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OXIDATION AND CORROSION BEHAVIOR OF NON-FLAMMABLE MAGNESIUM ALLOYS CONTAINING Ca AND Y

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Abstract

The combined addition of calcium and yttrium lead to significant increase in non-flammability and tensile properties, compared to conventional Ca-containing magnesium alloys. It means that we can reduce the amount of calcium addition to get certain amount of non-flammability in the alloys containing both calcium and yttrium together. Because the addition of calcium only can increase the ignition temperature but decrease the tensile properties, it should be minimize not to decrease the tensile properties. Corrosion behavior of calcium and yttrium containing alloys were also investigated systematically, and show that they have better corrosion resistance than the any other commercial alloys or calcium containing alloys. Detailed study on the corrosion behavior confirms that there are optimum amount of calcium and yttrium addition to get best corrosion resistance, and corrosion behavior of these alloys are quite different with other alloys.

Introduction

Magnesium alloys have many advantages, such as low density, high specific strength, good machinability and formability, good damping ability and easy recycling, therfore they have good prospects of applications in the fields of automobile, aerospace, electronics industry, etc.

However, the usage of magnesium alloys is still restricted due to their limited workability, formability, high reactivity (poor ignition/ corrosion resistance). Current technical issues in Mg alloys research are focused on how to solve the following problems [1-3]; low strength, poor formability, high cost, dilemma in use of rare earth elements, high reactivity, and poor chemical properties. Although many successful results in improving strength and formability and reducing production cost have been given so far, the control of fundamental nature of magnesium such as ignition and corrosion still remains unsolved. In order to meet strengthening demands for the use of magnesium alloys in addition to the social issues including environmental problem, the dramatic improvement in their safety and reliability as well as mechanical properties should be secured.

Magnesium and its alloys are very active, especially in a molten state, and are rapidly ignited or combusted when the clean surface of the melt comes into contact with oxygen in air. Flux or a cover gas has to be used to prevent ignition of magnesium alloys during melting. However, the above methods may cause many problems such as global warming and increased production costs, so many researchers are paying more attention to finding more essential methods to improve ignition resistance. Obviously, it is simple to prevent the ignition of magnesium alloys by the addition of alloying elements. However, it is difficult to select suitable elements, because only some of alloying elements have been proved to benefit the oxidation resistance of magnesium alloys [4-8].

Calcium is one of the promising elements that can improve ignition resistance. The ignition temperature increases by 250 K after an addition of 3 wt.% Ca- added into pure magnesium [9]. You et al. [10] investigated the oxidation behavior of a Mg-xCa alloy (x=0-3 wt.%), and they confirmed that a dense and compact protective MgO/CaO layer formed at elevated temperatures. However, a large amount of calcium addition generally lowers tensile strength and ductility because coarse Ca-compounds precipitate along the grain boundaries. Unfortunately, most of such studies have concentrated on either ignition resistance or tensile properties of magnesium alloys, but there has been no attempt to improve both them.

In fact, increasing both ignition temperature and tensile properties is difficult to achieve because of their contradictory aspects; that is, a large addition amount of ignition resistance improving alloying element is necessary to make ignition-proof magnesium alloys [5, 10-11], but at the same time it causes the deterioration of tensile properties due to the formation of coarse brittle phases. Fig. 1 clearly shows that more than 1wt.% Ca addition to AZ31 and AZ61 alloys can increase ignition temperature but at the same time deteriorate tensile properties, especially elongation. This indicates that instead of a large amount of a single alloying element, the combined addition of two or more alloying elements may suppress the formation of a large fraction of coarse brittle phase without sacrificing ignition resistance.

In this work, we therefore developed new non-flammable Mg alloys with both excellent mechanical properties and ignition/corrosion resistance. The effect of alloying elements on those properties of magnesium alloys was investigated, and the field application of newly-developed alloys was also performed in this work.

Experimental procedures

Several kinds of Mg-Al based alloys containing Ca and Y were prepared according to the nominal composition by pure magnesium (99.93 wt.%), pure aluminum (99.9 wt.%), pure zinc (99.9 wt.%), pure calcium (99.9 wt.%) and pure yttrium (99.9 wt.%) in an electric furnace using a low-carbon steel crucible heated to 720°C under a protecting gas (10% SF_6 and 90% CO_2). The melt was poured into a permanent mold preheated to 200°C and then cooled to ambient temperature in air atmosphere. The cast ingots were subsequently heated to 400°C for homogenization treatment and kept at this temperature for 20 hours. The ingots were hot-rolled at 400°C at a reduction rate of 30%/pass with a total reduction of 93%. The rolled sheets with a 1

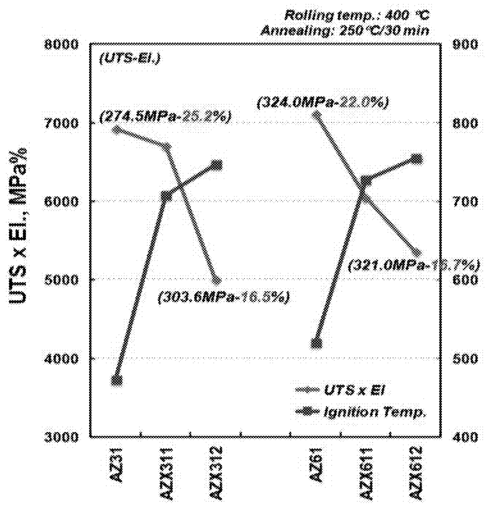

Fig. 1. Ignition temperature vs. mechanical properties. They are inversely related.

mm thickness were finally annealed at 250°C for 30 minutes. Ignition tests were carried out by inserting the chipped samples taken from the castings into a tube furnace held at 1000°C. The tests were carried out in air and at least five chipped samples were used. The ignition temperatures were determined as ones associated with both the appearance of flame and a significant temperature increase. Metallographic samples were prepared for microstructure observation according to a standard procedure. The distribution of alloying elements in the surface oxide layer that was formed on the melt was checked using an EPMA (electron probe micro-analyzer). Tensile tests were carried out using an Instron-4206 universal testing machine at a strain rate of 0.001/s at room temperature. Sheet-type tensile specimens with the dimensions of the ASTM E 8M standard were used. All the tensile specimens were taken in parallel to a longitudinal direction of the rolled sheet.

Results and discussion

Non-Flammability

Fig. 2 shows the change in ignition temperature of AZ-series alloy with an increase in Ca content or total amount of Ca and Y. It is found that larger amount of Al can increase ignition resistance of magnesium alloys; for instance, AZ91 alloys have higher ignition temperature than AZ31 regardless of whether Y is involved. In Fig. 2, the combined addition of Ca and Y to AZ-series alloys results in much higher ignition temperature than the only Ca addition. In addition, total amount of Ca and Y in AZ31 alloy can be reduced from 2.2wt.%Ca to 1.5wt.%(Ca+Y) for the target temperature of 750□C. In the case of AZ61 alloy, the required amount of Ca or Ca+Y for the target temperature of 750°C can be reduced from 1.7wt.%Ca to 1.1wt.%(Ca+Y). It indicates that the combined addition of Ca and Y has a very attractive synergistic effect on the ignition resistance, compared to the individual addition of those elements.

The reason why the small amount of Ca and Y can considerably increase ignition resistance of magnesium alloy is explained by oxide structure formed on the surface of melt. Fig. 3 clearly shows that the surface oxide of the AZX611-0.6Y sample held at 670°C for 10 minutes consists of two distinctive layers; dense and protective oxide layer that contains Ca and Y elements on the surface contacting with a Mg alloy melt in addition to an outer oxide layer that contains Mg, Al, and Ca elements. According to thermodynamic calculation, the following reactions can take place during the isothermal holding at 670°C:

Inner layer: $Ca + 2Y + 2O_2 \rightarrow CaO + Y_2O_3$
(ΔG = -2,155,620 J) (1)

Outer layer: $3Mg + 6Al + 3Ca + 15/2O_2 \rightarrow MgO + MgAl_2O_4 + Ca_3MgAl_4O_{10}$ (ΔG = -7,341,983 J). (2)

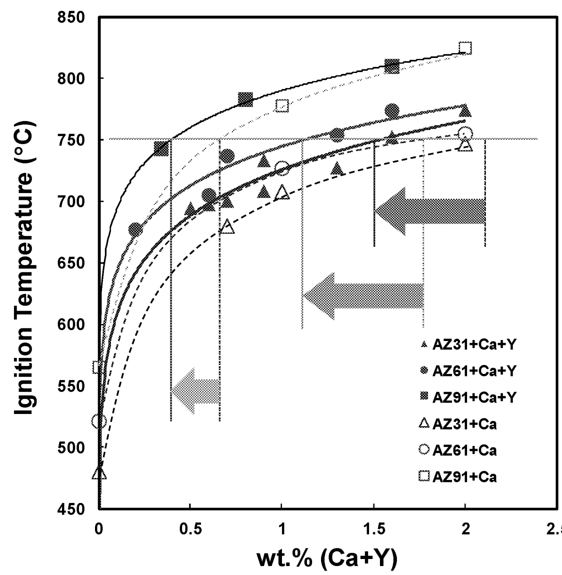

Fig. 2. Change in ignition temperature with the amount of Ca and Y (wt.%). Total addition amount of Ca and Y required to meet the target ignition temperature of 750°C is largely reduced, compared to the only Ca-added Mg alloys.

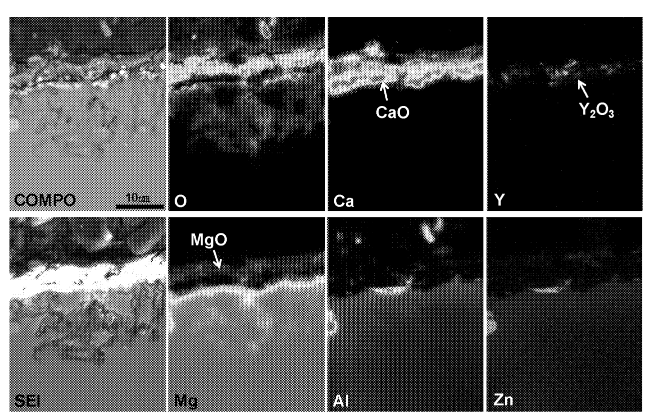

Fig. 3. EPMA result showing the surface oxide layer of the AZX611Y alloy held at 670°C for 10 min.

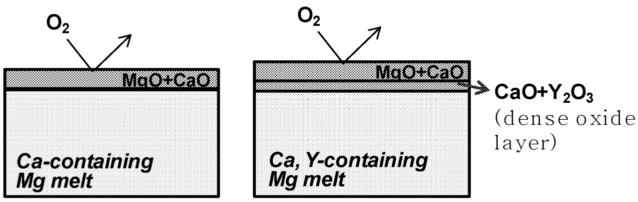

Fig. 4. Schematic illustration of the oxide structures of Ca-added and Ca and Y-added Mg alloys.

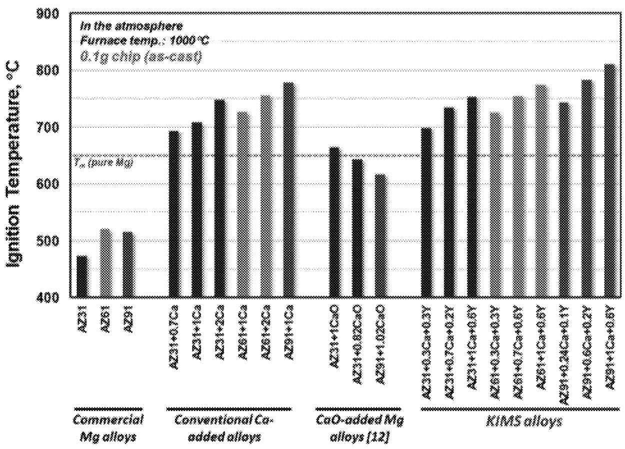

Fig. 5. Comparison of non-flammability between newly-developed non-flammable Mg alloys and conventional Mg alloys.

As the change in Gibbs energy of the reactions (1) and (2) is negative, an additional layer composed of CaO and Y_2O_3 can be formed on the surface of the Ca and Y-added magnesium alloys at 750°C. This duplex layered oxide structure can effectively prevent oxygen penetration into a melt as shown in Fig. 4 and finally increase ignition resistance of the magnesium alloys.

Fig. 5 shows the comparison of non-flammability of Ca and Y-added Mg alloys with commercial alloys and conventional Ca/CaO-added alloys. In this work, ignition tests were carried out by inserting the chipped samples taken from the castings into a tube furnace held at 1000°C. At least five chipped samples were used and the ignition temperatures were determined as ones associated with both the appearance of flame and a significant temperature increase. In Fig. 5, while the ignition temperatures of commercial AZ-series alloys are around 500°C, those of conventional non-flammable alloys with more than 1wt.% Ca are higher than 700°C. In the case of CaO addition, the ignition temperature of 0.82wt.%CaO-added AZ31 alloy is 642°C [12] and much lower than that of 0.7wt.%Ca-added AZ31 alloy (693□C). On the other hand, the ignition temperatures of the Ca and Y-added Mg alloys newly-developed alloys in this work are higher than 700°C and show better non-flammability than the Ca-added alloys even though only small amount of Ca and Y.

Based on the above results, it is obvious that the newly-developed Mg alloys with Ca and Y addition have much better ignition resistance than conventional Ca/CaO-added Mg alloys.

Tensile Properties

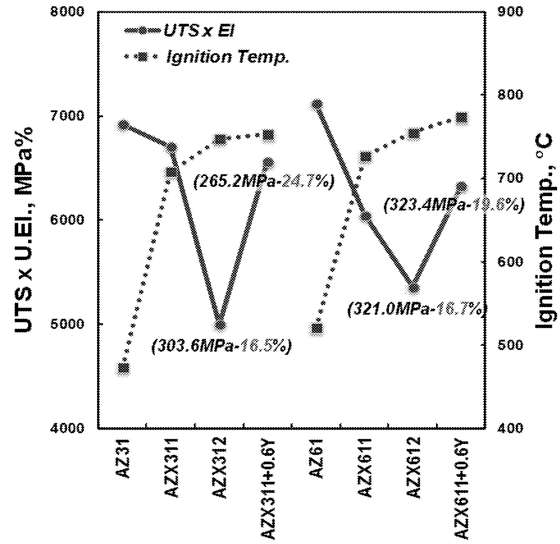

Fig. 6. The changes in ignition temperature and tensile properties with additions of Ca and Y. The combined addition of Ca and Y restored tensile properties with increasing ignition temperature.

The tensile properties of the hot-rolled sheets are shown in Fig. 6. As mentioned above, as Ca content increases from 1 wt.% to 2 wt.%, both yield and tensile strengths increase, but at the same time elongation greatly decreases due to a large amount of brittle Ca-containing phases [13,14]. Such a deterioration of elongation can be restored by reducing the calcium content and adding a small amount of yttrium. In Fig. 6, the elongations of the AZX311-0.6Y and AZX611-0.6Y alloys are 24.7% and 19.6%, respectively, which are similar to those of the AZX311 and AZX611 alloys. Furthermore, the ignition temperatures of the AZX311-0.6Y and AZX611-0.6Y alloys are higher than those of the AZX312 and AZX612 alloys, respectively. As an increase in elongation commonly gives rise to a decrease in strength, the multiplied values of ultimate tensile strength by uniform elongation are better to represent the overall tensile properties of the samples. In Fig. 6, the values significantly decreased in 2 wt.% Ca-added magnesium alloys, but they were restored to those of 1 wt.% Ca-added magnesium alloys by the combined addition of calcium and yttrium. The reduced amount of brittle and coarse Ca-containing phases is attributed to the improvement in tensile properties of those alloys.

Corrosion Resistance

Immersion test in 3.5% NaCl solution was carried out. Fig. 7 shows the surface of AZ31 and Ca and Y-added AZ31 alloys with different amount of Ca after immersion test for 1110 minutes. Compared to the AZ31 alloy of which surface were corroded excessively, the surfaces of AZ31-0.4Ca-0.3Y and AZ31-0.7Ca-0.3Y alloys were not quite corroded. As Ca content increases, the extent of corrosion on the surface becomes severe, and reaches a serious level at more than 1wt.%Ca. This is because the AZ31 alloys with more than 1wt.% Ca have coarse $(Mg,Al)_2Ca$ phase on grain boundary [14,15]. It indicates that Ca content in AZ31 alloys should be controlled less than 1wt.%, and thus the addition of small amount of Y is essential to improve corrosion resistance as well as ignition resistance.

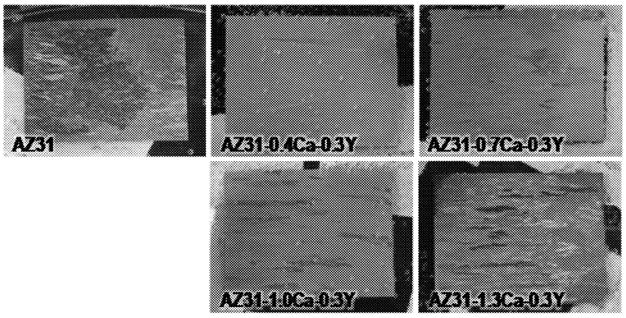

Fig. 7. Change in the surface of AZ31 and Ca, Y-added AZ31 with different amount of Ca after immersion test in 3.5% NaCl solution for 1110 min.

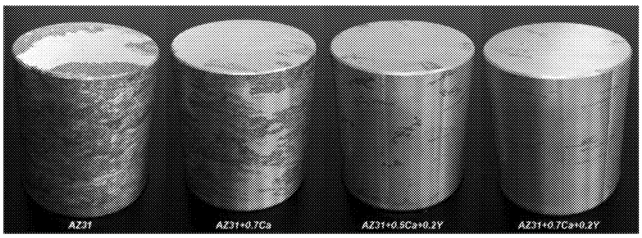

Fig. 8. Immersion test results of bulk samples. The Ca and Y-added alloys have much better corrosion resistance than the only Ca-added alloy.

Fig. 8 shows the immersion test results of bulk cast samples. It is obvious that the addition of Ca itself can improve corrosion resistance of AZ31 alloy, but the combined addition of small amount of Ca and Y can improve corrosion resistance much better than only Ca-added alloys.

Ignition Temperature - Tensile Properties

Fig. 9 shows the non-flammability and tensile properties of newly-developed Mg alloys for wrought applications. As mentioned above, conventional alloys including AZ31, AZ61, and ZK60 have poor ignition resistance, even though they have excellent mechanical properties. On the other hand, conventional Ca-added non-flammability Mg alloys have excellent ignition resistance, but their tensile properties are quite low. It implies that tensile properties and non-flammability are basically contrary to each other. However, the newly-developed non-flammable Mg alloys have both excellent tensile properties and ignition resistance as shown in Fig. 9. The reduction of volume fraction of brittle eutectic phase deteriorating elongation and the formation of multi-layered oxides effectively protecting oxygen penetration into Mg melt are attributed to improve both tensile properties and ignition resistance. In the cases of Mg-Zn based alloys containing Ca and Y, they have much improved tensile properties compared with those of AZXW alloys. In particular, it should be noted that Mg-4Zn-4Al-0.7Ca-0.6Y alloy has ignition temperature of higher than 750°C and tensile properties of approximately 10,000 MPa%.

Effect of Al on Non-Flammability, Tensile Properties

Fig. 10 shows the effect of aluminum on tensile properties and ignition resistance of newly-developed Mg alloys. Without Al

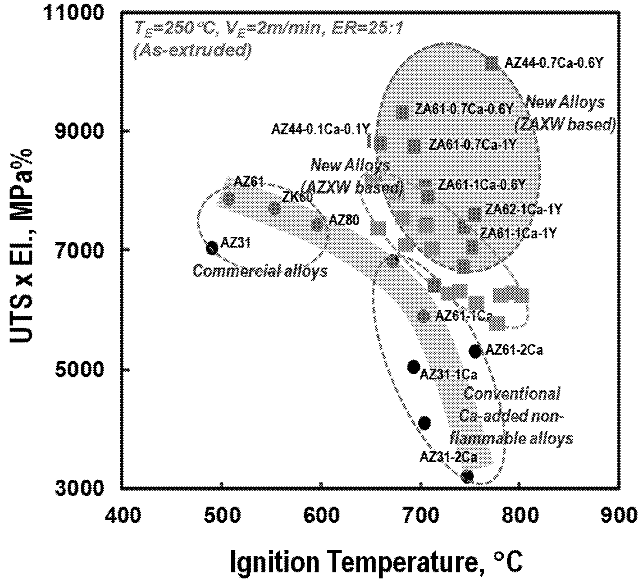

Fig. 9. Tensile properties and non-flammability of newly-developed non-flammable Mg alloys for wrought application.

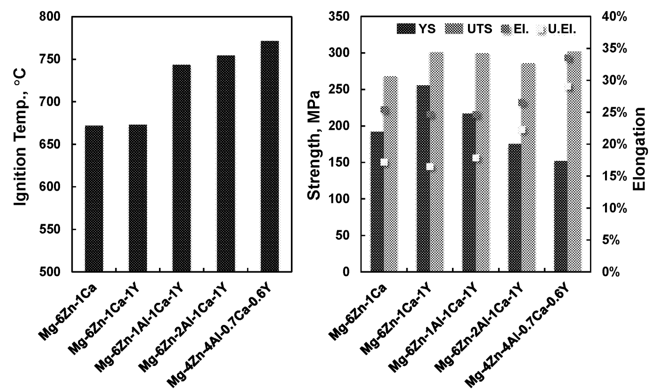

Fig. 10. The effect of Al addition on ignition temperature and tensile properties.

addition, Mg-6Zn-1Ca and Mg-6Zn-1Ca-1Y have ignition temperature of approximately 670°C. By the addition of Al, however, the ignition temperature of Mg-6Zn-1Ca-1Y-1Al alloy largely increases to 755°C. The effect of Al on ignition resistance is clearly shown in the result of EPMA analysis, where multi-layered oxide structure consisting of CaO, Y_2O_3, and $MgAl_2O_4$ formed on the surface of ZAXW6211 alloy melt (Fig. 11). In addition, Al can affect tensile properties: in Fig. 10, the addition of 1wt.% Al to ZXW611 alloy decreases yield strength but increase uniform elongation. More Al content in ZXW alloy results in lower yield strength and better uniform elongation, but does not change ultimate tensile strength.

Conclusions

- Calcium and yttrium addition can improve tensile properties, non-flammability, and corrosion resistance at the same time.
- The addition of Al in conjunction with calcium and yttrium leads to the formation of multi-layered oxide structure on

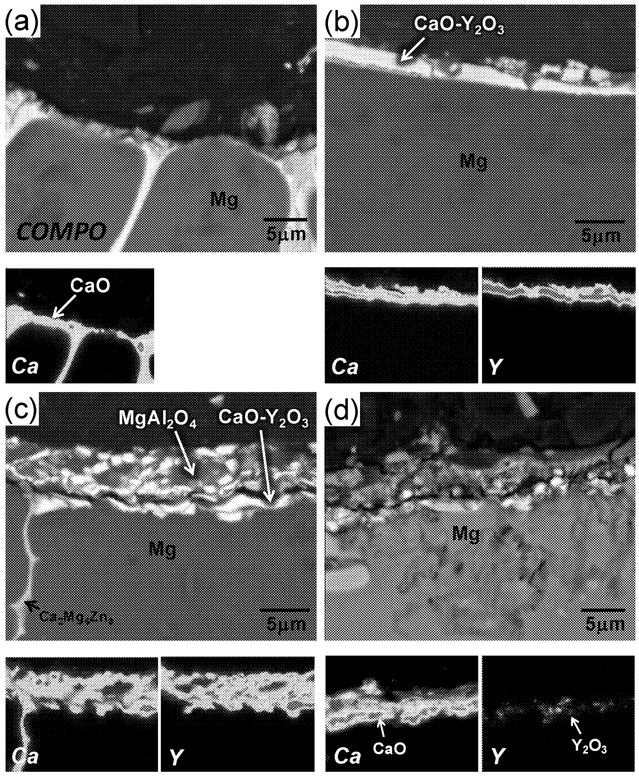

Fig. 13. EPMA results showing the effect of alloying elements on the structure of oxides formed on the surface of Mg melt: (a) ZX61, (b) ZXW611, (c) ZAXW6211, (d) AZXW6110

the surface, resulting in maximizing the efficiency of Ca and Y addition.

- Newly-developed non-flammable Mg alloys have high safety and reliability and don't need to use harmful SF_6 gas during melting, hot-working, and machining. Although the addition of only small amount of calcium and yttrium may increase material cost a little, it can provide better performance and safety and protect environment so that magnesium alloys can be used in wider variety of application areas with confidence.

Acknowledgements

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