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EFFECT OF PRESSURE ON MAGNESIUM COMBUSTION

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The use of powdered metals as fuels in energy generation equipment has stimulated a wide range of studies of the effects of various parameters on the combustion of such substances.

The effect of pressure on combustion of small particles [1-3] and ribbons [4] of magnesium has also been studied. Analysis of the solid residue after combustion of magnesium particles in the model engine of [1] revealed that the mass fraction of coarse-size particles (of the order of magnitude of the original particle size) increases with increase in pressure. The vapor-phase combustion time (time of visible light production) of a magnesium droplet measured in [2] decreased with increase in pressure. Similar results were achieved earlier in a model face combustion engine [3]; it was also found that the time required for complete chemical conversion of particles significantly exceeds the visible burning time. Qualitative observations of combustion of magnesium ribbon [4] at various pressures and oxygen concentrations in the surrounding medium have shown that at sufficiently high pressures about the ribbon there is formed a hollow tube of oxide, after which the reaction terminates. The authors proposed that the oxide shell was impermeable to oxygen. It should be noted that reaction termination can also set in with a partial reduction in oxygen supply, since in the given case the heat loss at the ribbon ends was significant, these being held in metal clamps.

It follows quite definitely from the studies referred to above that an increase in pressure in the surrounding oxidizing medium encourages accumulation of oxide about the burning specimen and reduction in the vapor-phase combustion time. However, the moment at which the combustion process is completed is not completely determined. The authors of [2] assumed that completion of vapor-phase combustion implied complete burnup of the droplet, as occurs at atmospheric pressure. At the same time, it follows from [3, 4] that this is not the case. From the existing results it is impossible to derive even a qualitative picture of the progress of combustion to the final stage, which can be quite lengthy and cause incomplete burnup.

The goal of the present study is to examine (qualitatively and quantitatively) the dynamics of the process of combustion of a droplet at various pressures of the oxidizing medium and to determine the effect of pressure on the combustion mechanism, using the broader possibilities afforded by the experimental technique employed.

The experiments studied magnesium specimens (99.9% pure) 6 mm in diameter. The large specimen size made qualitative observation easier and allowed measurement of several parameters in a single experiment. The oxidizing media used were air, or a mixture of oxygen with nitrogen or argon at room temperature. Studies were performed at pressures within the range 0.1-2 MPa. The experimental technique was described in [5]. The specimen was heated by an induction method until inflammation occurred, and further heating and combustion occurred without outside heat application.

The specimen was suspended from a thermocouple and placed within a solenoid driven by an hf generator. The specimen was isolated from the atmosphere by a quartz glass tube (26 mm in diameter), through which the oxidizing gas was pumped. Draft was supplied with a constant volume flow rate, so that the Reynolds numbers were identical at the various pressures. The draft velocity at a pressure of 0.1 MPa in all experiments comprised 60 cm/sec (arbitrarily selected). When pressure was increased, draft velocity was reduced in inverse proportion to pressure. Specimen temperature was measured continuously with a tungsten–rhenium thermocouple (0.35 mm thick), the signal from which was recorded by an oscilloscope. Also measured

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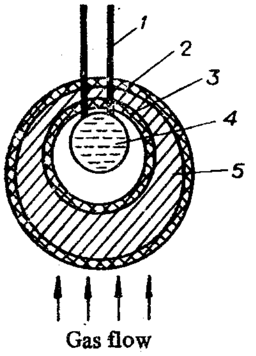

Fig. 1. Diagram of oxide residue in second stage of combustion process: 1) thermocouple; 2) external oxide shell; 3) internal oxide shell; 4) liquid metal droplet; 5) porous residue.

were combustion time (with a photocell), mixture composition, and flow rate. The condensed residue left on the thermocouple after burnup of the specimen was analyzed microscopically, chemically, and visually. Cinematography and visual observation of the burning process were also utilized. The uncertainty in temperature measurements comprised ±0.5%. The flow rate was determined to an accuracy of ±0.5%, and mixture composition to with ±1%.

Studies at higher pressures isolated two stages in the process of magnesium droplet combustion, and permitted tracing the dynamics of the process.

In the first stage, as is well known [2-4], vapor-phase combustion is realized. The cinematography and visual observations detected processes which change the character of combustion as time passes. Thus, during the time of vapor-phase combustion about the droplet, in the zone of the brightest luminescence (condensation zone) an oxide film is formed, which with the passing of time completely covers the droplet. It can be assumed that the appearance of the shell is due to sintering of finely dispersed oxide products, since this process occurs in the high-temperature region. The shell grows in the direction from the rear side to the sides. It thus displaces the brightly glowing condensation zone; i.e., where the oxide shell exists, there is no glowing zone. In the future we will call this shell the external shell. Simultaneously there is formed on the droplet surface yet another oxide shell (the internal one). Initially islets of oxide appear on the surface, which increase in width and length with the passing of time and join together in certain areas. Apparently the growth of these islets occurs because of deposition of finely dispersed combustion products from the condensation zone onto the droplet surface. Vapor-phase combustion disappears when the external shell completely covers the droplet.

Upon full termination of vapor-phase combustion the droplet does not extinguish itself. The oxide residue becomes incandescent, i.e., a quite intense chemical reaction begins to occur within the residue. This is the second stage of the combustion process. Significant heating of the oxide residue in this stage was observed visually. The thermocouple recorded the droplet temperature over the entire course of the process. In the second stage this temperature gradually decreased to ∿1100°K (although the shell was incandescent), which indicates a gradual reduction in the combustion rate. When the droplet has burned up completely, the brightness of the radiation from the residue and the temperature recorded by the thermocouple both dropped rapidly.

On the basis of the motion-picture photographs, visual observations, and analysis of the solid residue on the thermocouples after total burnup, it is possible to describe the structure of the residue and propose a mechanism by which the second stage of the process occurs (Fig. 1).

The residue consists of an internal hollow shell, the internal diameter of which is less than the original specimen size, comprising about 5 mm. The external shell, formed in the condensation zone, exceeds the original particle size by a factor of about 1.4 times. The space between the shells is filled with a porous material of dark-gray and yellowish color (combustion in air) or only dark-gray color (combustion in argon–oxygen mixture). Chemical analysis of the porous material obtained after burnup of a droplet in an argon–oxygen mixture at 1 MPa (mass fraction of oxygen c = 0.21) showed that it contained 3.8% (of the original specimen weight) of active metal. This explains the dark-gray color of the material.

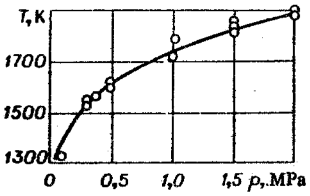

Fig. 2

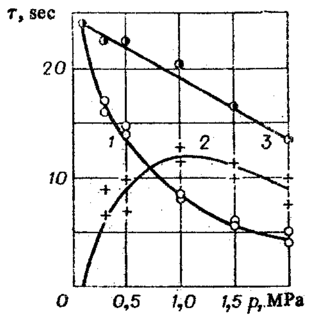

Fig. 3

Fig. 2. Steady-state droplet temperature during vapor phase combustion pressure in air flow.

Fig. 3. Duration of first (1) and second (2) stages of combustion process, and also duration of complete (3) combustion process, pressure in air flow.

For a vapor-phase reaction zone to exist, specific intensities of mass flow (oxygen, metal vapor) and heat flux (to the droplet and into the surrounding medium) are necessary. The oxide shells which form hinder intense heat and mass exchange, as a result of which self-maintaining vapor-phase combustion ends. However, the liquid metal is still heated to a high temperature and continues to evaporate, and oxygen diffuses through the external shell, although less intensely than previously. These two flows meet each other in the space between the inner and outer shells and react, as a result of which the residue becomes incandescent. Since the finely dispersed oxide products characteristic of vapor-phase combustion are not found in the porous layer and within the inner shell cavity, it can be proposed that the metal vapor condenses on the surface of the oxide formations in the porous layer and reacts there with the diffusing oxygen, i.e., the metal-oxygen reaction occurs not in the gaseous phase, but on the surface of the oxide formations. The gradual reduction in combustion rate (as indicated by the drop in droplet temperature) is apparently produced by gradual overgrowth of the pores in the oxide shells and reduction in the diffusion flows of the reagents. This may be the cause for the incomplete burning observed.

The studies also revealed some characteristic features of magnesium droplet combustion at elevated pressure in the vapor-phase combustion regime (first stage). It was found that the droplet temperature was constant and close to the boiling point of magnesium at the given pressure [6]. Results from measurements of this temperature as a function of the surrounding gas-phase (air) pressure are presented in Fig. 2. In [7] it was found that at atmospheric pressure the droplet temperature increased continually during the vapor-phase combustion regime, tending toward the boiling point of the metal. The present study found that at elevated pressure, after inflammation the droplet rapidly takes on a maximum temperature, which is practically constant in the first stage of combustion and then decreases gradually in the second stage.

Figure 3 shows measurements of the duration of the first and second stages, as well as the total droplet burning time, as functions of pressure in the oxidizing medium. On the basis of the experiments performed, factors can be indicated which apparently determine the features observed. The duration of the vapor-phase combustion period depends on the rate at which the external oxide shell is formed. With increase in pressure the boiling point increases, as does the vapor tension of the metal, which causes an increased concentration of solid products in the condensation zone. This factor decreases the time required for formation of the external oxide shell, i.e., the duration of the first stage of combustion. Curve 1 is qualitatively similar to the analogous curve obtained in [2], where smaller magnesium particles were used. However, [2] does not refer to the presence of a second combustion stage.

The duration of the second stage has a maximum value. To the left of this maximum, it can be said that the duration is shorter because there is a smaller quantity of metal left

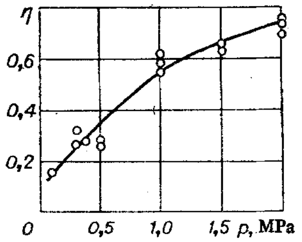

Fig. 4. Ratio of oxide residue mass on thermocouple to quantity of combustion products (η) vs pressure in air flow.

from the first stage, where the combustion times are still long. To the right of the maximum the decrease in duration can be related to the higher droplet temperatures, at which the second stage sets in an increase pressure. Moreover, the increase in pressure encourages intensification of free convection. The two latter causes also explain the dependence of total burn time on pressure.

Figure 4 shows the ratio of the mass of the oxide residue on the thermocouple to the total amount of combustion products as a function of pressure in the oxidizing atmosphere. It is evident that with increase in pressure the mass of the oxide residue increases. This apparently encourages more rapid formation of the outer oxide shell. As a result, a significant portion of the metal burns up in the regime characteristic of the second combustion stage, in which the oxides do not escape into the gas flow. The η dependence obtained is qualitatively similar to the results of [1], in which magnesium particles with a mean diameter of 11.6 μm were used.

It was not possible to perform exact measurements of the fraction of metal burned up in the second stage, or the droplet mass combustion rate in the vapor-phase regime, since under the experimental conditions projections of oxide were formed on the droplet surface, complicating processing of the motion-picture photographs. Moreover, near the moment of transition to the second combustion regime the droplet was totally covered with an oxide shell.

The general pattern of combustion at higher oxygen concentrations (c = 0.5) in a nitrogen–oxygen mixture over the same pressure interval does not differ from that described above. The duration of the first stage is of the same order of magnitude, while the second stage is more brief. At pressures of 0.3–0.5 MPa the inner oxide shell exists only in the lateral region. The outer shell exceeds the original droplet size by about 1.6 times, i.e., in this case more metal burns up in the vapor-phase regime. At higher pressures the oxide residue is similar to that described above for combustion in air. The value of η = 0.81–0.85 for a change in pressure from 0.5 to 2 MPa. According to [7], with increase in oxygen concentration the mass of the oxide residue also increases at atmospheric pressure.

Combustion of magnesium in a mixture of oxygen (c = 0.21) with argon showed some unique features. In the oxygen–nitrogen mixture, as the specimen heated up, its surface first foamed, and then the specimen took on a droplet form [7]. When the nitrogen was replaced by argon, foaming of the surface was also observed, but the specimen did not take on a droplet form, and the foaming surface was fixed at some point. Glowing hearths appeared on this surface, and then a vapor-phase combustion zone developed around the specimen. The shape of the foaming specimen surface was maintained throughout the combustion process, and an outer oxide shell was again formed around the specimen, suppressing vapor-phase combustion. The second stage took place as in air. Droplet temperature as a function of time behaved in an analogous manner, although in this case the mean temperature level was 30-50°C lower. In connection with this the total combustion time was 20-25% longer. The relationship between oxide residue weight and pressure corresponded to the results shown in Fig. 4.

As has already been noted, these results, obtained with coarse specimens, show qualitative similarity (in a number of features) with the results of [1-3], which used small particles. Use of large specimens made observation of the combustion process convenient in all stages. This made possible detection of the second combustion stage, which exists at high pressures, for the first time. This stage can significantly increase the total combustion time. With consideration of this stage, it is simple to explain the reason why in [3] the time required for complete chemical conversion of the microparticles significantly exceeded their visible burning time. It should be noted that the brightness of the radiation from the droplet in the first combustion stage is many times greater than that in the second. Apparently this is the reason why the second stage of small particle combustion was not recorded by still or motion-picture photography in the previous studies.

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FORMATION OF Co_2P IN THE COMBUSTION REGIME

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and A. N. Dubrov

Combustion of the system Co—P produces the compounds Co_2P, CoP, and CoP_3 [1], the first two being producible in the combustion regime, while for synthesis of stoichiometric Co_2P at normal argon pressure, an original mixture with a certain excess of phosphorus (21.5% as opposed to 20.79%) is required [2].

The present experiments were performed with electrolytic cobalt powder and red phosphorus with dispersion of less than 40 μm, using the technique described in [3]. The diameter of the pressed specimens was 20 mm and their relative density was 0.43, which permitted an adiabatic combustion regime. The external form of the specimens after reaction is shown in Fig. 1. Combustion occurred in a self-oscillating mode, as indicated by the layering of the specimens. Data from x-ray analysis indicated that only the phases Co and Co_2P were present.

A characteristic feature of combustion of compositions containing 15-19% phosphorus was an elongation and some expansion of the specimen. This required recalculation of the combustion rate values to allow for the changed dimensions, in a manner similar to that used in [4] to determine the true combustion rates in a Ti—B system. Figure 2 shows mass velocities and combustion temperatures found in experiment, together with a portion of the state diagram of the system Co—P [5]. Each point was obtained by processing the results of 5-8 experiments by the method of least squares.

Using the approximate technique of [6] and Co_2P thermodynamic data from [7], after calculating the heat of fusion (commencing from the closeness of the entropies of fusion of the

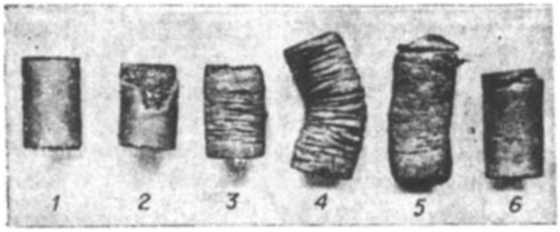

Fig. 1. External view of Co—P specimens after combustion. Mass fraction of bound phosphorus, %: 1) 11; 2) 14; 3) 15; 4) 16; 5) 18; 6) 21.

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