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Magnesium and Boron Combustion in Hot Steam Atmosphere

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ABSTRACT

This paper investigates the combustion of magnesium and boron powders in hot steam. A thermochemical analysis reveals theoretical results of such interactions. An experimental investigation demonstrates that stable exothermic oxidation takes place, resulting in actual combustion at 1100 °C for magnesium and 800 °C for boron. The reaction generates large quantity of gaseous products consisting of almost pure hydrogen and corresponding to about 60 per cent of a complete chemical reaction.

1. INTRODUCTION

The chemical interaction of different metals with steam is known, particularly with regards to hydrogen production, e.g., the steam-iron process, the cesium process, the tin oxide process, etc[1,2]. In this study, hydrogen evolution during magnesium and boron combustion in a hot steam atmosphere is investigated. Because of the high cost of magnesium and especially of boron, these processes may not be competitive with other methods of hydrogen production. Nevertheless, they may be useful for some practical applications, e.g., creating a hydrogen-protective atmosphere or establishing a local energy source.

2. THERMOCHEMICAL ANALYSIS

Table 1 presents the theoretical amounts of hydrogen and heat evolved for some metals during reactions proceeding according to the scheme:

$$aMe + bH_2O \rightarrow Me_aO_b + bH_2 \qquad (1)$$

where Me_aO_b is the highest oxide of the appropriate metal. The high heat release obtained for some metals indicates the possibility of stable combustion in a steam atmosphere and the use of this heat for metal and steam preheating. It can be seen that from this point of view magnesium and especially boron are the metals of particular interest (Table 1).

Table 1. Theoretical amount of hydrogen evolution and heat release for reactions of H_2O with different metals

Metal	Amount of hydrogen (l/g of metal)	Heat released per g of metal (KJ)
B	3.0	25.0
Al	1.2	18.0
Mg	0.9	15.0
Fe	0.5	0.9
Sn	0.3	0.8
Ti	0.9	9.0
Nb	0.6	3.7
Cr	0.6	4.0
Mn	0.8	0.7
Ni	0.4	0

Thermochemical analysis of the combustion temperature and equilibrium composition of the combustion products are carried out for the $Mg + H_2O$ and the $B + H_2O$ systems over a range of initial reactant ratios. The calculations are conducted for

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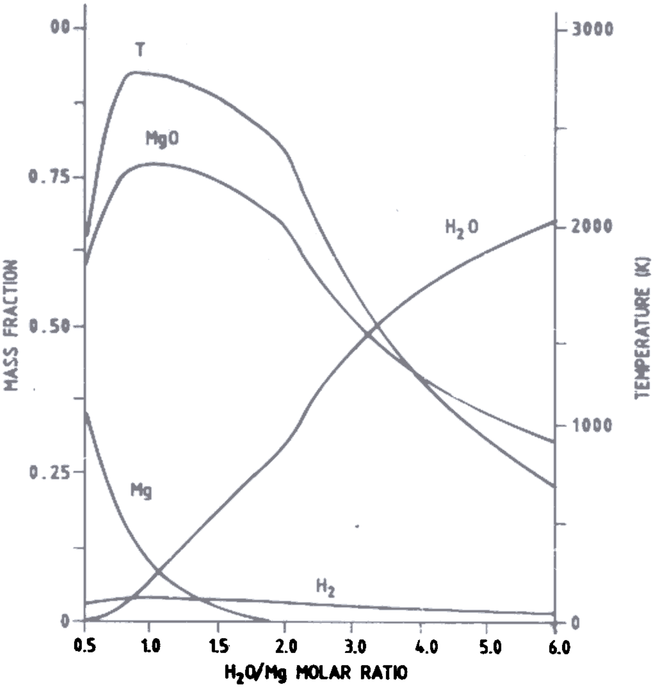

Figure 1. Thermochemical calculations of the $Mg + H_2O$ reaction system. $Mg + H_2O \rightarrow MgO + H_2$.

adiabatic conditions by thermodynamic potential minimisation method.

Figure 1 presents the calculated results of this analysis for the $Mg + H_2O$ system at 1 atm with different H_2O/Mg molar ratios. The combustion temperature (K) and the mass fractions of the main combustion products, viz., Mg, MgO, H_2O, H_2 correspond to the simple scheme:

$$Mg + H_2O \rightarrow MgO + H_2 \tag{2}$$

It can be seen that the highest theoretical combustion temperature (K) is achieved for the stoichiometric mixture ($Mg{:}H_2O$ = 1:1) and is about 2800 K. The $B + H_2O$ reaction system produces a complex composition of the combustion products (Fig. 2). Compounds, such as HBO_2, $B(OH)_3$ and $B_3(HO_2)_3$ are formed along with boron, B_2O_3, H_2 and H_2O. The trimeric form of metaboric acid, HBO_2 was indeed found in high-temperature gaseous systems[3]. The thermochemical analysis reveals that for small excess of steam in the mixture (molar ratio 1.5 < H_2O/B < 3), the reaction may be approximated by the scheme

$$2B + 3H_2O \rightarrow B_2O_3 + 3H_2 \tag{3}$$

while for a large excess of steam (molar ratio $H_2O/B > 6$), the scheme is:

$$2B + 4H_2O = 2\,BHO_2 + 3H_2 \tag{4}$$

Calculated amounts of hydrogen evolution as a result of the above-mentioned reaction schemes are presented in Fig. 3. It was observed that once the H_2O/B or H_2O/Mg molar ratio exceeds approx. 2, the amount of hydrogen evolved is kept constant and is equal to 3 l/g of metal for the $B + H_2O$ system and to 0.9 l/g for the $Mg + H_2O$ system in standard conditions. Hence, from the point of view of hydrogen production, the $B + H_2O$ system is preferable to the $Mg + H_2O$ system because boron has the additional advantage of higher density.

In practice, ignition and extensive oxidation reaction of magnesium with steam are well known[4]. On the other hand, the reaction of boron with steam has not been studied in detail. It is known that this reaction occurs only at high temperatures[3], and may slow down due to a protective liquid film of B_2O_3, which tends to cover the boron surface.

3. EXPERIMENTAL PROCEDURE

Preliminary tests on combustion of magnesium and boron in steam were carried out. The main objective of these experiments was to examine the existence of magnesium and boron combustion in H_2O and to determine the actual amount of hydrogen evolved in the process.

The experimental apparatus is shown schematically in Fig. 4. A given quantity of the metal powder under consideration (7) is placed in a porous ceramic or metal container (6) where argon is flowing in the chamber (4). The chamber with the metal powder is heated to a fixed temperature by an electrical heater (5). The temperature of the powder is measured by a thermocouple (8). When the necessary initial temperature (T_o) is attained, the Ar flow is switched to a steam flow. The steam is generated in an autoclave (1) at an overpressure of

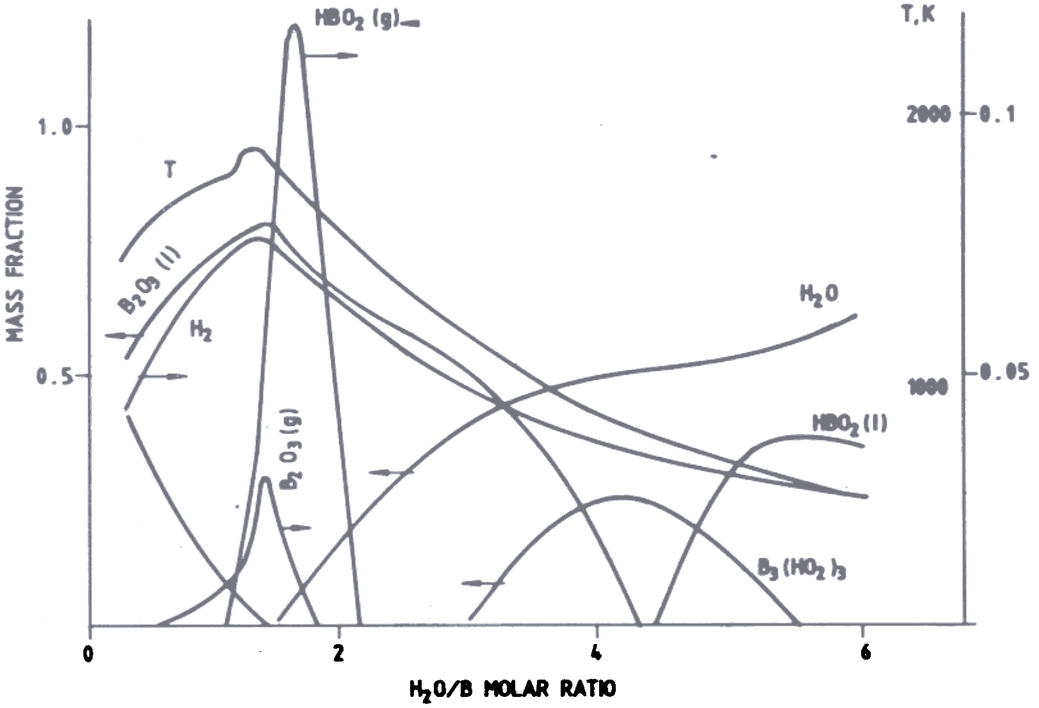

Figure 2. Thermochemical calculations of the B+H_2O reaction system.

about 0.5 atm, which is recorded by a manometer (2). Before feeding into the chamber, the steam is preheated to the chamber temperature by a heater (3).The gaseous products of reaction between the metal powder and the steam, together with excess steam, pass through a water condenser (10), where condensation of steam takes place, to the first glass cylinder (11). The remaining gaseous products (mostly hydrogen) drive out H_2O from the second glass cylinder (12), which was initially filled with H_2O, to the graduated cylinder (13). Taking into account the low solubility of hydrogen in H_2O, the volume of gases evolved for magnesium or boron interaction with steam is measured by the volume of liquid displaced. It was observed that the volume of H_2O condensed in cylinder (11) is much smaller than the volume of H_2O displaced.

Table 2. Test results

Sample	Mass (g)	V_g (ml)	V_g/V_{theor}
Mg			0.64
Mg			0.58
B			0.59
B			0.46

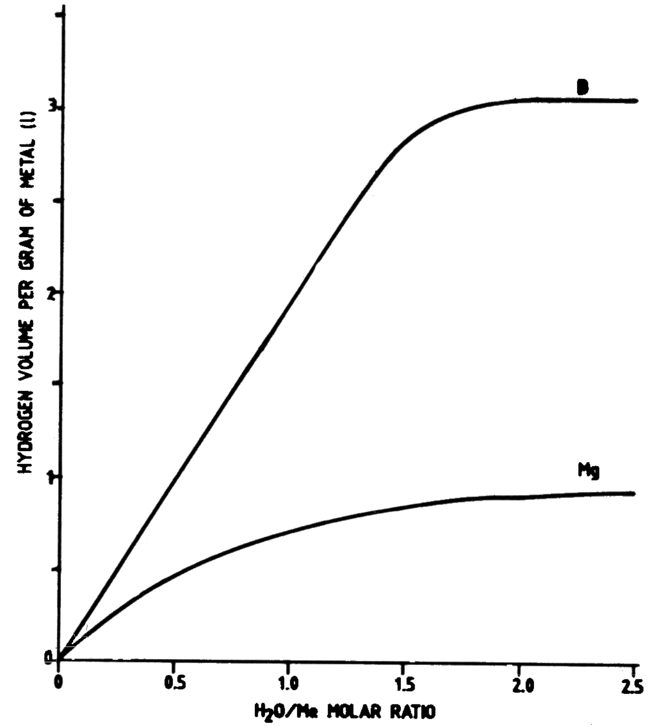

Figure 3. Theoretical dependence of hydrogen evolution on H_2O/metal molar ratio.

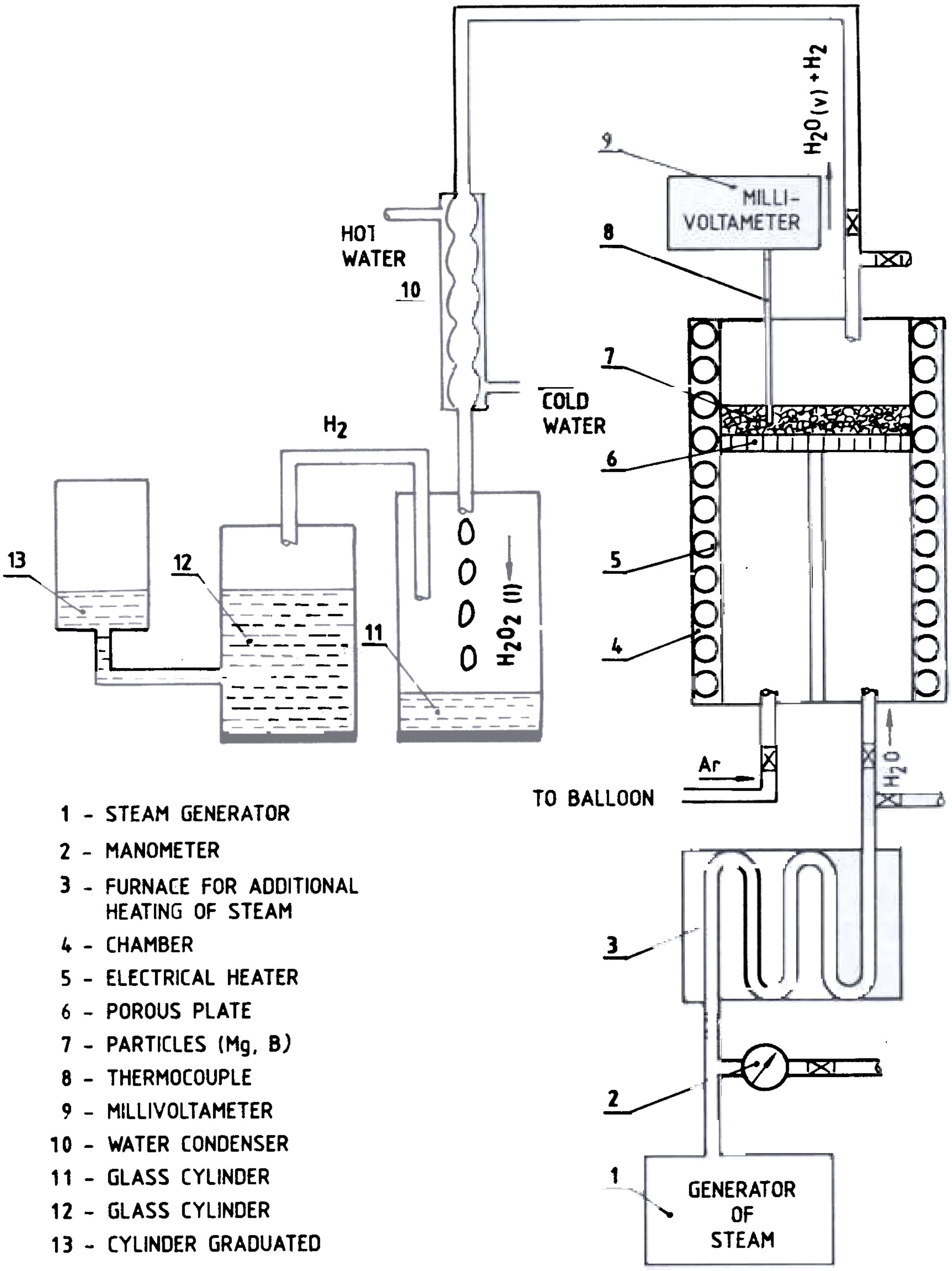

Figure 4. Schematic of the experimental installation

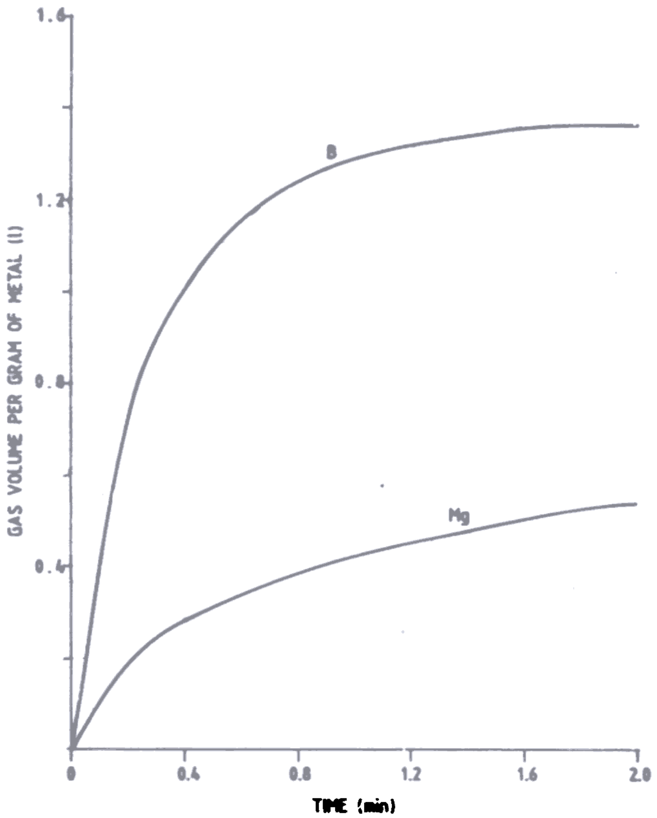

Figure 5. Test results of gas evolution *vs* time

4. EXPERIMENTAL RESULTS

Preliminary tests conducted without metal powders indicated the absence of gas evolution, eliminating the possibility of oxidative reactions between the metal container and the steam. For the reactive tests, fine powders of magnesium (average size 70 mm) and amorphous boron (average size < 1 µm) were used. T_o of magnesium powder was 450 °C and that of B powder 460-480 °C (just above the melting temperature of B_2O_3). The results are shown in Table 2. In this table, the mass of specimens, their T_o, T_{max} obtained during reaction, the actual volume of gas V_g evolved, and the volume ratio compared to the theoretical reaction schemes (2-4) are presented.

The metal powder temperature increases rapidly, in a matter of seconds, after the steam is supplied and then diminishes as the metal is burnt out. In the case of magnesium, the T_{max} achieved was of the order of the metal boiling temperature. For boron, the temperature increase due to reactive heating was more than 300 °C. The curves of gas evolution during experiments 2 and 4 (per 1 g of metal) are presented in Fig. 5 which shows that the gas evolution process is completed after two minutes.

The composition of the gases evolved were determined by the solid gas chromatographic method. The gas samples are extracted from the glass cylinder (12) in pre-evacuated glass bulbs. The gas is then injected into an HP 8900 series gas chromatograph equipped with a thermal conductivity detector. A molecular sieve column type 5A was used. The column temperature was 35 °C. *Ar* as a carrier gas flows at 30 ml/min through a thermal conductivity cell. The output of the thermal conductivity detector uses a Perkin-Elmer/Nelson analytical PC integrator card kit for gas chromatography. The unit performs instant area calculations and compares samples with standard sample runs. The chromatographic analysis results show that the gas samples of the metal combustion products contained about 100 per cent of hydrogen with traces of air.

5. CONCLUSIONS

Preliminary research on magnesium and boron combustion in a hot steam atmosphere has shown the possibility of hydrogen production by this method. It is possible that the observed intensive interaction of boron with steam is due to production of volatile HBO_2 by B_2O_3 hydration[5], according to equation:

$$B_2O_3(aq) + H_2O(g) \rightarrow 2\,HBO_2(g) \tag{5}$$

Such a reaction would remove the liquid layer from the boron particle surface which otherwise slows down the direct interaction between boron and H_2O.

The hydrogen yield obtained in these experiments accounts for about 60 per cent of the theoretical amount. Additional research is required to increase the hydrogen yield, which should include a systematic variation of metal and steam temperature, particle size, feed system and metal/steam ratio.

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