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THE ROLE OF MAGNESIA AND ALUMINA IN PROMOTING THE NITRIDATION OF MAGNESIUM AND ALUMINIUM

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ABSTRACT

The nitridation of magnesium, aluminium and their alloys is promoted by the addition of the oxides MgO or Al_2O_3. Non-isothermal kinetic measurements (TG and DTA) show that nitride formation proceeds to completion more rapidly in the presence of these oxides than when metal and gas only are present. The mechanisms of these reactions are discussed with reference to electron micrographs obtained for the magnesium/nitrogen reactions in the presence and absence of MgO, the only system where melting was absent. It is concluded that MgO provides an active surface across which there may be transport of reactants and products. MgO also accommodates the product Mg_3N_2 where it does not represent an adherent layer on the metal constituting the barrier to solid (Mg)/gas (N_2) interaction that opposes the uncatalyzed reaction.

INTRODUCTION

The reductions of oxysalts by various substances, and by metals in particular, have been studied in the thermobalance [1]. Sometimes these reactions are accompanied by further chemical changes, such as, for example, the nitridation of a metal. Some of these accompanying or secondary rate processes are well known, as in the interaction of magnesium or aluminium with nitrogen gas [2] where nitridation may be a preferred process [3]. However, the indirect evidence concerning the occurrence and the significance of these processes during reduction studies is not easily interpreted. Extents of reactions have been measured by chemical analyses and the experimental conditions used have not always allowed the separate observation of the possible contributory physical processes including melting and evaporation. While kinetic investigations of certain nitridation reactions have been reported, for example the nitridation of magnesium [4–6], some-

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times the results are difficult to interpret where perhaps more than a single experimental parameter has been varied between the observations being compared. In particular, the role of oxide during metal nitridation is difficult to establish unambiguously. In the present report we have specifically investigated the influences of oxides (MgO and Al_2O_3) during the nitridation of magnesium and aluminium.

EXPERIMENTAL

Reactions were investigated through the complementary use of a thermogravimetric balance (TG) and differential thermal analysis (DTA), together with some microscopic studies. From the measured weight changes, the extent of nitridation could be determined and the occurrence of reaction, as well as any instances of melting and/or volatilization, were also readily detected from the DTA responses. Temperatures corresponding to the initiation of reaction were considered reliable only when satisfactory agreement was reached from both the TG and the DTA measurements. Reactions were characterized through the range required for their completion: this could be expressed alternatively as a time or as a temperature interval. The occasional instances of reactant metal volatilization were investigated by experiments in an argon atmosphere.

The primary objective of the present investigation was to compare the nitride formation reactions of the metals magnesium, aluminium and an alloy of these metals in N_2 gas, in the presence and in the absence of the oxides of these metals but under otherwise identical conditions. In each experiment 50 mg samples of metal filings of analytical purity, alone or admixed with oxide, were placed in a ceramic (Alox) crucible and heated at 10°C min^{-1} in a nitrogen stream at 5 l h^{-1}.

RESULTS AND DISCUSSION

Thermogravimetric measurements

From the thermogravimetric records in Fig. 1, and the measured temperature intervals required for the completion of nitridation (Table 1), it is evident that magnesium is nitrided below its melting point (645°C), aluminium at the melting point (660°C), and the alloy appreciably above the melting point (445°C).

An admixture of these metals with MgO significantly promoted nitridation (Fig. 1 and Table 1) by lowering the initiation temperature and/or reducing the temperature interval required for its completion. This decrease in the temperature of onset of reaction was most striking for the alloy (~ 350°C) though here the metal reacted in the molten phase. The reaction of molten magnesium metal with nitrogen was slower than that of the mixtures with oxides (Fig. 1) where completion corresponded to the melting point. The promoting activity of prepared MgO was the same as that of oxide resulting from $MgCO_3$ decomposition. Doping of MgO (with added Li_2O or TiO_2, both 0.3 and 2.0%) did not cause any detectable further change in the influence of MgO on magnesium nitridation and accordingly investigations of the effects of these MgO-incorporated additives were not continued.

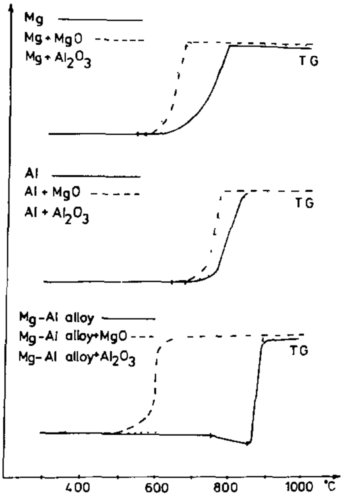


Fig. 1. TG curves for Mg, Al and Mg–Al alloy with MgO and Al_2O_3 additives.

The influence of Al_2O_3 on the nitridation of these metals was less than that of MgO. Indeed Al_2O_3 apparently caused a slight delay in the onset of aluminium nitridation (Table 2). In contrast, Al_2O_3 lowered both the temperature of onset and the interval for reaction of the alloy. Reaction of

TABLE 1

Formation of metal nitrides

No.	Substance	Temp. of nitride formation (°C)		
		Initial	Final	Interval
1	Mg	575	660	85
2	Al	670	820	150
3	Mg–Al alloy	890	920	30
4	Mg + MgO	585	625	40
5	Mg + $MgCO_3$	580	620	40
6	Al + MgO	620	750	130
7	Mg–Al alloy + MgO	540	680	140

TABLE 2

Nitride formation in the presence of aluminium(III) oxide of different surface

No.	Substance	Surface of Al(III) oxide ($m^2 g^{-1}$)	Temp. of nitride formation (°C)		
			Initial	Final	Interval
1	Mg	60	600	700	100
2	Mg	160	550	680	70
3	Al	60	710	930	220
4	Mg-Al alloy	60	640	700	60
5	Mg-Al alloy	160	580	670	90

magnesium started earlier and proceeded more rapidly when a high area sample of Al_2O_3 was used (Table 2).

Experimental results reporting the influences of factors expected to exert some control over reaction rates, together with the phases detected by X-ray diffraction measurements for the solid products, are summarized in Table 3. Available oxygen may react to form a surface layer (see Nos. 1, 5, 6 and 7 in Table 3): this may influence the rate of nitridation [4–6].

The temperature of onset of magnesium nitridation is not markedly changed by the addition of MgO or Al_2O_3 but reactions were completed more rapidly as the quantity of oxide added was increased (Table 3, compare Nos. 1, 2 and 4, 5, 6 and 7). Pelleting, or the presence of high area additives did not reduce the temperature interval for reaction (Table 3, Nos. 3, 8 and

TABLE 3

The reaction of magnesium with nitrogen to form magnesium nitride in the presence of various additives

No.	Reactant mixture (added to magnesium)	Temp. range for nitride formation (°C)	Temp. interval of nitride formation (°C)	Phases identified by X-ray diffraction measurements
1	None	575–660	85	Mg_3N_2, MgO
2	+25% MgO	585–625	40	Mg_3N_2, MgO
3	As 2, pelleted	580–685	105	
4	+80% MgO	570–590	20	
5	+25% Al_2O_3	550–620	70	Mg_3N_2, MgO, AlN
6	+31% Al_2O_3	580–615	35	Mg_3N_2, MgO, AlN
7	+50% Al_2O_3	570–605	35	Mg_3N_2, MgO, AlN, spinel
8	+25% SiO_2	500–600	100	
9	+25% active carbon	605–750	145	
10	$N_2/H_2O(g)$	510–680	170	

9), though the presence of SiO_2 reduced and that of carbon increased the temperature of onset of nitridation. Initiation of reaction was promoted by saturated water vapour (Table 3, No. 10), but the duration was considerably extended, behaviour not influenced by the presence of MgO or Al_2O_3.

Differential thermal analysis

DTA studies (25–630°C) showed two response peaks between 400 and 600°C. This is attributed to the nitridation reaction and, in addition, some oxidation since MgO was identified in the products by X-ray analysis (Table 3, Nos. 1, 2, 6, 7 and 8). Interestingly, aluminium nitride was also produced in the Al_2O_3 promoted reaction ($Mg + N_2$) and the spinel phase ($MgAl_2O_4$) appeared when the mixture contained 50% Al_2O_3.

Microscopic studies of magnesium nitridation

Only the magnesium nitridation reaction was selected for detailed microscopic study since this metallic component did not melt. Surface textures were examined in a scanning electron microscope (Cambridge Stereoscan S180).

Magnesium ribbon

Comparative experiments, intended to identify the role of MgO in promoting magnesium nitridation, were performed as follows. A strip of magnesium metal ribbon (~ 10 cm in length), the surface cleaned by abrasion, was placed in the reaction vessel so that the lower half was embedded in MgO powder (previously ignited with outgassing to remove CO_2 and H_2O). The upper half, extending above, was out of contact with solids. After evacuation, with heating to reaction temperature (500–550°C), pure nitrogen was admitted (200 or 500 Torr) for periods of up to 300 min. Eight such experiments were performed within the range of conditions specified. In all of these, that portion of the magnesium ribbon which had been embedded in and was in contact with MgO during the heating with nitrogen had undergone greater textural modification of the surface (Fig. 2a) than that part beyond the oxide and which had been exposed concurrently to N_2 gas alone (Fig. 2b). These photographs (Fig. 2a, b) are typical, representative and indicate the occurrence of the breakaway reaction [4]. Inspection showed that after longer reaction times at higher temperatures, within the stated intervals, the magnesium metal strip which had been in close contact with MgO had disintegrated, whereas that exposed to gas, but remote from the oxide, remained coherent. These results clearly demonstrate that direct Mg/MgO contact promotes nitridation, compared with that of the $Mg + N_2$ reaction in the absence of MgO contact. During these experiments the reaction vessel walls above the MgO powder became coated with a brown

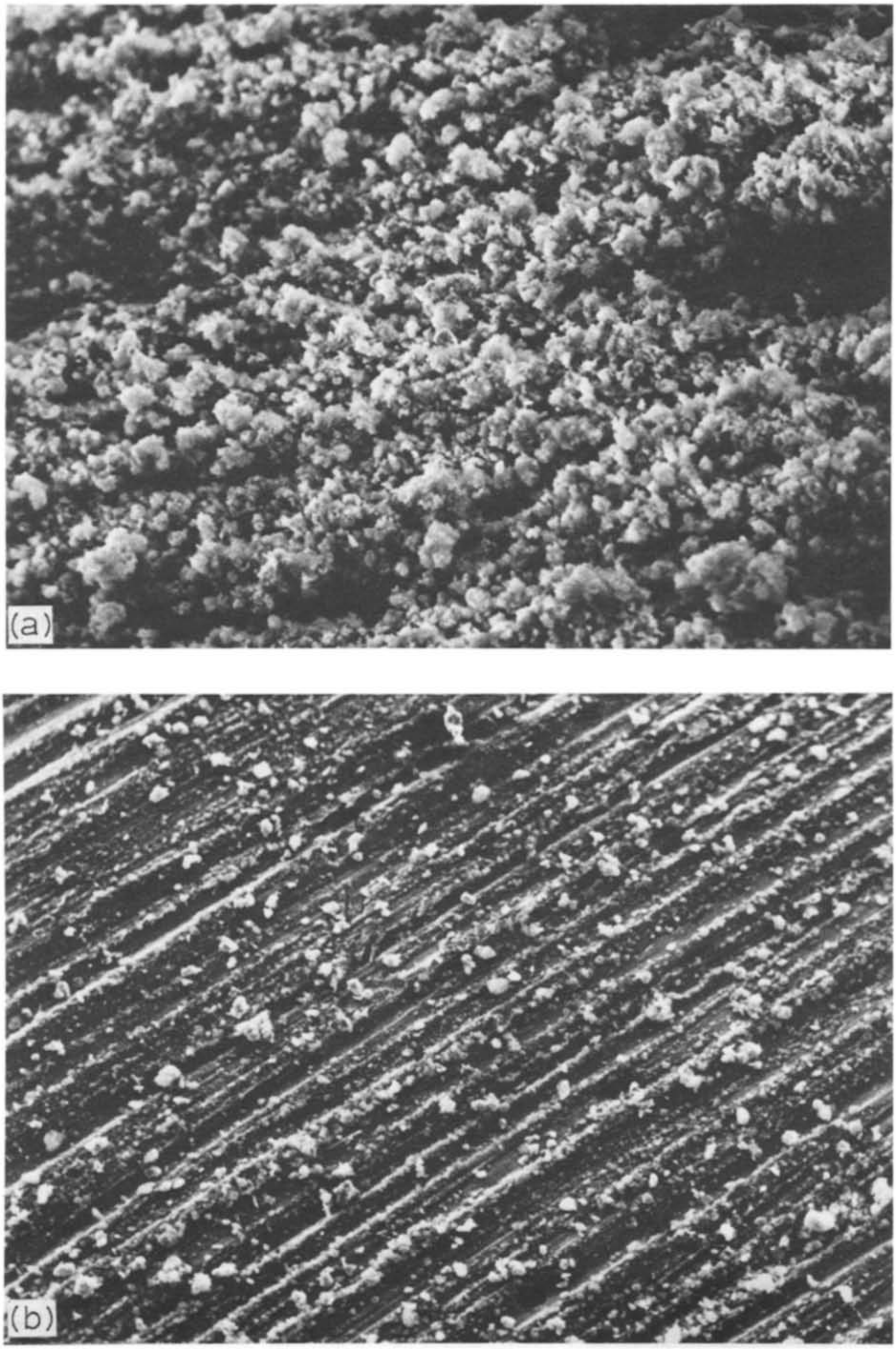


Fig. 2. Two areas of the same strip of magnesium ribbon which had been reacted under comparatively mild conditions: 150 min at 510°C in 240 Torr N_2. (a) This area of ribbon had been embedded in loose MgO powder and was seen to have undergone more extensive surface modification than a different area of the same ribbon (b) that had been concurrently exposed to the same atmosphere of N_2 but was not in direct contact with MgO. Magnification: 10 mm = 100 μm.

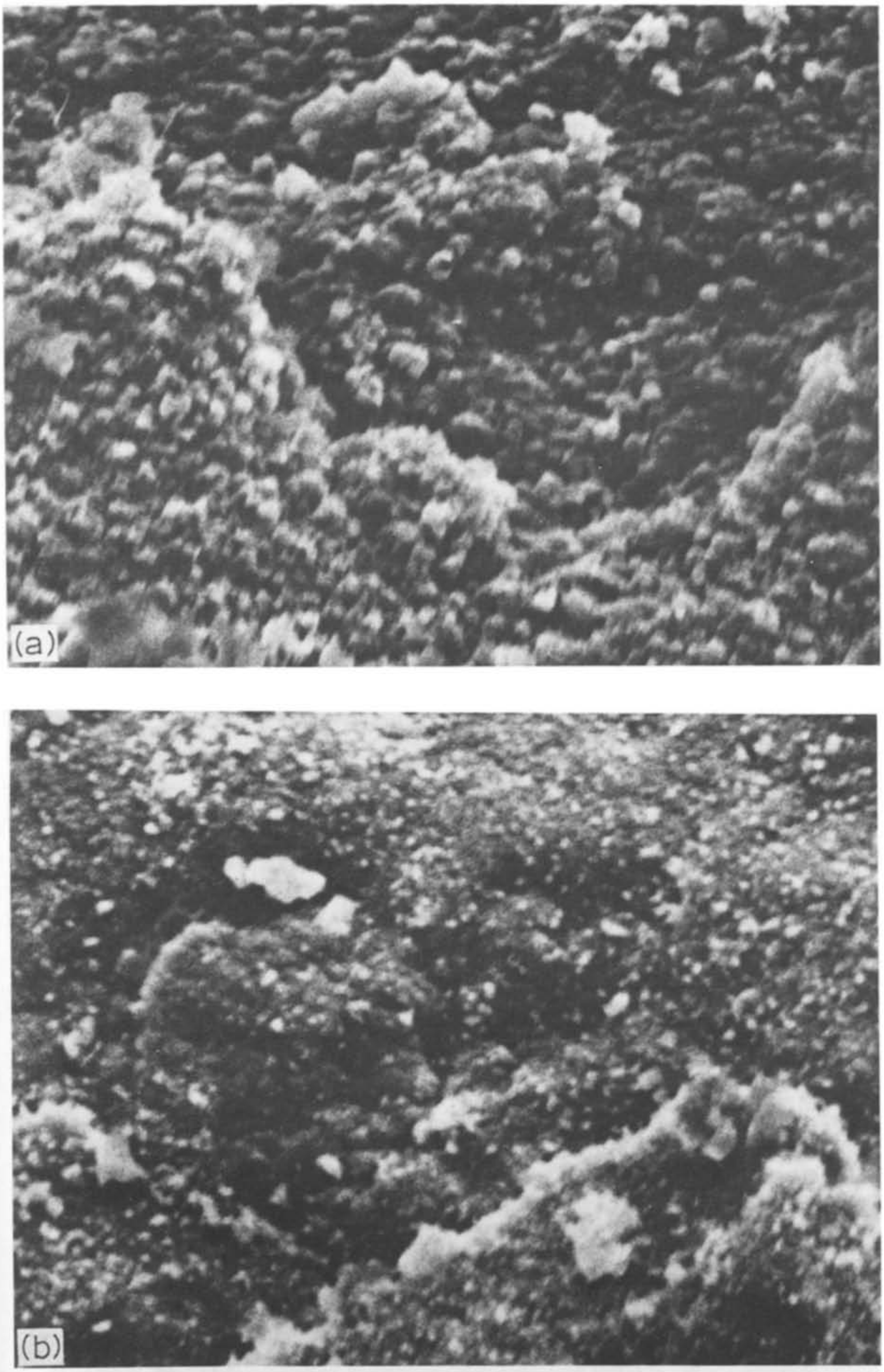
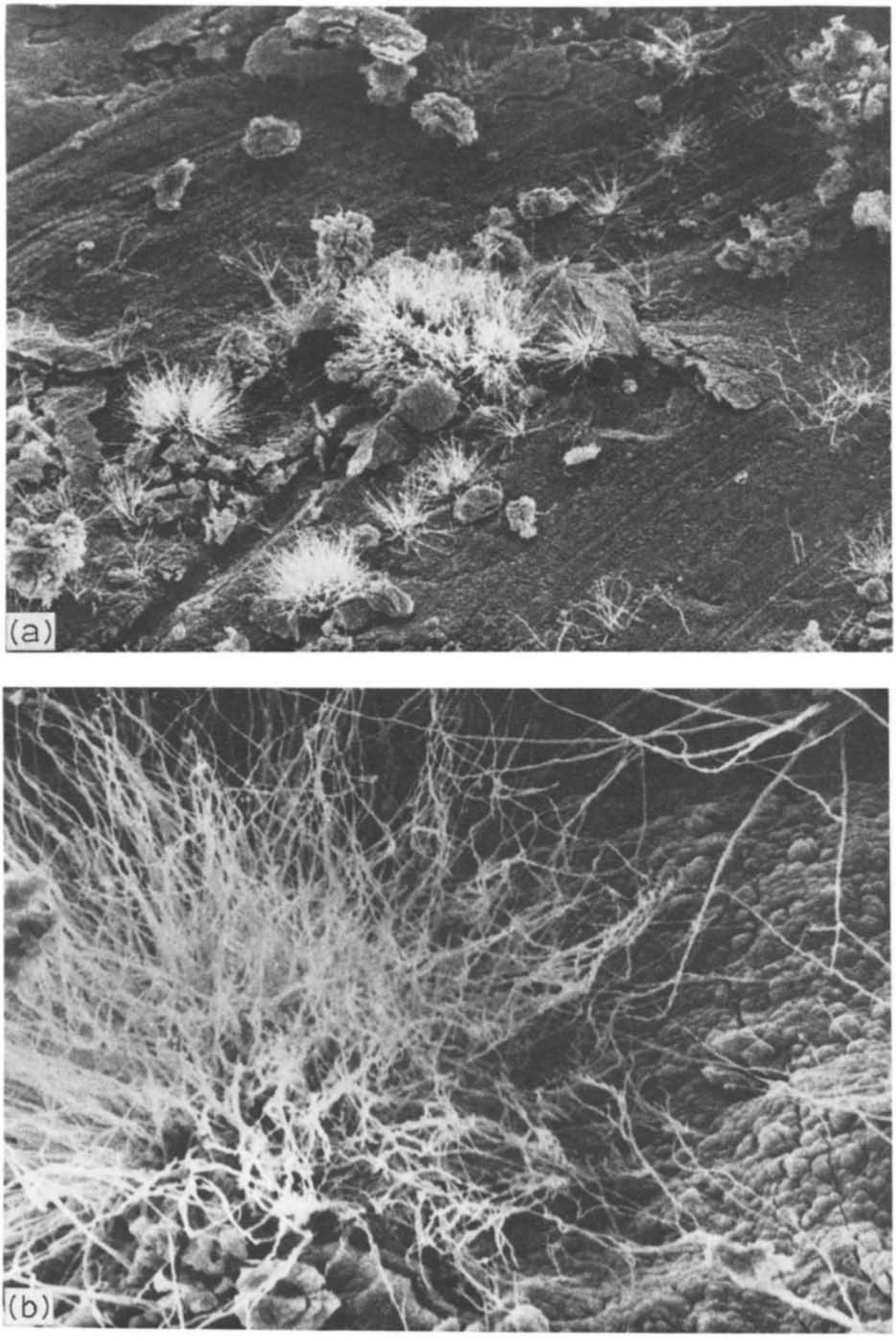


Fig. 3. Two areas of the same fracture surface of an MgO pellet that had been partly covered by a strip of magnesium ribbon during 30 min reaction at 580°C in 760 Torr N_2. That area of the MgO pellet surface in close contact with the Mg metal (a) had undergone more intensive textural modification than that more remote from the effects of metal volatilization (b). Magnification: 10 mm = 10 μm.

deposit which was shown, by chemical analysis, to consist largely of magnesium metal with some nitrogen as Mg_3N_2. This adherent film dissolved in acid only with difficulty, evolving small (< 0.5 mm) bubbles within which the gas exploded with a yellow flame. Magnesium reacts with silica at 549°C



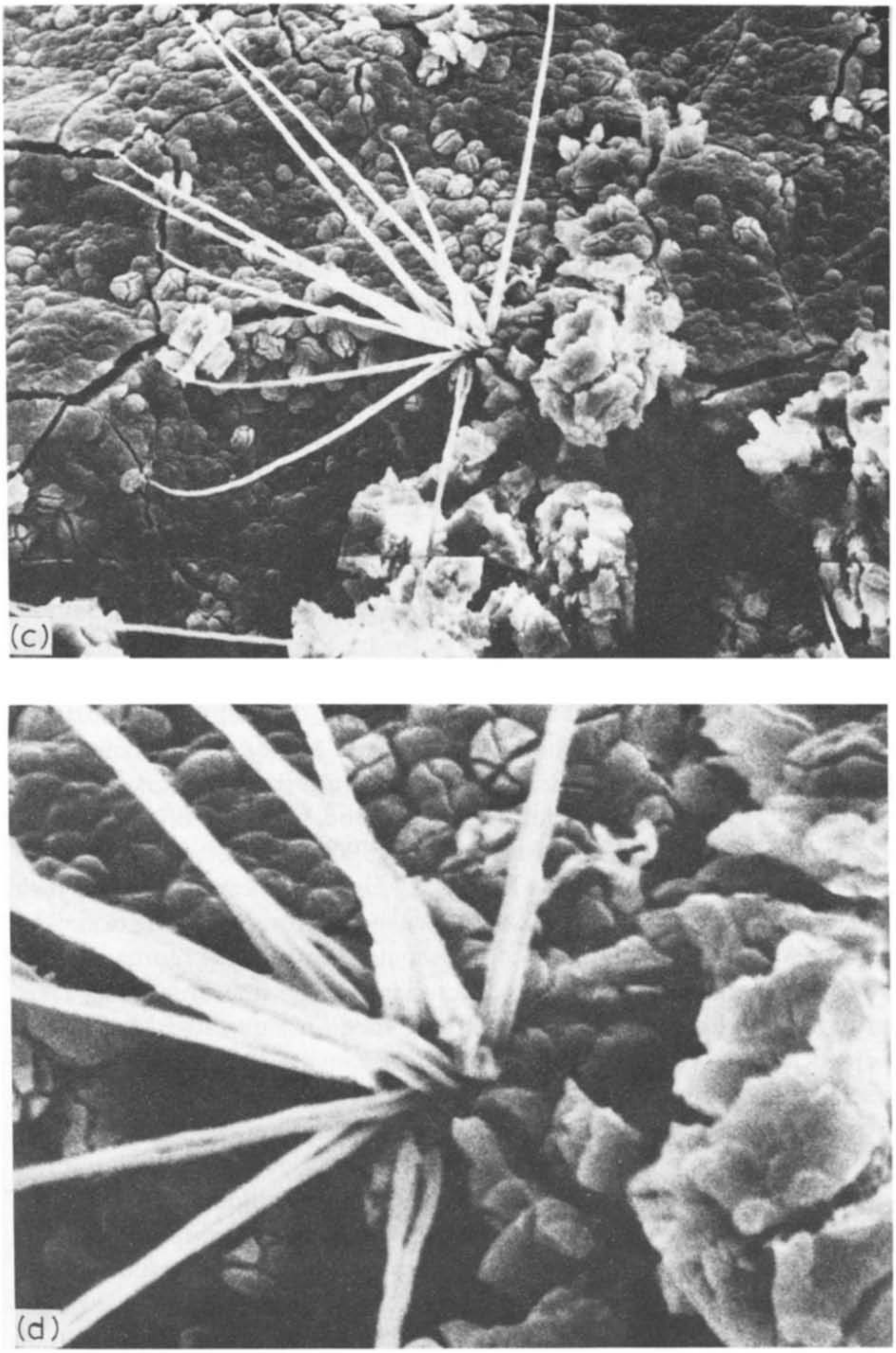


Fig. 4. Typical groups of fibre-like growths developed on the surface of MgO pellet when heated in close juxtaposition with magnesium metal (550°C in 760 Torr N_2). Sites active in fibre promotion were within an adherent layer of product Mg_3N_2 and were irregularly disposed across surfaces (a). Groups of fibres were sometimes rather dense (b). Fibre development from an active generation site or sites is shown in greater detail at two magnifications in (c) and (d). Magnifications: 10mm represents (a) 30 μm, (b) 10 μm, (c) 10 μm, and (d) 3 μm.

[7]. We conclude that nitride (Mg_3N_2) formation occurs on or after Mg volatilization [5].

Magnesium oxide pellets

Textural modifications of MgO surfaces during concurrent nitridation of magnesium metal in close contact were investigated through electron microscope examinations of pelleted MgO. Freshly fractured surfaces of such pellets were used to avoid possible artefact development at surfaces formed during compression. Groups of these pellet fragments were reacted concurrently, to permit reliable comparisons. MgO fragments were disposed in a closely spaced linear array in the reaction vessel tube, every second oxide sample supporting a small strip of magnesium ribbon. Comparative studies were made of the textural changes occurring at the bare and at the metal covered surfaces of the MgO pellet fragments, after 30–60 min reaction in 760 Torr N_2 at 500–580°C.

On heating under these reaction conditions only the MgO pellet surfaces which had been in close contact with magnesium metal became yellow, attributed [4] to the formation of Mg_3N_2 on or after metal volatilization. Those surfaces which were not in direct contact with magnesium remained white. Electron microscopic examination showed that all MgO surfaces underwent superficial textural modification when heated under conditions appropriate for nitridation. The extent of such modification, however, was varied by the presence of Mg metal. Figure 3(a and b) shows different areas of the same surface after 30 min reaction at 580°C in 760 Torr N_2. The central part of the pellet fragment (Fig. 3a), which had been in contact with metal, was coloured yellow and showed extensive textural modification. The MgO surface not in direct contact with the metal showed less reorganization than the texture, retaining features characteristic of the fractured pellet face.

A novel and significant textural feature detected only on those MgO pellet surfaces which had been heated in contact with magnesium metal was the development of groups of fibres. Representative illustrations of these features are shown in Fig. 4(a–d). Fibre development was found only on yellow coloured surfaces, ascribed to the presence of Mg_3N_2, produced during reactions for 60–120 min at 530–570°C in 760 Torr N_2. The distribution of fibres across surfaces was highly irregular (Fig. 4a), some groups being very dense (Fig. 4b). The component fibres from any group originated from a localized and specialized surface site [Fig. 4(c and d)] sometimes associated with superficial cracking. Fibres were unbranched and sometimes bent and distorted after higher temperature reactions. These structures were never detected as a feature of the surface modifications of MgO heated without close contact with magnesium metal. Comparisons indicate that when Mg metal is presented Mg_3N_2 formation occurs in the MgO surfaces since these become yellow. The evidence of surface cracking and the development of rounded features [Fig. 4(c and d)] only on these surfaces further supports this view.

Unfortunately attempts to examine the surfaces of magnesium metal after extensive nitridation had to be discarded as being unreliable, since the effects of hydrolysis by even small traces of water vapour could not be positively eliminated. Thus we have no evidence concerning the structures developed on the metal strips produced during the several series of reactions represented in Fig. 4.

SURFACE AND INTERFACE CHEMISTRY OF THE MAGNESIUM NITRIDATION REACTION

Although MgO is a particularly refractory solid (m.p. 2800°C) there is ample evidence that, under reaction conditions, participants in the chemical changes described above possessed appreciable mobility. Magnesium metal is volatile and Mg_3N_2 sublimes in vacuum (presumably through dissociation). It is believed [4] that the nitride layer initially formed on magnesium metal constitutes a protective film but later breakaway, mechanical distortion or disintegration occurs, thereby permitting volatilization of Mg metal. We have obtained evidence that interactions between the anionic and cationic constituents of originally solid reactants yield new crystalline substances: MgO, AlN and the spinel $MgAl_2O_4$ were formed during the reactions of $Mg + N_2$ in the presence of Al_2O_3 (Nos. 5, 6 and 7 in Table 3). The photomicrographs in Fig. 4 support the view that Mg_3N_2 is developed on MgO surfaces and fibre growth also requires the movement of material.

This evidence of the mobility of the participants in the reactions does not itself explain the role of MgO. The mechanism is discussed, therefore, with reference to the following considerations.

Growth of Mg_3N_2 on MgO

Whereas the growth of a barrier nitride layer on the metal progressively opposes the reaction, the same reaction on the outer face of Mg_3N_2 supported by MgO may be limited only by the availability of Mg volatilized to this outer reactant surface. Not all solids can be accepted as supports for product Mg_3N_2, however, carbon is shown (No. 9, Table 3) to be unsuitable. We envisage, therefore, initial defect formation on MgO through reaction with condensed Mg metal. The imperfect and non-stoichiometric surface zone may then chemisorb nitrogen and preferential reaction ($3\ Mg + N_2 \rightarrow Mg_3N_2$) can be expected in this area of defects and dislocations containing excess magnesium (as metal Mg or possibly Mg^+, and/or Mg^{2+} with F-centres) and also possibly including oxide ions (from the MgO support). During growth of product on this surface, remote from the metal reactant, condensation will maintain the enhanced reactivity of the Mg_3N_2 or MgO surface by generation of imperfections. The reactivity and mobility of the adsorbed phase will, therefore, remain greater than that of the outer face of a nitride barrier layer on Mg metal.

The fibres (Fig. 4) are identified as MgO and not nitride since these are not hydrolized by water vapour. We conclude that whisker growth provides a mechanism for removal of excess oxide from the nitride layer. Possibly aggregation of oxide contributes to the breakaway of adherent nitride during uncatalyzed reactions, some reactions are accelerated by oxygen [4].

Surface mobility of adsorbed material on MgO

Magnesium melting, migrating metal and mobility of marginal material may all contribute towards the movement of reactants, intermediates and products during these chemical changes. The generation of a zone of surface imperfection on proximate MgO particles from reactions following metal condensation and nitrogen chemisorption must be expected to enhance the ease of surface mass transfer processes. Also, contacts between oxide and nitride phases may result in chemical interactions leading to impurity incorporation (e.g., N^{3-} in MgO and/or O^{2-} in Mg_3N_2). Migrations within the active and imperfect surface zones provide an explanation for the appearance of new phases [e.g., the formation of MgO, AlN and spinel from $Mg + N_2(Al_2O_3)$; Table 3]. Similar enhanced mobility on the surface of added oxide may contribute to the breakup or diffusive removal of adherent nitride from the metal surface. Added MgO could, therefore, provide an acceptable recipient phase for withdrawal of product that would otherwise oppose contact between the reactant metal (Mg) and the gas (N_2).

CONCLUSIONS

We conclude, therefore, that MgO catalyses the nitridation of magnesium by providing a compatible surface on which enhanced mobility of superficial adsorbed material promotes diffusive removal of the Mg_3N_2 barrier and permits retention of this product. In the absence of MgO from the reaction mixture the accumulated product (Mg_3N_2) constitutes a barrier layer between the solid (Mg) and gaseous (N_2) reactants. Probably the same surface chemical or diffusional factor controls both catalyzed and uncatalyzed reactions since both are first detected at ~ 585°C. The role of the catalyst is envisaged as increasing the effective participating area of reactants, thereby permitting its more rapid completion.

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