Article

Effect of Ca Additions on Ignition Temperature and Multi-Stage Oxidation Behavior of AZ80

Chunlong Cheng®, Qing Lan, An Wang, Qichi Le *, Fan Yang and Xiaoqiang Li

Key Laboratory of Electromagnetic Processing of Materials, Ministry of Education, Northeastern University, Shenyang 110819, China; cchlennann@163.com (C.C.); qian1990@163.com (Q.L.); anwangneu@163.com (A.W.); chengchunlong@ sina.com (F.Y.); lixiaoqiang@ sina.com (X.L.)

* Correspondence: iolxvxlo@163.com; Tel.: +86-132-3402-1373

Received: 13 September 2018; Accepted: 24 September 2018; Published: 26 September 2018

Abstract: AZ80, AZX801, and AZX802 alloys were prepared to investigate the ignition temperature and multi-stage oxidation behavior in air. Besides, the microstructures of alloys before and after oxidation were compared. The results reveal that AZX802 exhibits the characteristics of higher ignition temperature and best oxidation resistance compared to AZX801 and AZ80, which contributes to the increase of melting temperature of secondary phase in matrix due to the formation and increase of Al₂Ca, with the addition of Ca in AZ80. In addition, the incubation periods before accelerated oxidation and the beginning of the accelerated oxidation temperatures of AZ80, AZX801, and AZX802 are different during multi-stage oxidation, which also contributes to the different onset melting temperature of the secondary phase. And the beginning of the accelerated oxidation of Mg alloys at high temperature is always accompanied by the onset melting of the low melting temperature of the secondary phase and the growth of oxide nodule on the surface.

Keywords: AZ80; oxidation; ignition temperature; calcium

1. Introduction

As the lightest of structural materials, magnesium (Mg) alloys have increased interest in the aerospace and automotive industries thanks to their characteristics of high specific strength and stiffness, low density, and high rigidity [1–4]. Mg alloys have also been intensively studied for their biomedical applications due to their mechanical strength and biodegradability [5]. However, the limitation of Mg alloy applications is the high chemical activity and high attraction to nitrogen and oxygen. Mg alloys represent inflammability and poor resistance to high-temperature oxidation [6–9]. Mg and Mg alloys are easily oxidated or burned in manufacturing processes at elevated temperatures (such as extruding, welding, forging, and heat treatment), which is attributable to their active chemical properties. In addition, Aluminum alloys form a compact oxidation film on the surface, while magnesium alloys generate only a loose porous structure of MgO, providing limited protection for the substrate from being further oxidized, especially for temperatures above 400 °C [10–12].

It is proved that alloying (such as the addition of Ca or rare-earth elements in Magnesium alloys) is a commendable way to increase the ignition temperature and oxidation resistance of Mg alloys, especially for the high temperatures [13–15]. Lee et al. [16] have found that the oxidation rate of AZ31, oxidized between 450 °C and 650 °C, was remarkably suppressed after adding a small amount of Ca. However, many researchers adopt a different ignition temperature test device for investigation, and there is no specialized equipment for the study of magnesium alloy’s ignition temperature [17]. Fan et al. [18] studied the ignition temperature of Mg-Y-Ce ternary magnesium alloy by a semi-closed resistance furnace ignition temperature test device. However, the oxygen in the mold cavity of the device could not be replenished once consumed, and the obtained ignition
point was not accurate due to the reduction of oxygen content during testing. Prasad et al. [4] investigated the influence of Al and Y on the ignition and flammability of Mg alloys, using a flame injection ignition temperature test device. And the specimens were exposed to air directly during testing, resulting in the detected temperature being affected by many factors, such as wind and placement of thermocouple. So the ignition temperature of alloys might not be accurate. Liu et al. [19] researched the flammability and oxidation kinetics of the magnesium alloys AZ31, WE43, and ZE10 by a cone calorimeter ignition temperature test device, which was an expensive and complicated operation for the ignition temperature test, so it could not be widely used by researchers. Our equipment provides sample operation, accurate temperature monitoring, and air convection to acquire the ignition temperature of samples. In addition, the ignition temperature and oxidation resistance of Ca adding magnesium alloys at elevated temperatures have been researched by some scholars, however the multi-stage oxidation behavior of AZ80 alloying with Ca has not been studied by researchers. Moreover, the effect of Ca on the microstructure and melting point of the secondary phase of AZ80 is not well known. In this paper, devices providing sample operation, accurate temperature monitoring, and air convection were adopted to acquire the ignition temperatures of samples. And AZ80, AZ80-0.8 wt.% Ca (AZX801), and AZ80-2.0 wt.% Ca (AZX802) magnesium alloys were prepared. The influence of calcium additions on ignition temperature and multi-stage oxidation behavior of AZ80 were studied, and the melting point of secondary phase of alloys were investigated.

2. Experiment

2.1. Alloy Preparation

AZ80, AZX801, and AZX802 alloys were prepared with MnCl$_2$, commercially pure Zn, pure Al and pure Mg, and Mg-25 wt.% Ca master alloys. The alloys were melted by a crucible heating in a small electric resistance furnace at 710, protected with a mixed gas of 99 vol.% CO$_2$-1 vol.% SF$_6$. Mg was heated to 710 °C and when it melted completely, Mg-Ca master alloy, Al, and Zn were added into the melt. After that, the melt was heated at 730 °C for the addition of MnCl$_2$ and the refine agent. Then, the melt was held at 730 °C for about 30 min to make sure all the alloying elements were absolutely dissolved in the melt. Following this, the melt was cast at 690 °C into a steel mold, which had been pre-heated at 150 °C for 2 h. Three kinds of ingots (AZ80, AZ80-0.8Ca, and AZ80-2.0Ca) were obtained. Table 1 displays the actual chemical compositions of AZ80, AZX801, and AZX802 alloys.

| Alloy   | Al  | Zn  | Mn  | Ca  | Others | Mg   |
|---------|-----|-----|-----|-----|--------|------|
| AZ80    | 8.23| 0.56| 0.33| -   | <0.1   | Bal. |
| AZX801  | 8.19| 0.61| 0.28| 0.83| <0.1   | Bal. |
| AZX802  | 8.21| 0.59| 0.35| 1.97| <0.1   | Bal. |

2.2. Oxidation Evaluation

A sample of about 20 mm × 15 mm × 15 mm, chamfered in each arris, cut from ingots, is used to test the ignition temperature in air after polishing with 400, 800, 1000, 1500, and 3000 grades SiC papers, respectively, and was then degreased in acetone for 10 min. The experimental device for the ignition point test is shown in Figure 1, which exhibits characteristics of sample operations and air convection. And each time a sample is heated in a small furnace with a corundum crucible at a rate of 5 °C/min, the temperature of the sample is measured by a K-type thermocouple placed in a small hole drilled into the center of the sample. Moreover the interstice between the small hole and thermocouple is filled with refractory mortar to avoid flames being generating from there.
and the surface morphologies of alloys with different oxidation times are also observed. X-ray (Carl Zeiss AG Inc., Heidenheim, Germany), equipped with Electronic Differential System (EDS), is used to observe the microstructures of as-cast or oxidized AZ80, AZX801, and AZX802 alloys. An OLS4100 (Olympus Inc., Tokyo, Japan) 3D measurement laser microscope is used to observe the 3-dimensional morphology of sample surface after multi-stage oxidation. A ULTRA PLUS FESEM (Carl Zeiss AG Inc., Heidenheim, Germany) electron microscope is used to observe the microstructures of as-cast or oxidized AZ80, AZX801, and AZX802 alloys. The ignition temperature is identified by the sharp increase of the sample temperature measured by a K-type thermocouple placed in a small hole drilled into the center of the sample.

The sample mentioned above is dried at 70 °C for 2 h to investigate the multi-stage oxidation behavior by a tube type resistance furnace equipped with a high precision analytical balance named METTLER TOLEDD-XS (METTLER TOLEDD Inc., Shanghai, China), to record the weight change during the multi-stage oxidation in air. The multi-stage oxidation process shown in Figure 2 is as follows: room temperature 1 °C/min 150 °C 4 h 150 °C 1 °C/min 250 °C 4 h 250 °C 1 °C/min 350 °C 4 h 350 °C 1 °C/min 450 °C 4 h 450 °C 1 °C/min 550 °C 3 h 550 °C. In addition, using a NETZSCH STA449F3 (NETZSCH Inc., Selb, Germany) differential scanning calorimeter (DSC) apparatus to detect the fusing point of secondary phase of alloys, the heating rate of sample is 10 °C/min and sample is Φ 5 mm × 2 mm in size.

**Figure 1.** The schematic diagram of ignition temperature test device. The ignition temperature is identified by the sharp increase of the sample temperature measured by a K-type thermocouple placed in a small hole drilled into the center of the sample.

**Figure 2.** The scheme of multi-stage oxidation process. The scheme shows the details of multi-stage oxidation process.

### 2.3. Microstructure Characterization

An OLS4100 (Olympus Inc., Tokyo, Japan) 3D measurement laser microscope is used to observe the 3-dimensional morphology of sample surface after multi-stage oxidation. A ULTRA PLUS FESEM (Carl Zeiss AG Inc., Heidenheim, Germany), equipped with Electronic Differential System (EDS), is used to observe the microstructures of as-cast or oxidized AZ80, AZX801, and AZX802 alloys. And the surface morphologies of alloys with different oxidation times are also observed. X-ray diffraction (XRD) is used to perform the phase identification to obtain detailed information of phase in the specimens.
3. Results and Discussion

3.1. Microstructure Characterization

Figure 3 displays the microstructures of AZ80, AZX801, and AZX802 with the EDS mapping. Combined with XRD pattern of AZ80, as shown in Figure 4, α-Mg, divorced eutectic β-Mg17Al12, α-Mg + β-Mg17Al12 intermetallic, and few Al3Mn5 can be observed in Figure 3a, and the eutectic micro-constituent, consisting of α-Mg and β-Mg17Al12, mainly distribute along the dendrite boundaries of the α-Mg. In contrast to AZ80, the microstructures of AZX801, shown in Figure 3b, exhibit that α-Mg + β-Mg17Al12 lamellar eutectic is partially replaced by a chain-shaped phase considered as β-Mg17Al12 + Al2Ca eutectic micro-constituent, combined with the XRD pattern of AZX801, which is consistent with some researches [20–24]. The chain-shaped phase is fragmented after multi-stage oxidation, as given in Figure 5a,b. From the morphology of AZX802, as shown in Figure 3c, the network structure considered as β-Mg17Al12 + Al2Ca eutectic micro-constituent uniformly scatters in α-Mg matrix. The same phenomenon is observed in the microstructure of AZX802 after multi-stage oxidation, where the network structure is also fragmented and replaced by spherical and rod-like structures, as shown in Figure 5c,d. In addition, the dark spots in Figure 5a,c are burnt structures. Table 2 gives the EDS results taken from different positions as denoted in Figures 3 and 5. The atomic ratios of Al/Ca are shown in Table 2, from which we can see that the atomic ratios of Al/Ca in the microstructure of as-cast are a little higher than that of microstructure after multi-stage oxidation, which verifies that chain-shaped phase and network structure are β-Mg17Al12 + Al2Ca eutectic micro-constituent. Furthermore, the fragmenting of the chain-shaped phase and network structure can also be explained by the dissolution of β-Mg17Al12 which is thermolabile and can easily dissolve into α-Mg matrix when exposed to homogenization treatment [25–27].
Figure 4. XRD patterns of as-cast AZ80, AZX801 and AZX802 alloys. XRD patterns of as-cast alloys show the phase composition.

Table 2. EDS results taken from different positions as denoted in Figures 8 and 10.

| Zone | Mg (at.%) | Al (at.%) | Ca (at.%) | Al/Ca | Phase       |
|------|-----------|-----------|-----------|-------|-------------|
| A    | 74.67     | 23.27     | 2.27      | -     | Mg17Al12    |
| B    | 59.62     | 30.3      | 10.09     | 3.00  | Mg17Al12 + Al2Ca |
| C    | 58.63     | 29.93     | 11.44     | 2.62  | Mg17Al12 + Al3Ca |
| D    | 59.64     | 28.5      | 11.85     | 2.41  | Mg17Al12 + Al2Ca |
| E    | 60.26     | 38.33     | 1.41      | -     | Mg17Al12    |
| F    | 9.78      | 63.38     | 26.85     | 2.36  | Al2Ca       |
| G    | 53.24     | 33.40     | 13.36     | 2.50  | Al2Ca       |

Figure 5. Microstructures of (a), (b) AZX801 and (c), (d) AZX802 alloys after multi-stage oxidation in air. The chain-shaped phase, new lamellar eutectic and network structure which are considered as β-Mg17Al12 + Al2Ca eutectic micro-constituent are fragmented after oxidation.
3.2. Ignition Temperature

Figure 6 shows the ignition temperature test curves and ignition temperatures of all alloys. It is obvious that AZ80 shows the lowest ignition temperature 556 °C, compared with AZX801 (667 °C) and AZX802 (769 °C). This indicates that adding calcium can significantly improve the ignition temperature of magnesium alloys, which is attributable to the formation and increasing of Al2Ca in the matrix seen in Figure 3. The vapor pressure of Mg will increase in order of magnitude once magnesium alloys melt, thus causing Mg vapor to easily diffuse out the surface of the sample and rapidly react with oxygen in air [15,28–30]. So when the temperature is heated to 556 °C in Figure 6a, the alloy of AZ80 is semi-solid according to the phase diagram of Mg-Al, and magnesium vapor will permeate into the air and promptly react with oxygen, releasing an enormous amount of heat and cause AZ80 flaming. Figure 6b shows the small fluctuations of the ignition temperature test curve of AZX801 before burning, due to the small sparks generated during heating.

![Figure 6](image_url)

**Figure 6.** The ignition temperature test curves of the studied alloys (a) AZ80, (b) AZX801, (c) AZX802 and ignition temperatures of all alloys (d). The sample is heated in a small electric resistance furnace with a corundum crucible at a rate of 5 °C/min from room temperature.

3.3. Multi-Stage Oxidation Behavior

Figure 7 gives the weight gain data and surface morphologies with different oxidation times of AZ80, AZX801, and AZX802 alloys during multi-stage oxidation. Figure 7 shows the whole oxidation process of each alloy, including two oxidation stages. The first stage considered to be the initial parabolic stage means an incubation period during oxidation [25–27], within which the compact and uniform oxide film formed on the sample surface could offer enough protection for the matrix alloy at low temperature. On the contrary, the second stage shows an accelerated oxidation, which indicates the fracture of the oxide film at high temperature as shown in Figure 7, and implies the linear oxidation kinetics [31,32]. However, the incubation periods of different alloys are variant during multi-stage oxidation. The incubation period of AZ80 is 1100 min, meanwhile the weight gain is 0.142 mg/cm². After that, the accelerated oxidation stage begins at about 420 °C and the oxidation rate increases with elevated temperature. Finally, AZ80 alloy burns when oxidized at 550 °C, because the ignition point is 556 °C, as shown in Figure 6a,d. The incubation period of AZX801 is 1360 min and the weight gain is 0.097 mg/cm². After that, the AZ80 accelerated oxidation stage begins at a temperature of about 460 °C and oxidation accelerates with increases of temperature. Finally, even oxidized at 550 °C for 3 h,
AZX801 do not ignite because the ignition temperature is 667 °C, as exhibited in Figure 6b,d, and also the overall weight gain of AZX801 is 2.772 mg/cm². The incubation period of AZX802 is 1500 min, and the weight gain of AZX802 is 0.058 mg/cm², correspondingly. After that, the AZ80 and AZX801 accelerated oxidation stages of the AZX802 alloy begin at a temperature of about 510 °C, while the oxidation rate is lowest compared with AZ80 and AZX801. In the end, even oxidized at 550 °C for 3 h, AZX802 does not ignite because the ignition temperature is 769 °C, as is given in Figure 6c,d, and the overall weight gain of AZX802 is just 0.312 mg/cm².

Furthermore, Figure 8b–d exhibits the surface morphologies of AZ80, AZX801, and AZX802, respectively, after multi-stage oxidation. From the surface morphologies in Figure 8c,d, we can intuitively see that AZX801 alloy is massively oxidized compared with AZX802. Large-scale oxide nodules scatter on the surface of AZX801, while oxide nodules on the surface of AZX802 are smaller and fewer. The interesting thing is that the appearance of oxide nodule is accompanied by the beginning of accelerated oxidation as show in Figure 7, meaning accelerated oxidation is accompanied by a growth of the oxide nodule. The weight gain curve and surface morphology, after multi-stage oxidation, indicate that the addition of calcium can enhance the oxidation resistance of AZ80 remarkably, and increased Ca improves the oxidation resistance. Figure 9 presents the surface microscopic images of AZX801 and AZX802 after multi-stage oxidation. The surface of AZX801 is rough and inhomogeneous with lots of oxide ridges observed from Figure 9a,b, and some dark positions and porous scatter on the oxide layer as seen from Figure 9c. While the surface of AZX802 is smooth and homogeneous with just a few oxide particles, the grain boundary can even be seen clearly in Figure 9e. Because the Ca content of AZX801 is just 0.8 wt.% and the majority of Ca exiting in Al₂Ca couldn’t diffuse out from matrix at high temperature, the Ca reaction with oxygen is inhibited. The CaO/MgO composite layer formed in the surface is not densified enough for substrate protection [26]. Micro-cracks are generated after oxidation due to the different coefficient of thermal expansion of MgO, CaO, and Mg matrix [26,33,34]. The cracks act as channels for penetration of oxygen, and therefore, the substrate is continuously oxidized during multi-stage oxidation. The result in Figure 9 also indicates that increasing Ca content can improve the oxidation resistance of AZ80, even at remarkably high temperatures. Combined with microstructures of alloys, the improved oxidation resistance of alloys can also be attributed to the formation and increase of Al₂Ca in matrix with Ca addition. The melting temperature of Al₂Ca is 1079 °C as seen from the phase diagram of Al-Ca, which is thermostable and cannot dissolve into a α-Mg matrix during homogenization treatment [24]. So the presence of Al₂Ca in α-Mg matrix with Ca addition in AZ80 increases the ignition point of alloy and protects AZ80 from long-term oxidation.

**Figure 7.** The weight gain curves and surface morphologies of AZ80, AZX801 and AZX802 alloys during multi-stage oxidation. The weight gain curves show all oxidation process with two oxidation stages: (i) the initial parabolic stage, and (ii) an accelerated oxidation stage. The first stage is considered to be an incubation period.
stages: (i) the initial parabolic stage, and (ii) an accelerated oxidation stage. The first stage is considered to be an incubation period.

Figure 8. The size (a) of sample for test, and macroscopic images of alloys after multi-stage oxidation in air: (b) AZ80-ignited, (c) AZX801, (d) AZX802. The macroscopic images of alloys after oxidized indicate that the addition of Ca can improve oxidation resistance of AZ80 remarkably and the more Ca content the better oxidation resistance.

Figure 9. The surface microscopic images of alloys after multi-stage oxidation in air: (a)-3D, (b)-3D and (c) of AZX801; (d)-3D, (e)-3D and (f) of AZX802. The surface of AZX801 after oxidation is rough and inhomogeneous with some porous and dark positions scattered on. While the surface of AZX802 after oxidation is smooth and homogeneous just with few oxide particles which the grain boundary can even be seen.

3.4. DSC Analysis

The oxidation of magnesium alloys at high temperature is always accompanied by a transformation of microstructure or even the partial melting of matrix alloys [30]. Figure 10 displays the differential scanning calorimeter (DSC) curves for AZ80, AZX801, and AZX802. The beginning point of the DSC valley means melting in the secondary phase [35]. Figure 10 shows the onset melting...
temperature of the secondary phase in AZ80 is 428 °C, approximating to 437 °C for the melting temperature of β-Mg17Al12. The onset melting of the secondary phase in AZX801 and AZX802 are 471 °C and 510 °C, respectively. Thus, the addition of Ca can remarkably increase the onset melting of the secondary phase in AZ80. In addition, the onset melting temperatures of the secondary phases in AZ80, AZX801, and AZX802, as presented in Figure 10, consist in the beginning of the accelerated oxidation temperatures shown in Figure 7. Furthermore, the melting in the second phase causes local high Mg vapor, and cracks are generated in the oxide at certain regions. Mg vapor can easily diffuse out of the substrate through the crack, making oxidation of the substrate continue at high oxidation temperature out of the substrate through the crack, making oxidation of the substrate continue at high oxidation temperature.

**Figure 10.** DSC analysis of AZ80, AZX801 and AZX802 at a heating rate of 10 °C/min. The onset point of the DSC valley represents the melting of the eutectic micro-constituent and the area of the valley represents the total heat absorbed to melt the eutectic micro-constituent.

**Figure 11.** The schematic representation of the evolution of alloy oxidation. A hypothesis for the evolution of alloy oxidation is schematically depicted in Figure 11.
4. Conclusions

(1) With the increase of Ca content in AZ80, the divorced eutectic $\beta$-Mg$_{17}$Al$_{12}$ and $\alpha$-Mg + $\beta$-Mg$_{17}$Al$_{12}$ intermetallics, in a lamellar eutectic micro-constituent, are replaced by a chain-shaped phase and network structure, considered as a $\beta$-Mg$_{17}$Al$_{12}$ + Al$_2$Ca eutectic micro-constituent scattering in a $\alpha$-Mg matrix. After multi-stage oxidation in air, the chain-shaped phase and network structure are fragmented and replaced by Al$_2$Ca of spherical and rod-like structures.

(2) The addition of Ca in AZ80 can remarkably improve ignition point and oxidation resistance by increasing the melting temperature of the secondary phase due to the formation and increase of Al$_2$Ca in alloys.

(3) The incubation periods and beginning of the accelerated oxidation temperatures of AZ80, AZX801, and AZX802 are different during multi-stage oxidation, thus contributing to the different onset melting temperature of the secondary phase. The beginning of the accelerated oxidation of Mg alloys at high temperature is always accompanied by the onset melting of the low melting temperature of the secondary phase and growth of oxide nodule on surface.

Author Contributions: C.C. and Q.L. (Qing Lan) conceived and designed the experiments; A.W. performed the experiments; Q.L. (Qichi Le) analyzed the data; F.Y. and X.L. wrote the paper. All authors have discussed the results, read and approved the final manuscript.

Funding: This work described in this paper was supported by the National Key Research and Development Program of China (2016YFB0301104) and Nation Natural Science Foundation of China (51771043).

Acknowledgments: The authors are grateful to the National Key Research and Development Program of China (2016YFB0301104) and Nation Natural Science Foundation of China (51771043).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Song, G.L.; Atrens, A. Corrosion mechanisms of magnesium alloys. *Adv. Eng. Mater.* 1999, 1, 11–33. [CrossRef]

2. Jafari, H.; Idris, M.H.; Ourdjini, A.; Payganeh, G. Effect of thermomechanical treatment on microstructure and hardness behavior of AZ63 magnesium alloy. *Acta Metall. Sin. Engl. Lett.* 2009, 22, 401–407. [CrossRef]

3. Wei, Y.; Hou, L.; Yang, L.; Xu, B.M.; Kozuka, M.; Ichinose, H. Mechanical properties of die casting components with various thicknesses made of AZ91D alloy. *J. Mater. Process. Technol.* 2009, 209, 3278–3284. [CrossRef]

4. Prasad, A.; Shi, Z.; Atrens, A. Influence of Al and Y on the ignition and flammability of Mg alloys. *Corros. Sci.* 2012, 55, 153–163. [CrossRef]

5. Micro, P.; Jan, T.; Filippo, B. Mg and its alloys for biomedical applications: Exploring corrosion and its interplay with mechanical failure. *Metals* 2017, 7, 252.

6. Aydin, D.S.; Bayindir, Z.; Hoseini, M.; Pekguleryuz, M.O. The high temperature oxidation and ignition behavior of Mg-Nd alloys. Part I: The oxidation of dilute alloys. *J. Alloys Compd.* 2013, 569, 35–44. [CrossRef]

7. Zhao, S.; Zhou, H.; Zhou, T.; Zhang, Z.; Lin, P.; Ren, L. The oxidation resistance and ignition temperature of AZ31 magnesium alloy with additions of La$_2$O$_3$ and La. *Corros. Sci.* 2013, 67, 75–81. [CrossRef]

8. Aydin, D.S.; Bayindir, Z.; Pekguleryuz, M.O. The high temperature oxidation behavior of Mg-Nd alloys. Part II: The effect of the two-phase microstructure on the on-set of oxidation and oxide morphology. *J. Alloys Compd.* 2014, 584, 558–565. [CrossRef]

9. Ravi Kumar, N.V.; Blandin, J.J.; Suéry, M.; Grosjean, E. Effect of alloying elements on the ignition resistance of magnesium alloys. *Scr. Mater.* 2003, 49, 225–230. [CrossRef]

10. Felu, S.; Samaniego, A.; Barranco, V.; El-Hadad, A.A.; Llorente, I.; Serra, C.; Galván, J.C. A study on the relationships between corrosion properties and chemistry of thermally oxidized surface films formed on polished commercial magnesium alloys AZ31 and AZ61. *Appl. Surf. Sci.* 2014, 295, 219–230. [CrossRef]

11. Gobara, M.; Shamekh, M.; Akid, R. Improving the corrosion resistance of AZ91D magnesium alloy through reinforcement with titanium carbides and borides. *J. Magn. Alloys* 2015, 3, 112–120. [CrossRef]

12. Mirak, A.R.; Davidson, C.J.; Taylor, J.A. Characterization of fresh surface films formed on molten Mg-Nd alloy protected by different atmospheres. *Appl. Surf. Sci.* 2014, 301, 91–98. [CrossRef]
13. Kim, Y.M.; Yim, C.D.; Kim, H.S.; You, B.S. Key factor influencing the ignition resistance of magnesium alloys at elevated temperatures. *Scr. Mater.* 2011, 65, 958–961. [CrossRef]

14. Li, W.; Zhou, H.; Zhou, W.; Li, W.P.; Wang, M.X. Effect of cooling rate on ignition point of AZ91D-0.98 wt.% Ce magnesium alloy. *Mater. Lett.* 2007, 61, 2772–2774. [CrossRef]

15. Czerwinski, F. Controlling the ignition and flammability of magnesium for aerospace applications. *Corros. Sci.* 2014, 86, 1–16. [CrossRef]

16. Lee, D.B. High temperature oxidation of AZ31+0.3 wt.% Ca and AZ31+0.3 wt.% CaO magnesium alloys. *Corros. Sci.* 2013, 65, 958–961. [CrossRef]

17. Tekumalla, S.; Gupta, M. An insight into ignition factors and mechanisms of magnesium based materials: A review. *Mater. Des.* 2017, 113, 84–98. [CrossRef]

18. Fan, J.F.; Yang, C.L.; Han, G.; Fang, S.; Yang, W.D.; Xu, B.S. Oxidation behavior of ignition-proof magnesium alloys with rare earth addition. *J. Alloys Compd.* 2011, 509, 2137–2142. [CrossRef]

19. Liu, C.; Lu, S.; Fu, Y.; Zhang, H. Flammability and the oxidation kinetics of the magnesium alloys AZ31, WE43, and ZE10. *Corros. Sci.* 2015, 100, 177–185. [CrossRef]

20. Allameh, S.H.; Emamy, M.; Maleki, E.; Pourbahari, B. Effect of microstructural refinement on tensile properties of AZ80 magnesium alloy via Ca addition and extrusion process. *Proc. Cells Mater. Sci.* 2015, 11, 89–94. [CrossRef]

21. Min, X.G.; Du, W.W.; Xue, F.; Sun, Y.S. Analysis of EET on Ca increasing the melting point of Mg17Al12 phase. *Chin. Sci. Bull.* 2002, 47, 1082–1086. [CrossRef]

22. Liang, S.M.; Chen, R.S.; Blandin, J.J.; Suery, M.; Han, E.H. Thermal analysis and solidification pathways of Mg–Al–Ca system alloys. *Mater. Des.* 2008, 39, 1225–1235. [CrossRef]

23. Suzuki, A.; Saddock, N.D.; Jones, J.W.; Pollock, T.M. Solidification paths and eutectic intermetallic phases in Mg–Al–Ca ternary alloys. *Acta Mater.* 2005, 53, 2823–2834. [CrossRef]

24. Wang, Z.J.; Xu, Y.; Zhu, J.; Li, S.L. Effect of homogenizing heat treatment on microstructure and hardness of AZ80–2.0Ca magnesium alloy. *Spec. Cast. Nonferrous Alloys* 2012, 32, 500–504.

25. Czerwinski, F. The reactive element effect on high-temperature oxidation of magnesium. *Int. Mater. Rev.* 2015, 60, 264–296. [CrossRef]

26. Sakamoto, M.; Akiyama, S.; Ogi, K. Suppression of ignition and burning of molten Mg alloys by Ca bearing stable oxide film. *J. Mater. Sci. Lett.* 1997, 16, 1048–1050. [CrossRef]