

Influence of the composition of the redox system on the thermo-oxidative degradation of intercalated graphites

V.S. Osipchik, R.A. Yakovleva, E.Yu. Spirina, T.N. Obizhenko, E.A. Rybko, and A.V. Kondratenko

D.I. Mendeleev Russian Chemico-Technological University, Moscow, Russia

Khar'kov State Technical University of Building and Architecture, Khar'kov, Ukraine

University of Civil Protection of Ukraine, Khar'kov, Ukraine

Selected from International Polymer Science and Technology, 37, No. 4, 2009, reference PM 09/10/38; transl. serial no. 16244

Translated by P. Curtis

SUMMARY

An examination was made of the influence of the concentration of an oxidative solution of potassium bichromate in sulphuric acid on processes of thermo-oxidative breakdown and the coefficient of swelling of intercalated graphites. It was established that the resistance of intercalated graphites to thermal oxidation depends not only on the concentration of the oxidative solution used for intercalation but also on the graphite/potassium bichromate/sulphuric acid ratio.

A great deal of attention has recently been paid to the study of processes of the production and the physicochemical properties of intercalated graphite compounds possessing a regular lamellar structure, a high anisotropy of properties, and also an unusual nature of the bond of the substances introduced with the graphite matrix. Continued interest in intercalated graphite compounds is due to the potential scope for the development of materials with the given combination of properties.

Graphite and intercalated graphite (IG) are widely used as fillers of polymer composites for the fireproofing of building structures [1]. The effectiveness of fireproofing coatings depends largely on the resistance of IG to thermo-oxidative degradation (TOD).

There are numerous technologies for IG production, which means that their physicochemical properties should differ according to the production method. To date, the

method that has been most widely used on an industrial scale is IG production technology using sulphuric acid in the presence of potassium bichromate as an oxidant [2].

In the light of their great practical importance, numerous studies have been devoted to investigating processes of interaction of carbon materials, including graphites, with air oxygen. In particular, the heterogeneous oxidation of non-volatile coke residue (flameless combustion, smouldering) presents a serious risk of the possible spread of fire [3].

Therefore, study of the behaviour of different graphite materials, including chemically oxidised graphites, in the process of intercalation under conditions of increased temperatures in the presence of air oxygen is an important scientific and practical problem.

The aim of this work was to study the effect of the oxidative solution used for intercalation on the breakdown rate and the coefficient of swelling of intercalated graphites.

Graphite of grade GSM-2 and products of its treatment with sulphuric acid were studied in the present investigations. The procedure for graphite oxidation is described in the literature [4]. In the present investigations, graphite powder of 200–160 µm fraction was added to a freshly prepared solution of potassium bichromate in concentrated 96% sulphuric acid. Here, the content of bichromate and sulphuric acid was varied (**Table 1**).

A suspension of graphite in the reaction mixture was intensively mixed using a magnetic stirrer at room temperature for 30 min. At the end of intercalation, the

Table 1. Graphite/oxidant/sulphuric acid ratio

Graphite number	GSM-2/K ₂ Cr ₂ O ₇ /H ₂ SO ₄			Concentration (K ₂ Cr ₂ O ₇ in H ₂ SO ₄), g/L
	m _{GSM-2} , g	m _{K₂Cr₂O₇} , g	m _{H₂SO₄} , g	
1	2	3	4	5
1	2	3	4	5
1*	10	—	—	—
2	10	1.2	50	24
3	10	1.2	40	30
4	10	1.6	50	32
5	10	1.2	30	40
6	10	1.6	40	40
7	10	1.6	30	53

* Initial GSM-2

mixture was diluted with water, the solid phase was filtered out, and it was washed to pH ~6 and dried to constant weight at a temperature of 100°C.

Processes of the TOD of graphite were studied on a derivatograph in a dynamic regime with a heating rate of 10°C/min to 1000°C in an air atmosphere. The specimens weighed 20 mg.

Figure 1 gives curves of thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the initial graphite (GSM-2) (1) and of IG (2) in air.

From experimental TG and DTA curves we calculated the temperature and weight characteristics of the

process of TOD of graphites ($T_{\text{endo,e}}$ is the temperature of the endothermic effect, $T_{\text{exo,e}}$ is the temperature of the exothermic effect, T_{infl} is the temperature of the inflection point, Δm is the weight loss), and also the maximum breakdown rates ($\Delta m/\Delta \tau$). Calculated data are presented in **Table 2**.

Analysing the presented curves and data in **Table 2**, it can be noted that the weight loss of the initial graphite begins at 650°C and proceeds in a single stage at a constant rate up to 950–1000°C. The weight loss at 900°C amounts to 46.1%. This process is accompanied with a significant exothermic effect, and it can therefore be concluded that the weight loss of the initial specimen is connected with oxidation of the graphite and with the liberation of gaseous products of oxidation.

The DTA curve for the initial graphite (**Figure 1**, curve 1) in the region 300–600°C has a slightly exothermic nature, which may be due to the adsorption of molecular oxygen on the surface of the graphite.

The shape of the TG curves of the IG (curves 2–7) indicates the occurrence of thermo-oxidative breakdown in two stages. In the first stage, in the 30–600°C range, up to 33.8 wt% is lost (curve 3, TG) and the process proceeds with heat absorption, as indicated by endotherms with maxima at temperatures of 130, 140, 210, and 220°C (**Figure 1**, DTA). The greatest weight loss at 600°C is observed in the case of IG numbers 2 and 3 with K₂Cr₂O₇ concentrations in H₂SO₄ of 24 and 30 g/L respectively, and the smallest weight loss in the case of graphites 5–7 with concentrations of 40 and 53 g/L. Thus, the more oxidised the graphite, the lower is its weight loss at the first stage of the process of decomposition, and the slower the rate of weight loss.

A characteristic feature of this stage of the process is that, on the TG curves (2–7), an abrupt change in weight loss is observed at 205–240°C, and in this narrow range up to 14 wt% is lost. On the DTA curves, a marked endothermic peak is observed in the low-temperature region at 140°C, which can be attributed to

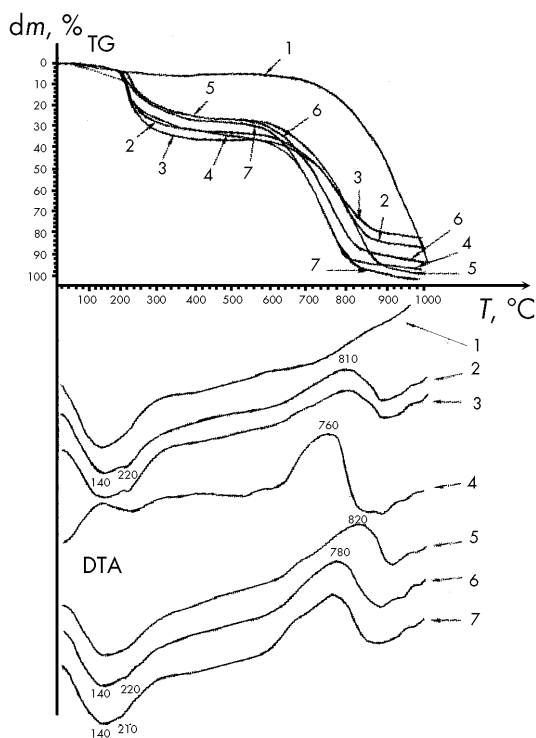


Figure 1. TG and DTA curves during the thermal degradation of the initial graphite GSM-2 (1) and of GSM-2 oxidised by a mixture of K₂Cr₂O₇ and H₂SO₄ in different ratios: 2, 1.2:50; 3, 1.2:40; 4, 1.6:50; 5, 1.2:30; 6, 1.6:40; 7, 1.6:30 for 10 g of graphite

Table 2. Temperature and weight characteristics of the TOD process of the graphites used

Stage of TOD process	Characteristics	Graphite number							
		1	2	3	4	5	6	7	
I	Temperature range, °C	—	30–600						
	$T_{\text{endo.e1}}$, °C	140	140	130	—	140	140	140	
	$T_{\text{endo.e2}}$, °C	210	220	220	220	220	220	210	
	T_{m} , °C	—	206	213	209	240	220	220	
	$\Delta m/\Delta \tau$, mg/min	—	0.20	0.26	0.15	0.10	0.13	0.13	
	Δm , %, at 600°C	6.8	30.4	33.8	31.5	22.5	28.1	31.5	
II	Temperature range, °C	600–900							
	$T_{\text{endo.e1}}$, °C	—	810	810	760	820	780	780	
	$T_{\text{endo.e2}}$, °C	950	775	790	760	805	750	745	
	T_{m} , °C	0.13	0.15	0.13	0.13	0.18	0.20	0.20	
	$\Delta m/\Delta \tau$, mg/min	47.2	49.5	47.2	60.8	72.0	63.0	72.0	
	Δm , %, at 600°C	46.1	81.0	78.8	91.1	94.5	90.0	100	

phase transitions, as the process is not accompanied with weight loss of IG specimens. These processes evidently can be attributed to the formation of gaseous products of introduced substances – water vapour, residual hydrates of sulphuric acid, and products of its breakdown, which are produced by the reaction



and, possibly, products of the oxidation of carbon at higher temperatures:



With a further increase in temperature, these gaseous products expand, which leads to deformation of the graphite layers and, ultimately, to swelling of the graphite along axis C at 205°C and to the removal of gaseous products up to 600°C. Furthermore, as noted in reference [5], in the process of thermal expansion, splitting of crystallites along axis A can occur. It must be noted that, in the 205–600°C temperature range, small endothermic effects are observed on the DTA curves at 210 and 220°C, and this indicates the Van der Waals nature of interaction of the graphite matrix and intercalate.

After swelling (expansion) of IG at temperatures of 600°C and up to 900°C, a second stage proceeds, which is noted for intense weight loss. At this stage, up to 72 wt% of the oxidised graphite itself is lost, and the total weight loss of the IG specimen at 900°C amounts to 100% (Table 2; Figure 1, curve 7). It can be noted that, with increase in the degree of oxidation of graphite, there is an increase in weight loss at the second stage of

graphite breakdown. The rate of weight loss of the most oxidised graphites (numbers 5–7) is 1.5 times greater than the breakdown rate of the initial natural graphite GSM-2. The greatest contribution to increase in the rate of oxidation of IG is probably made by the magnitude of the surface area of the graphite particles, which increases considerably as a result of thermal splitting at 205°C. On the DTA curves (curves 2–7) there are pronounced exothermic peaks with maxima at 760, 780, 810, and 820°C in the 600–900°C temperature range (Table 2), indicating the oxidative nature of the breakdown process. The most intense peak is seen for graphite number 4 with a concentration of 32 g/L with a maximum at 760°C, and the least intense peak for graphite number 5 (concentration 40 g/L) with a maximum at 820°C. Thus, the oxidation resistance of IG depends not only on the concentration of the oxidative solution used for intercalation but also on the graphite/oxidant/sulphuric acid ratio (the more $\text{K}_2\text{Cr}_2\text{O}_7$, the earlier is the start of oxidation).

In the production of fire-resistant materials using IGs, it is important to know the coefficient of swelling of the latter. For this, heat treatment of the IG was conducted by shock heating (by insertion in a muffle furnace heated to a given temperature and by holding for 1 min). The capacity to swell during heating was expressed quantitatively by the coefficient of swelling $K_v = \rho^{\text{HEG}}/\rho^{\text{IG}}$, i.e. the ratio of the bulk densities of heat-expanded graphite and the initial intercalated graphite respectively [5]. The results are given in Table 3.

As can be seen, with increase in the concentration of oxidative solution there is a reduction in the coefficient of swelling. This is in good agreement with TOD data, as, at the first stage of breakdown of graphites, the rate of weight loss decreases.

Table 3. Properties of intercalated graphites

Graphite number	Concentration ($K_2Cr_2O_7$ in H_2SO_4), g/L	Stage I of TOD	Stage II of TOD	K_v	
		$\Delta m/\Delta \tau$, mg/min	$\Delta m/\Delta \tau$, mg/min	600°C	800°C
1	—	—	0.13	—	—
2	24	0.20	0.15	11.12	29.24
3	30	0.26	0.13	12.52	28.72
4	32	0.15	0.13	9.65	29.07
5	40	0.10	0.18	8.73	22.02
6	40	0.13	0.20	8.75	25.16
7	53	0.13	0.20	8.74	22.31

CONCLUSIONS

1. The greater the oxidation of graphite, the lower is the rate of its weight loss at the first stage of the breakdown process, and the greater the rate of its weight loss at the second stage of the oxidation process.
2. The oxidation resistance of IG depends not only on the concentration of the oxidative solution used for intercalation but also on the graphite/oxidant/sulphuric acid ratio.
3. With increase in concentration of oxidative solution there is a reduction in the coefficient of swelling of the graphites, which is in good agreement with data of thermo-oxidative degradation.
4. On the basis of the investigations carried out it is possible to predict the effect of graphite fillers on the thermo-oxidative degradation of filled epoxy polymer composites and their fireproofing characteristics, and the yield of coke residue. The data obtained can be used to develop intumescent fireproofing composites filled with intercalated graphites.

REFERENCES

1. I.G. Romanenkov and F.A. Levites, *Fireproofing of Building Structures*. Stroizdat, Moscow, 1991, 320 pp.
2. I.G. Chernysh and I.D. Buraya, Investigation of the process of oxidation of graphite by a solution of potassium bichromate in sulphuric acid. *Khimiya Tverdogo Topliva*, No. 1, 1990, pp. 123–127.
3. R.M. Aseeva and G.E. Zaikov, *Combustion of Polymeric Materials*. Nauka, Moscow, 1981, 280 pp.
4. I.V. Nikol'skaya *et al.*, The formation of graphite bisulphate in systems containing graphite, H_2SO_4 , and oxidant. *Zhurnal Obshchei Khimii*, **54**, No. 12, 1989, pp. 2653–2658.
5. G.I. Titel'man *et al.*, Thermal splitting of the breakdown products of graphite–acid intercalation compounds under conditions of shock and linear heating. *Khimiya Tverdogo Topliva*, No. 4, 1991, pp. 79–84.