Journal of Thermal Analysis and Calorimetry, Vol. 74 (2003) 647–651

INFLUENCE OF SOLID CORRODENTS ON HIGH-TEMPERATURE OXIDATION OF COBALT POWDER

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Abstract

The oxidation of a fine cobalt powder mixed with solid corrodents was investigated in the air. NaCl, Na_2SO_4, $CaCl_2$, mixture of NaCl with Na_2SO_4, mixture of NaCl with MgO, and mixtures of Na_2SO_4 with V_2O_5, MoO_3 and Fe_2O_3, respectively, were chosen as corrodents. Thermoanalytical diagrams were recorded within the temperature range from 20 to 1200ºC. It was stated that none of the corrodents induced the cobalt oxidation to start at a lower temperature. NaCl and mixture of NaCl with Na_2SO_4 accelerated the oxidation slightly but addition of MgO stopped this effect.

Keywords: cobalt powder, DTA, oxidation, solid corrodents, TG

Introduction

Metals and alloys in many industrial high-temperature applications are often exposed to various corrosive environments.

By complete combustion of coal and petroleum the main reaction products are CO_2 and $H_2O_{(g)}$. If the combustion is incomplete, CO is also formed. The gas may contain some nonreacted hydrocarbons. The combustion products also include ashes due to impurities in the fuels. These may be deposited on the walls of reactors.

Both coal and fuel oils contain varying amounts of sulphur, which when combusted yield SO_2 followed by partial oxidation to SO_3. At low temperatures, SO_3 and water vapour react and form sulfuric acid. NaCl – present either as impurity in the fuel or in the air – reacts with SO_3 and $H_2O_{(g)}$ at combustion temperatures to yield Na_2SO_4.

Thus, metals and alloys in combustion gases may be exposed to various corrosive agents depending upon the composition of fuel, temperature and reaction conditions. Beside oxygen gas, important corrosive agents are SO_2, SO_3, molten salts like Na_2SO_4 or sulphate mixtures, sodium vanadates and NaCl deposited on the metal surface. The presence of combustion gases may cause enhanced corrosion. It is very important to study high temperature corrosion. Some authors [1–7] have studied the corrosion of metals such as nickel, titanium and chromium.The results show that

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

sulphates induce hot corrosion of nickel, while chlorides–hot corrosion of chromium. The influence of salts on the high-temperature oxidation of cobalt and cobalt alloys have not yet been studied in detail [1, 8].

The oxidation behaviour of powder metals or oxides can be investigated by employing the TG, DTA and DSC techniques [9, 10].

In the present work the oxidation of cobalt powder in air with the presence of chlorides, sulphates and their mixtures with oxides was studied.

Experimental

The study of oxidation behaviour of a fine cobalt powder (made by Fluka) mixed with solid corrodents was carried out in the air within the temperature range from 20 to 1200ºC. NaCl, Na_2SO_4, $CaCl_2$ and mixtures of NaCl with Na_2SO_4, NaCl with MgO, Na_2SO_4 with V_2O_5, MoO_3 and Fe_2O_3, respectively, were chosen as corrodents. All the samples of the cobalt powder were mixed with the agents (30% mass) and put into platinum crucibles. Mass of each sample was 65 mg.

TG/DTG and DTA curves were recorded using a METTLER Thermoanalyzer 2. The thermogravimetric investigation was carried out at heating rate of 10ºC min^{-1} and air flow of 5 dm^3 h^{-1}. Al_2O_3 was used as a reference sample.

Selected oxidized samples, cooled in nitrogen were subjected to X-ray diffraction analysis for the phase identification. The X-ray diffractograms in the range of 20 to 120° 2θ of the samples were obtained using X-ray diffractometer with goniometer HZG4. Commercial cobalt powder was also investigated by X-ray diffraction analysis to verify content of cobalt oxides.

Results and discussion

Thermoanalytical curves, DTA and TG, for cobalt and selected mixtures (cobalt with NaCl, cobalt with NaCl plus Na_2SO_4) are presented in Fig. 1. For the other samples DTA curves are given in Fig. 2.

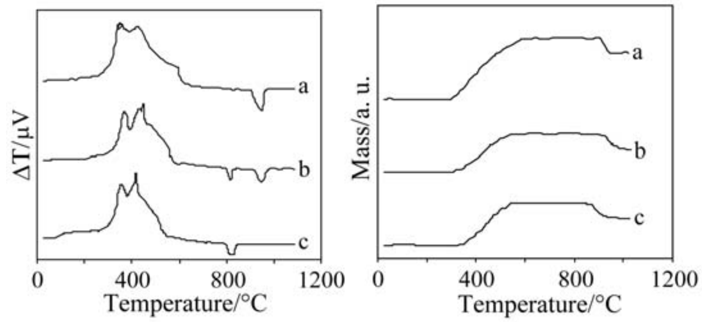

Fig. 1 DTA and TG curves for: a – cobalt; b – cobalt with 30% NaCl; c – mixture of cobalt with 15% NaCl and 15% Na_2SO_4

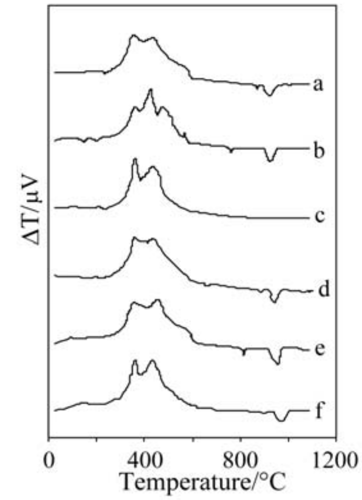

Fig. 2 DTA curves for different mixtures: a – Co+30% Na_2SO_4; b – Co+30% $CaCl_2$; c – Co+15% Na_2SO_4+15% MoO_3; d – Co+15% Na_2SO_4+15% V_2O_5; e – Co+15% NaCl+15% MgO; f – Co+15% Na_2SO_4+15% Fe_2O_3

The results reveal that none of the investigated corrodents decreases the start temperature cobalt oxidation, although some of them enable cobalt to oxidize slightly faster. As it can be seen in Fig. 1 the cobalt oxidation in the presence of NaCl and NaCl with Na_2SO_4 finished at a lower temperature i.e. proceeded in a smaller temperature interval comprising to pure cobalt. However this effect did not appear when NaCl was mixed with MgO (curve e in Fig. 2 comprising with curves b and c in Fig. 1). Each studied sample of pure cobalt or cobalt mixed with corrodents weighted 65 mg, so the contents of cobalt in the mixture samples were 45 mg. To avoid the influence of the smaller mass of cobalt on the results presented above, the termoanalytical curves were obtained for pure cobalt of 45 and 65 mg as well. Both curves were similar.

As it can be seen in Fig. 2 all corrodents affected the shape of DTA curves. Especially, the shape of the curves for cobalt with $CaCl_2$ was distinct.

The obtained thermal and mass curves indicated oxidation of cobalt to CoO and Co_3O_4 at higher temperature, while at the temperature over about 930°C the mass drop has occurred due to the decomposition of Co_3O_4 to CoO and oxygen, as it was expected. To determine the presence of these oxides, the heating processes were interrupted at different temperatures and the samples cooled in nitrogen were subjected to X-ray diffraction analysis. The results for cobalt samples at 360 and 450°C are given in Fig. 3 (cases a and b). The presence of Co_3O_4 and CoO was noticed for the both temperatures with increasing ratio of Co_3O_4 to CoO content by temperature increase.

The same analyses were carried out for cobalt and a mixture of cobalt with NaCl after heating to 1030°C. The first sample after cooling in nitrogen did not contain CoO because of the oxidation of CoO to Co_3O_4 by the residual oxygen content in nitrogen. Nevertheless, the sample of cobalt with NaCl, prepared in the same way, retained some amount of non-oxidized CoO (c and d in Fig. 3).

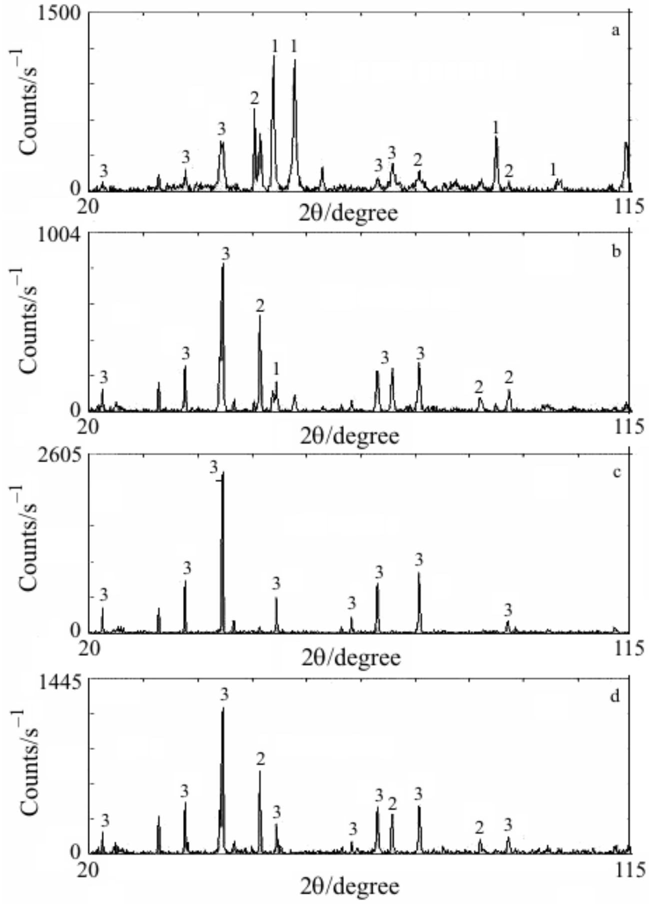

Fig. 3 X-ray diffraction patterns (1 – Co, 2 – CoO, 3 – Co_3O_4) for cobalt and a mixture of cobalt with NaCl: a – cobalt, 360°C; b – cobalt, 450°C; c – cobalt, 1030°C; d – cobalt with NaCl, 1030°C

X-ray diffraction of commercial cobalt powder showed that there were not any oxides of cobalt (CoO and Co_3O_4). Two allotropic forms of cobalt hexagonal and cubic were detected.

Conclusions

The performed analyses indicate that the studied salts are not highly corrosive, yet they affect the process of cobalt oxidation.

None of the corrodents decrease the start temperature of cobalt oxidation, however NaCl slightly accelerates the oxidation process.

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