Thermochimica Acta, 91 (1985) 213–222
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MUTUAL THERMAL INTERACTION BETWEEN COBALT AND TANTALUM OXIDES

N.M. GHONEIM and G.A. EL-SHOBAKY

National Research Centre, Dokki, Cairo (Egypt)

(Received 21 March 1985)

ABSTRACT

The effect of Ta_2O_5 additions (1.5–12 mol%) on the thermal stability of Co_3O_4 and reactivity of CoO towards reoxidation by O_2 to give Co_3O_4 was investigated. The induced thermal decompostion of Ta_2O_5 was also studied. The techniques employed were DTA, with controlled heating and cooling rates, X-ray and IR spectrometry.

The results obtained revealed that Ta_2O_5 increased both the thermal stability of Co_3O_4 and the reactivity of CoO. The thermal treatment of cobalt oxides doped with Ta_2O_5 in air at 1000°C led to a partial decomposition of Ta_2O_5 to TaO and the formation of $CoTa_2O_6$ together with a well-crystalline, new compound. The *d*-spacings of the newly formed compound were calculated and found to be 2.78_x, 3.02_7, 4.49_6 Å.

The observed increase in the thermal stability of Co_3O_4 due to treatment with Ta_2O_5, was attributed to the increase in the oxidation character of the treated solid resulting from substitution of some of Co^{4+} ions by Ta^{2+} ions. The liberation of O_2 degassed from the partial decomposition of Ta_2O_5 to TaO might also account for the increase in the oxidation character of cobaltic oxide and for the increase in the reactivity of cobaltous oxide.

INTRODUCTION

Cobaltous oxide is one of the well-known oxides that are traditionally employed as colouring agents in the glass and glaze industries. Different grades of blue colourations (cobalt blue) can be obtained through the addition of different amounts of CoO, either alone or together with other colouring oxides, followed by heat treatment under various conditions [1,2]. Cobaltous oxide is considered the most stable and reliable glaze colourant. However, its characteristic colouring effects are greatly influenced by its partial oxidation to Co_3O_4. Such a transformation could be effected by treating with other oxides. The effects of different oxides (Li_2O, Na_2O, MgO, Al_2O_3, ZrO_2, ThO_2, V_2O_5, MoO_3 and BeO) on the reactivity of CoO towards reoxidation by O_2 to yield Co_3O_4 was the object of our series of investigations [3–8].

The present work was devoted to the study of the effect of Ta_2O_5 on the reactivity of CoO and the thermal decomposition of Co_3O_4. Tantalum oxide is known to exist as stable Ta_2O_5 and is relatively inert chemically [9]. Being

0040-6031/85/$03.30

known to behave as a stable pentavalent oxide made it worthy to investigate its effect upon the thermal behaviour of cobalt oxides.

EXPERIMENTAL

Materials

A series of cobalt oxide samples treated with different proportions of tantalum pentoxide was prepared by thermal decomposition of basic cobalt carbonate mixed with various amounts of Ta_2O_5 solids in air at 1000°C for 4 h. The amount of Ta_2O_5 was varied between 1.5 to 12 mol% Ta_2O_5. Being added as a powder required a prolonged grinding to ensure the homogeneous distribution of the foreign oxide throughout the whole mass of the basic cobalt carbonate employed. An automatic agate mortar was employed for this purpose.

Techniques

Differential thermal analysis (DTA) of pure and treated basic cobalt carbonate was carried out using a DuPont 990 thermal analyser with a differential scanning calorimeter cell. The rate of heating and cooling was kept constant at 20°C min^{-1} and the sensitivity was 1 mV/in. A 30-mg sample of each solid specimen was employed in each case.

An X-ray investigation of the thermal products of pure and treated basic cobalt carbonate was performed with a Philips diffractometer (type PW 1390). The patterns were run with iron-filtered cobalt radiation, $\lambda = 1.7889$ Å, at 40 kV and 30 mA with a scanning speed of 2° in 2θ min^{-1}.

An IR absorption spectrum was determined for each solid using a Beckman IR 4250 spectrometer. The IR spectra were determined from 4000 to 300 cm^{-1}, but only the portion between 1500 and 300 cm^{-1} was considered in the present work. A 2-mg sample of each solid was dispersed by grinding for 3 min in a vibratory ball mill, placed in a steel die 30 mm in diameter, and subjected to a pressure of 12 tonnes.

RESULTS

Thermal behaviour of pure and Ta_2O_5-treated cobalt oxides

Figure 1 represents the DTA (heating and cooling) of pure basic cobalt carbonate and cobalt carbonate treated with different proportions of Ta_2O_5. A strong endothermic peak with its maximum at about 915°C was observed in all cases. This peak corresponds to the decomposition of Co_3O_4 to CoO [3]. A strong exothermic peak was found during the cooling of both pure and treated solids. Such a peak indicates the oxidation of CoO to Co_3O_4 [4]. The

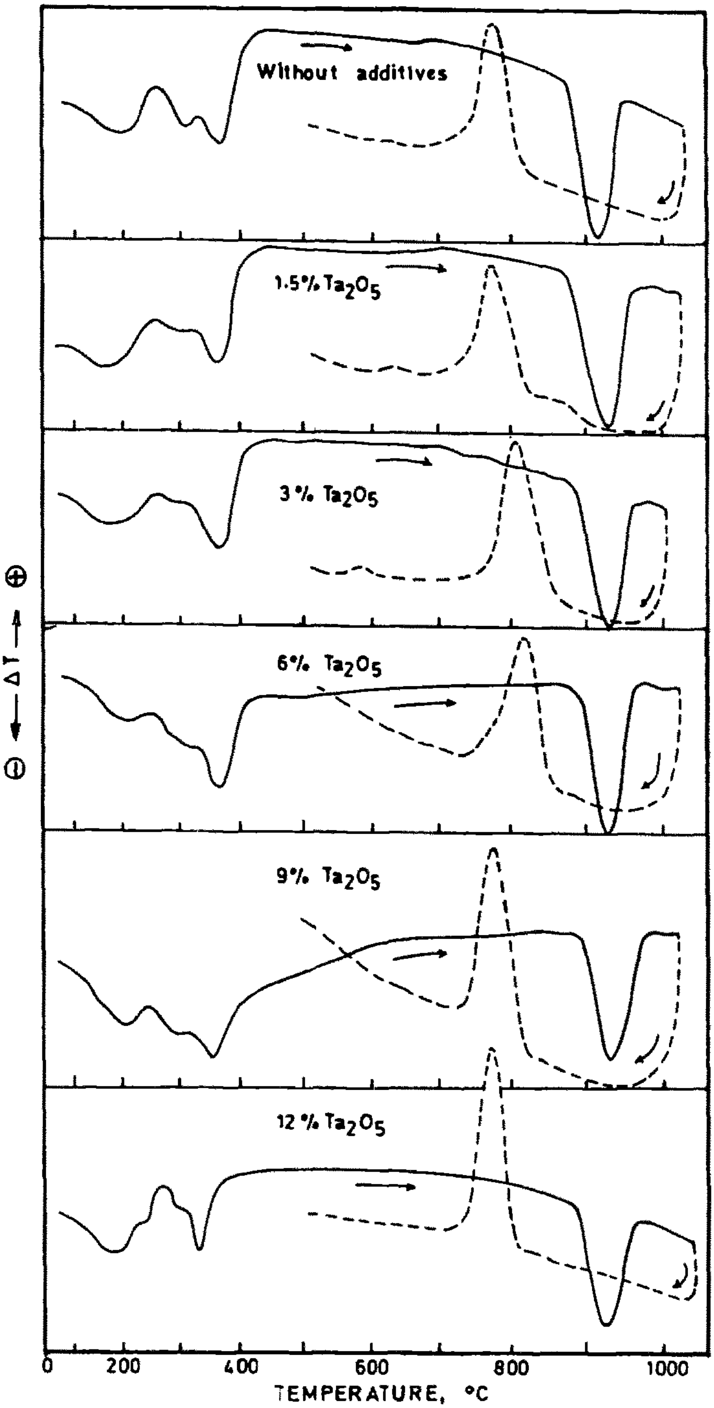

Fig. 1. DTA heating and cooling curves of pure and Ta_2O_5-treated specimens of basic cobalt carbonate.

TABLE 1

The effect of Ta_2O_5-treatment on the peak area of the DTA curves of the thermal decomposition of Co_3O_4 and reoxidation of CoO

Solid	Peak area (arbitrary units)		Percentage change in area of endothermic peak [a]	Ratio between the area of exothermic and endothermic peaks
	Endothermic peak	Exothermic peak		
Pure basic cobalt carbonate	25.60	20.51	0.0	0.80
Basic cobalt carbonate +				
1.5% Ta_2O_5	25.80	19.28	−0.78	0.75
3.0% Ta_2O_5	24.22	27.14	+5.39	1.12
6.0% Ta_2O_5	23.90	26.70	+6.64	1.12
9.0% Ta_2O_5	23.40	33.40	+8.59	1.43
12.0% Ta_2O_5	18.62	29.22	+27.27	1.57

[a] These data were obtained by subtracting the area of the endothermic peak for each solid from 25.60 (that for the pure solid). The negative and positive signs indicate a decrease and increase in the thermal stability of Co_3O_4, respectively.

maximum of this peak was found at 770 and 805°C for pure solid and those treated with 3 or 6 mol% Ta_2O_5, respectively.

The areas of endothermic and exothermic peaks were determined and are given in Table 1. This table also includes the percentage change in the area of the endothermic peak due to treating with Ta_2O_5 and the ratio between the area of exothermic and endothermic peaks for each solid. The percentage change in the area of the endothermic peak was considered as a measure of the thermal stability of Co_3O_4 and the ratio between the area of exothermic and endothermic peaks indicated the reactivity of CoO towards reoxidation by O_2 to yield Co_3O_4.

Table 1 shows that the addition of a small amount of Ta_2O_5 (1.5 mol%) to Co_3O_4 causes a very small decrease in its thermal stability which suffers a progressive increase by increasing the extent of the foreign oxide to the range 3–9 mol%. Increasing the amount of Ta_2O_5 to 12 mol% led to a sudden increase in the thermal stability of Co_3O_4 from 8 to 27%. The reactivity of the CoO produced towards reoxidation by O_2 to yield Co_3O_4 was found to increase on increasing the amount of doping oxide added.

X-ray investigation of pure and Ta_2O_5-treated cobalt oxides

The X-ray diffraction patterns were performed for pure and treated solids heated in air at 1000°C and subjected to both slow and rapid cooling to room temperature. All the diffraction lines of the Co_3O_4 phase were only detected in the X-ray diffraction patterns of pure solid subjected to slow

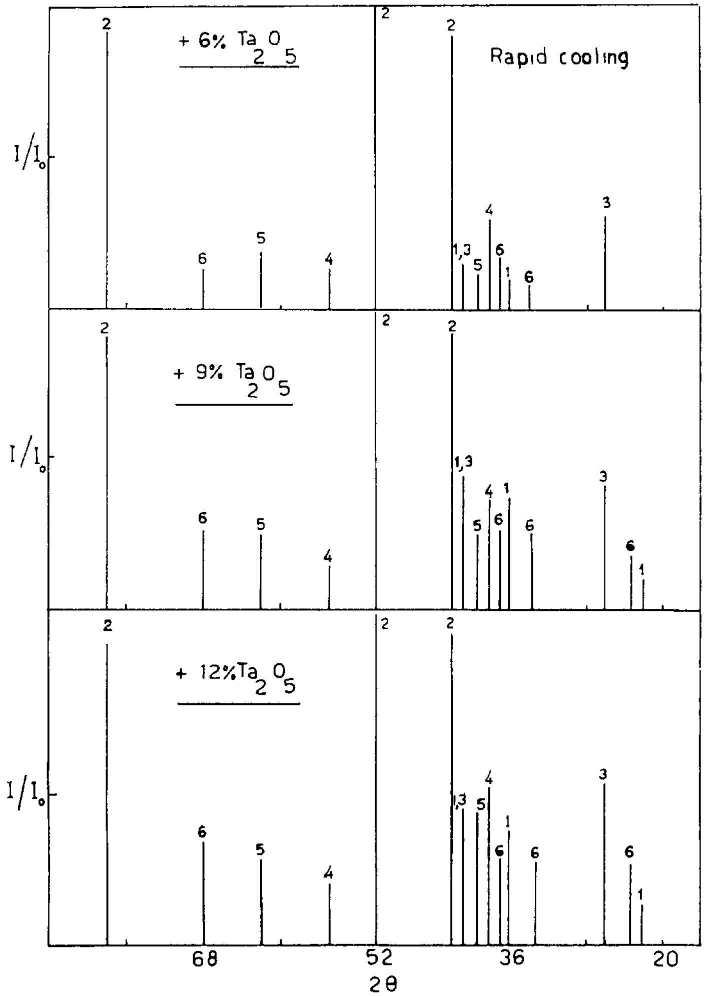

Fig. 2. X-ray patterns of Ta_2O_5-treated cobalt oxides heated in air at 1000°C and subjected to rapid cooling. (1) Co_3O_4 phase; (2) CoO phase; (3) Ta_2O_5 phase; (4) TaO phase; (5) $CoTa_2O_6$ phase; (6) a new compound.

cooling. By contrast, in the case of the rapidly cooled pure solid, the characteristic diffraction lines of both the CoO and Co_3O_4 phases were found, indicating an incomplete oxidation of CoO to Co_3O_4.

Figure 2 represents the X-ray diffraction patterns of cobalt oxide treated with different proportions of Ta_2O_5, heated at 1000°C then subjected to rapid cooling. All the characteristic lines of both the CoO and Co_3O_4 phases, together with several new lines, were detected. However, the intensity of the cobaltous oxide lines is, as expected, much more pronounced than that of the cobaltic oxide lines. Indeed, the intensity of the Co_3O_4 lines increases markedly on increasing the amount of Ta_2O_5 added from 6 to 9 mol%. It then remained almost unchanged by a further increase in the amount of the foreign oxide. These results indicate that Ta_2O_5 being added to Co_3O_4 led to an increase in its thermal stability. The newly detected diffraction lines may point to the formation of new compounds. The ASTM matching [10] with the newly observed lines revealed the appearance of the following phases: Ta_2O_5, TaO, and $CoTa_2O_6$ together with a new compound. The 2θ values and *d*-spacings of this new compound were calculated and found to be the following.

2θ (°)	37.4	34.5	23.0
d-spacing (Å)	2.78_x	3.02_7	4.49_6

It is worthy to observe the partial thermal decomposition of Ta_2O_5 to a

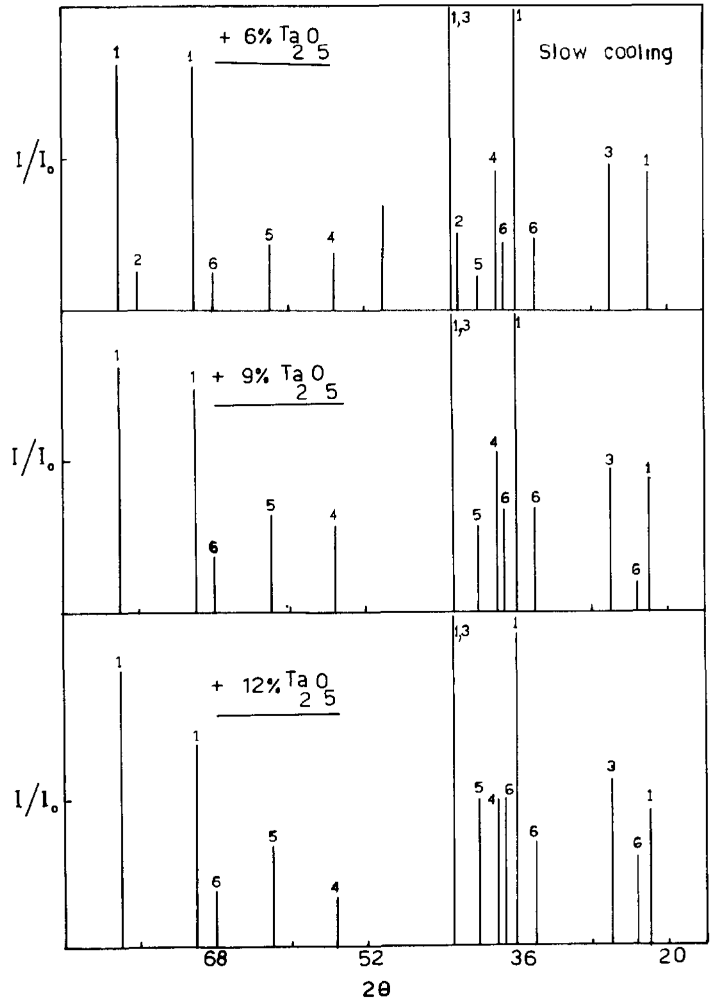

Fig. 3. X-ray diffraction patterns of Ta_2O_5-treated cobalt oxides heated in air at 1000°C and subjected to slow cooling. (1) Co_3O_4 phase; (2) CoO phase; (3) Ta_2O_5 phase; (4) TaO phase; (5) $CoTa_2O_6$ phase; (6) a new compound.

stable TaO phase, in the presence of cobalt oxides. This reaction might proceed according to

$$\mathrm{Ta_2O_5} \underset{(\mathrm{CoO},\ \mathrm{Co_3O_4})}{\overset{1000^{\circ}\mathrm{C}}{\rightleftharpoons}} 2\,\mathrm{TaO} + 3/2\ \mathrm{O_2}\ (\mathrm{g}) \qquad (1)$$

The oxygen evolved could be consumed either in raising the oxidation character of cobalt oxide effecting an increase in its thermal stability and/or in oxidizing the CoO produced into Co_3O_4. Based on this assumption, the observed increase in the thermal stability of cobaltic oxide due to treatment with Ta_2O_5 might be achieved, in part, by the effectiveness of the above-mentioned reaction.

Figure 3 represents the X-ray diffraction patterns of cobalt oxide treated with different proportions of Ta_2O_5, heated in air at 1000°C then subjected to slow cooling to room temperature. All the characteristic lines of the Co_3O_4 and CoO phases, together with the same new lines as found in the case of the rapidly cooled solids, were detected in the diffraction patterns of the cobalt oxide sample treated with 6 mol% Ta_2O_5. The lines of the CoO phase disappeared when cobalt oxide samples were treated with 9 and 12 mol% Ta_2O_5. The absence of the CoO phase in these two solid specimens revealed an enhanced reactivity of such a phase towards reoxidation by O_2 to produce Co_3O_4. The oxygen evolved from the reaction given by eqn. (1) might account for the complete oxidation of CoO into Co_3O_4 by treating with Ta_2O_5 (9–12 mol%). The phases present in the slowly cooled solids treated with Ta_2O_5 are: Ta_2O_5, TaO, $CoTa_2O_6$ and a new compound, the same as those found in the case of the rapidly cooled solids. The presence of free tantalum oxides indicated a limited solubility of these oxides in cobalt oxide solids.

IR investigation of pure and treated cobalt oxides

Figure 4 represents the IR spectra of pure and treated cobalt oxide specimens heated in air at 1000°C and subjected to slow cooling to room temperature. All the characteristic absorption bands of Co_3O_4 [4,6] were only detected in the case of pure and Ta_2O_5-treated cobalt oxides. However, the percentage transmission of the absorption bands of the solid treated with 12 mol% Ta_2O_5 was found to suffer a small decrease due to a possible interference with the IR bands of free tantalum pentoxide. In fact, it has been shown that Ta_2O_5 heated in air at 1000°C exhibited a very strong broad band extending between 400 and 620 cm^{-1} and three other weak bands at 750, 830 and 930 cm^{-1}.

Figure 5 represents the IR spectra of pure and Ta_2O_5-treated cobalt oxides heated at 1000°C and subjected to rapid cooling to room temperature. This figure shows that pure and treated solids exhibit a very strong band located at 300–550 cm^{-1} which characterizes a CoO structure [4].

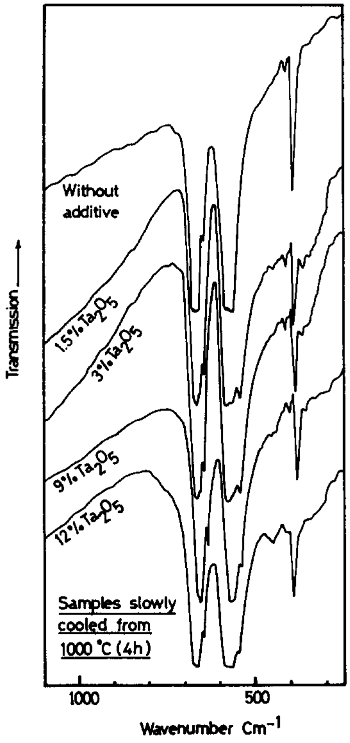

Fig. 4. IR absorption spectra of pure and Ta_2O_5-treated specimens of basic cobalt carbonate heated at 1000°C and subjected to slow cooling.

Other bands corresponding to the Co_3O_4 structure at 560, 640 and 655 cm^{-1} were also observed in the case of Ta_2O_5-treated cobalt oxide specimens. The percentage transmission of these bands increases on increasing the amount of the foreign oxide added. In other words, the extent of Co_3O_4, in the rapidly cooled solids, increases on increasing the amount of Ta_2O_5 added. These results are, thus, in good agreement with those of the DTA and X-ray investigations (cf. Table 1 and Figs. 2 and 3). The fact that no IR bands relative to the phases detected by the X-ray investigation (Ta_2O_5, TaO, $CoTa_2O_6$ and a new compound) were found in the IR spectra of treated cobalt oxide solids might indicate that these compounds exhibit their characteristic IR bands in the same vicinities as those of the cobalt oxides (CoO and Co_3O_4).

DISCUSSION

The results obtained in this investigation clearly indicate that the addition of Ta_2O_5 induced an increase in the thermal stability of cobaltic oxide and in the reactivity of cobaltous oxide towards reoxidation by oxygen to yield

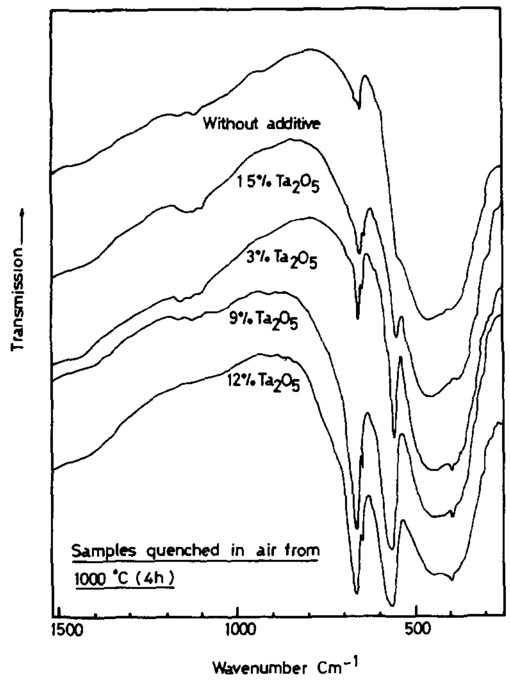

Fig. 5. IR absorption spectra of pure and Ta_2O_5-treated specimens of basic cobalt carbonate heated at 1000°C and subjected to rapid cooling.

Co_3O_4. Such an increase was proportional to the amount of the foreign oxide added. However, the addition of a small amount of Ta_2O_5 (1.5 mol%) was followed by a very small decrease in the thermal stability of Co_3O_4. The ionic radius of Ta^{5+} is 0.73 Å and those of Co^{2+} and Co^{4+} are 0.78 and 0.58 Å [11], respectively. The substitution of some Co^{2+} ions of the Co_3O_4 solid by Ta^{5+} seems geometrically possible. This process could be simplified, adopting Kröger's notions [12], as follows

$$Ta_2O_5 + 6\ Co^{3+} \rightarrow 2\ Ta(Co^{2+}) + 3/2\ O_2(g) \qquad (2)$$

$Ta(Co^{2+})$ are pentavalent tantalum ions located in the positions of some of the host Co^{2+} cations of the Co_3O_4 lattice, and Co^{3+} are charge carrier ions present in the non-stoichiometric cobaltic oxide sample [13]. The amount of Ta^{5+} dissolved in the Co_3O_4 lattice according to mechanism (2) is limited by the number of Co^{3+} ions or by the extent of deviation of Co_3O_4 from the stoichiometric composition. The dissolution of Ta^{5+} ions in cobaltic oxide according to reaction (2) is accompanied by degassing of oxygen and subsequent transformation of some of the Co^{3+} into Co^{2+} ions, effecting a decrease in the oxidation character of the doped solid [12]. Such a decrease could account for the observed decrease in the thermal stability of Co_3O_4 doped with 1.5 mol% Ta_2O_5. The progressive increase in the thermal stability of cobaltic oxide specimens treated with Ta_2O_5 (3–12 mol%) could not be explained in terms of the location of Ta^{5+} ions in the positions of any of the host cobalt cations. We might assume the presence of Ta^{2+} ions in the tantalum pentoxide-treated cobalt oxides. Such a speculation has been confirmed by X-ray investigation (cf. Figs. 2 and 3). The dissolution of Ta^{2+} ions in Co_3O_4 via substitution of some of its Co^{4+} ions is followed by an increase in the oxidation character of the treated solids, leading to a corresponding increase in their thermal stability. This process could be simplified as follows

$$TaO + 1/2\ O_2(g) \rightarrow Ta(Co^{4+}) + 2\ Co^{3+} \qquad (3)$$

$Ta(Co^{4+})$ are divalent tantalum ions located in the positions of the host cations of the Co_3O_4 solid. However, one cannot ignore the effect of cobalt oxides upon the induced partial decomposition of Ta_2O_5 to TaO. Such a reaction is accompanied by the liberation of active oxygen (reaction 1) which might also contribute to the increase in the oxidation character of Co_3O_4 and the subsequent increase in its thermal stability. This active oxygen might also be responsible for the observed increase in the reactivity of the CoO produced towards reoxidation by O_2 to yield Co_3O_4. In other words, a mutual effect took place between Ta_2O_5 and the cobalt oxides. Such an effect resulted in a decrease in the extent of thermal decomposition of Co_3O_4 and an enhancement of the thermal decomposition of Ta_2O_5 to TaO. The fact that free tantalum oxides were detected in all treated cobalt oxides revealed that most of the Ta_2O_3 added was involved in solid–solid interactions leading to the formation of $CoTa_2O_6$ together with a new compound.

REFERENCES

1 F. Singer and S.S. Singer, Industrial Ceramics, Chapman and Hall, London, 1963.
2 D. Rhodes, Clay and Glazes for the Potter, Chilton Book Company, Randor, PA, 1973.
3 G.A. El-Shobaky, I.F. Hewaidy and N.M. Ghoneim, Thermochim. Acta, 53 (1980) 105.
4 G.A. El-Shobaky, N.M. Ghoneim, I.F. Hewaidy and I.M. Morsi, Thermochim. Acta, 61 (1983) 107.
5 G.A. El-Shobaky, N.M. Ghoneim and I.M. Morsi, Thermochim. Acta, 67 (1983) 293.
6 G.A. El-Shobaky, N.M. Ghoneim and I.M. Morsi, Thermochim. Acta, 70 (1983) 325.
7 N.M. Ghoneim and G.A. El-Shobaky, Thermochim. Acta, 80 (1984) 165.
8 G.A. El-Shobaky and N.M. Ghoneim, Thermochim. Acta, 89 (1985) 63.
9 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, New York, 1972.
10 Powder Diffraction File (JCPDS), International Centre for Diffraction Data, Swarthmore, PA, 1979.
11 N.N. Greenwood, Ionic Crystal Lattice Defects and Non-Stoichiometry, Butterworths, London, 1968.
12 F.A. Kröger, Chemistry of Imperfect Crystals, North-Holland, Amsterdam, 1964.
13 P. Kostad, Non-Stoichiometry of Imperfect Crystals and Electrical Conductivity in Binary Metal Oxides, Interscience, New York, 1972.