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MICROCALORIMETRIC STUDY OF THE AGING REACTIONS OF ATOMIZED MAGNESIUM POWDER

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13. ABSTRACT (*Maximum 200 words*)

Magnesium powder is used widely as a fuel in pyrotechnic compositions, e.g., in illuminating flare formulations. Powdered magnesium chemically is a very reactive metal and it is prone to undergo relatively slow surface reactions at room temperature with moist air. In this study the technique of microcalorimetry has been used to characterize these undesired magnesium degradation reactions. Experiments have been carried out using large magnesium samples to simulate a storage environment and small magnesium samples to simulate the magnesium powder in a pyrotechnic production line environment.

Powdered magnesium can react with both water vapor and oxygen found in air with the reaction with water vapor being at least an order of magnitude more rapid. The degradation reactions are relatively slow, e.g., at 70°C and 100% relative humidity 1% magnesium degradation requires approximately 15 hours reaction time. However, a 1% degradation of the powdered magnesium translates into as much as 8% decrease in the burn rate of a pyrotechnic composition which incorporates the degraded magnesium.

Results will be described that show the degradation reaction with water vapor is strongly dependent on the exposed magnesium surface area, temperature and relative humidity.

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FOREWORD

A summary of this report was presented at the 1991 Annual Meeting of the American Defense Preparedness Association, Ammunition Technology Division, Pyrotechnics and Explosives Application Section, held 8-10 October 1991 at the Chemical Research, Development, and Engineering Center, Aberdeen Proving Ground, Maryland.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Magnesium is a very widely used pyrotechnic fuel. For example, it is used as a fuel in illuminating flares, various other flares, and igniters. Despite its widespread use in pyrotechnic items, magnesium is known to be a relatively reactive metal, prone to undergo relatively efficient oxidation reactions on its exposed surfaces. Specifically, the following two aging (degradation) reactions are known to occur:

$$Mg(s) + 2\ H_2O(g) = Mg(OH)_2(s) + H_2(g) \qquad \Delta H_{rx} = -440.99\ \text{kJ/mole} \qquad (1)$$

$$2\ Mg(s) + O_2(g) = 2\ MgO(s) \qquad \Delta H_{rx} = -597.88\ \text{kJ/mole} \qquad (2)$$

where ΔH_{rx} is the heat of the reaction.

It is known that reaction (1), the degradation reaction with water, is approximately an order of magnitude faster than the corresponding reaction with oxygen, reaction (2).

In our effort to find a satisfactory analytical technique to study these aging reactions we learned that the technique of microcalorimetry has been successfully used to study analogous pyrotechnic aging reactions by the AB Bofors Company (Sweden) and others over the last decade.[1-11] The unique feature of this technique is the extremely low levels of heat flow (as low as 0.1 microwatt) that can be measured. This is two to three orders of magnitude lower than the levels of heat flow that can be monitored using conventional differential scanning calorimetry (DSC) instrumentation. Obviously, this makes possible the monitoring of relatively slow pyrotechnic aging reactions which might take as long as a century to effect complete degradation of the sample under normal temperature/humidity storage conditions. In the past, the only practical way to study such slow reactions was to speed them up by a rather sizeable temperature increase. However, it was often found that the results obtained at elevated temperatures could not be straightforwardly extrapolated back to ambient storage conditions owing to temperature dependent changes in the overall reaction mechanism.

Accordingly, we are engaged in an ongoing microcalorimetric investigation of the aging reactions of atomized magnesium powder. Small samples (approximately 50 mg) have been studied to simulate magnesium degradation in a production line environment, while larger samples (approximately 3.5-4.0 grams) were used to simulate degradation in a non-airtight containerized storage environment.

EXPERIMENTAL

A Thermometrics/LKB Model 2277 Thermal Activity Monitor Microcalorimeter equipped with a Gas Flow Ampoule System (GFAS) and a dedicated data system has been used to study magnesium degradation as a function of temperature (25° - 70°C), relative humidity (0 - 100%) and sample size/shape (exposed surface area).

In all runs, a flow rate of 30 cc/hr of air at a precisely known temperature and relative humidity was maintained through the gas flow ampoule which contained the sample of magnesium.

Figure 1 has been included to show a cutaway view of the microcalorimeter instrument. It can be seen that the unit contains a relatively large volume constant temperature water bath (thermostat). This ample volume of water makes possible the very precise control of temperature in the measuring cylinder, i.e., temperature stability to 0.001°C. Under such stable conditions, the arrays of Peltier detectors in the measuring cylinder walls are able to detect heat flows as small as fractions of a microwatt either into or out of the sample in the GFAS which is inserted into the measuring cylinder.

The GFAS portion of the system is illustrated schematically in Figure 2. Four principal elements make up the GFAS. The first element in the flow system is the water filled humidifier unit which is maintained at a preset temperature, T_H. The exact value of T_H is dictated by the desired value of the relative humidity. The second element is the stainless steel transfer line through which the gas stream flows between the humidifier and the sample ampoule. It should be noted that the transfer line passes through a heat exchanger just before entering the sample ampoule. The function of the heat exchanger is to ensure that the temperature of the flowing gas has been raised to and equilibrated at the temperature of the water bath, T_B, prior to its entrance into the sample ampoule. As shown in Figure 1, the thermostated water bath surrounds the measuring cylinder. The stainless steel sample-containing ampoule, which has a volume of 4.5 cm^3 and dimensions of 1.2 cm in diameter and 4.0 cm in height, is the third element of the GFAS. The fourth and final element of the GFAS consists of the remainder of the transfer line and the peristaltic pump which maintains the preset gas flow rate through the GFAS.

When hot humid air flows through these stainless steel transfer lines and the empty sample ampoule, a measurable quantity of heat is produced by a slow corrosion type reaction at least in the early stages of the experiment (first several hours). This is shown by the dashed curve appearing in the heat flow versus time plot in Figure 3a. The solid curve in this same plot is the corresponding raw heat flow versus time trace produced when an approximately 50 mg sample of magnesium is present in the sample ampoule under the same gas flow conditions (25°C and 50% relative humidity). Accordingly, the corresponding empty cell background signal was routinely subtracted from the raw signal obtained in each magnesium-containing run. When this was done for the run shown in Figure 3a, the net heat flow (in microwatts) versus time plot shown in the lower curve, Figure 3b, was obtained. The next step in the data analysis process was to divide each net heat flow curve by the sample mass, thereby normalizing to a hypothetical one gram sample size (units of microwatts/g). In that way differing sample sizes can be compared on a common basis. If we make the simplifying

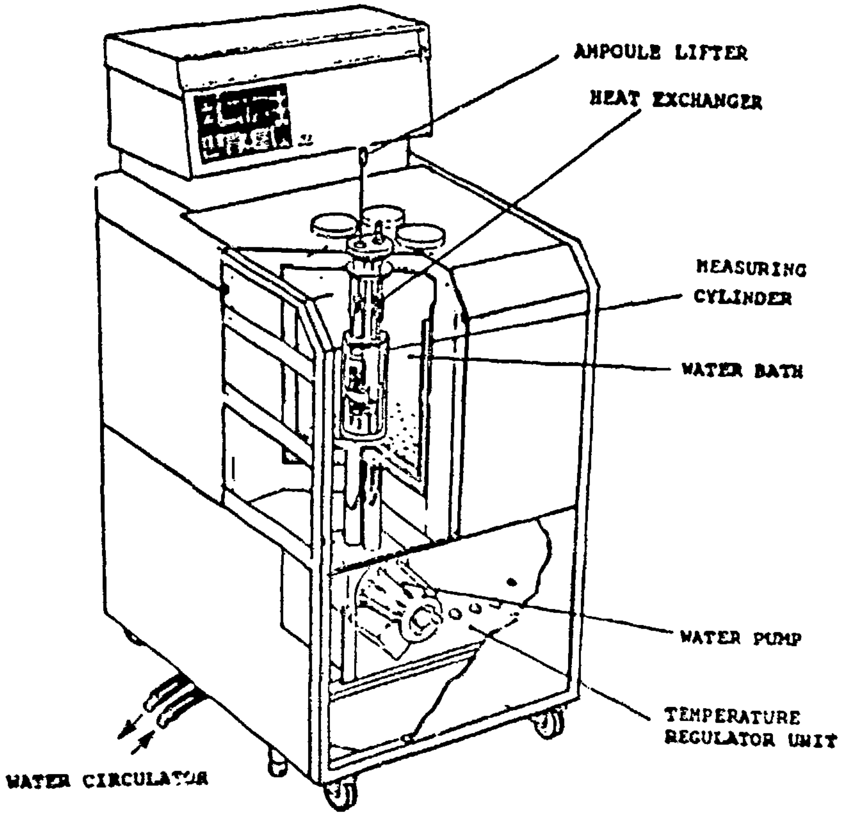


Figure 1. Cutaway View of the Thermometrics/LKB Model 2277 Microcalorimeter

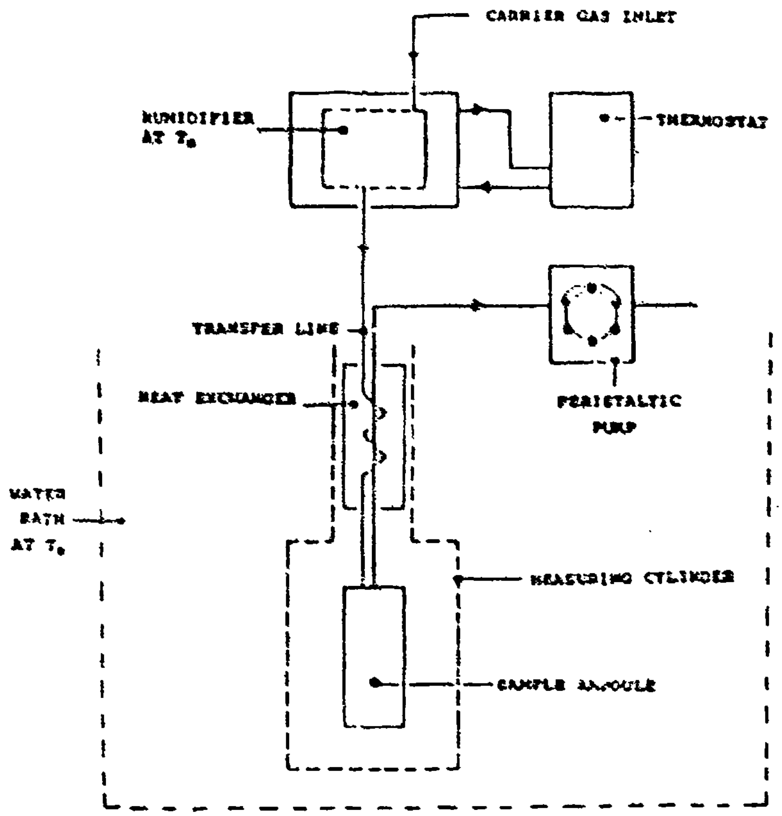
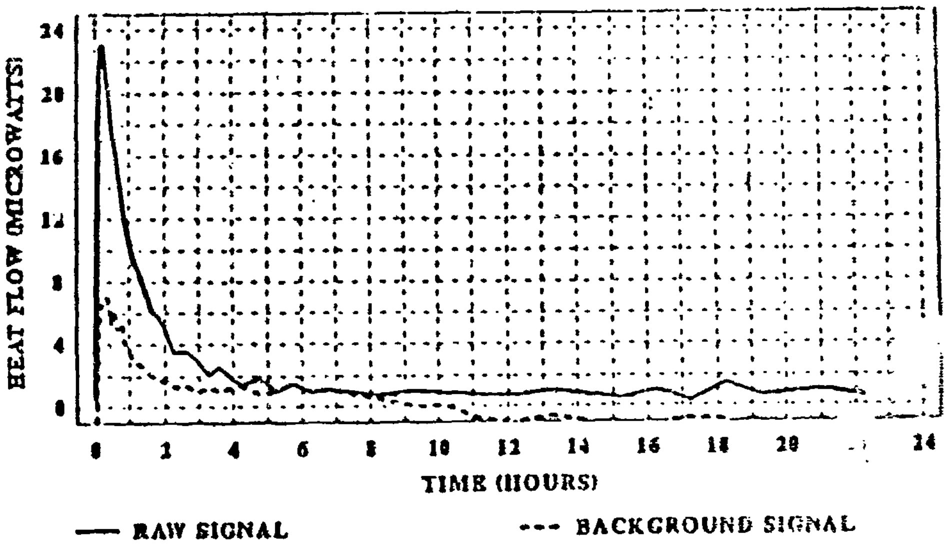
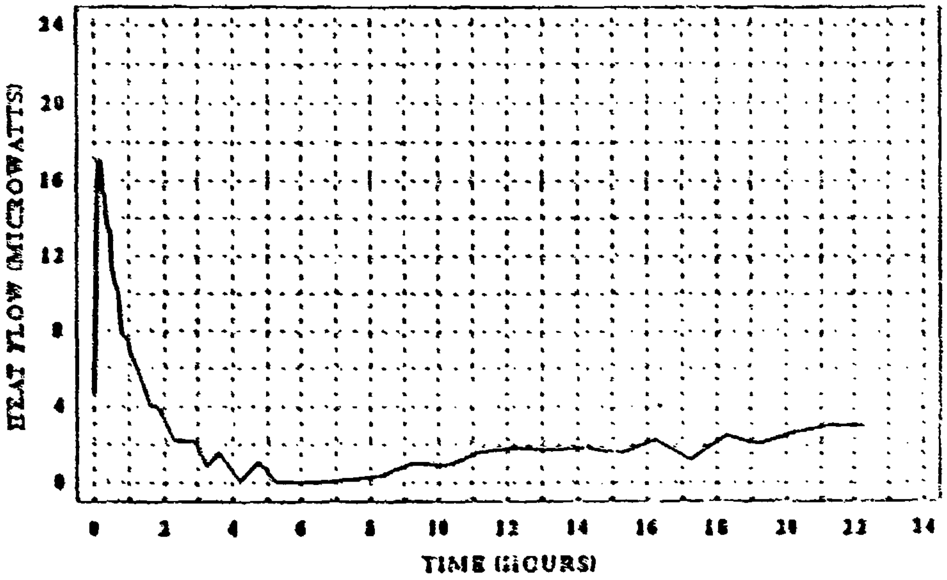


Figure 2. Schematic Diagram of the Gas Flow Ampoule System



(a) Background Signal Without Samples (dashed line) and Uncorrected Sample Signal (solid line)



(b) Corrected Sample Signal Obtained When Background is Subtracted from Raw Sample Signal

Figure 3. Procedure Used to Correct Microcalorimeter Data

assumption that the observed heat flow is due exclusively to reaction (1), we can then straightforwardly calculate the time required for 1% degradation of each magnesium sample. Complete degradation would liberate 440,990 J/mole or 18,144 J/g of magnesium. Therefore, a 1% degradation would liberate 181.44 J/g. By multiplying the observed heat flow in W/g (J/sec.g) by the number of seconds in a day (86,400 sec/day) and dividing the result into 181.44 J/g, one calculates the estimated time required for 1% degradation of the magnesium.

The atomized magnesium samples used in this study were obtained from Hart Metals, Inc., Tamaqua, Pennsylvania. The purity of the atomized magnesium was stated as 99.7%. The atomized magnesium sample was sized classified to pass a 200 mesh U.S. Standard screen and be retained on a 325 mesh U.S. Standard screen. This material is typical of magnesium used in manufacturing pyrotechnic compositions. It is noted that the atomized magnesium is passivated to a controlled extent during its manufacture by exposing it to a low concentration of oxygen for a short exposure time. During this study no effort has been made to characterize the extent of oxide layer on the particle surfaces.

RESULTS AND DISCUSSION

Effect of Relative Humidity:

The effect of relative humidity on the aging of both large and small samples of magnesium maintained at an ambient temperature of 25°C was investigated. Runs were made at relative humidities of 0%, 25%, 50%, and 75%.

With the large sample sizes (3.5-4.0 gram) used to simulate containerized storage environments, the heat flow curves shown in Figure 4 were obtained. It should be mentioned at this point that the general shape of the heat flow versus time curves shown in Figure 4 are typical of the shapes obtained in all of the magnesium-containing microcalorimeter runs, i.e., at the start of a run, heat flow increases with time to some maximum or peak value before decreasing until eventually reaching some steady state value which does not change with time. It is seen that both the peak and steady state observed heat flows increase rapidly with increasing relative humidity. Furthermore, the steady state heat flows are not reached until after approximately two weeks.

The same type of direct dependence of the observed peak and steady state heat flows on relative humidity was also observed with the small sample sizes (approximately 50 mg) used to simulate production line environments, as shown in Figure 5. However, two significant differences from the larger sample results are apparent. Firstly, the heat flows from the smaller samples were typically several times higher than the corresponding heat flows from the larger samples at the same relative humidity. Secondly, the steady state heat flow levels

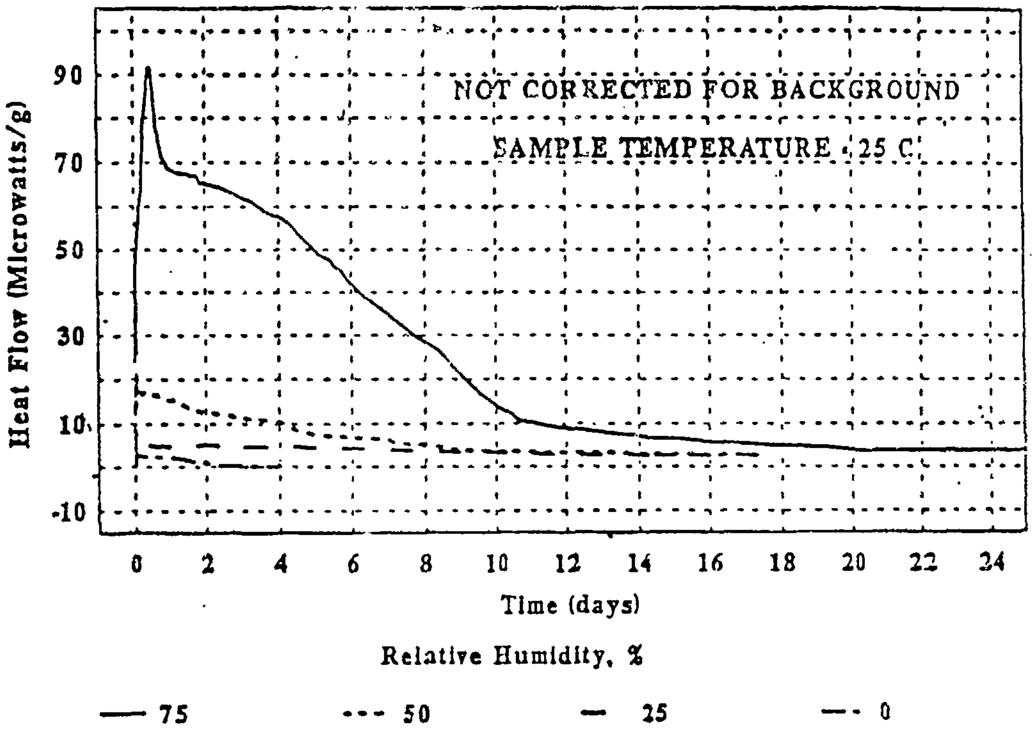


Figure 4. Effect of Relative Humidity on Magnesium Samples Simulating Storage Environment (3.5-4.0 g)

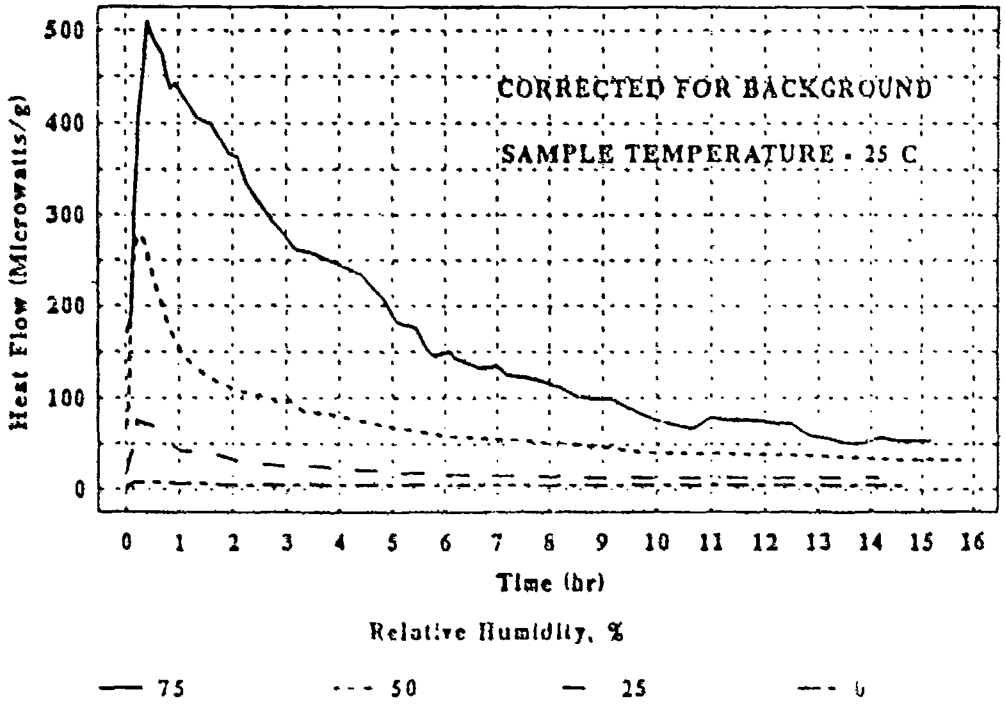


Figure 5. Effects of Relative Humidity on Magnesium Samples Simulating Production Line Environment (0.04-0.05 g)

of the small samples were reached much more quickly than was the case with the larger samples. While the larger samples required approximately 14 days to reach steady state, the smaller samples required only approximately 14 hours.

The information appearing in Figures 4 and 5 has been summarized and quantified in Table 1. In addition to tabulations of the observed values of both the peak and steady state heat flows of both sample sizes, the table contains calculated estimates of the times that would be required for a 1% degradation of each magnesium sample assuming (1) peak heat flow, and (2) steady state heat flow. For the case of the larger samples simulating a containerized storage environment, the time for 1% degradation at the steady state heat flow level is certainly more realistic than the value based on peak heat flow, but should be regarded as an upper limit. This is because the maximum heat flow corresponds to the heat flow occurring during the relatively rapid early stages of the attack of a freshly exposed magnesium surface to the flow of moist air, while the steady state heat flow corresponds to the much slower (diffusion controlled) subsequent attack of subsurface magnesium once easily accessed exposed surface magnesium has been coated with magnesium hydroxide. For the case of the smaller samples simulating the production line environment, the actual time for a 1% degradation probably lies somewhere between the peak and steady state estimates, and will depend upon how much mechanical agitation the magnesium sample undergoes on the production line, that is, how rapidly previously unexposed magnesium surfaces are exposed to the humid air as a consequence of shaking, mixing, pouring, or otherwise agitating the magnesium. In order to avoid possible underestimation of the degradation times of magnesium on the production line, it is probably more realistic to rely on the estimate derived from the peak heat flow case and regard it as the minimum (lower limit) time required for a 1% degradation.

Table 1. Results at 25°C as a Function of Relative Humidity Level for Magnesium Sample Sizes in (A) 50 mg Range and (B) 3.5-4.0 gram Range

% RH	Sample Size	Maximum Heat Flow (μw/g)	Time Required[a] for 1% Degradation (day)	Steady State Heat Flow (μw/g)	Time Required[b] for 1% Degradation (day)
0	A	7.46	282	4.32	486
0	B	2.96	709	0.13	16153
25	A	75.2	28	12.3	171
25	B	8.29	253	2.52	833
50	A	260.	8.1	37.2	56
50	B	21.0	100	3.07	684
75	A	500.	4.2	40.0	52
75	B	91.5	23	3.76	559

[a] Calculated Assuming Maximum or Peak Heat Flow
[b] Calculated Assuming Steady State Heat Flow

Based upon the above considerations, it is apparent from Table 1 that a small (production line environment) sample at the highest relative humidity studied, 75%, may undergo a 1% degradation in as little as 4.2 days. The corresponding minimum degradation time when all water vapor is excluded (0% relative humidity) is 282 days. For the case of the larger (storage environment) samples, the predicted maximum degradation time at 75% humidity is 559 days, while at a relative humidity of 0% the predicted maximum degradation time is 16,153 days, or approximately 44 years. It is obvious from these results that magnesium can be stored without significant degradation for truly long periods of time provided that water vapor can be excluded from the magnesium. These results verify the statement made in the introduction that reaction (1) with water is approximately an order of magnitude faster than reaction (2) with oxygen, at least at a sample temperature of 25°C.

Effect of Temperature:

Only a few preliminary runs at a single relative humidity (75%) with small magnesium samples simulating a production line environment have been made to study the effect of temperature on the rate of the water degradation reaction. The temperatures studied included 25°C, 50°C, and 70°C. The results are shown graphically in Figure 6. It is observed that the peak heat flow values increase significantly with increasing temperature. However, all three runs appear to converge to a common steady state heat flow before the end of the first day. Table 2 has been included to summarize the peak and steady state heat flows obtained at each temperature, as well as to show the calculated times that would be required for a 1% degradation of the magnesium assuming (1) peak heat flow, and (2) steady state heat flow. As in the study of the effect of relative humidity, it is probably more realistic for a production line environment sample to use the maximum heat flow in the calculation of the time for 1% degradation but to regard the resulting time estimate as a lower limit. From Table 2 it is observed that a minimum of approximately 4.2 days would be required for a 1% degradation at a temperature of 25°C, while a minimum of only approximately 1.8 days would be required for a 1% degradation at 70°C. However, if the steady state heat flows are used to calculate an upper limit of the time for 1% degradation, an estimate of 52 days irrespective of temperature is obtained. A measurable decrease in the time for a 1% degradation with increasing temperature certainly seems more reasonable based upon chemical kinetic considerations.

It is planned to further study the effect of temperature on the magnesium degradation rate. The effect of relative humidity on the temperature dependence will be investigated by repeating these runs at a lower relative humidity than 75%. Furthermore, the effect of temperature on the larger magnesium samples simulating a storage environment will similarly be investigated.

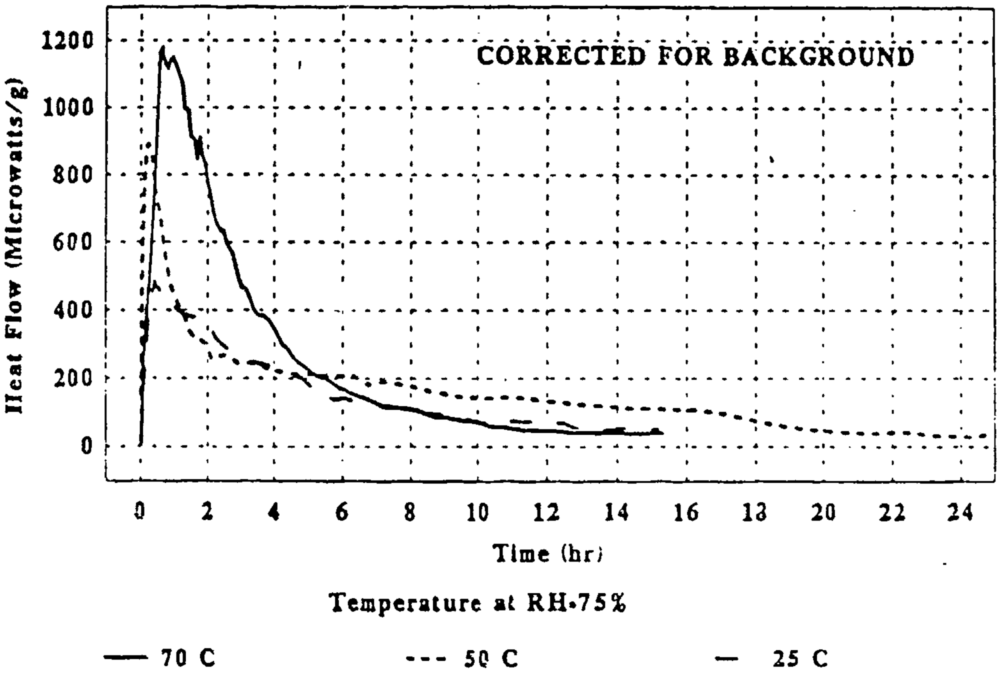


Figure 6. Effect of Temperature on Magnesium Samples Simulating Production Line Environment (0.04-0.05 g)

Table 2. Results at RH 75% as a Function of Temperature for Magnesium Sample Sizes in 50 mg Range

Temperature (°C)	Maximum Heat Flow (μw/g)	Time Required[a] for 1% Degradation (day)	Steady State Heat Flow (μw/g)	Time Required[b] for 1% Degradation (day)
25	500	4.2	40	52
50	875	2.40	40	52
70	1200	1.75	40	52

[a] Calculated Assuming Maximum or Peak Heat Flow
[b] Calculated Assuming Steady State Heat Flow

Effect of Magnesium Degradation on a Pyrotechnic Composition Burn Rate:

Having obtained estimates for the time required for a 1% degradation of magnesium samples in both storage and production line environments as a function of relative humidity and temperature, it was desired to determine what effect degradation of the magnesium would have on the performance characteristics of a typical magnesium-fueled pyrotechnic composition. Burn rate was chosen as a typical performance characteristic.

In order to determine the effect of magnesium degradation on burn rate, four samples of magnesium were used to prepare four batches of a typical magnesium-fueled pyrotechnic composition. The first magnesium sample was obtained directly from the can used to store the magnesium under a dry, inert environment following its receipt from Hart Metals. The next three samples were weighed initially, subjected to accelerated aging for 20, 24, and 72 hours in a temperature and humidity chamber maintained at 70°C and 100% relative humidity, and then reweighed so that the percent degradation of the magnesium to the magnesium hydroxide product could be calculated gravimetrically. After the four batches of composition were prepared from identical proportions of the magnesium and the other ingredients, approximately six gram pellets of measured length were pressed from each batch. A computer-controlled photoptic detector was used to obtain accurate measurements of the burn time of the pellets made from each of the four batches. The resulting measured burn rates are plotted in Figure 7 as a function of the gravimetrically determined percent of magnesium degradation. A linear least squares regression of the data yielded the solid line shown in the figure. The slope of this line yielded an estimate of an 8% decrease in the burn rate for each 1% degradation of the magnesium fuel. Generally similar results have been obtained for other pyrotechnic compositions.[10]

CONCLUSIONS

The rate of atomized magnesium degradation has been shown to depend on a number of factors including relative humidity, temperature, and exposed surface area of the sample.

Relative Humidity of the gaseous air flow was found to have a strong effect on the rate of magnesium degradation. Specifically, increasing the relative humidity between 0% and 75% was observed to greatly accelerate the magnesium degradation rate. This was true for both large and small samples.

Increasing temperature at a constant relative humidity of 75% was found to increase the peak heat flow rate (i.e., the peak magnesium degradation rate) for the case of small magnesium samples simulating a production line environment. Continuing work will address the behavior of larger magnesium samples which simulate typical storage environments.

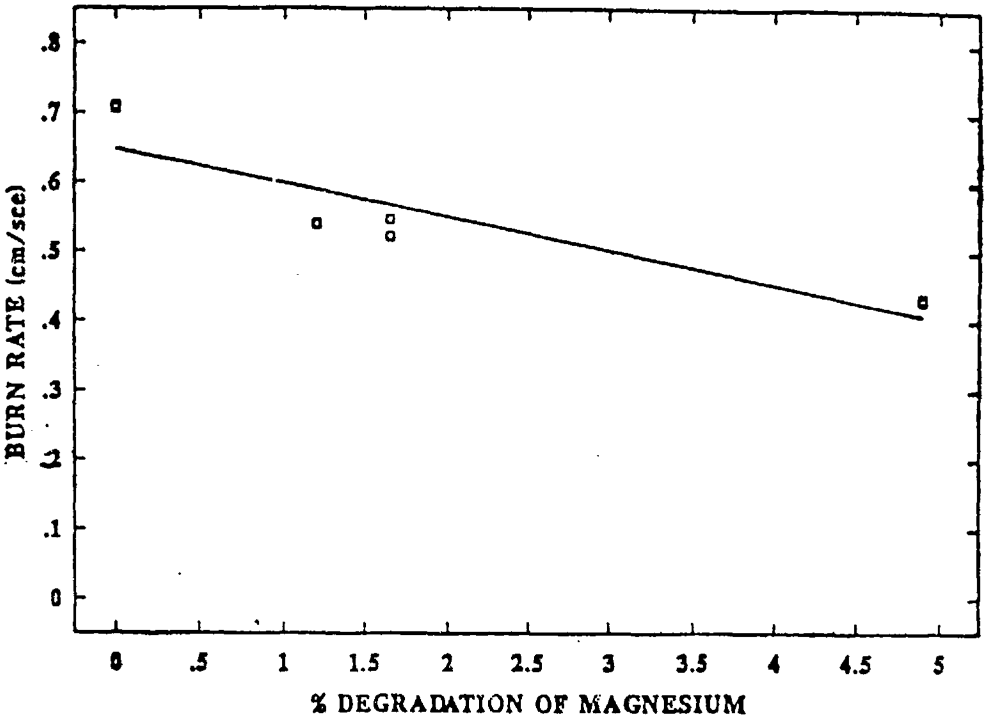


Figure 7. Burn Rate as a Function of
% Degradation of Magnesium

Owing to the fixed dimensions of the instrument sample ampoule, the smaller samples had a proportionately much larger percentage of their surface area exposed to the gas flow. As expected, this was found to have a significant effect on the degradation rate. Smaller samples always had higher values of the peak and steady state heat flows (units of microwatts/g) than did the larger samples, and the peak and steady state heat flow levels were reached on a much faster time scale with the smaller samples than with the larger samples.

It was verified that the reaction of magnesium with water vapor, reaction (1), is approximately an order of magnitude faster than the reaction with oxygen, reaction (2). Hence, it was determined that magnesium could be stored with very little degradation at 25°C and 0% relative humidity (i.e., under completely dry conditions) for years and years.

The effect of degraded magnesium on the performance characteristics of pyrotechnic compositions has been shown. That is, the burn rate of a composition was observed to decrease approximately 8% for every percent magnesium degradation.

It is apparent that the microcalorimeter/gas flow ampoule technique is in fact an effective analytical tool for measuring the degradation rate/lifetime of pyrotechnic materials. Furthermore, there are several additional surface analytical techniques which could presumably provide complementary mechanistic information in the case of magnesium-fueled compositions. These analytical techniques include infrared absorption spectroscopy,[12,13] X-Ray Diffraction,[12,14] Auger Electron Spectroscopy, X-Ray Photoelectron Spectroscopy,[15-17] and Scanning Electron Microscopy. It is planned to utilize combinations of these techniques as part of our ongoing investigation of pyrotechnic material aging.

REFERENCES

1) C. J. Elmqvist, P. E. Lagerkvist and L. G. Svensson, "Stability and Compatibility Testing Using a Microcalorimetric Method," J. Hazardous Materials, 7, 281 (1983).

2) L. G. Svensson, P. E. Lagerkvist, and C. J. Elmqvist, "Ampoule Microcalorimetry for Stability and Compatibility Testing of Explosives and Materials," LKB Application Note 332, Bofors, Sweden (1983).

3) P. E. Lagerkvist, L. G. Svensson, and C. J. Elmqvist, "Ampoule Microcalorimetry for Stability Testing of Primary Explosives and Pyrotechnics, Application of Gas Flow Microcalorimetry to Stability and Compatibility Testing of Pyrotechnic Systems," Proc. of the 9th International Pyrotechnics Seminar, Colorado Springs, Colorado, 323 (1984).

4) L. G. Svensson, P. E. Lagerkvist, and N. G. Gellerstedt, "Microcalorimetry and Impact Testing Applied to the Study of Explosive/Polymer Compatibility," Proc. of the ADPA Symposium on Compatibility of Plastics and Other Materials with Explosives, Propellants and Pyrotechnics, Hilton Head Island, South Carolina, 19 (1985).

5) T. Lindblom, P. E. Lagerkvist, and L. G. Svensson, Proc. of the 7th Symposium on Chemical Problems Connected with the Stability of Explosives, Sweden, 247 (1985).

6) L. G. Svensson, D. E. Taylor, C. K. Forsgren, and P. O. Backman, "Stability and Compatibility Testing Using a Microcalorimetric Method," Proc. of the ADPA Symposium on Compatibility of Plastics and Other Materials with Explosives, Propellants and Pyrotechnics, Long Beach, California, 86 (1986).

7) J. Suurkuusk and I. Wadso, "A Multichannel Microcalorimetry System," Chemica Scripta (Sweden), 20, 155 (1982).

8) F. Taylor, L. R. Lopez, and P. L. Farnell, "Study of the Storage Stability of a Zr/Ni Delay System Using Ampoule Microcalorimetry," Proc. of the 15th International Pyrotechnics Seminar, Boulder, Colorado, 899 (1990).

9) M. A. Bohn and F. Volk, "Investigation of the Aging Behavior of Propellants with Heat Generation, Stabilizer and Molar Mass Degradation," Proc. of the 16th International Pyrotechnics Seminar," Jonkoping, Sweden, 719 (1991).

10) L. G. Svensson, H. Nyhlen, C. K. Forsgren, N. G. Gellerstedt, "A Study of Longer Term Pyrotechnic Degradation Using Microcalorimetry and Burn Rate Tests," A. B. Bofors, Sweden, Report dated 22 June 1988.

11) J. Isler, "Self-Ignition of Nitrocellulose," in Propellants, Explosives and Pyrotechnics, 9, 130 (1984).

12) D. Barasin and I. Batinic-Haberle, "Aging of Pyrotechnic Compositions. The Investigation of Chemical Changes by IR Spectroscopy and X-Ray Diffraction," Propellants, Explosives, Pyrotechnics, 14, 162-169 (1989).

13) I. Batinic-Haberle, D. Barasin, and I. Spasojevic, "Aging of Pyrotechnic Compositions. Kinetics of Magnesium Hydroxide Formation," Proc. of the 20th International Annual Conference ICT, 61/1-61/13 (1989).

14) D. Barisin and I. Batinic-Haberle, "Aging of Pyrotechnic Composition. The Reliability of X-Ray Diffraction Data for Estimation of the Quality of Signal Mix," Propellants, Explosives, Pyrotechnics, 14, 255-259 (1989).

15) A. I. Nizovski, V. I. Savchenko, V. K. Duplyakin, "Applicability of Ultra-Soft X-Ray Radiation for the Investigation of Initial States of Metal Oxidation and Impurity Segregation," Poverkhnost, 1990 (5), pp 134-140. (Russian)

16) W. Holzinger and C. Scholz, "Surface Analysis of Powdered Pyrotechnic Components by Photoelectron Spectroscopy (ESCA)," Proc. of the 14th International Annual Conference ICT, Karlsruhe, Germany, 1983, pp 657-674. (German)

17) H. Nakamura, Y. Ban, Y. Hara, and H. Osada, "Study on the Reactivity of Metallic Powder Used for Explosives," Kogyo Kayaku, 48, 151-157 (1987). (Japanese)