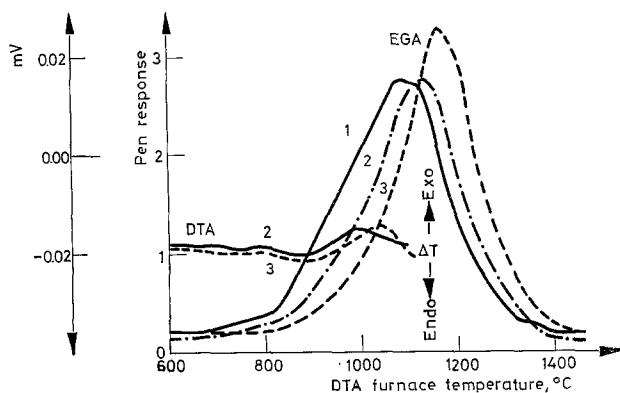


Fig. 2. Effect of particle size on EGA peak position for titanium nitride and the DTA curves; Weight of TiN = 4.36 mg; O<sub>2</sub> flow rate = 2.0 ml · min<sup>-1</sup>; Heating rate = 12.1° · min<sup>-1</sup>; Particle size 1. < 20 μ; 2. < 37 μ > 20 μ; 3. > 37 μ; N · B For clarity the DTA trace of the < 20 μ fraction is not included as it is only slightly lower in position than that of fraction 2

(b) to determine the DTA peak positions, together with the temperatures corresponding to the maxima of the nitrogen curves on the chromatograms in order to examine the feasibility of using DTA/EGA results for nitride identification.

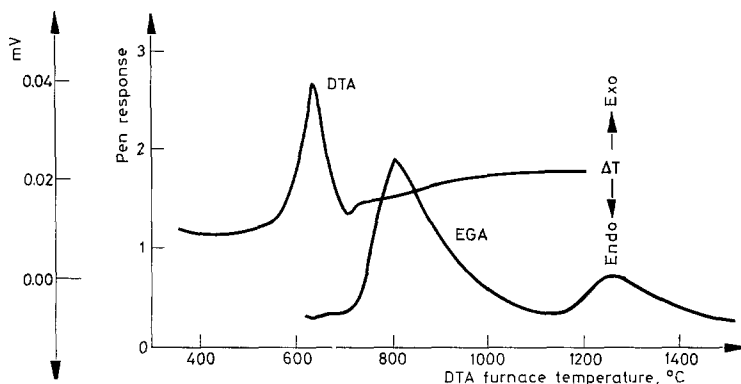


Fig. 3. Zirconium nitride in an oxygen atmosphere. Weight = 5.15 mg;  $O_2$  flow rate =  $2 \text{ ml} \cdot \text{min}^{-1}$ ; heating rate =  $12.1^\circ \cdot \text{min}^{-1}$

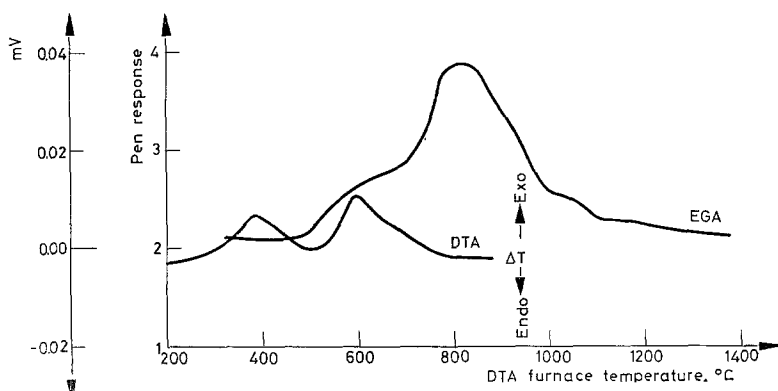


Fig. 4. Oxidation of residue extracted from zirconium bearing iron base alloy: Weight of residue = 8.48 mg;  $O_2$  flow rate =  $2 \text{ ml} \cdot \text{min}^{-1}$ ; heating rate =  $12.1^\circ \cdot \text{min}^{-1}$ ;  $CO_2/CO$  absorption train in position; carbon content: 0.003%

The results for the nitrogen contents of the commercial nitride powders are summarized in Table 1 and for the residues in Table 2. In Table 3 a comparison of the DTA/EGA data for the various types of sample is made. Typical DTA traces are given in Figs 2–5.

Table 3

Comparison of DTA/EGA data for nitrides isolated from iron base alloys with those from commercial nitride powders

Nitride <sup>+</sup>	Source	carbon in alloy %	DTA exotherm, °C										EGA peak positions, °C						
Silicon	C	—															1455		
	Alloy (T)	0.003															1441		
Chromium	C	—																	1489
	Alloy (T)	0.003	305 304	341 341	568 550													572–696P	801
Aluminium	C	—	1208w 1223w																
	Alloy (T)	0.003																560–630P	817
Boron	C	—																	
	Alloy (T)	0.005			986 992													533vw 554vw	1122 1130
	Alloy (Q)	0.22	262 251	371w 365w	927 886														749w 737w
Titanium	C	—																	
	Alloy (T)	0.017		400sh 399sh	460 447														
	Alloy (Q)	0.10	269 269																
	Alloy (Q)	0.17	235 239		475sh 465														
Zirconium	C	—																	
	Alloy (T)	0.003		376 390	563 596														
	Alloy (Q)	0.18	223 234	385 377	612 586														
Vanadium	C	—	480vw 476vw	532w 532w	632w 529w	662 671													
	Alloy (T)	0.003		300sh 295sh	370sh 364sh	438 411													
Niobium	C	—																	
	Alloy (Q)	0.21	237 243	393sh 390sh	476 470														
Molybdenum	C	—	509 495																
Tungsten	C	—	407vw 404vw	517sh 513sh	569 532														

N.D. — no distinct peak(s) on DTA curve.

sh — shoulder

P — plateau

w — weak

vw — very weak

(T) — ternary iron base alloy

(Q) — quaternary iron base alloy

C — commercial nitride powders.

+ — sample weight in range: 2–22mg for the commercial nitride powders; 4–31mg for the nitride containing residues

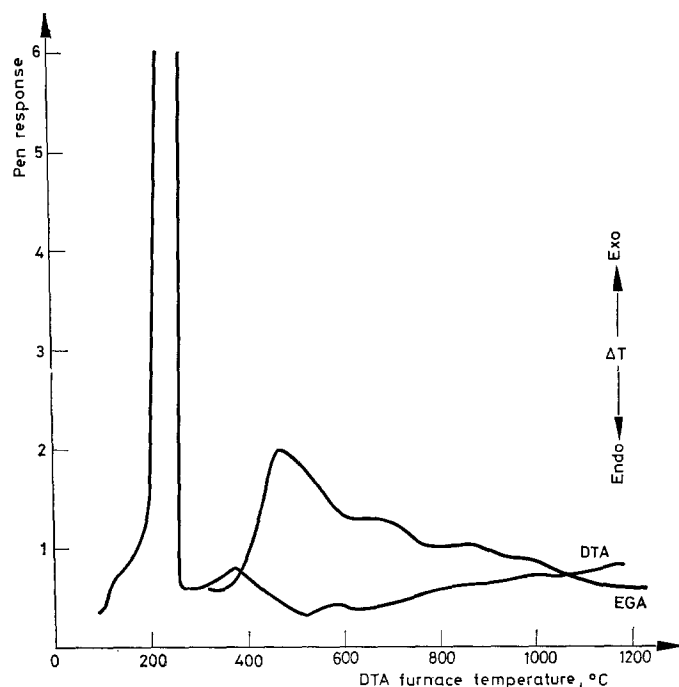


Fig. 5. Oxidation of residue extracted from zirconium bearing iron base alloy. Weight of residue = 15.68 mg;  $O_2$  flow rate =  $2 \text{ ml} \cdot \text{min}^{-1}$ ; heating rate =  $12.1^\circ \text{ min}^{-1}$ ;  $CO/CO_2$  absorption train in place; carbon content: 0.18%; aluminium content: 0.023%

### *Effect of particle size*

The effect of particle size and sample weight on the DTA/EGA results has been examined using commercial samples of titanium nitride and aluminium nitride respectively. Titanium nitride was sieved to give three fractions *viz.*  $< 20 \mu$ ,  $> 20 \mu$ ,  $< 37 \mu$ , and  $> 37 \mu$ . Equal weights of each fraction were examined using the DTA/EGA procedure and the results are shown in Fig. 2.

## Discussion of results

### *Suitability of nitride samples for DTA/EGA studies*

In order to compare the DTA/EGA results for the commercial nitrides and nitrides contained in the extracted residues the characterization of the nitrides present was obviously important. This was done by X-ray examination. The results in Table 1 indicate that of the ten commercial nitride powders studied only six, *viz.* the nominal zirconium, aluminium, titanium, vanadium, silicon and chromium nitride powders contained appreciable amounts of the correspond-



Table 2  
X-ray diffraction data and nitrogen contents by DTA/EGA and chemical analysis of nitride residues extracted from experimental alloys

Cast number	X-ray diffraction examination — main compound(s) found	% nitride forming element	% carbon	% nitrogen <sup>1</sup> by chemical analysis	% nitrogen <sup>2</sup> by DTA/EGA	Average % nitrogen by DTA/EGA	+Δ%
<i>Ternary Alloys</i>							
K769	The exact vanadium compound could not be identified — see text Pattern did not correspond to any of the CrN patterns in the J.C.P.D.S. file	V	0.003	0.0145	0.0196	0.0187	+29.0
K770		Cr	0.003	0.0095	0.0178	0.0112	+17.9
K773	AlN	Al	0.003	0.0170	0.0120	0.0192	+12.9
K774	No pattern obtained	Si	0.003	0.0020	0.0191	0.0028	+40.0
K821	TiN+TiC	Ti	0.017	0.0220	0.0249	0.0234	+ 6.4
K933	Pattern did not correspond to any of the BN compounds in the J.C.P.D.S. file	B	0.005	0.0215	0.0218	0.0155	-27.9
K1391	ZrN	Zr	0.003	0.0190	0.0173	0.0174	- 8.4
<i>Quaternary Alloys</i>							
K1094	TiN+TiC TiN+TiC	Ti	0.10	0.0115	0.0174	0.0113	- 1.7
K1219		Ti	0.17	0.0220	0.0120	0.0240	+ 9.1
K1098	ZrN	Zr	0.18	0.0195	0.0219	0.0194	- 0.5
K1110	NbN	Nb	0.21	0.0215	0.0181	0.0189	-12.1
K1111	Could not obtain a satisfactory X-ray pattern	B	0.22	0.0260	0.0207	0.0195	-55.4
		0.05			0.0139	0.0116	

+ Δ% =  $\frac{100(\% \text{ nitrogen by DTA/EGA (average)} - \% \text{ nitrogen by chemical analysis})}{\% \text{ nitrogen by chemical analysis}}$

1. By method of Beeghly [2] + method set out in BS 11 21/Part 39.
2. Sample weight in range 4–31 mg for each determination.

J.C.P.D.S. — Joint Committee of Powder Diffraction Standards.

ing crystalline nitride. The X-ray examination of the residues from the ternary alloys (Table 2) only positively identified aluminium, titanium and zirconium nitrides. However, DTA/EGA examinations revealed the presence of nitrides where vanadium, chromium, boron and silicon were the supposedly nitride forming elements in the alloys.

From the lattice parameter ( $a_0 = 4.127 \text{ \AA}$  for a cubic diffraction pattern) it seems probable that where vanadium is the nitride forming element in the alloy the residue contains vanadium carbonitride [12] ( $\text{VC}_x\text{N}_y$ ) rather than VN ( $a_0 = 4.28 \text{ \AA}$ ) for a cubic diffraction pattern [11]. This conclusion agrees with work by Krapf [14].

The large differences between the DTA/EGA results (Table 3) for the residue from the chromium ternary alloy and the commercial chromium nitride powder (in which CrN and  $\beta\text{-Cr}_2\text{N}$  were identified) suggest that the nitride in the residue is not CrN and differs markedly from the commercial chromium nitride powder. It may possibly consist of  $(\text{Fe, Cr})_4\text{N}$  as suggested by Bandi [12].

Comparison of the DTA/EGA results (Table 3) for the residue expected to contain boron nitride with those of the commercial boron nitride powder suggests that both samples contain similar nitrides although their presence was not detected by X-ray diffraction.

The ternary alloy prepared to contain inclusions rich in silicon nitride contained 2.75% silicon (Table 2) and during extraction, the inclusions became mixed with silicic acid; this probably accounted for the failure to detect  $\text{Si}_3\text{N}_4$  by X-ray diffraction. Support for this suggestion is the similarity of the DTA/EGA traces with those for the commercial silicon nitride sample (see Table 3) which definitely contained  $\text{Si}_3\text{N}_4$  (Table 1).

Titanium nitride, zirconium nitride and niobium nitride have been positively identified in the residues extracted from the corresponding quaternary alloys (Table 2). The presence of additional features on the DTA/EGA traces for the residue from the titanium quaternary alloy (Table 3) suggests the presence of a carbonitride ( $\text{TiC}_x\text{N}_y$ ) as Bandi [6] found in similar residues. Again the presence of BN in the corresponding quaternary alloy has not been detected although the similarity of the DTA/EGA results in Table 3 with those for the residue from the boron ternary alloy and the commercial nitride powder suggests that all the samples contain a similar form of the nitride.

#### *Nitrogen recovery from the nitride samples by DTA/EGA*

Although the nitrogen values of the commercial nitride samples determined by chemical means and DTA/EGA are reasonably reproducible the DTA/EGA values are generally higher. A possible explanation is provided by ISI Special Report 62 where different nitrides were subjected to Kjeldahl nitrogen analysis [9]. Certain nitrides, e.g. those of aluminium, boron, chromium, niobium, silicon, titanium, vanadium and zirconium were found to be acid resistant; in particular those of boron, niobium, titanium and vanadium could only be dissolved by

intense fuming in concentrated sulphuric acid and silicon nitride could not be decomposed quantitatively. The nitrides of molybdenum and tungsten appeared to exhibit variable behaviour. Such varying resistance to acid attack could lead to incomplete dissolution of the nitride residues and hence low results. The DTA/EGA values resulting from combustion in oxygen at temperatures up to 1400–1500° may thus be generally the more reliable. This is evident in the case of the vanadium and silicon nitrides where the recoveries of nitrogen are more than 100 per cent higher by DTA/EGA than by “wet” chemical means.

Both techniques for determining nitrogen yield values lower than those calculated from the nitrides found to be present by X-ray diffraction (Table 1). This is compatible with the presence of impurities and with unidentified diffraction lines obtained during the X-ray examination. In the particular case of the silicon nitride powder, X-ray examination showed the sample to be reasonably pure; the low analytical values have resulted from incomplete decomposition or oxidation of the sample.

Apart from the residues of the boron alloys, reasonable agreement was obtained between the EGA nitrogen values and those obtained by chemical analysis (Table 2) for the ternary and quaternary alloy residues. The chemical values for the silicon and vanadium bearing residues were presumable low because of their acid resistant nature. The EGA nitrogen values for the boron containing residues are considerably lower than those obtained chemically (Table 2) and although this effect has already been observed by Bandi [6], no satisfactory explanation is available. Since the discrepancy is greater for the quaternary alloy residue which contains significant amounts of carbon, mechanical loss arising from rapid carbon oxidation was considered a possible cause.

#### *Effect of particle size and sample weight on the DTA/EGA results*

Since the positions of the DTA/EGA oxidation peaks are dependent on reaction rates, and thus theoretically on such variables as particle size and sample weight, the effect of these have been investigated. The results in Fig. 2 for titanium nitride show that by decreasing the particle size the temperatures of the peak maxima decrease for both the DTA and EGA traces for example the EGA peak maximum decreases from 1162° for the  $> 37 \mu$  fraction to 1080° for the  $< 20 \mu$  fraction. Mackenzie and Mitchell [10] have considered the effect of particle size on DTA peak temperatures and shapes and concluded that for surface reactions, such as the oxidation of nitrides, particle size would be expected to have a marked effect. The high specific surface area associated with a small particle size would accelerate oxidation and hence tend to reduce the temperatures of the reaction peaks. This effect is also evident from the DTA/EGA results in Table 3 when comparing the results of the commercial nitride powder with those of the corresponding nitride containing residue which has in general a much finer particle size.

Variations in the temperatures of EGA peaks from differences in sample weight are apparently minor. Thus the values of the temperature peaks for alu-

minium nitride sample weights of 1.9, 2.7, 2.8, 4.92, 5.0 and 5.16 mg were 1340°, 1359°, 1323°, 1306°, 1329° and 1337° respectively giving a mean value of 1332° with a standard deviation of  $\pm 18^\circ$ . A similar conclusion was reached on the influence of sample weight for the residues examined.

#### *Nitride identification by DTA/EGA*

The EGA peaks (Table 3) in general occur at apparently higher temperatures (approximately 200°) than the corresponding DTA oxidation peaks because the furnace temperature is increasing with time and a time lag exists between the nitrogen leaving the DTA unit and entering the chromatograph column. Making allowance for this enables EGA peaks to be associated with the corresponding DTA maxima. The data in Table 3 have been grouped for each nitride forming element for easy comparison. Data in Table 3 indicate that EGA traces are generally simpler than DTA curves and their peaks are often well defined and therefore potentially useful for nitride identification (cf. silicon, chromium and aluminium nitride data in Table 3). This is corroborated by the reasonable agreement obtained between the EGA peak temperatures of residues from the ternary-alloys and the corresponding commercial nitride powders (Table 3). Any differences which do exist can be accounted for by different forms of the nitride being present in the samples as shown by X-ray examination (e.g. when chromium and vanadium are the nitride forming elements) or a particle size effect when the same nitride has been detected by X-ray examination in the two types of sample (e.g. when aluminium is the nitride forming element).

Unfortunately difficulties arise when the comparison of the nitride powder data is extended to the residues from the quaternary alloys. The presence of elemental carbon which oxidizes at approximately 260° sometimes causes appreciable premature nitride oxidation as for example with zirconium nitride (compare series of Figs 3–5 where carbon content of sample increases from 0 to 0.18%) and niobium nitride giving rise to EGA traces different from the corresponding pure nitrides. Nitrides which normally oxidize at relatively high temperatures (those of boron and titanium) are not so seriously affected. Both Bandi [12] and White [8] have recorded the problem of free carbon and Bandi [12] has attempted its removal prior to analysis by ashing at a sufficiently low temperature to prevent nitride oxidation. While this was apparently accomplished, any carbides present were oxidized and some decomposition of carbonitrides appeared to occur. It is generally concluded that since elemental carbon would normally be present in the extracted residues from steels, EGA curves would not be helpful in identifying nitrides such as those of zirconium and niobium which oxidize at temperatures lower than approximately 600°. Of course the EGA curves would provide estimates of the total nitrogen present in the residues.

In the absence of carbon oxidation interference, the identification of nitrides by EGA traces still requires adequate temperature differences between the oxidation peaks of the various nitrides present. Table 4 shows the decreasing order of

nitride oxidation temperatures as determined from the major EGA peak temperatures, using the commercial nitride powders and the residues from the ternary and quaternary alloys. For comparison purposes data are included from the work of White [8], and Bandi [5, 6, 13]. Several conclusions can be drawn from Table 4.

(i) The temperature order found for the ternary quaternary alloy nitride residues agrees with that of Bandi [5, 6, 13] obtained for residues from steel.

Table 4  
Nitride EGA peaks from various sources

Sample type	Commercial powder	Residues from ternary, quaternary alloys	White [8] residues from ternary alloys	Bandi [5, 6, 13] steel residues
Decreasing Temperature	Cr			
	Si	Si		
	Al	Al	Al	
	Ti			
	B	B	B	B
		Ti	Ti	Ti
	Zr	Zr	Zr	Zr
		Cr		
		Nb	Nb	Nb
	V	V		V
	Nb		Cr	
		V		

(ii) Comparison of the commercial powder results with those from the ternary and quaternary alloy residues shows discrepancies for Cr, Ti and a reversal in the order for V and Nb. Undoubtedly these variations arise chiefly from the differing forms of nitride in the commercial powder and residue samples as noted in the discussion of the X-ray examination of these samples.

(iii) Apart from chromium, the present temperature order of the nitrides from the ternary and quaternary alloys agree with White [8].

It is generally concluded that in the absence of elemental carbon as, for example, in the residues from the ternary alloys, EGA peaks may be used to distinguish the nitrides of silicon, aluminium, boron, titanium and zirconium. In the presence of carbon (e.g. in residues from the quaternary alloys), the nitrides of silicon, aluminium, boron, titanium may be identified, the nitrides of zirconium, niobium, chromium and vanadium requiring additional X-ray diffraction data.

## Conclusions

The following general conclusions are based on the application of oxidation DTA/EGA to commercially available nitride powders, the residues from specially prepared iron base ternary and quaternary alloys and comparison of the results with published data. All the samples used contain one predominant nitride; the behaviour of mixed nitrides and carbides has not been studied.

1. In general EGA traces are more useful than DTA results; the traces are simpler and the peaks sharper.

2. The EGA trace can be used to estimate the total nitrogen in a residue and in some cases (e.g. silicon and vanadium nitrides) is more reliable than chemical dissolution methods.

3. In cases where the DTA or EGA peaks are well separated on the temperature co-ordinate, the technique is useful in nitride identifications. Examples are the nitrides of silicon, aluminium, boron, titanium, zirconium, niobium and vanadium.

4. When DTA/EGA is applied to the residues from steels containing easily decomposable carbides (e.g. cementite) the sample may contain elemental carbon. During the analysis, this oxidizes at a low temperature and the heat evolved can cause premature partial oxidation of the nitrides. This effect complicates both the DTA and EGA traces and is particularly troublesome when nitrides are present having low oxidation temperatures. The nitrides of silicon, aluminium, boron and titanium have relatively high oxidation temperatures and are not seriously affected.

5. In general DTA/EGA is useful for detecting the presence of certain nitrides and providing estimates of the total nitrogen content in the sample. It should not be regarded in isolation but as an ancillary to other forms of examination such as X-ray diffraction.

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RÉSUMÉ — On a effectué une étude préliminaire pour rechercher si l'emploi conjugué de l'analyse thermique différentielle et de l'analyse des gaz émis (ATD/AGE) pouvait servir à l'identification et à l'estimation de la teneur des nitrures présents dans les résidus d'extraction des alliages à base fer. On a également examiné une série de nitrures en poudre disponibles commercialement.

Les résultats ont montré que les enregistrements d'AGE fournissent davantage de renseignements que les courbes ATD car ils donnent en plus la valeur de l'azote total présent. Les résidus d'extraction des aciers contiennent souvent du carbone élémentaire, ce qui complique l'interprétation des enregistrements d'ATD et d'AGE. L'étude permet de conclure qu'en général la technique d'ATD/AGE est utile pour identifier les nitrures, mais qu'elle devrait être utilisée comme méthode auxiliaire vis-à-vis d'autres techniques, par ex. la diffraction des rayons X.

ZUSAMMENFASSUNG — Eine Vorstudie wurde durchgeführt um die Einsatzmöglichkeit der Differentialthermoanalyse/Emittierte Gasanalyse (DTA/EGA) zur Identifizierung und Abschätzung der Nitride in aus Eisenbasenlegierungen extrahierten Rückständen zu prüfen. Eine Reihe handelsüblicher Nitridpulver wurde ebenfalls untersucht.

Die Ergebnisse zeigten, daß EGA-Spuren informativer sind als die DTA-Beobachtungen und überdies eine Schätzung des Gesamtstickstoffgehaltes gestatten. Rückstände aus Stählen enthalten oft Kohlstoff und dies erschwert die Deutung der DTA- und EGA-Spuren. Im Allgemeinen kann gefolgert werden, daß die DTA/EGA-Technik bei der Identifizierung von Nitriden nützlich ist, doch nur als Ergänzung anderer Techniken, wie z. B. die Röntgen-diffraktion, eingesetzt werden sollte.

Резюме — Было проведено предварительное изучение возможности применения дифференциального термического анализа и анализа выделенного газа (ДТА/ЕГА) для идентификации и определения нитридов в остатках, извлеченных из сплавов на основе железа. Ряд коммерчески доступных нитридных порошков был также исследован. Результаты показали, что техника анализа выделенного газа более информативна, чем ДТА наблюдения и к тому же она позволяет определить наличие общего азота. Остатки от сталей часто содержат элементарный углерод, что усложняет интерпретацию ДТА и ЕГА. В общем сделано заключение, что техника ДТА/ЕГА является полезной при идентификации нитридов, но должна быть дополнена другими методами, такими как диффракция рентгеновских лучей.