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DTA–EGA OBSERVATIONS OF VANADIUM PRECIPITATES IN LOW ALLOY STEEL

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ABSTRACT

Differential thermal analysis–evolved gas analysis (DTA–EGA) has been used, along with x-ray diffraction and microchemical techniques, to study the effect of varying the concentrations of vanadium, carbon, and nitrogen added to steels upon the composition of the second-phase compounds isolated. It was thus possible to identify and quantitatively measure vanadium carbide, nitride, and carbonitride in the presence of one another in the isolated residues. The effect of various heat treatments of the steels upon the composition of the second-phase compounds will also be presented.

INTRODUCTION

Vanadium has been added to steel for almost 70 years as a means of increasing the yield strength. Its effect as a secondary-hardening element is well known[1]. Despite the widespread use of vanadium as an alloying element, the literature is quite contradictory on the carbide, nitride, and carbonitride phases that precipitate in steel.

A number of investigators[2–9] indicate that the vanadium carbide precipitated in steel is usually V_4C_3, while some workers believe that the most common precipitate is VC_xN_y[6,8,9]. However, on the basis of X-ray diffraction, VC_xN_y cannot be differentiated[8,10] from either the carbide or the nitride because the lattice constants of the compounds overlap one another, and in many studies the amount of non-stoichiometry of the precipitated phase, which affects the lattice parameter, has not been reported. The formula of the vanadium compound cannot be determined readily by physical methods of separation because of interfering compounds in the residue isolated. Chemical analysis of residues isolated from steel containing vanadium carbide, nitride, and carbonitride phases is not dependable because of the interference of compounds such as $(Fe, V)_3C$[11].

This study is concerned with the identification and determination of vanadium precipitates using differential thermal analysis (DTA)–evolved gas analysis (EGA) techniques supplemented by X-ray diffraction and microchemical analysis.

EXPERIMENTAL

Materials

Table 1 shows a partial chemical analysis of the steels used in this work and the pertinent heat-treating data. Sample 1 was obtained from K & K Laboratories, Plainview, N.Y.; it was analyzed chemically for carbon and nitrogen and identified by X-ray diffraction as face-centered cubic (fcc) VC. Sample 2 was chosen because from previous chemical and EGA work it was believed to contain V_4C_3 and because it had high vanadium and low nitrogen concentrations and a high vanadium–carbon ratio. Sample 3 was also low in nitrogen, but it had a low vanadium–carbon ratio, and was heat-treated to promote the formation of VC rather than V_4C_3.

TABLE 1

COMPOSITION AND HEAT TREATMENT OF SAMPLES USED[a]

Sample No.	*% C*	*% N*	*% V*	*Heat treatment*
1	17.14	<0.001	82.86 By difference	—
2	0.14	0.002	0.60	Hot-rolled
3	0.22	0.001	0.038	Austenitized at 1094°C for 1/2 h, water-quenched, tempered at 600°C for 24 h
4	0.21	0.027	0.038	Austenitized at 1094°C for 1/2 h, water-quenched, tempered at 600°C for 24 h
5	0.20	0.008	0.045	Silicon-killed, hot-rolled
6	0.20	0.008	0.045	Silicon-killed, hot-rolled, normalized at 950°C
7	0.20	0.008	0.046	Aluminum-killed, hot-rolled
8	0.20	0.008	0.046	Aluminum-killed, hot-rolled, normalized at 950°C
9	0.001	0.011	0.034	Decarburized
10	0.001	0.013	0.034	Decarburized
11	0.009	0.012	0.034	Decarburized
12	0.003	0.014	0.034	Decarburized
13	0.001	0.005	5.60	Hot-rolled

[a] Only residual amounts of other carbide and nitride alloying elements are present in these samples.

Samples 4 through 8 are vanadium–carbon–nitrogen-bearing steels. Sample 4 is the same as sample 3, except that an abnormally high amount of nitrogen was added so that carbonitrides rather than carbides would be formed. Samples 6 and 8 differed from samples 5 and 7 because the former received a normalizing treatment at 950°C after rolling. Samples 5 and 6 were silicon-killed so that any effect on the precipitation of VC_xN_y caused by the possible presence of AlN in samples 7 and 8 would be detected.

Samples 9 through 12 have compositions similar to those of enameling steels, but they have been decarburized and contain more than enough nitrogen to combine with all of the vanadium. Sample 13 is a specially produced steel with a very high vanadium–nitrogen ratio so that at least on the basis of composition, formation of V_4N_3 would be favored over VN.

Isolation of vanadium phases for DTA–EGA

From 0.5 to 4 g of steel millings were dissolved under an argon atmosphere in (1 + 1) HCl at 40°C. The residues were separated by filtration, dried, and weighed for DTA–EGA, microchemical, and X-ray diffraction examinations by procedures that have been previously described[12–14].

DTA–EGA procedures

The following instrumental and experimental parameters were used in this work.

DTA. Instrument: modified R. L. Stone 12 BC_2 for carbide, specially built for nitride. Sample holder and compartment: specially constructed Inconel for carbide, specially constructed ceramic for nitride. Heating rate: 10°C min^{-1}. DTA temperature accuracy: ±10°C with reference to quartz. Differential thermocouples: Platinel. DTA sensitivity: 15 μV $in.^{-1}$ = 0.33°C $in.^{-1}$. DTA reference: Al_2O_3. Atmosphere: dynamic O_2 (3 ml min^{-1}).

EGA	*CO_2*	*N_2*
Measurement	Thermal conductivity	Chromatographic–thermal conductivity
Column	None	Molecular sieve 5a
Thermal conductivity cell	Gow-Mac Model TRIIIA	Gow-Mac Model TRIIIA
Power supply	Gow-Mac Model 9999	Gow-Mac Model 9999
Bridge current	6 mA	6 mA
Recorder span	1 mV/10 in.	1 mV/10 in.
Carrier gas	O_2 (3 ml min^{-1})	O_2 (3 ml/min^{-1})
Reference gas	O_2 (3 ml min^{-1})	He (70 ml/min^{-1})
Sensitivity	5 μg CO_2 at power supply setting of 8	10 μg nitrogen evolved in 20 min at power supply setting of 16

DTA–EGA responses for the carbides and the carbonitrides were obtained by established procedures[12–14], and complex EGA responses were resolved into the component peaks by use of the DuPont curve resolver.

EGA nitrogen recordings for the nitrides and the carbonitrides were obtained with the modified DuPont instrumentation[15].

By comparing EGA responses for residues, which because of the composition of the steels could contain only nitride (no carbide or carbonitride), with EGA responses for samples which because of composition contained carbonitrides, it was possible to determine which peaks were associated with the carbonitride in the more complex responses. By similar comparisons of EGA responses, chemical analysis of the residue, and composition of the steel, the determination of V_4C_3, VC_xN_y, and VN in the presence of each other seemed possible.

DISCUSSION

Figure 1 is the DTA–EGA response obtained for commercially prepared vanadium carbide. X-ray diffraction analysis confirmed that the carbide was fcc VC. The peak temperatures for combustion of the VC and evolution of CO_2 occur at 630 and 680°C, respectively. The large endotherm is characteristic of the melting of V_2O_5. Figure 2 is the DTA–EGA response obtained for a residue isolated from sample 2, which had a high vanadium-to-carbon ratio which would favor the V_4C_3 carbide structure. There is a large difference in the combustion temperature of the two samples. Even though X-ray diffraction could not confirm the presence of V_4C_3, we have assumed that this compound is the prevalent vanadium carbide in sample 2. This assumption is supported by microchemical analysis of the residue and the chemical composition of the steel.

The resolution of the EGA curve in Fig. 3 shows three major peaks for the evolution of CO_2. From previous knowledge[12], the peak at 380°C can be attributed to cementite. Because the peak at 430°C is common to all vanadium–carbon steels, it appears that it was caused by the combustion of V_4C_3. However, the residue isolated from sample 2 contained approximately 70% vanadium (3.5 to 3.7 mg of vanadium per gram of steel dissolved), whereas the CO_2 evolved at 430°C represented only 0.6 mg of carbon (equivalent to 2.6 mg V) per gram of steel. Because the vanadium is present in excess over that needed for V_4C_3, it appears that vanadium

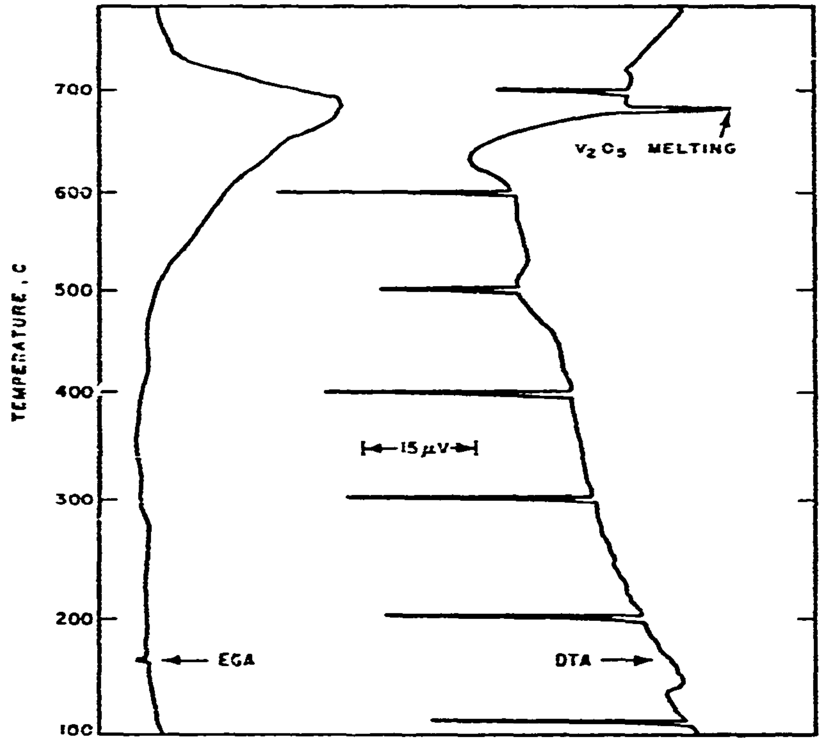

Fig. 1. 0.34 mg of DTA/EGA response for commercially prepared vanadium carbide (sample 1).

was present in the cementite which gave rise to the response at 380 °C, or was present in the compound responsible for the response at 310 °C in Fig. 3.

In spite of the attempts to form stoichiometric VC in sample 3, Figs. 4 and 5 show that more than half the CO_2 was evolved from the combustion of V_4C_3, with peak temperature at 430 °C. It appears that the adjustment of conditions to enhance the formation of VC was not successful. This agrees with the conclusion of Cochnar and Cadek[11] who found that even after tempering 5000 h at 650 °C the formula computed from chemical analysis of an isolated residue was $V_{3.5}C_3$.

Figure 4, which is the DTA–EGA response for a residue isolated from sample 3, is a typical response for the programmed combustion of a residue containing V_4C_3 and Fe_3C. This conclusion is based on X-ray diffraction identification. In the resolution of the EGA response of Fig. 4, the most noticeable difference between Figs. 3 and 5 is the absence of the EGA peak at 310 °C in Fig. 5. The three main EGA peaks are the result of the combustion of Fe_3C, V_4C_3, and elemental carbon; the EGA temperature maxima are at 360, 430, and 470 °C, respectively.

Table 2 summarizes the CO_2 evolution measurements and also lists pertinent X-ray diffraction, DTA, and microchemical information for the samples. It shows that programmed combustion of residues isolated from the vanadium-bearing samples always caused evolution of CO_2 at 350 to 390 °C (Fe_3C) and 410 to 440 °C (V_4C_3 or VC_xN_y). In addition, CO_2, from the combustion of amorphous carbon, was also evolved at 460 to 500°C for all but one residue.

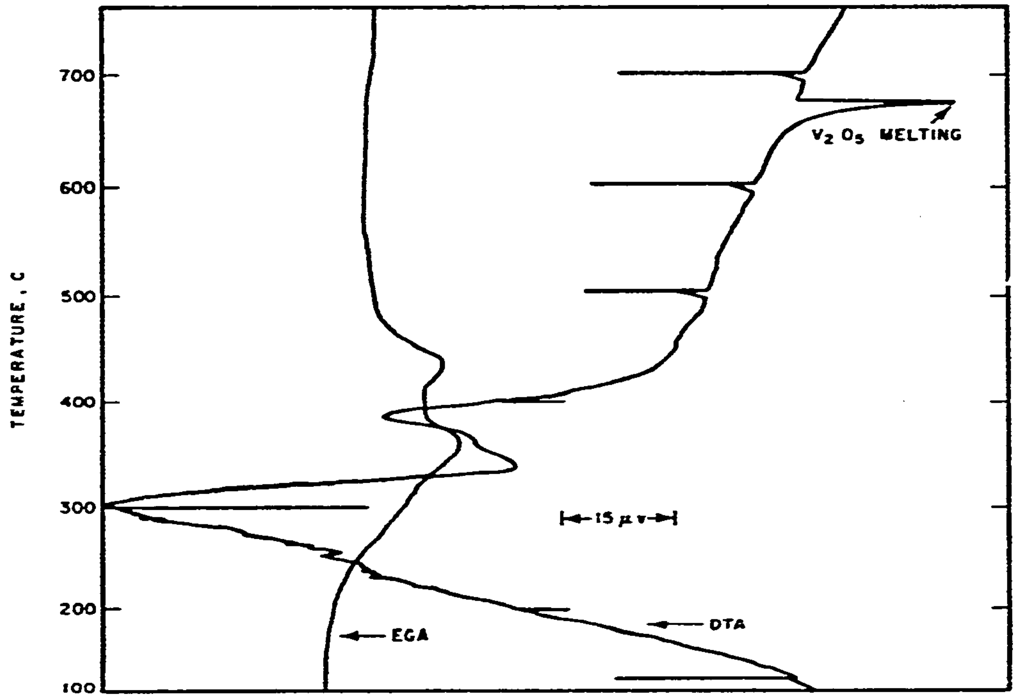

Fig. 2. DTA–EGA response for 0.45 mg of residue isolated from sample 2.

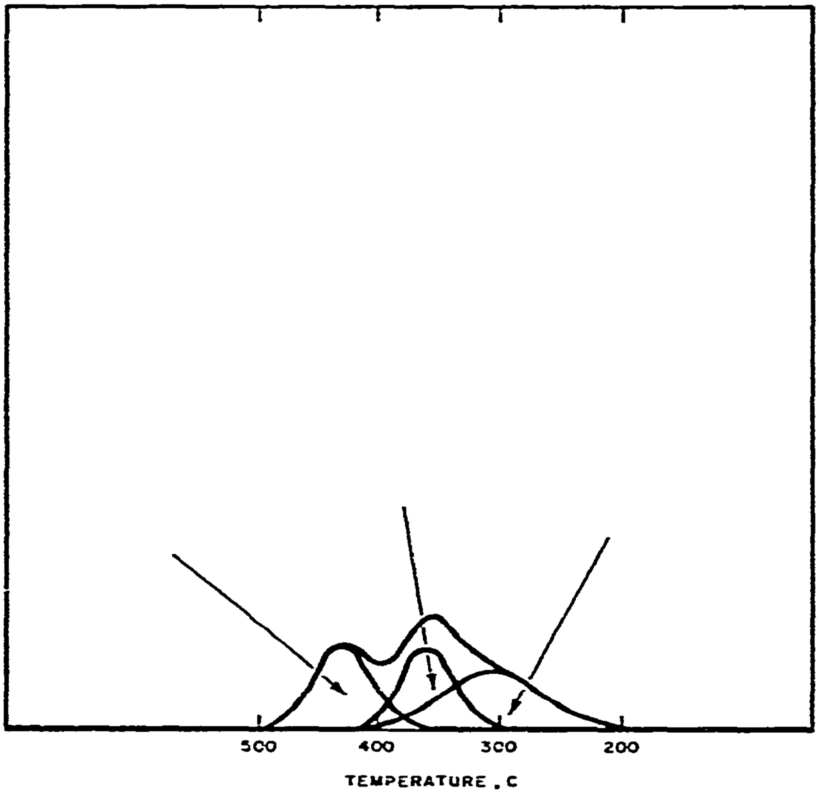

Fig. 3. Resolution of CO_2 EGA response for 0.45 mg isolated from sample 2.

TABLE 2

ANALYTICAL DATA FOR VANADIUM–CARBON-BEARING RESIDUES

Sample No.	*Probable compound*	*CO_2 evolved at indicated temperature, %*				*X-Ray diffraction identification*
		350 to 390°C	*410 to 440°C*	*460 to 500°C*	*Other*	
2	V_4C_3	30	30	None	40 at 310°C	VC or V_4C_3
3	VC or V_4C_3	20	52	18	10 at 520°C	VC and Fe_3C
4	VC_xN_y	26	54	11	7 at 320°C	Fe_3C
5	VC_xN_y	22	30	49	None	VC+vanadium oxides
6	VC_xN_y	44	39	25	None	VC+vanadium oxides
7	VC_xN_y	33	24	44	None	Not examined
8	VC_xN_y	36	44	23	None	Not examined
9	VN	44	8	43	5 at 290°C	Not examined
10	VN	18	23	49	10 at 290°C	Not examined
11	VN	50	16	29	5 at 300°C	Not examined
12	VN	56	15	15	22 at 520°C	VC+unidentifiable diffraction lines
13	VN or V_4N_3	29	5	61	3 at 610°C	VN

Figure 6 is a typical DTA–EGA response for most of the residues from the samples listed in Table 2, which show VC_xN_y as the vanadium compound isolated. This particular response was obtained for a residue isolated from sample 5. The resolution of the EGA response shows that 30% of the carbon in the residue was isolated as VC_xN_y and is represented by an EGA peak at 440°C. Ignoring for the moment N_y, the C_x corresponds to 0.01% vanadium in the steel. The DTA response shows only a trace of the V_2O_5 endotherm between 640 and 700°C, which is prominent in Figs. 1, 2, and 4, because the concentration of vanadium in the isolated residue is not as high as that in residues from samples 2 and 3.

In addition to the CO_2 response at 440°C, the residue from sample 5 also evolved nitrogen at 450°C, as shown in Fig. 7. This nitrogen response is typical of that for all the samples in Table 2 that have been designated as containing VC_xN_y. It is small and nearly constant, representing 0.001 to 0.002 absolute percent nitrogen in the steel. A possible explanation is that in these samples V_4C_3 formed first, and nitrogen tended to fill the vacancies in the lattice.

The EGA decomposition observations made for VC_xN_y are different from those made previously for NbC_xN_y[14] by DTA–EGA. The combustions of the M_4C_3 carbide and of the MC_xN_y carbonitride take place over the same temperature range, however, CO_2 and N_2 are evolved simultaneously from VC_xN_y. VC was identified by X-ray diffraction in several samples which appeared to contain the carbonitride by EGA

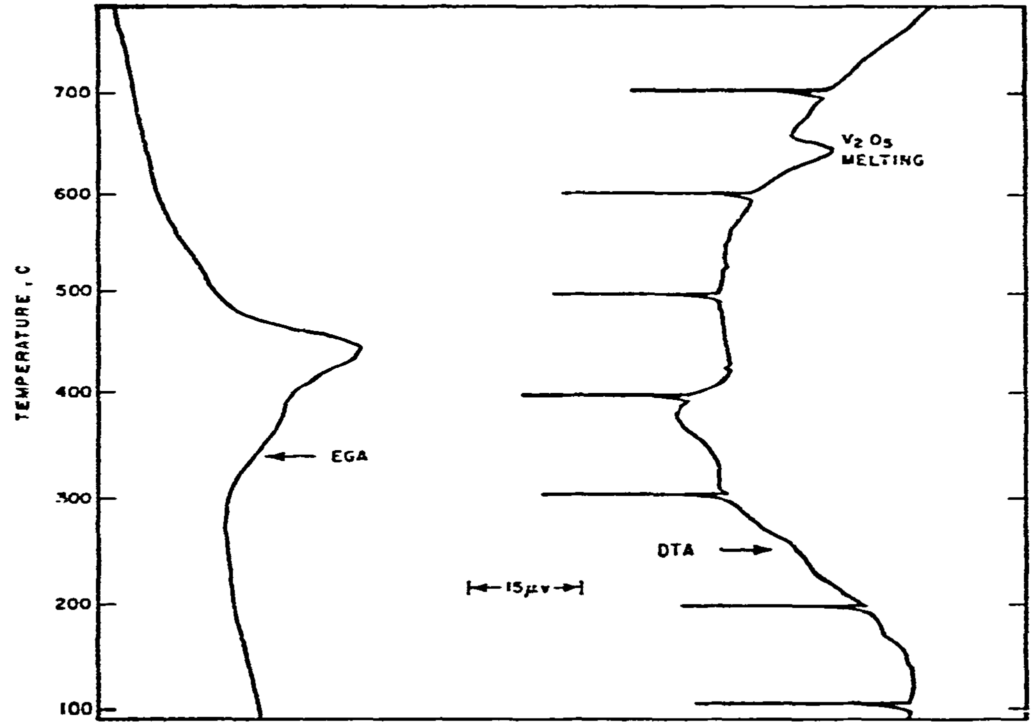

Fig. 4. DTA–EGA response for 0.14 mg of residue isolated from sample 3.

observation. This confirms the contention that VC or VC_{1-x} cannot be distinguished from VC_xN_y by X-ray diffraction and is also in agreement with a similar diffraction observation for niobium carbide and niobium carbonitride[14]. Therefore, in order to determine whether the precipitated vanadium is present as V_4C_3 or as VC_xN_y, it is necessary to determine whether nitrogen is being evolved simultaneously with the CO_2 during combustion.

Residues from steels 9 through 12 after decarburization contained nitrogen as nitride (0.006 to 0.008%) which indicated that all or nearly all of the vanadium was combined as VN. There were large endotherms from the melting of V_2O_5 and microchemical analysis of isolated residues showed high vanadium concentrations. The EGA responses from all four samples showed either three or four nitrogen evolution peaks (Figs. 8 and 9). Table 3 summarizes the results obtained from the resolution of these responses. Because the residue from sample 13 showed a single nitrogen-evolution peak at 480°C, and because cubic VN has been identified by X-ray diffraction in this residue before heating to 480°C, it is assumed that the corresponding peaks for the residues from samples 9 through 12 were also due to this compound.

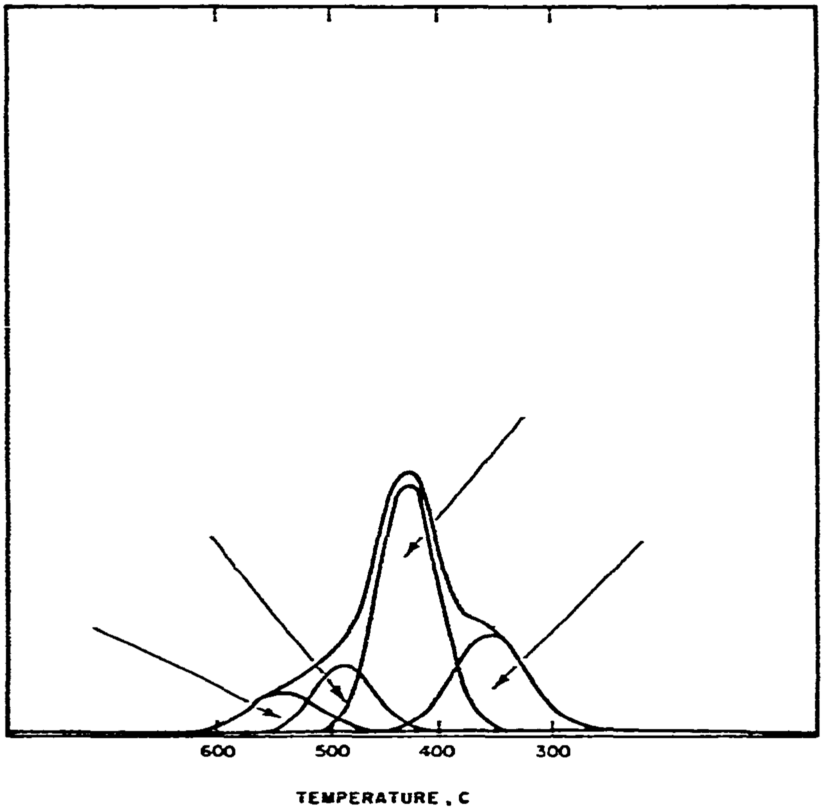

Fig. 5. Resolution of CO_2 EGA response for 0.14 mg of residue isolated from sample 3.

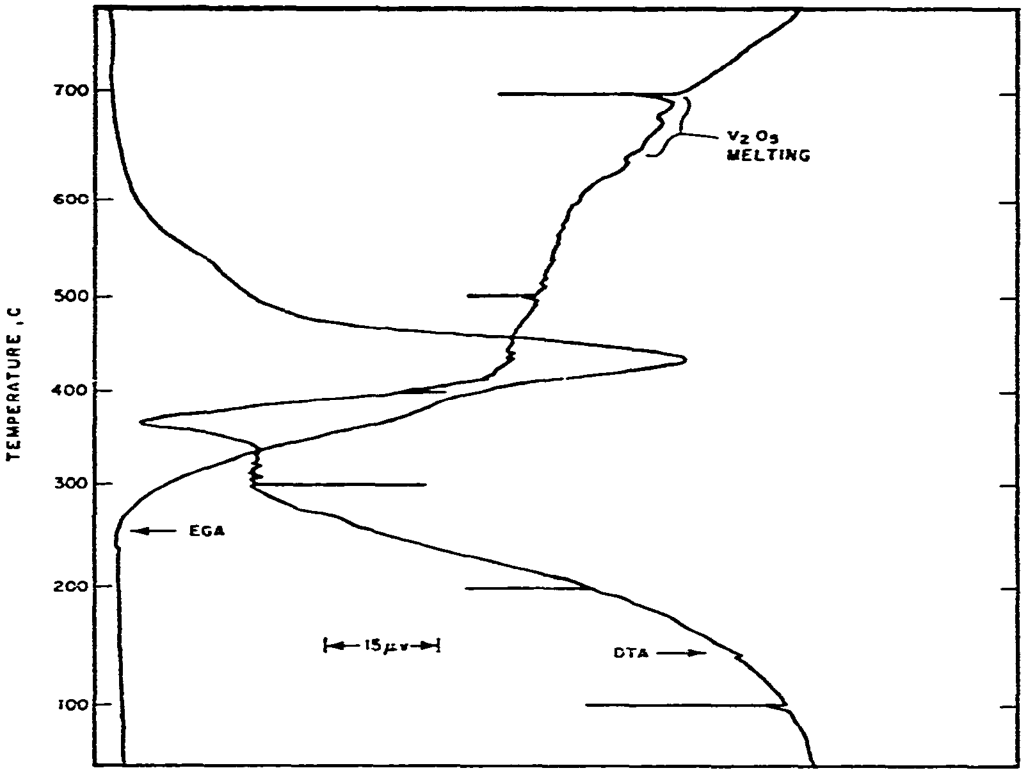

Fig. 6. DTA–EGA response for 0.68 mg of residue isolated from sample 5.

TABLE 3

EGA NITROGEN DATA FOR DECARBURIZED VITRENAMEL SAMPLES

Sample no.	*Total N in isolated residue (%)*	*Percent of total nitrogen detected*			
		Peak No. 1	*Peak No. 2*	*Peak No. 3*	*Peak No. 4*
9	0.008	35 at 380°C	—	30 at 480°C	35 at 550°C
10	0.006	18 at 380°C	17 at 450°C	28 at 500°C	38 at 550°C
11	0.006	15 at 380°C	10 at 420°C	22 at 460°C 52 at 510°C	—
12	0.008	3 at 390°C	34 at 420°C	63 at 500°C	—

The nitrogen evolved from 420 to 450°C appears to be due to vanadium carbonitride, because carbon dioxide and nitrogen were evolved over this temperature range. Although the microchemical and quantitative EGA evidence indicates that the two remaining nitrogen-evolution peaks must also result from the decomposition of VN, there is no evidence to explain this phenomenon. In previous work on NbN[16], two minor peaks in addition to the major response caused by fcc NbN[16], were identified by X-ray diffraction as being due to hexagonal NbN and epsilon NbN; however, corresponding vanadium compounds have not been identified.

CONCLUSIONS

Vanadium carbide, nitride, and carbonitride precipitates in low alloy, vanadium-bearing steels have been chemically isolated from the matrix and examined by DTA–EGA, microchemical, and X-ray diffraction methods. The results show:

1. When there was little nitrogen and much carbon available to combine with the vanadium, the precipitated phase was V_4C_3 which burns in a dynamic atmosphere of oxygen in the DTA–EGA apparatus over the temperature range 330 to 360°C to

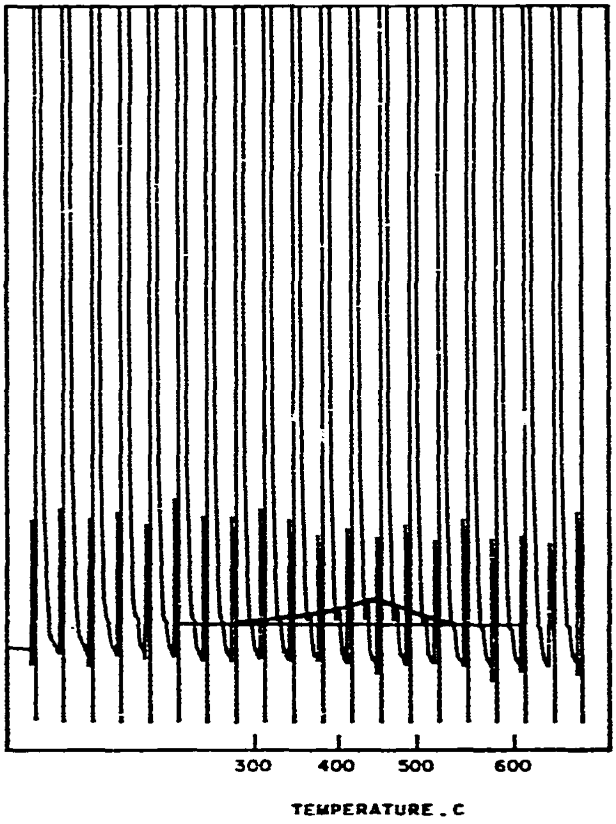

Fig. 7. EGA response for nitrogen evolved from 0.33 mg of residue isolated from sample 5.

evolve CO_2. No evidence for the formation of VC was found.

2. When both carbon and nitrogen were available for combination with vanadium, the only compound found was VC_xN_y.

3. In samples of a Fe–V–N alloy, only a single EGA nitrogen evolution peak was observed, which was caused by the decomposition of VN or V_4N_3.

4. For residues isolated from decarburized low alloy, vanadium-bearing steels, three and sometimes four nitrogen evolution peaks were observed during the decomposition of the residues isolated. It appears that two of these peaks result from the decomposition of VC_xN_y and VN, but a reason for the existence of the other two peaks has not been found.

5. Because V_4C_3 and VC_xN_y burn in oxygen over the same temperature range, the only way to differentiate between the two is to determine the amounts of CO_2 and nitrogen evolved.

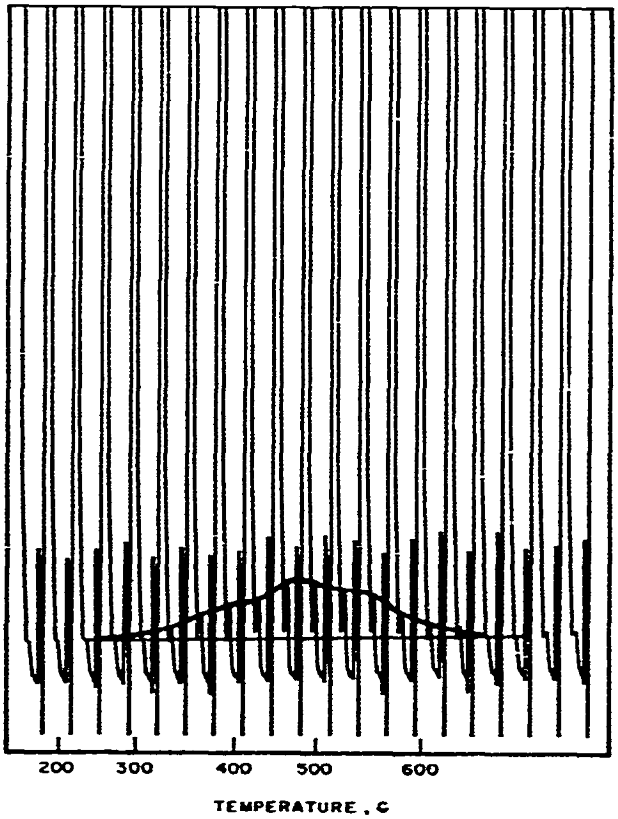

Fig. 8. EGA response for nitrogen evolved from 0.31 mg of residue isolated from sample 9.

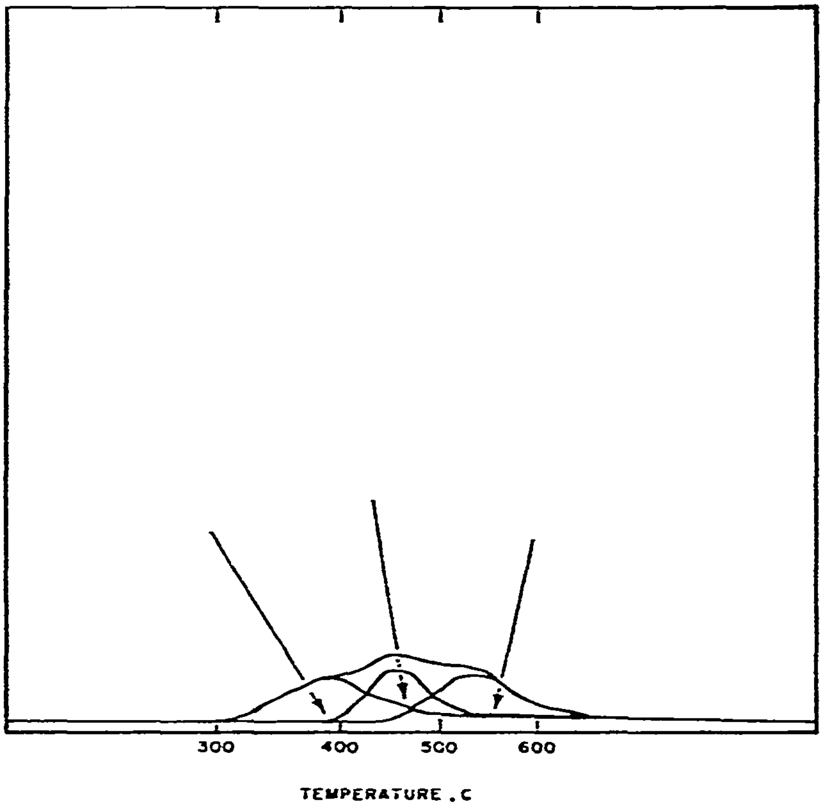

Fig. 9. Resolution of EGA nitrogen response obtained for 0.31 mg of residue isolated form sample 9.

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