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INVESTIGATION OF THE OXIDATION BEHAVIOUR OF Mg-CONTAINING INTERMETALLICS BY THERMAL ANALYSIS

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ABSTRACT

The oxidation behaviour of AB_2-type intermetallics, namely Mg_2Ni and Mg_2Cu, was studied by thermogravimetry and differential thermal analysis. The phases formed at different temperatures were identified by XRD. Mg_2Ni showed two DTA peaks with peak maximum temperatures 495 and 637 °C, whereas Mg_2Cu exhibited three DTA peaks at 498, 543.5 and 645.5 °C. These peaks have been attributed to the different oxidation processes occurring in these systems.

INTRODUCTION

Intermetallic compounds containing transition metals have been found to be a good substitute for supported catalysts owing to the in situ oxidation of the intermetallics during reaction or activation resulting in the formation of a supported system with the transition metal as the active species [1–3]. The supported catalysts prepared from intermetallics are found to be free from impurities [4] and are found to be more active than conventionally prepared supported catalysts [5]. Analysis of the fresh and spent catalysts by XPS, AES and EELS revealed that the surface of the intermetallics contains transition metal and oxide of the other component, and that the exposed transition metal is the active species for the hydrogenation/dehydrogenation reactions [6,7]. When oxygen-containing reactants are used, bulk oxidation of the intermetallics occurs resulting in the formation of a supported system with the transition metal as the active species [2,8]. The high activity of La_2CuO_4 in the presence of intermetallics has been attributed to the oxidation of the intermetallics during pretreatment with oxygen, leading to the high dispersion of oxidised species over La_2CuO_4 [9,10]. Therefore, identification of the species formed during oxidation is important in ascertaining the active species for the catalytic reactions. However, only a few reports are available on the oxidation behaviour of intermetallics [11–14]. It is, therefore, necessary to study the oxidation behaviour of these inter-

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metallics to determine the phases formed at different temperatures. In continuation of our earlier work [11,12], an attempt has been made to study the oxidation behaviour of AB_2-type intermetallics, namely, Mg_2Ni and Mg_2Cu, by thermogravimetry (TG) and differential thermal analysis (DTA); the phases formed at different temperatures were characterised by X-ray diffraction (XRD).

EXPERIMENTAL

Commercial samples of Mg_2Ni and Mg_2Cu employed in this investigation were obtained from Ergenics Corporation, U.S.A., with the designation Hystor 301 and 302 respectively. TG–DTA experiments were carried out using Stanton Redcroft, U.K., thermal analysis equipment with ~ 10 mg of sample in the temperature range 30–900 °C. The heating rate was 10 °C min^{-1} and the flow rate of oxygen was 50 ml min^{-1}. The phases formed upon oxidation in a tubular furnace at different temperatures were determined using a Philips X-ray diffractometer (model PW 1130) provided with an online recorder and a dot matrix printer.

RESULTS AND DISCUSSION

Studies on Mg_2Ni

The TG–DTA pattern for the oxidation of Mg_2Ni in a flow of oxygen is shown in Fig. 1. The total weight change corresponds to the complete oxidation of Mg_2Ni to MgO and NiO (44.72%). The DTA pattern of Mg_2Ni showed two peaks with peak maximum temperatures of 495 and 637 °C.

In order to assign these two peaks to different oxidation processes, Mg_2Ni was oxidised at different temperatures in a tubular furnace for 8 h. The XRD patterns of Mg_2Ni oxidised at various temperatures is shown in Fig. 2 along with that of the fresh Mg_2Ni alloy. It has been reported that the fresh surface of Mg-based alloys undergoes decomposition leading to the pronounced enrichment of Mg on the surface which is then oxidised upon exposure to air [15,16]. However, XRD of the fresh Mg_2Ni did not show any phases other than Mg_2Ni, indicating that the bulk of the sample is not affected by exposure to air. The formation of MgO was observed along with the separation of metallic nickel when the alloy was oxidised at 200 °C. Mg_2Ni oxidised at 400 °C showed the formation of NiO indicating oxidation of Ni. The peaks of Mg_2Ni disappear at 550 °C indicating complete disintegration of the alloy. However, oxidation of Ni to NiO was complete only at temperatures above 800 °C.

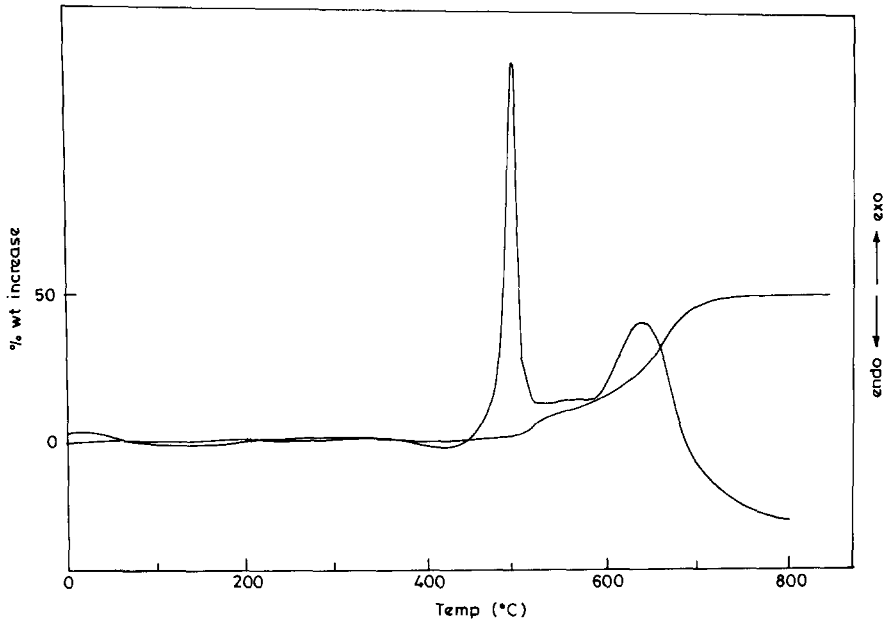

Fig. 1. TG–DTA pattern for the oxidation of Mg_2Ni.

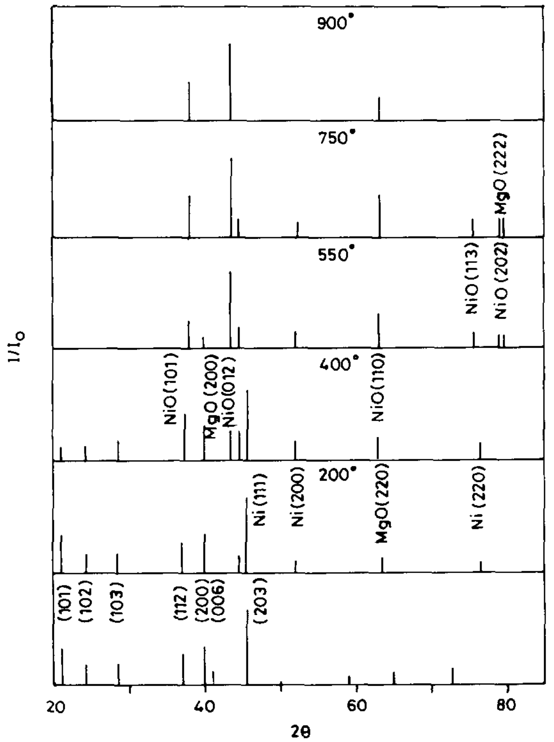

Fig. 2. XRD patterns for the oxidation of Mg_2Ni at various temperatures.

TABLE 1

Standard free energy formation, heat of formation of oxides [18] and surface energy of metals [19]

Metal oxide	$\Delta G_f^\ominus$ (kJ mol^{-1})	$\Delta H_f^\ominus$ (kJ mol^{-1})	Surface energy of metal (mJ m^{-2})
MgO	−569.4	−601.7	790
Cu_2O	−146.0	−168.6	1850
CuO	−129.7	−157.3	–
NiO	−211.7	−239.7	2450

According to the theory of oxidation [17], the thermodynamic driving force consists of four contributions, namely, the free energy change of the oxidation reaction, the oxidation temperature, the oxygen activity and the oxide film thickness. In the present investigation, TG–DTA studies were carried out using the same oxygen pressure and hence the contribution from oxygen activity is not considered. It is evident from XRD that Mg is initially oxidised to MgO which has a high ΔG value (Table 1), followed by the oxidation of Ni at higher temperatures. From the XRD results and ΔG values, the DTA peak at 495 °C can be assigned to the bulk oxidation of Mg, and the peak at 637 °C can be attributed to the oxidation of Ni. In order to study the effect of Mg on the oxidation behaviour of Ni, a TG–DTA run was carried out on pure nickel powder obtained from Koch-Light Laboratory Ltd., U.K. The sample was heated in a flow of oxygen up to 900 °C. During such a run, only a 4% increase in weight was observed. This may be due to formation of NiO layers which probably cover the unreacted nickel and prevent it from oxidation. In these cases, the diffusion of oxygen into the bulk will govern the oxidation process. In addition, DTA did not show sharp maxima indicating the slow oxidation of Ni. Thus, the complete oxidation of Ni to NiO in Mg_2Ni may be due to the large amount of heat evolved during the oxidation of Mg to MgO.

Studies on Mg_2Cu

Figure 3 shows the TG–DTA pattern for the oxidation of Mg_2Cu. The weight increase in the TG curve corresponds to the complete oxidation of Mg_2Cu to MgO and CuO (43%). The DTA pattern of Mg_2Cu exhibited three peaks with peak maximum temperatures of 498, 543.5 and 645.5 °C. To assign these peaks to various oxidation processes, Mg_2Cu was oxidised in a tubular furnace at different temperatures. The various phases formed during oxidation are shown in Fig. 4. Formation of MgO was observed at 200 °C, as in the case of Mg_2Ni. XRD patterns of Mg_2Cu oxidised at 300 °C showed the formation of CuO, and the Mg_2Cu peaks disappeared

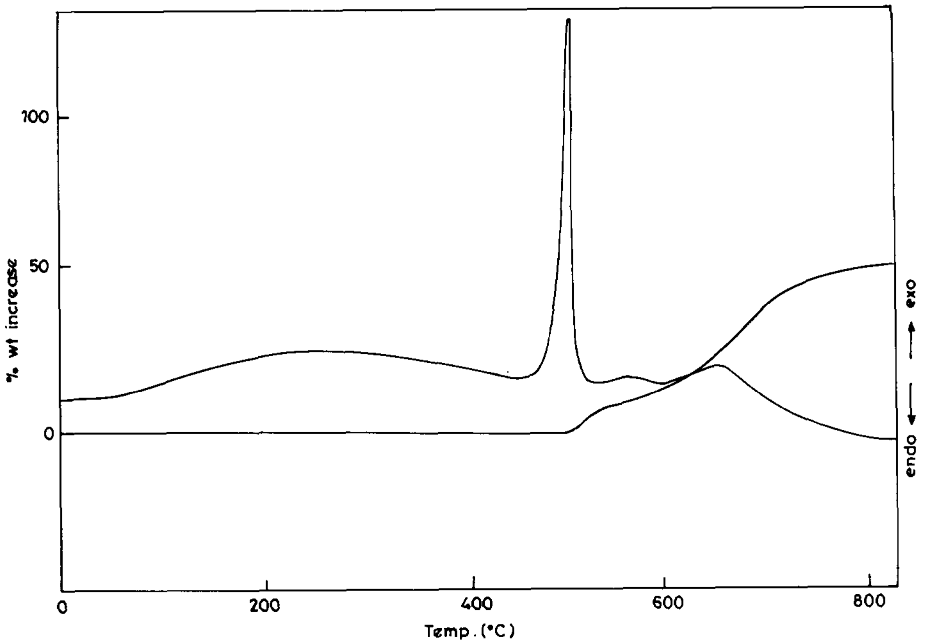

Fig. 3. TG–DTA pattern for the oxidation of Mg_2Cu.

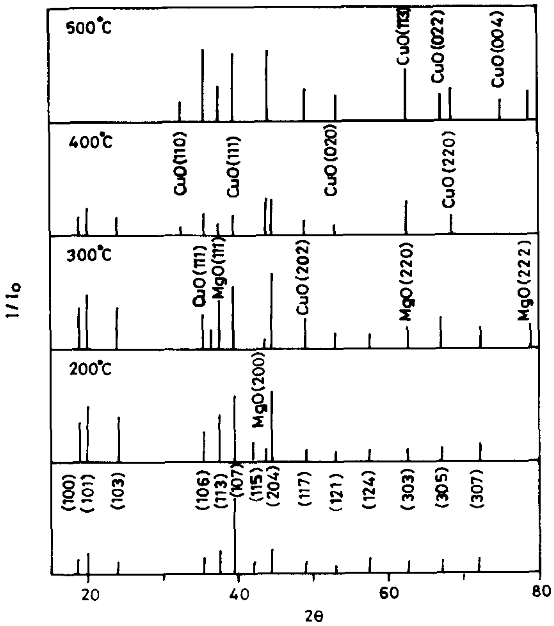

Fig. 4. XRD patterns for the oxidation of Mg_2Cu at various temperatures.

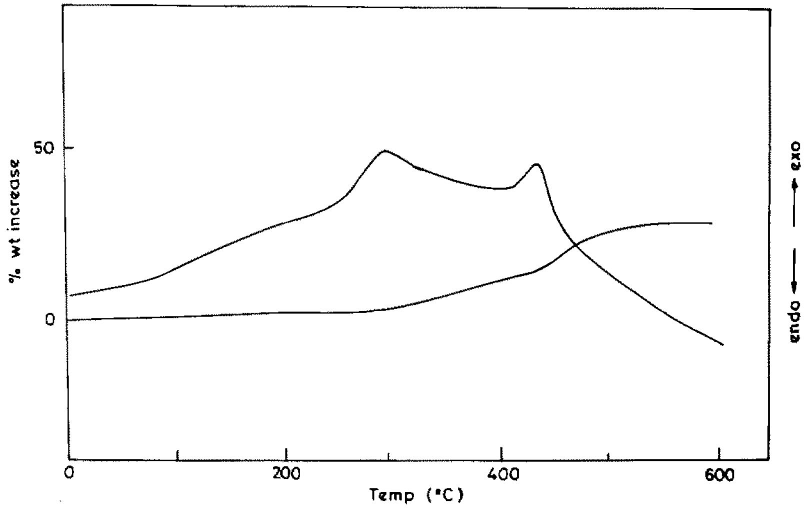

Fig. 5. TG–DTA pattern for the oxidation of metallic copper.

when the alloy was oxidised at 500 °C, indicating the completion of oxidation at this temperature.

It is known that the oxidation of metallic Cu always leads initially to the formation of Cu_2O followed by CuO, and the growth of the latter does not take place until the growth of Cu_2O is completed [20,21]. Recently, Hay et al. [13] have reported the formation of Cu_2O for the system $CeCu_x$ oxidised in different atmospheres. XPS studies on Mg_2Cu carried out in our laboratory confirmed the presence of Cu_2O [22]. As most of the *d* values of Cu, Cu_2O, CuO and Mg_2Cu coincide with one other, XRD could not confirm the formation of Cu_2O in the present case. Therefore, to understand the oxidation behaviour of copper, a TG–DTA run was carried out using metallic copper (obtained by decomposing $Cu(NO_3)_2 \cdot 3H_2O$ in a flow of hydrogen at 400 °C).

Figure 5 shows the TG–DTA pattern of metallic copper. Two steps in the TG curve and two DTA peaks with peak maximum temperatures of 280 and 438 °C can be observed. Based on the ΔG values (Table 1), the peaks were assigned to the oxidation of Cu to Cu_2O and CuO respectively. Thus, TG–DTA of copper explains the formation of CuO via Cu_2O. Wakasa and Yamaki [23] studied the oxidation behaviour of metallic copper and reported the formation of Cu_2O and CuO with transition temperatures of 285.6 and 587.8 °C. The lower oxidation temperatures in the present case might be due to the difference in the particle size of the metal powders.

Considering the results of the oxidation of copper and the ΔG values, the three peaks observed in the oxidation of Mg_2Cu can be due to the formation of MgO, Cu_2O and CuO respectively. The peak maximum temperatures of Cu_2O and CuO in Mg_2Cu (Fig. 4) are shifted to higher temperatures compared to metallic copper (Fig. 5), which can be attributed to the segregation of Mg to the surface which has a low surface energy (Table 1) compared to copper, thereby preventing the interaction of oxygen with copper. In such cases, the diffusion of oxygen to the bulk controls the rate of oxidation and hence, oxidation of copper takes place at higher temperatures in Mg_2Cu. A similar escapusulation of copper has been reported for $CeCu_x$ intermetallics [13].

It is evident from the oxidation behaviour of Mg_2Ni and Mg_2Cu investigated by TG–DTA that oxidation of Mg occurs at 495 and 498 °C respectively. The small difference in the peak maximum temperatures can be due to the difference in crystal structure: Mg_2Ni is hexagonal and Mg_2Cu is orthorhombic. Although the heat evolved for the oxidation of Mg is the same in both cases, the amount of heat evolved is sufficient for the oxidation of copper in Mg_2Cu at lower temperatures compared to the oxidation of Ni in Mg_2Ni. This may be due to the fact that Ni has a high energy of activation compared to copper, as reported by Wakasa and Yamaki [23]. Also, Mg_2Cu has a brittle nature which is easily decomposed and therefore facilitates the formation of oxides.

CONCLUSION

The following conclusions have been drawn from the high-temperature oxidation behaviour of Mg_2Ni and Mg_2Cu: the magnesium in Mg_2Ni and in Mg_2Cu is oxidised at the same temperature; the oxidation of copper in Mg_2Cu takes place via Cu_2O; and the copper in Mg_2Cu is oxidised at lower temperatures than the nickel in Mg_2Ni.

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