



Degradation of the surface appearance of magnesium and its alloys in simulated atmospheric environments

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Abstract

An environmental simulation system was developed to simulate and control natural atmospheric environments. Purity magnesium and AZ91D and AM60 ingots were exposed to constant temperatures and humidity in a humidity chamber as well as to cycling temperature and humidity conditions in the environment simulation system in order to investigate the surface degradation of magnesium and its alloys during storage and transport. To quantify the change in surface brightness of a metal, a luminance measurement method using a light meter was established. With this method, the surface degradation of the specimens was determined. It was found that the specimen surfaces exposed to the simulated atmospheric environments became duller and the degradation process was accelerated at a higher environmental temperature or higher relative humidity. Temperature and humidity cycling led to an accelerated surface degradation process probably due to condensation of aqueous droplets, resulting in “white spots” on the specimen surface. The presence of salt fog was quite detrimental to the specimen surfaces, which made the condensation of aqueous droplets become possible at lower relative humidity on the specimen surfaces. AZ91 and AM60 with aluminium as a major alloying element were more resistant to the surface degradation than commercial purity magnesium. It is concluded that controlling humidity is a practical way of preventing rapid surface degradation of magnesium and its alloys during their storage and transport.

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1. Introduction

Surface appearance is an important aspect of the quality of a magnesium or its alloy ingot. It is a psychological factor affecting the relationship between the customer and the supplier. Ideal surface appearance of a newly cast ingot is relatively shiny. However, it can rapidly degrade, becoming duller or less shiny, with time under certain environmental conditions. In some cases, “white spots” or “white pits” may even appear on the surface which make the ingot quite unattractive to a customer.

Surface degradation of an ingot can occur in many natural environments where its exposure to moisture can not be avoided. For example, in magnesium production and manufacturing, the storage and transport of magnesium ingots are inevitable procedures. In addition, magnesium ingots usually experience long-term transport and storage when they need to be shipped overseas. In these cases, magnesium ingots are usually exposed to an environment of variable temperature and relative humidity. Sometimes, the temperature and relative humidity may be cycling daily, and the relative humidity could even achieve 100% at night because of condensation. Moreover, when magnesium ingots are transported overseas, the storage containers or cargoes for the ingots could be contaminated by aggressive salt. Thereby, a silver-like ingot from a magnesium producer may finally turn into a dull block after one month when the smelter is ready to use it.

Faced with ingots of degraded surface appearance, customers normally become suspicious about the quality of the ingots, even though casting performance is not necessarily connected with the surface appearance of the ingots.

For effective prevention of such surface degradation, it is important to understand the surface degradation behaviour of magnesium and its alloys in a practical environment where temperature and relative humidity cycle daily. A good understanding of the influences of temperature and relative humidity and their combined effect on the surface degradation is of commercial significance. It may lead to the development and adoption of suitable measures to mitigate surface degradation of magnesium and its alloys.

Surface degradation of magnesium and its alloys in nature is a process of oxidation or corrosion. Some fundamental work has been conducted to reveal the detailed mechanisms involved in the interaction of magnesium alloy surfaces with the environment [1,2]. It has been known that magnesium has a good resistance to oxidation at normal ambient temperature in dry environments [3–5]. The presence of moisture can deteriorate the corrosion or oxidation resistance and lead to rapid surface degradation. On the other hand, temperature is another well known factor that can affect the rates of most reactions. In this regard, high temperature oxidation appears to be more interesting to many researchers than the oxidation behaviour at low temperature (e.g. room temperature). It has been generally accepted that at temperatures below 450 °C in dry oxygen or at 380 °C in moist oxygen, the oxide film on magnesium is protective for considerable lengths of time [5,6].

Although the above fundamental investigations have to some extent deepened the understanding of surface degradation and the nature of surface films on magnesium and its alloys, they cannot guide practical storage and transport of the ingots of magnesium and its alloys. There are some practical issues that have not been well addressed. For example, it is still unclear how to quantitatively define or to measure the degree of surface degradation in practice. So far, reports on the dependence of surface degradation on the relative humidity are quite scarce. To the best of the authors' knowledge, published investigations into the oxidation of magnesium alloys below 380 °C are also very rare,

let alone the effect of temperature on the surface degradation of magnesium and its alloys at ambient temperatures. It seems that the combined effect of temperature and relative humidity on surface degradation of magnesium and its alloys has not, to date, been systematically investigated.

This study intends to address these issues through quantifying and measuring the degradation of surface appearance of magnesium and its alloys using a conventional photographic method to investigate the influences of salt; temperature and relative humidity on the surface degradation in a low temperature range. This will be done by simulating the natural daily cycling of temperature and relative humidity conditions in a storage container to understand the effect of temperature and relative humidity on surface degradation of ingots of Mg, AZ91 and AM60. The objective of this study is to provide a guide to practical storage and transport of the ingots of magnesium and its alloys for the magnesium industry.

2. Experimental

2.1. Constant temperature and relative humidity

A humidity chamber (Contherm Chamber) was used to control a series of constant temperatures and relative humidities. Considering the stability of the chamber for precise control of temperature and relative humidity, the temperature and relative humidity were controlled within the ranges of 30–60 °C and 30–90% in this study.

2.2. Environment simulation system

To simulate the actual temperature and relative humidity cycles likely to be experienced in a container or a storage chamber, an environment simulation system was built and used in this study. The system consisting of two chambers is schematically presented in Fig. 1.

The storage chamber is 150 cm in length, 80 cm in width and 60 cm in height with a 25 cm high triangular prism shaped lid on the top. The chamber can be heated up to 50 °C in the daytime by heaters mounted on the side walls outside the chamber. The heaters were automatically switched off at night to let the chamber cool down to room temperature. The heat generated by the heaters simulates the day time temperatures outside the chamber. To monitor the changes in temperature and relative humidity inside the chamber during testing, temperature and relative humidity (*R/H*) sensors were also installed in the chamber. A few shelves were mounted in the chamber, which allow specimens to be placed in high and low positions in the chamber for testing.

Through a tube, the chamber is connected to an environment chamber in which the environmental atmospheric media is simulated. The tube connecting the storage chamber to the environment chamber simulates the leakage of a practical storage container in practice.

In the environment chamber, the environmental atmospheric media is generated by spraying a solution, such as tap water or 3.5 wt.% NaCl, the concentration of which is the same as seawater through a water pump. The water fog generated through the pump from the tap water simulates the atmospheric media where the storage of ingots is far away from seawater. The salt fog generated from the salt water in the environment chamber

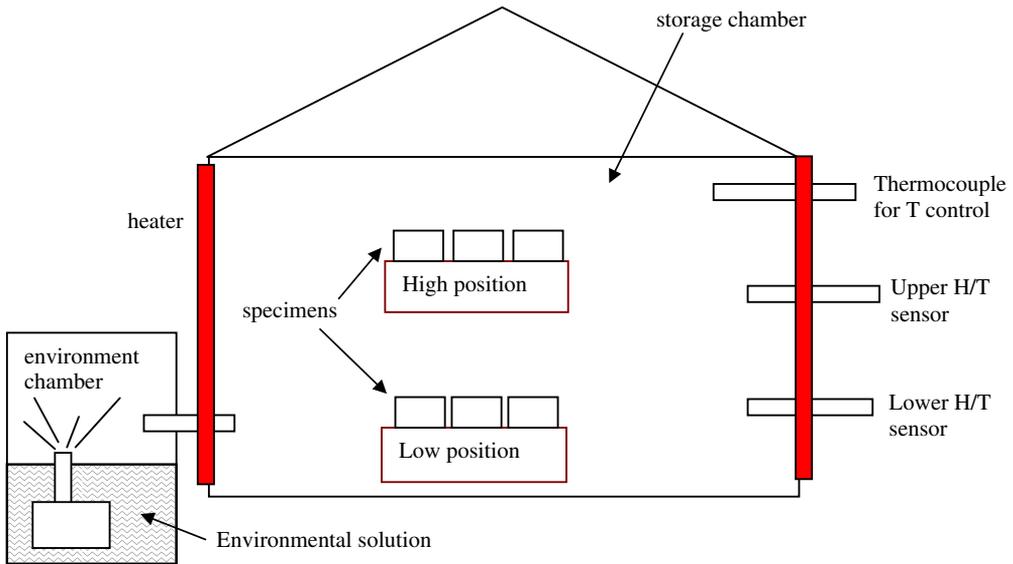


Fig. 1. Schematic diagram of the environmental simulation system.

simulates the environmental conditions when the ingots are stored somewhere close to the coast or transported over sea.

During operation, the air originally in the storage chamber will be expelled from the chamber during heating due to the heating-expansion effect of the air in the chamber. This simulates the situation in a container or cargo during storage or transport in the day time. After heating is switched off and the storage chamber starts cooling down, the fog from the environment chamber is sucked into the storage chamber because of the cooling and contraction of the air remaining in the storage chamber. This process simulates the conditions experienced during the night part of the cycle.

To check whether the simulated relative humidity and temperature in the storage chamber can reasonably represent the actual atmospheric environment experienced in a storage tank, a metallic container (see Fig. 2) was set up out-door (outside the laboratory) and the temperature and humidity inside and outside the container were measured simultaneously by humidity and temperature meters for two days.

2.3. Quantitative measurement of surface appearance

The most common form of surface degradation of magnesium and its alloys under natural atmospheric conditions is dulling or discolouring. There is no standard ranking to follow in rating or measuring the surface dulling or discolouring degree. To investigate surface degradation behaviour, it is therefore essential to be able to quantify the degree of surface degradation.

Traditional corrosion methods, such as measurement of weight loss or gain, are not sensitive enough to detect changes resulting from surface dulling or discolouring. Although some microscopic techniques may be sensitive enough to reveal the changes in micro-structure and composition of the surface, they are inconvenient for illustrating

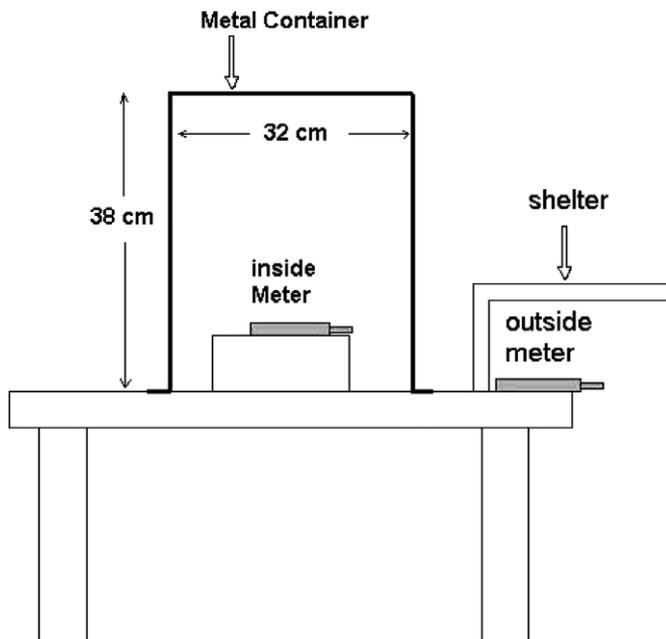


Fig. 2. Schematic diagram of the apparatus for measuring the humidity and temperature inside and outside an outdoor metal container.

optical information over a large area. Unfortunately, surface quality is an overall visual parameter measured by the human eye.

Theoretically, photography can record such a visual change and therefore some parameters of photography that are associated with the reflectivity of an objective surface could be used to quantitatively rank the surface appearance of an ingot. After conducting a product technique survey, it was found that a light meter is an objective and off-the-shelf technique to measure reflectivity or brightness of a surface. It can quantitatively measure the luminance from the surface, which truly reflects visual quality.

Fig. 3 schematically shows the principle of a light meter in a dark room measuring the brightness of a specimen surface. It should be noted that the luminance reading from the light meter depends on the brightness of the light source, measured surface area and relative positions of the light source, light meter and specimen. For a meaningful measurement, specimens were placed behind a black window which allowed only an area of 4 cm by 5 cm of the specimen surface to be exposed to the light source and to be measured by the light meter. For the luminance reading to sensitively reflect the brightness or reflectivity, the incident angle was set to be equal to the reflection angle. In addition, the brightness of the light source and all the relative positions of the light, window, specimen and light meter were carefully controlled and fixed in all measurements. In each measurement the brightness of the light source was calibrated with a standard grey card that had a standard luminance reading.

It should be stressed that a change in measured luminance reading reflects the change in brightness of the whole measured specimen surface. It cannot very sensitively reflect a small change in brightness of a small local area, such as local pitting or “white spots” appearing on a degraded surface. In this study, it was found that the degradation of

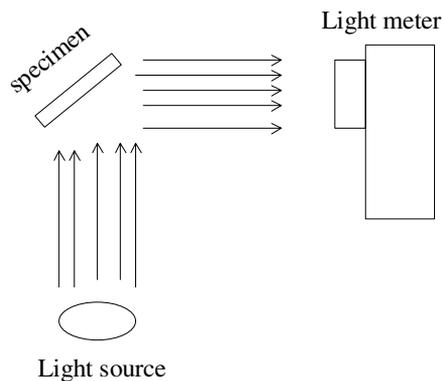


Fig. 3. Schematic diagram of the set-up for measurement of the luminance of a specimen surface using a light meter in a darkroom.

surface appearance as measured by brightness was not very severe and dulling or discolouring is the major form of surface degradation. A decreased luminance reading should reliably illustrate the degree of surface degradation.

3. Testing procedures

Cross-section plates cut from Mg, AZ91D and AM60 ingots were polished to 1200# grade with SiC paper. The surfaces of the polished plates were measured in a dark room for their initial luminance readings (Lux1). After that, they were then exposed in the humidity chamber for 4 days and in the storage chamber for 11 days. In some cases, 2 kg of silica gel desiccant was also put in the storage chamber to absorb the moisture in the chamber in order to examine the effect of controlled relative humidity on the surface degradation in that chamber.

After exposure in the chamber, the degraded surfaces of the specimens were measured in the dark room again for their final luminance readings (Lux2). The degree of degradation of the surface appearance of a specimen is expressed by the decrease in the luminance in percentage, $\Delta\text{Lux}\%$:

$$\Delta\text{Lux}\% = [(\text{Lux1} - \text{Lux2})/\text{Lux1}]\%$$

Three specimens for each exposure condition were measured for their $\Delta\text{Lux}\%$ values. The average of these three results is reported in this study.

After exposure, XPS analyses with a Mg $K\alpha$ X-ray as the X-ray source and an argon ion beam at 4 μA –4 keV etching the surface film, were performed on representative specimens to detect the compositions of their degraded surfaces.

4. Results

4.1. Dependence of surface degradation on temperature and relative humidity

The dependence of the surface degradation of Mg, AZ91D and AM60 on temperature and relative humidity, as measured by reduced luminance readings in percentages, is pre-

sented in Figs. 4–6. Iso- $\Delta Lux\%$ curves are plotted on the charts and the numbers in the grids next to the curves denote the values of the iso- $\Delta Lux\%$ curves.

Although the $\Delta Lux\%$ values are relatively scattered, some basic trends of the influences of temperature and relative humidity on surface degradation can be summarized as follows:

1. At a given temperature or relative humidity, the $\Delta Lux\%$ value increases with increasing relative humidity or temperature (Figs. 4–6). In other words, surface degradation of the specimens in the humidity chamber became more severe as environmental temperature or relative humidity increases.
2. The $\Delta Lux\%$ values for Mg (Fig. 4) in general are larger than those for AZ91D and AM60 (Figs. 5 and 6), which suggests that at the same humidity and temperature, the surface of pure Mg degraded more rapidly than that of AZ91D or AM60.
3. According to the locations of the iso- $\Delta Lux\%$ curves in the charts (Figs. 4–6), it appears that the influence of relative humidity on surface degradation is more significant than that of temperature, as the increase of iso- $\Delta Lux\%$ has a steeper gradient along the humidity axis compared with that along the temperature axis.

The above findings are consistent with the visual appearance of the specimens after 4 days of exposure in the humidity chamber.

The above results indicate that on a H-T map (Figs. 4–6) the upper right hand corner is the most detrimental zone and the lower left hand corner is the least aggressive zone. The

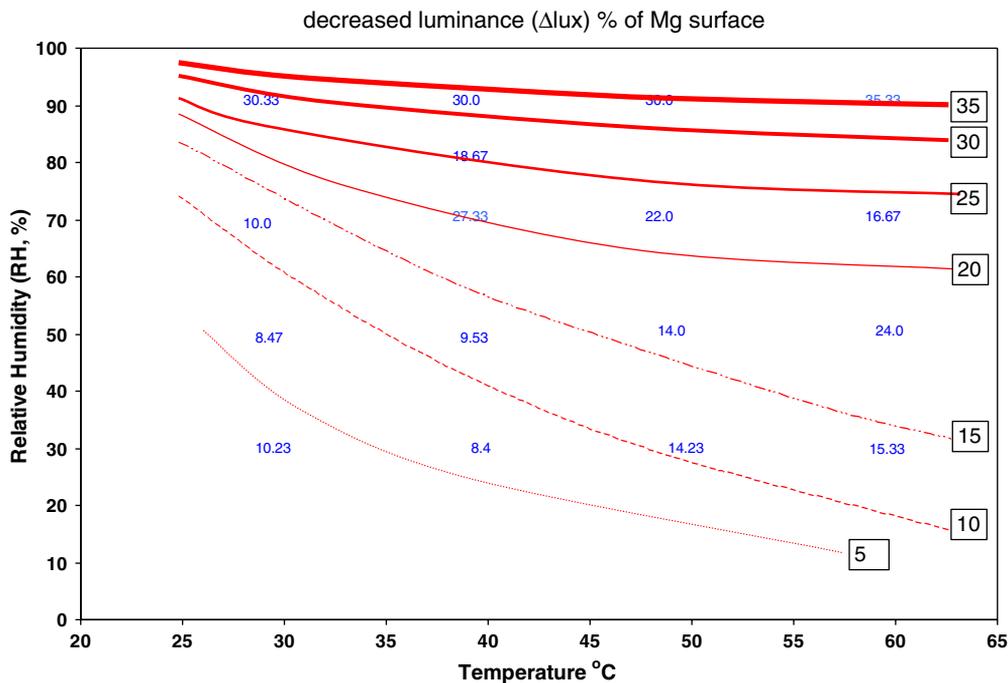


Fig. 4. Dependence of decreased luminance of the specimen surface of Mg on temperature and humidity.

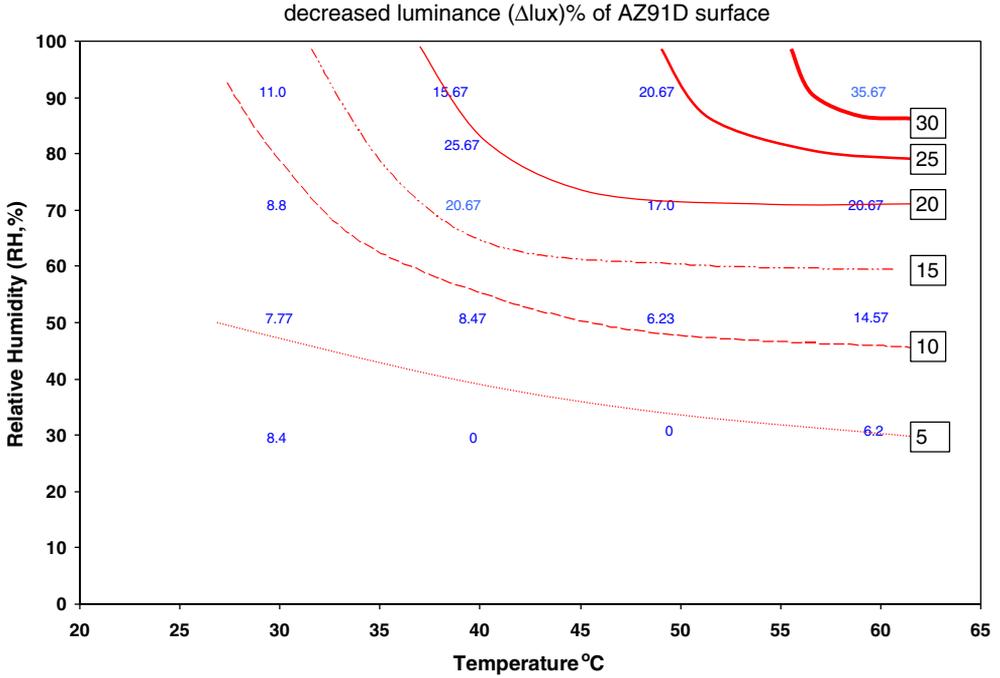


Fig. 5. Dependence of decreased luminance of the surface of AZ91D on temperature and humidity.

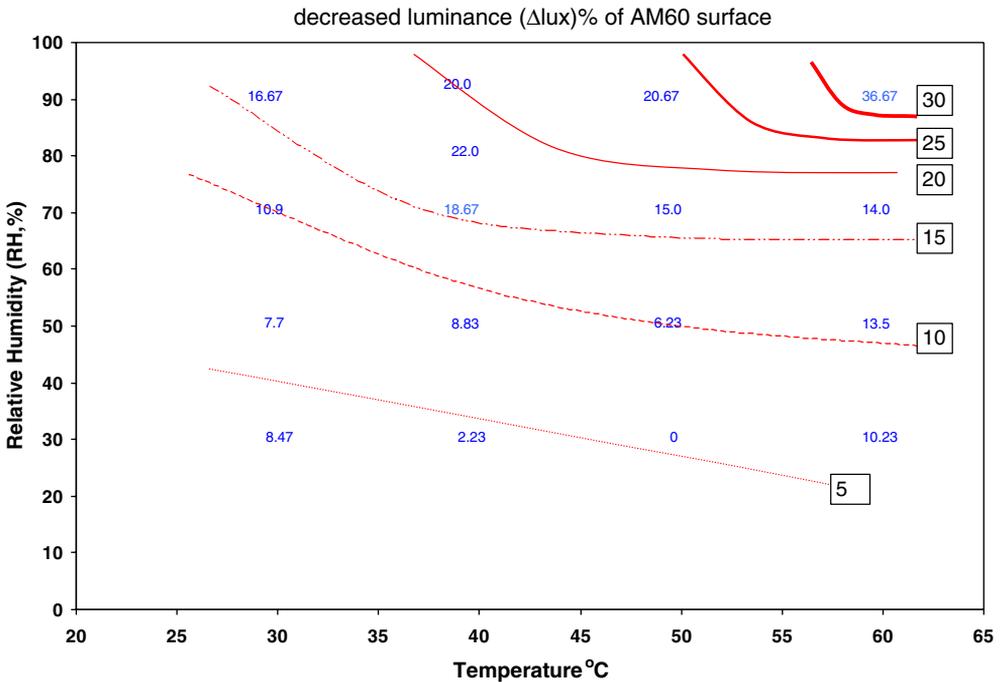


Fig. 6. Dependence of decreased luminance of the surface of AM60 on temperature and humidity.

aggressiveness gradually increases as the H-T conditions shift from the lower left hand corner to the upper right hand corner.

It should be noted that the iso- Δ Lux% curves were obtained after 4 days of exposure in a chloride-free environment. They could shift in the direction of lower temperature and lower humidity if the exposure time is extended or if the environment is polluted by chlorides or some other aggressive substances.

4.2. Simulation of cycling of temperature and relative humidity

In a real environment, the temperature and relative humidity cannot be constant parameters. To understand the surface degradation behaviours of magnesium and its alloys stored or transported in a practical environment, specimens should be tested under conditions similar to a real environment. The environment simulation system was built for this purpose. It is important to check if the simulated environment by the system is reasonable or not.

The natural temperature and relative humidity measured inside and outside the outdoor metal container are shown in Fig. 7. The temperatures inside and outside the container varied within the range 20 °C–40 °C. In the day time, the temperature rose and maintained a high level and then dropped and remained low during the night time. The inside temperature is about 10 °C higher than the outside. The relative humidities inside and outside the container varied oppositely to the temperature with time within the range 20–100%. The humidity was high, over 90%, at night but dropped below 50% during the day time. The inside relative humidity is always higher than that outside and sometimes reached 100% at night. It should be noted that the measurement of the two-day natural humidity

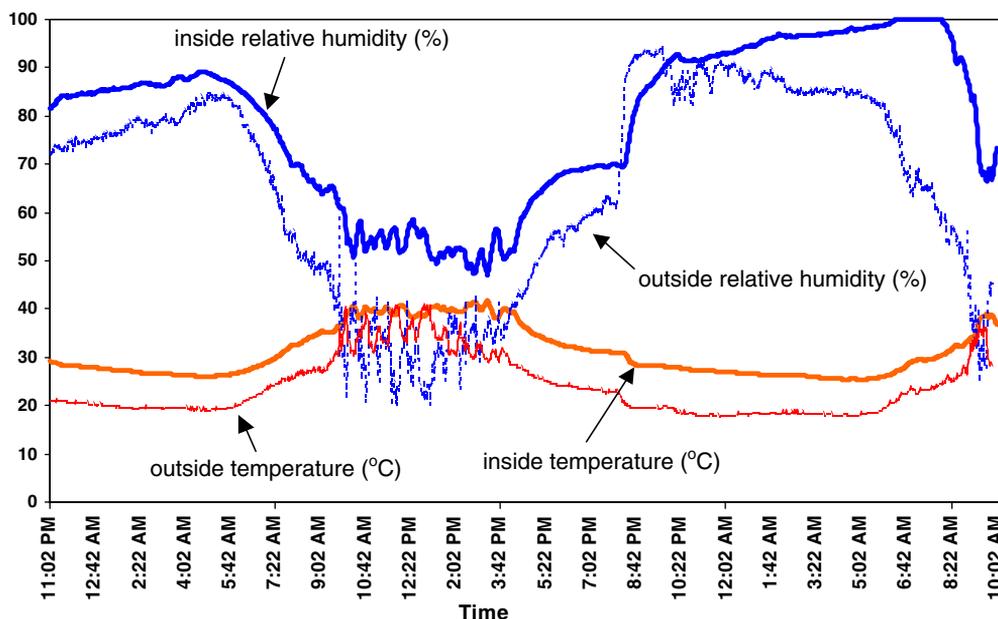


Fig. 7. The natural daily cycling of temperature and humidity outside and inside the outdoor metal container.

and temperature inside and outside the metal container was conducted at a campus about 15 km away from the ocean where the climate conditions are relatively mild. In a location closer to sea, the temperature and humidity conditions could be even harsher.

Figs. 8–11 show the cycling temperatures and relative humidities in the storage chamber. The cycling temperature and humidity in the storage chamber simulate very well the basic features of the cycling of the natural temperature and humidity inside the outdoor metal container (see Fig. 7).

When the chamber was heated up, the temperatures inside the chamber became higher than the room temperature outside. After heating was switched off, the inside temperatures

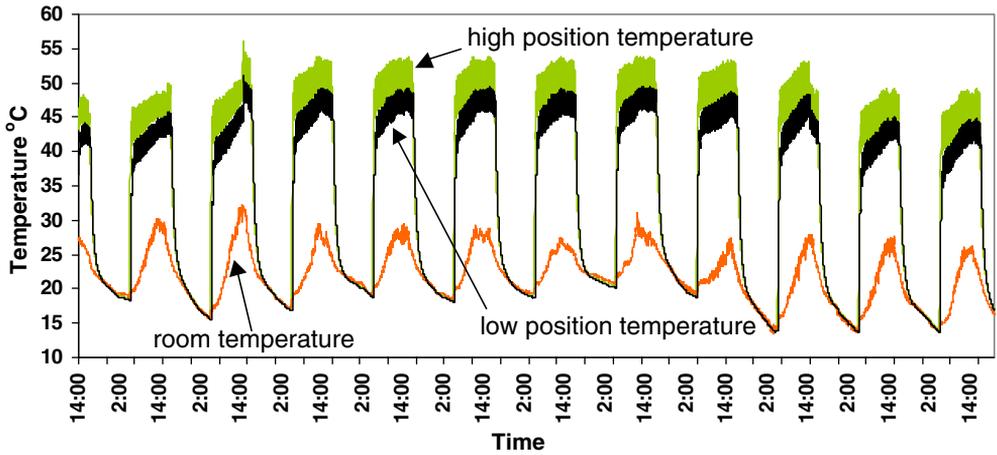


Fig. 8. Typical daily cycling of ambient temperature outside the storage chamber and the temperatures inside the storage chamber during the 11 days of test (the presented result was obtained with water fog in the environmental chamber. The cycling of temperatures with salt water in the environmental chamber or desiccant in the storage chamber are similar to this typical one).

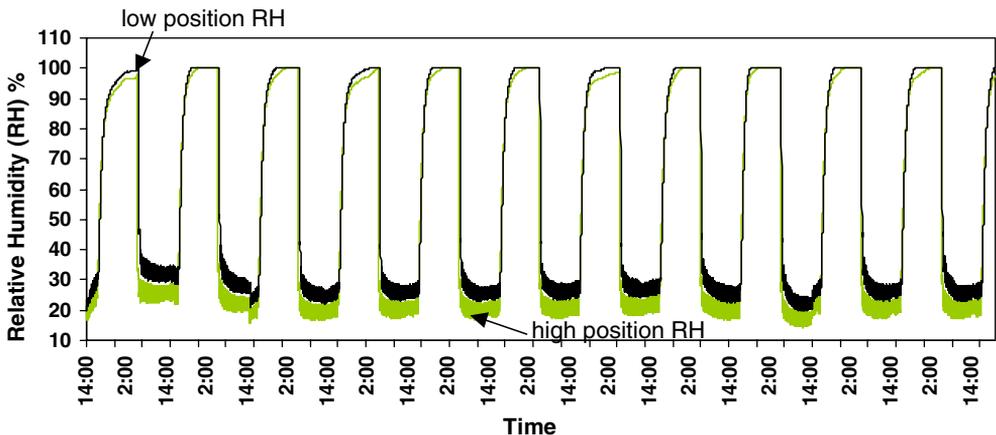


Fig. 9. The daily cycling of relative humidity in the storage chamber during the 11 days of test with water fog in the environmental chamber.

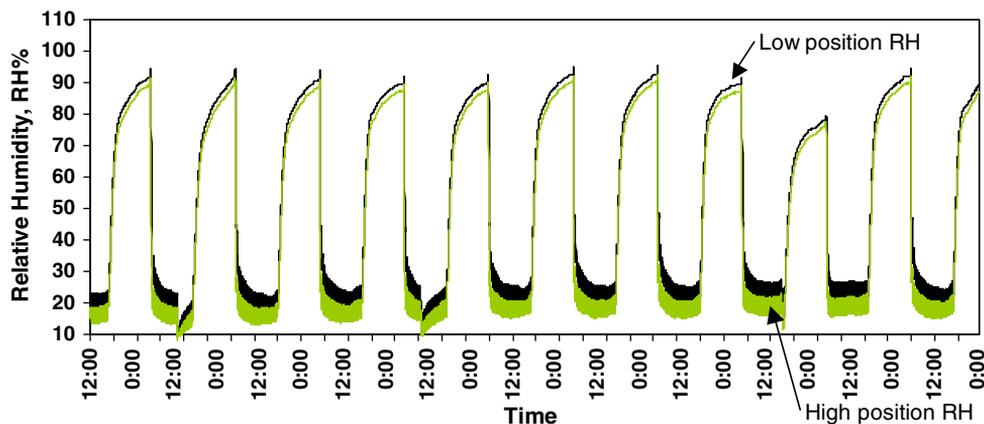


Fig. 10. The daily cycling of relative humidity in the storage chamber during the 11 days of test with salt fog in the environmental chamber.

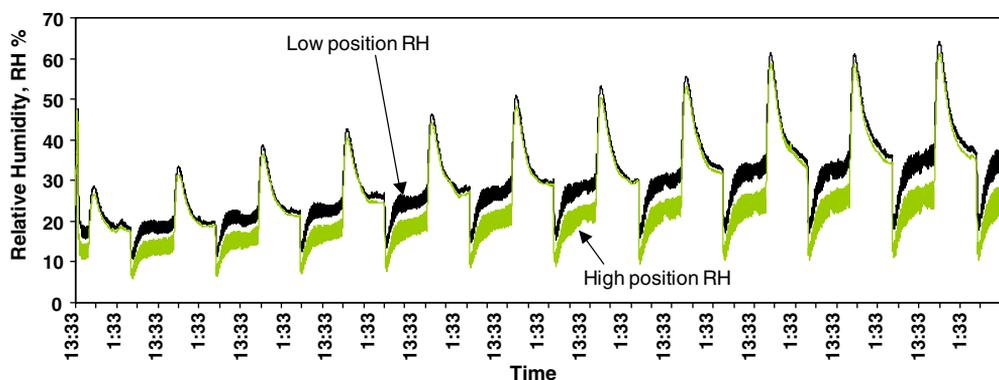


Fig. 11. The daily cycling of relative humidity in the storage chamber during the 11 days of test with desiccant in the storage chamber and salt fog in the environmental chamber.

became close to the outside temperature. This is typical of the temperature inside a not well insulated container. In the day time under the sun, the temperature inside the container is always much higher than the temperature outside. However, the inside temperature gradually drops down to a level close to the outside temperature during the night time.

The opposite cycling of temperature and relative humidity is clearly shown in Figs. 8–11. It is noticed that even though the relative humidity decreased to a very low level in the day time while the chamber was hot, it approached 100% after the chamber cooled down to room temperature at night if desiccant was not used in the chamber (Figs. 9 and 10).

The distribution of temperature and humidity in the chamber was not uniform. There was about 5 °C difference in temperature and 3–5% difference in relative humidity between high and low positions in the chamber (see Figs. 9–11) as measured by the upper and lower T/H sensors (Fig. 1). The differences in temperature and relative humidity are natural phenomena that would be experienced inside a practical container.

In general, the cycling behaviours of temperature in the storage chamber with water fog and salt fog in the environment chamber with and without desiccant in the storage chamber are quite similar and can be illustrated by a typical chart (Fig. 8). However, the corresponding cycling behaviours of relative humidity were different. The relative humidity in the storage chamber with salt fog is systematically slightly lower than that with water fog, which could be due to the fact that the water content is slightly lower in the salt fog than in the water fog. The presence of desiccant in the chamber significantly changed the cycling manner of humidity in the chamber (see Fig. 11), which can be demonstrated in the following two aspects: (1) The relative humidity in the high and low positions in the chamber decreased dramatically in the first few hours at the beginning of the test. Such an initial decrease in humidity was not observed in the chamber without desiccant, and can be ascribed to the absorption of moisture in the chamber by fresh desiccant. (2) The waveform of the cycling of relative humidity in the storage chamber with desiccant is characterised by two extra peaks in each relative humidity cycle compared with the cycling relative humidity in the chamber without desiccant.

The differences between the typical humidity cycles in the storage chamber with and without desiccant are schematically demonstrated in Fig. 12. The relative humidity increases (a–b) as temperature decreases. This process is the same as the humidity variation in a desiccant-free environment. After the relative humidity becomes high enough in the low temperature period, the desiccant starts to absorb moisture from air. The absorption capability decreases with time, hence the relative humidity decreases quickly at the beginning (b–b') and then the rate of decrease slows down (b'–c) until a sudden drop in relative humidity (c–d) when the chamber temperature starts to rise. The sudden decrease in relative humidity is caused by the increase of temperature. During the high temperature period, water is desorbed from the desiccant, leading to an increasing relative humidity. Similarly, the desorption capability of moisture from desiccant decreases with

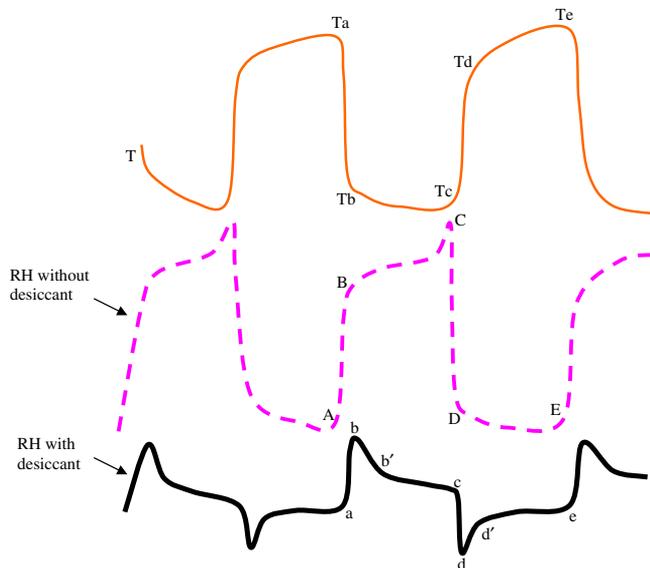


Fig. 12. Typical daily temperature and humidity cycles with and without desiccant.

time, so the relative humidity increases quickly at first (d–d') and then gradually stabilises (d'–e). In summary, the complicated humidity cycling behaviour actually results from a rapid response of relative humidity to temperature and a relatively slow temperature dependent absorption and desorption of moisture by the desiccant. It can be seen in Fig. 12 that the peaks of the humidity cycles increase with exposure time. This is because the absorption and desorption capabilities of desiccant decreased with exposure time.

4.3. Surface degradation in the storage chamber

Fig. 13 shows the decrease of luminance of Mg, AZ91D and AM60 after exposure in the storage chamber for 11 days. The following points can be made from this figure:

1. The decrease in luminance for the Mg surface was in general more significant than for AZ91D and AM60. Among these specimens, AZ91D appears to be the most stable in terms of surface degradation.
2. In general, the surface brightness of a specimen in a lower position decreased more than that of a plate in a higher position in the storage chamber.
3. The salt fog produced in the environment chamber attached to the storage chamber accelerates the surface degradation of the specimens in the storage chamber. The decrease in luminance of the specimens with salt fog in the environment chamber is much more evident than that with only water fog produced in the environment chamber.
4. When desiccant was used in the storage chamber, the decrease in the luminance of the specimen surfaces became insignificant.

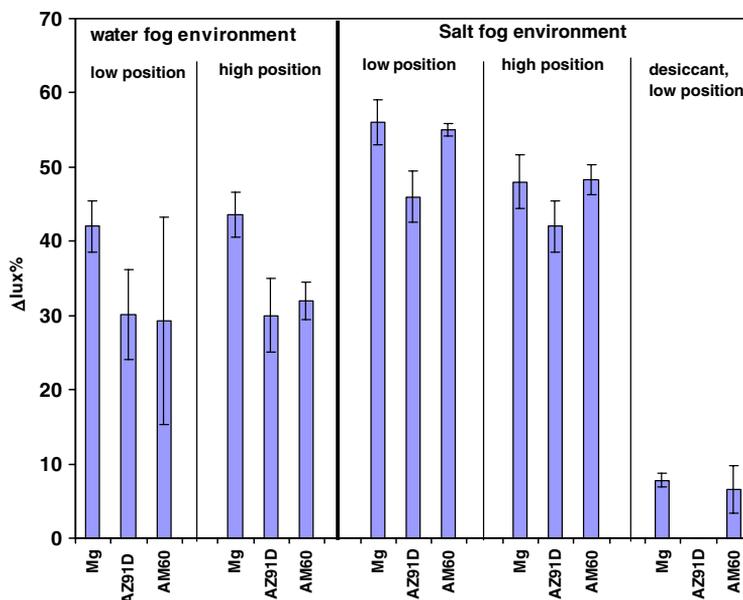


Fig. 13. Decrease of luminance of the surfaces of Mg, AZ91D and AM60 after storage in the storage chamber for 11 days.

The above findings were confirmed by visual observation with the naked eye.

Compared with the specimens after 4 days in the humidity chamber, the specimens stored for 11 days in the storage chamber without desiccant are slightly different in surface degradation morphologies. There were no visible “white spots” or pitting on the former (in the humidity chamber), while “white spots” and pitting were strikingly evident on the latter (in the storage chamber). Fig. 14 shows typical appearances of the specimens in the storage chamber without desiccant. These kinds of “white spots” did not appear on the specimens in the storage chamber with desiccant.

4.4. Surface composition

Typical compositions of degraded surfaces are listed in Table 1. Basically, the degraded surfaces were covered with oxide films mainly consisting of Mg, O and C. According to the ratio of $O/Mg \approx 2$, the main composition of the surface films of the ingots should be $Mg(OH)_2$. The C signal may either come from air pollution or the surface film component, e.g. $MgCO_3$, which should be responsible for the deviation of the measured ration of O/Mg from 2. It has been found that CO_2 in the atmosphere can dissolve in water to form carbonic acid and react with a surface film to form magnesium carbonates [7].

After ion beam etching, the main difference in surface composition between the specimens exposed in salt-free and salt-contaminated environments is the different amounts of NaCl present in their surface films. The Na and Cl signals can be detected from the surface of the specimen exposed in the storage chamber with salt fog. The surface of the specimen kept in the salt-free chamber had very weak (almost no Na and Cl signals). These results indicate that NaCl from the salt fog had deposited on the specimen surface and participated in film formation and growth. The trace amount of NaCl on the specimen exposed to the salt-free environment could simply come from the air in the laboratory where salt spray tests are normally carried out. The salt only stayed on the top of the surface film and was not incorporated into the surface film.

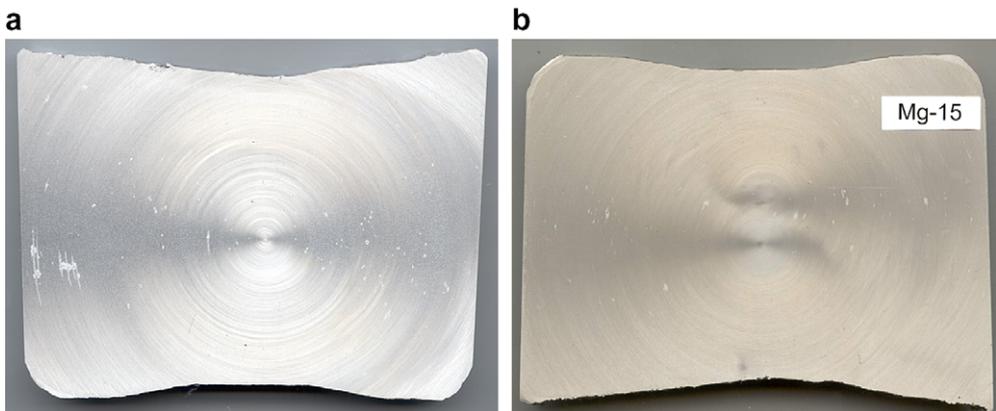


Fig. 14. Typical appearance of Mg plates after exposure in the storage chamber without desiccant for 11 days with (a) water fog and (b) salt fog in the environmental chamber.

Table 1

Compositions of degraded surfaces after exposure in a salt free environment and a salt-fog contaminated environment

| Elements in the surface film | Salt free environment (atm.%) | | Salt-contaminated environment (atm.%) | |
|------------------------------|-------------------------------|------------------------------|---------------------------------------|------------------------------|
| | Before ion-beam etching | After 5 min ion-beam etching | Before ion-beam etching | After 5 min ion-beam etching |
| O | 45.1 | 62.1 | 47.3 | 44.1 |
| Mg | 17.2 | 30.8 | 18.4 | 28.5 |
| Cl | 0.5 | | 1.1 | 0.8 |
| Na | 0.3 | | 1.3 | 1.2 |
| C | 36.7 | 7.1 | 31.9 | 25.3 |
| S | | | 0.4 | |

5. Discussion

5.1. Oxidation and electrochemical corrosion induced surface degradation

At low temperatures, magnesium can react with oxygen and water to form a film on its surface [1,2]. In this case, the surface degradation of magnesium and its alloys is an oxidation process. The dulling and discolouring of a shiny ingot can be attributed to the formation and growth of an oxide or hydroxide film on the surface. The oxidation results in dulling and discolouring of a specimen probably through two mechanisms: (1) the formed surface film which is not completely transparent more or less absorbs incident and reflective light to and from the metal surface; (2) due to the non-uniformity of the magnesium surface, the formation and growth of the surface film further leads to a rougher surface at a micro-scale, which increases diffusive reflection and reduces the reflectivity of the surface to a greater degree.

In respect of oxidation of magnesium, a three stage process has been proposed [1,8], which includes oxygen chemisorption, nucleation and lateral growth of an oxide film and thickening of the film on magnesium. In this study, as the specimens after polishing had already been exposed to air for many hours before being put into the chambers, there was already an initial surface film covering their surfaces. Therefore, the oxidation of the specimen surfaces was already in the third stage and thus the contributions of the first two stages of oxidation to the surface degradation should not be considered. Hence, surface degradation should only be associated with the third stage, i.e., the film thickening process.

The above oxidation mechanism was proposed based on the results obtained at a very low water vapour partial pressure [1], so it is particularly relevant for the surface degradation of a specimen in an environment with a relatively low content of moisture.

For a specimen in a very moist environment, e.g. the relative humidity of which is close to 100%, electrochemical corrosion cannot be excluded. This is because at such a high relative humidity, some aqueous droplets can preferentially form through condensation on a specimen, particularly in some micro-dented, depressed or hollow sites whose surfaces have a certain micro-concavity. These sites can be caused by scratches, non-uniform oxidation, pitting or casting pores which often exist on a practical specimen surface. These sites with the aqueous droplets acting as electrolyte will be electrochemically corroded much more rapidly than a normal oxidation process at room temperature. It has been

recently revealed that in a simulated atmospheric environment, severe corrosion can even lead to cavities formed in the matrix phase of AZ91D [9]. In theory, electrochemical corrosion in this case often results in localised corrosion or pitting, resulting in white corrosion products, known as “white spots”, on the specimen surface (e.g. see Fig. 14). Normally, oxidation at room temperature cannot lead to severe localised pitting or “white spots” on a specimen. It should be noted that the composition of the electrolyte droplets can significantly affect the electrochemical corrosion. If some aggressive salt dissolves in the electrolyte, the “white spots” should become more evident.

Since temperature and humidity are oppositely cycling, the oxidation and electrochemical corrosion mechanisms should alternately operate in the surface degradation of an exposed specimen. At a high temperature but low relative humidity, the surface degradation is an oxidation process. It will turn into electrochemically-induced surface degradation when the temperature drops and correspondingly the relative humidity approaches the condensation point. At a temperature lower than 100 °C, electrochemical corrosion should be much faster than an oxidation process. Therefore, if a specimen suffers from surface degradation in such an environment, condensation-related electrochemical corrosion should be a major cause.

5.2. Effect of temperature and relative humidity

As the controlled relative humidity in the humidity chamber was always lower than 90%, the condensation of water on the specimen surfaces should be insignificant and therefore the electrochemical reaction should play a less important role than oxidation in the surface degradation of the specimens.

Figs. 4–6 show that the surface of the specimens degraded more severely at a higher temperature or a higher humidity. As discussed earlier, the dulling and discolouring of the specimen surfaces can be associated with the thickening and roughening of the surface films on the specimens. Oxidation is normally facilitated by raising the temperature. Since at low temperature the thickening rate of an oxide film can be described by the Cabrera and Mott equation where the thickness of the film is proportional to temperature [1,10], then the dulling of the specimen surfaces should be more significant at a higher temperature, as indicated by Figs. 4–6.

With regard to the influence of relative humidity on surface degradation, Figs. 4–6 indicate that the presence of water vapour can facilitate surface degradation. The measured detrimental effect of moisture is in agreement with Splinter et al.’s theory [1,10] that water vapour can dissociate on the surfaces of magnesium and its alloys and participates in the surface oxidation process. This theory predicts that a surface film thickens more quickly at a higher exposure of water vapour resulting in a thicker film. This explains the detrimental effect of relative humidity on the surface degradation in this study.

5.3. Influence of cycling temperature and relative humidity

Under cycling temperature and relative humidity conditions, surface degradation should be associated with changes in temperature and relative humidity. However, these two factors oppositely change with time (see Figs. 8–12). Their influence on surface degradation could to some extent counteract each other, which makes the analyses of the overall effect of the two factors on the surface degradation relatively difficult.

For a better understanding of the overall effect of cycling temperature and relative humidity on surface degradation, the traces of the cycling temperature and relative humidity are plotted on a T – H map as shown in Fig. 15. As the cycling of temperature and relative humidity in the storage chamber without desiccant was relatively stable (see Figs. 8–10), only one or two typical T – H cycles are plotted on the T – H map. For the chamber with desiccant, the cycling of temperatures and relative humidity changed with time (i.e., the cyclic relative humidity increased with time (see Fig. 11)), so all 11 cycles are plotted on the T – H map.

From Fig. 15, it can be seen that the T – H cycling in the low position of the chamber is located relatively close to the upper right hand corner on the T – H map compared with that in the high position. In other words, the cycling temperature and relative humidity conditions in the low position of the storage chamber were more aggressive than those in the high position. The difference in aggressiveness of the cycling temperature and humidity conditions should be responsible for the phenomenon that the specimen surfaces degraded more severely in the low position than in the high position in the chamber (Fig. 13).

Apart from the relatively different locations of the traces of cycling temperature and humidity in the T – H map, the condensation effect was another factor that could contribute to the difference in the surface degradation between the specimens in the low and high positions in the storage chamber without desiccant. Figs. 9 and 15 show that the specimens in the lower position were exposed to 100% relative humidity for a longer period of time

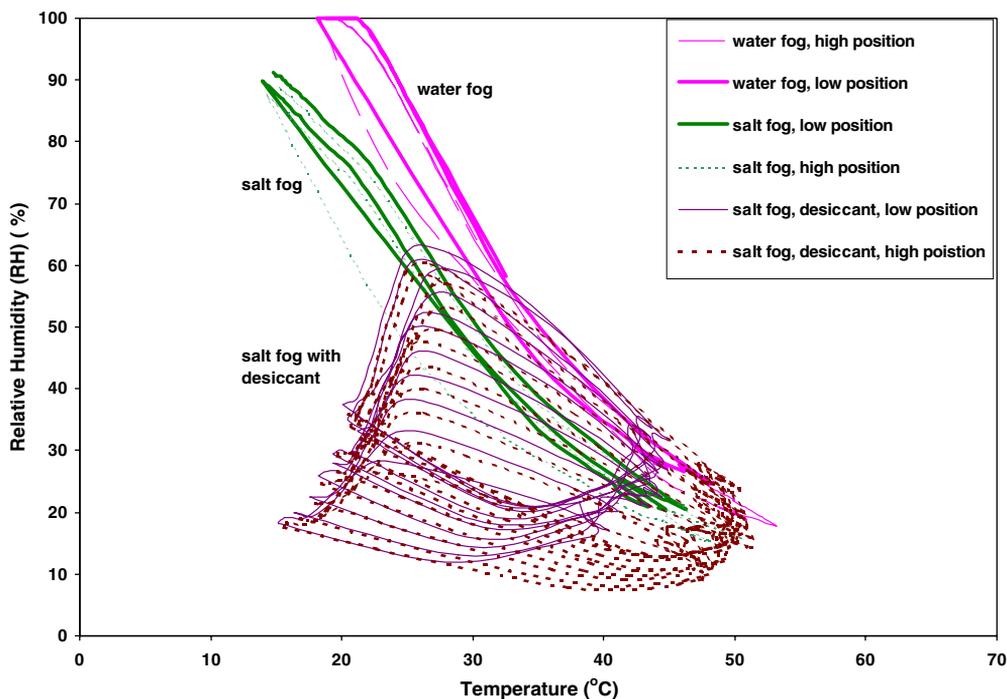


Fig. 15. Traces of temperature and relative humidity on a T – H map.

over a wider temperature range. This means that these specimens suffered more aggressive electrochemical corrosion attack for a longer time than the specimens in the high position. This was confirmed by the naked-eye observation that relatively more “white spots” appeared on the specimens in the low position than in the high position. This to some extent provides experimental evidence that surface degradation is caused by condensation-induced electrochemical corrosion.

Similar condensation-induced electrochemical corrosion can also occur in the chamber with salt fog without the presence of desiccant, which is illustrated in the next section.

5.4. Effect of salt

If the cycling temperature and relative humidity in the salt-fog contaminated chamber without desiccant is compared with those in the salt-fog free chamber, it can be found that the cycling of temperature and relative humidity with salt-fog is located closer to the lower left hand corner on the T – H map, a relatively less aggressive zone (see Fig. 15). This contradicts the surface degradation results (Fig. 13) whose surface degradation of specimens was more severe in the salt-contaminated chamber than in the salt-free chamber.

It should be borne in mind that when the exposing atmospheric environment is contaminated by salt, the surface degradation of the exposed specimens should not simply be dependent on temperature and humidity alone. In this case, the presence of salt should have a more profound influence on the surface degradation process. Table 1 has indicated that NaCl participated in the formation of the film on the degraded surface. The presence of chlorides in a surface film is detrimental to the protectiveness of the film on magnesium or its alloy. Thus, it is not surprising that the specimens suffer from more severe surface degradation even under relatively mild temperature and humidity conditions in a salt-contaminated environment than under aggressive temperature and humidity conditions in a salt-free environment.

It should be noted that a salt solution has a lower water vapour pressure and correspondingly its relative humidity is lower than that of pure water at the same temperature. For example, the relative humidity of a saturated NaCl solution is about 75% at 25 °C. In a salt-contaminated environment, salt is likely to deposit on a specimen surface. If the hygroscopic salt is present on the specimen surfaces, condensation of water from the salt-contaminated air can occur at a relative humidity much lower than pure water. Therefore, even though the maximum of the relative humidity in the storage chamber with salt fog was around 95%, condensation of the salt fog on the specimen surfaces was quite likely to occur in practice. In this sense, the specimens in an salt-contaminated environment were more likely subjected to more detrimental electrochemical corrosion attack. In fact, in a salt-contaminated environment, electrochemical corrosion should be the main mechanism responsible for the surface degradation of the specimens, rather than oxidation.

With this understanding, it is easy to interpret the beneficial effect of desiccant on the surface degradation in the salt-fog contaminated chamber. Firstly, with desiccant in the chamber, the maximum relative humidity in this chamber was less than 70%, even lower than the relative humidity of saturated NaCl. In this case, the condensation of water from the fog could not occur, so the possibility of the electrochemical corrosion-induced surface degradation could be excluded. In experiments, the fact that no “white spots” appeared on the specimens in the storage chamber with desiccant is good evidence that no electrochemical corrosion is involved in the surface degradation. Secondly, even though there were a

few cycles of temperature and relative humidity in the chamber with desiccant that are located closer to the upper right hand corner in the T – H map than those in the chamber without desiccant (Fig. 15), this only occurred in a few cycles and only for a short period of each cycle. In most cycles the T – H traces were still located closer to the lower left hand corner. This means that the temperature and humidity conditions in general were milder in the chamber with desiccant than in the chamber without desiccant.

5.5. Influence of composition

To interpret the more severely degraded surface of magnesium compared to the most stable surface of AZ91D under the same temperature and humidity conditions (Figs. 4–6 and 13), both oxidation and electrochemical corrosion mechanisms should be taken into account.

It has been illustrated by Splinter and McIntyre [1] that aluminium in a substrate magnesium alloy can increase the activation energy for ion movement and consequently retard the thickening of the surface film at room temperature. This theory can well explain the different surface degradation degrees of Mg, AZ91D and AM60 plates in the humidity chamber (Figs. 4–6) where oxidation is mainly responsible for their surface degradation.

In the storage chamber, not only oxidation but also electrochemical corrosion was responsible for the surface degradation. In the low humidity range during T – H cycling, electrochemical corrosion could not occur and oxidation was the main reason for the surface degradation. So, Mg should be expected to have the fastest oxidation rate and AZ91D to be the most stable for the same reason for the different surface degradation degrees of Mg, AZ91D and AM60 in the humidity chamber. In the high humidity range during T – H cycling when the electrochemical corrosion mechanism operated, since the presence of Al in a magnesium alloy is also beneficial to its electrochemical corrosion resistance [3,4,11–14], then the electrochemical corrosion induced surface degradation should also be most severe on Mg and least degradation should occur on AZ91 according to their different aluminium contents. Therefore, in general the surface degradation degree increases in the following sequence: AZ91D < AM60 < Mg.

6. Concluding remarks

6.1. Findings

This investigation has led to the following findings:

- (1) Luminance measurement using a light meter is a convenient method of quantifying the surface degradation of magnesium and its alloys.
- (2) The developed environmental simulation system reproduced the basic characteristic changes of the environmental parameters in a container used for storage and transport of ingots of magnesium and its alloys.
- (3) At low temperature (lower than 100 °C), a higher relative humidity or temperature can lead to more rapid surface degradation of magnesium, AZ91D and AM60 alloys.
- (4) The surface of pure magnesium degraded faster than that of AZ91D or AM60. The different aluminium contents in these metals is most likely responsible for their different degrees of surface degradation.

- (5) The cycling of temperature and relative humidity in the storage chamber led to condensation of aqueous droplets on the specimen surfaces, resulting in more severe surface degradation of Mg and its alloys.
- (6) The presence of salt in the atmosphere accelerated the surface degradation of Mg and its alloys, resulting in “white spots” on the specimen surfaces by an electrochemical corrosion mechanism.
- (7) When the relative humidity was low enough, surface degradation could be significantly reduced even in a salt-contaminated environment.

6.2. Significance of findings to storage and transport of magnesium and its alloys

The above findings are of significance to practical storage and transport of Mg and its alloys.

- (1) A cost-effective way to prevent surface degradation is to maintain a low relative humidity in a container by using desiccant. The desiccant should be placed in high relative humidity areas, for example, on the bottom of a container, next to leakage or ventilation sites, etc.
- (2) Leakage in a container can reduce the effectiveness of desiccant. Sealing containers or using a sealed container is recommended. Ventilation is not encouraged.
- (3) Variation of temperature can accelerate the suction of moisture into a container. Hence, it is recommended to insulate a container, which will reduce the temperature variation inside the container. The transport of ingots of magnesium and its alloys in a sealed container containing desiccant provides very good protection from excessive surface degradation.

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