Article ID: 1003-6326(2003)06-1260-05

Purification technology of AZ91 magnesium alloy wastes①

WU Guo-hua(吴国华)[1], XIE Min(谢　敏)[2], ZHAI Chun-quan(翟春泉)[1],
ZENG Xiao-qin(曾小勤)[1], ZHU Yan-ping(朱燕萍)[1], DING Wen-jiang(丁文江)[1]
(1. State Key Laboratory of Metal Matrix Composites,
Shanghai Jiaotong University, Shanghai 200030, China;
2. School of Adult Education, Shanghai Jiaotong University, Shanghai 200030, China)

Abstract: The effects of different purification processes on the mechanical properties, structure and fracture pattern of AZ91 magnesium alloy wastes were studied. The results show that the inclusions in the Mg melt can be removed effectively by the treatment of the fluxes with MgO foam ceramic filter. Therefore, the properties of magnesium alloy wastes can be improved substantially. Tensile strength and elongation of the magnesium alloy wastes after purification treatment can reach 194.6 MPa and 5.12% respectively, which are comparable to the mechanical properties of AZ91 fresh stuff. The metallographic analysis results show that the purification treatment has not obvious effect on metallurgical structure. The fracture mechanism of AZ91 is not changed, and its fractures are still quasi-cleavage crack. It is discovered that for AZ91 magnesium alloy, the fluxes containing TiO_2 can decrease the Fe content of magnesium alloy wastes to below 0.0056%. The results also show that TiO_2 is helpful for the precipitation of γ phase in granular or small island shape and can refine the grain size effectively.

Key words: magnesium alloy; purification; flux; structure; TiO_2

CLC number: TG 146 **Document code:** A

1 INTRODUCTION

Because magnesium alloy has the advantages of low density, high specific strength and rigidity, excellent damping effect, good tolerance to impact, excellent machinability and polishing ability[1, 2], it is widely used in the fields of automobile manufacturing, aviation and spaceflight, communication, optic instruments and computer manufacturing[3-5]. However, the yield of magnesium alloy is low in the production of die casting. At present, the utilization ratio can only be about 30%-50%. In the process of die casting, a large quantity of waste chips and leftovers are produced, which are required to be recycled as a consideration of sustained development and environment protection[6-8]. However, no effective recycling method has been found at present.

Introduction of Fe element in the course of die casting results in decrease of corrosion resistance and mechanical properties. Therefore, how to reduce the content of Fe in the magnesium alloy waste shows a great importance[9]. The aim of this paper is to seek an effective purification treatment of Mg melt to remove oxide inclusions and to eliminate the Fe element. In the meantime, the effects of purification conditions on the microstructure and properties of recycled magnesium alloy are also studied so as to improve the utilization ratio of Mg waste.

2 EXPERIMENTAL

The composition of die casting AZ91 alloy wastes used in the experiment was (mass fraction, %): Al 9.47, Zn 0.832, Mn 0.18, Be 0.00027, Fe 0.0168, Cu< 0.01, Si 0.0327, Ni 0.0032, Mg balanced. Tools, raw material and refining agents used in the experiment were heated to 200 ℃ in the stove before experiment in order to eliminate the water. 10 kg Mg waste was melted in a 7.5 kW resistance furnace, and a thermal couple was immersed in the melt directly to control the melt temperature. The melt was refined at 730-740 ℃ for 15 min. And the mixed protecting atmosphere of CO_2 and SF_6 was employed. Then, the melt was poured into a metallic mould. The castings were cut to obtain the tensile samples[10]. Tensile tests were conducted on the SHIMADZU AG-100KNA tensile test machine. Five specimens under the same condition were used and the final values of test were obtained in term of their average value. PHILIPS SEM 515 was employed to analyze the fractograph.

3 RESULTS AND ANALYSES

3.1 Inclusion removing

The experimental parameters and results are list-

① **Foundation item:** Project(00233AA1100) supported by the National Advanced Materials Committee of China
Received date: 2002-12-13; **Accepted date:** 2003-03-03
Correspondence: WU Guo-hua, PhD, Associate professor; Tel: +86-21-62932164; E-mail: ghwu@mail.sjtu.edu.cn

ed in Table 1, where RJ2 is the ordinary refinement agent for magnesium alloy, and JDMJ is a new kind of flux developed by Shanghai Jiaotong University[11].

Table 1 Experimental parameters and mechanical properties of samples

Sample No.	σ_b/ MPa	δ/ %	Experimental parameter		
			Refining agent	Filter	Pouring temperature/ ℃
1	143.4	2.27	No refining	Iron wire	720
2	165.2	2.51	3% RJ2	Iron wire	720
3	163.7	2.53	2% JDMJ	Iron wire	720
4	169.5	2.61	3% JDMJ	No filter	720
5	172.6	2.79	3% JDMJ	Iron wire	720
6	173.1	3.13	3.5% JDMJ	Iron wire	720
7	171.3	2.89	4% JDMJ	Iron wire	720
8	170.0	2.73	3% JDMJ	Iron wire	730
9	166.8	2.67	3% JDMJ	Iron wire	740
10	180.9	4.35	3% JDMJ	Foam ceramic	720

Sample 1 in Table 1 shows that the mechanical properties of Mg waste without refinement are very poor with σ_b and δ only of 143.4 MPa and 2.27% respectively. It is also discovered that the melt is difficult to fill up the mould because of its high consistency. When being treated by the conventional refining agent RJ2, σ_b and δ of sample 2 are improved to be 165.2 MPa and 2.51% respectively. Samples 3－7 represent those refined with different contents of JDMJ flux. The contents of JDMJ flux were increased from 2% to 4% step by step. It is concluded that the specimen treated by 3.5% JDMJ shows optimum mechanical properties. The mechanical properties will decrease when the content of JDMJ flux reaches 4%. Because the purification treatment of the magnesium melt can be envisioned as dynamic balance between purifying and pollution. The amount of inclusions will increase when the addition of flux surpasses a certain content.

Table 1 also shows the effect of pouring temperature on the mechanical properties with the same content of flux after iron wire filtration. It can be inferred that the mechanical properties of the alloy will decrease with the increase of pouring temperature. This may be that the oxidization and gas-absorption become more serious with the increase of temperature. Therefore, more oxidized inclusions and pores are formed to decrease the mechanical properties of the alloy.

Samples 4, 5 and 10 in Table 1 were purified by 3% JDMJ refining agent and their pouring temperatures are all 720 ℃. But their filtration conditions are different. It can be seen that the mechanical properties of Sample 10 with MgO foam ceramic filter are the best. Its σ_b and δ reach 180.9 MPa and 4.35% respectively. Fig. 1 shows morphology of MgO foam ceramic filter used in this experiment. The skeleton of dense and tiny ceramic branches forms a continuous three-dimensional structure. Its filtration mechanism is fairly complicated. At present, the dominant views related to its filtration mechanism include the following three aspects. The first factor is filtering action. That is, inclusion particles are counterchecked by tiny holes in the filter in order that the accumulation of inclusions even leads to the formation of inclusion cakes. Furthermore, the formed inclusion cakes help to hold the smaller inclusion particles in the melt. The second factor is the existence of many winding tiny tunnels in the filtration medium. Some tiny particles deposite at the corners of the passage due to fluctuation of the fluid speed. The third factor is its excellent absorption capability. This is because that the huge surface of the skeleton, which was not wetted by the metal melt, has stronger adsorption for solid tiny inclusion. But the ceramic surface can be wetted by the smelting inclusion drops, such as flux inclusion or intermetallic compounds with low melting points. This kind of filter can not only remove the solid inclusion particles with a diameter of less than 10－20 μm, but also eliminate the liquid flux inclusions to which the traditional filter are powerless.

The SEM fractograph of Sample 10 is shown

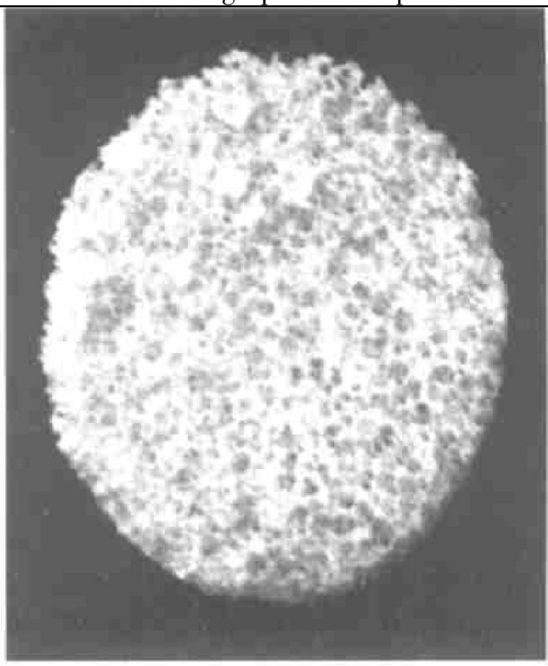

Fig. 1 Morphology of MgO foam ceramic filter

in Fig. 2. The results show that the purification treatment has no obvious effect on metallurgical structure. The fracture mechanism of AZ91 has not been changed, and the fracture type is still quasi-cleavage crack. During the tensile test, the crack track is affected by the distribution of inclusion particles, and no longer determined by the crystallography orientation. Accurately, the fracture belongs to transgranular one, which is mixed with small cleavage plane, steps or tear arrises and rivers.

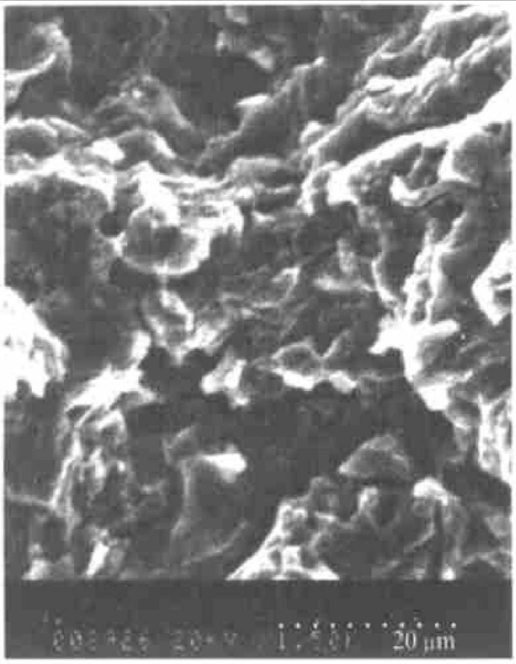

Fig. 2 SEM fractograph of Sample 10

The microstructure of unrefined AZ91 magnesium alloy scraps is shown in Fig. 3. The white matrix phase is Mg, the gray grains are γ phase ($Mg_{17}Al_{12}$), and black particles are inclusions. It shows that there exist more inclusions in the microstructure of unrefined magnesium alloys. But the microstructure of sample purified by the combination of MgO ceramic filter and JDMJ flux shows that the inclusions are reduced substantially.

3.2 Fe removing

It can be inferred from Samples 11 and 12 in Table 2 that RJ and JDMJ are invalid in Fe elimination. No difference in Fe content was observed before and after refinement. The effects of TiO_2 containing flux on the Fe content in the magnesium alloys are also revealed in Table 2. The degree of Fe elimination is improved with the increment of TiO_2 addition. The Fe contents are reduced to 0.006 9% and 0.005 6% when the contents of TiO_2 are increased to 30% and 40% respectively. Hence, the refinement with TiO_2 shows a great potential in Fe elimination. The chemical composition of alloy treated by flux agent in Table 2 are as follows (mass fraction, %): Al 9.47, Zn 0.832, Mn 0.18, Be 0.000 27, Fe 0.016 8, Cu< 0.01, Si 0.032 7, Ni 0.003 2, Ti 0.01, Mg balanced. It can be seen that alloy compositions don't change except that Fe content is decreased and Ti content is increased after refinement treatment. And the increase of Ti content is helpful for increasing the mechanical properties. The chemical composition of the molten slag of alloy treated by 70% JDMJ+ 30% TiO_2 flux agent is listed in Table 3. It is shown that the Fe content increases in the slag.

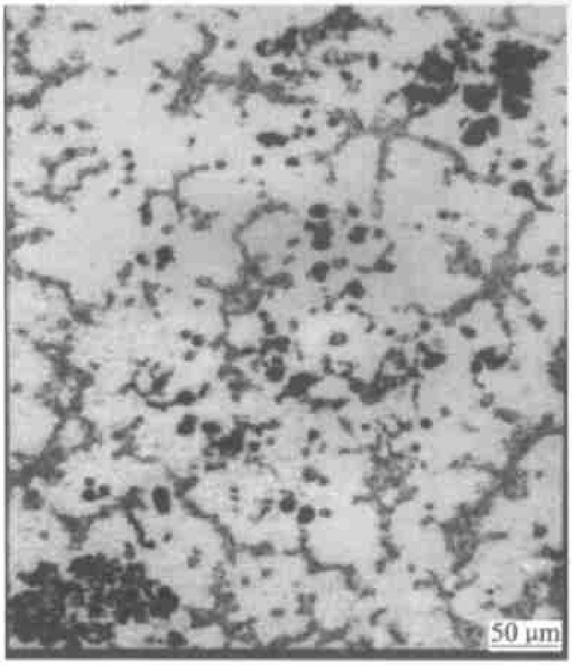

Fig. 3 Microstructure of Sample 1

The effects of TiO_2 on the mechanical properties of refined alloys are also listed in Table 2. It is

Table 2 Constituents of fluxes, Fe content and tensile properties of samples

Sample No.	Constituent of flux: w(RJ2)/%	w(JDMJ)/%	w(TiO_2)/%	w(Fe)/%	σ_b/MPa	δ/%
11	100			0.016 8	168.9	3.13
12		100		0.016 8	180.9	4.35
13		80	20	0.012 2	187.3	4.71
14		70	30	0.006 9	194.6	5.12
15		60	40	0.005 6	189.2	4.94

Table 3 Chemical composition of molten slag of alloy treated by 70% JDMJ+ 30% TiO_2 (mass fraction)

Element	Mg	Al	Zn	K	Ca
Content	88.78	5.41	0.268	4.41	0.16
Element	Na	Fe	Ni	Ti	Si
Content	0.32	0.52	0.004 5	0.032	0.099

obvious that mechanical properties were improved as a result of reduced Fe content. The σ_b and δ of recycled scraps reached 194.6 MPa and 5.12% respectively after purification by the JDMJ flux containing 30% TiO_2. That is, the mechanical properties are comparable to those of AZ91 fresh stuff. But when TiO_2 content increase to 40%, although the Fe content decreases further to 0.005 6%, the σ_b and δ of magnesium alloy decrease. This may be because that too much TiO_2 increase the inclusion content in the magnesium melt. Fig. 4 shows the microstructure of the specimen treated by refining agent containing 30% TiO_2. Continuous coarse γ phase($Mg_{17}Al_{12}$) located in the border area of grains diminishes gradually, and the distribution of γ particles in the grains becomes more even. That is, as a result of the introduction of TiO_2, granular and tiny islands of γ phase form. Due to dispersion strengthening effect, the mechanical properties are improved greatly. Therefore, the addition of TiO_2 can not only reduce Fe content in the magnesium alloys, but also refine the grains, helping to further improve mechanical properties. From the chemical compositions of the alloy, it is known that Ti content of alloy increases after refinement treatment with TiO_2 containing flux.

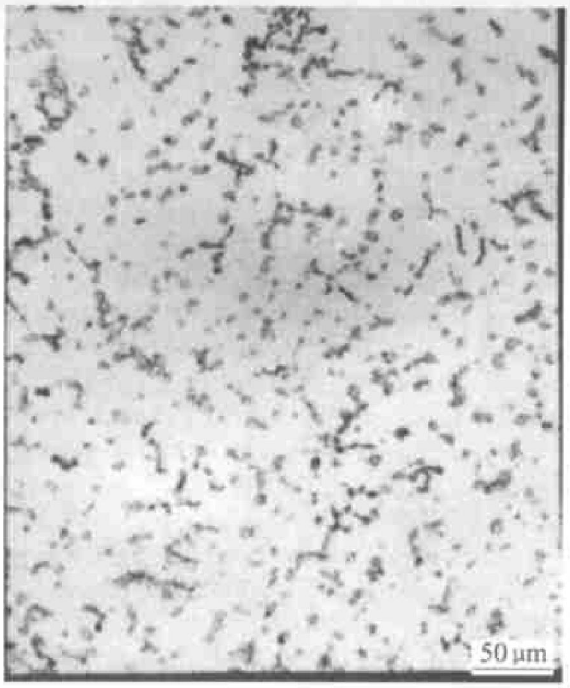

Fig. 4 Microstructure of Sample 14

4 DISCUSSION

It can be concluded from the above experimental results that JDMJ agent is superior to RJ2. JDMJ is mainly composed of $MgCl_2$, NaCl and KCl, and Table 4 lists a series of characteristics of this system. Their initial melting points are all below those of magnesium alloys. As a result, the melt can get effective protection throughout the whole refining process. Other kinds of salts are added to JDMJ in order to adjust the flux density, consistency and the slaggability, such as CaF_2, MgO and $BaCl_2$. Especially, a kind of special inorganic compound is added to the flux to blister the flux in order to increase its specific surface area greatly. Therefore, the absorption ability of flux for oxidization inclusions is improved. In addition, the gasses discharged by the flux help to remove the dissolved gas in the melt, resulting in further improvement of refining ability. The above factors explained the excellent refining ability of JDMJ agent.

One of the conventional techniques for eliminating the inclusions in the casting production of magnesium alloys is to install a filter at a proper site of the gate system. Porous iron disc, steel wool and multi-layer steel mesh are often used as filtering medium. The major defect of these mediums is that the absorptivity of the medium surface for inclusions is very poor. This makes it difficult to eliminate the tiny particles whose diameters are less than 20 μm, and let alone to clear the liquid melting flux drops. Therefore, these mediums are difficult to be used in the production of high quality cast parts.

Foam ceramic filter is a kind of highly efficient filtering medium for alloy melt developed recently. As a filtering material of melt, an excellent elevated temperature property is essential. That is, it not only meets the requirement of a good tolerance to the thermal shock and the mechanical impact of high temperature melt, but also has chemical stability under high temperature, and does not react with alloy elements. Within recent ten years, a variety of ceramic mediums have been developed abroad according to the different properties of the alloys. These ceramic mediums have been exten-

Table 4 Melting point and compositions of $MgCl_2$-NaCl-KCl ternary system

Melting point/ ℃	Eutectic composition			Composition of solid phase
	$x(MgCl_2)$/%	x(NaCl)/%	x(KCl)/%	
400	35	18	47	$KCl\cdot MgCl_2$, NaCl, $2KCl\cdot MgCl_2$
395	46	32	22	$KCl\cdot MgCl_2$, $NaCl\cdot 2MgCl_2$, $2NaCl\cdot MgCl_2$
400	39	36	25	$KCl\cdot MgCl_2$, $2NaCl\cdot MgCl_2$, NaCl

sively used to filter the liquid aluminum alloys, copper alloys, cast iron, cast steel and high temperature alloys. Several kinds of foam structure ceramics have been developed in our country too, which employed as the filtration medium of aluminum alloys and high temperature alloys.

Due to the active chemical behavior and the oxidizing susceptibility of the magnesium alloy, the smelting process of the magnesium is very complicated, including the difficulty to remove the oxide inclusions and flux inclusions. But ordinary ceramic foam structure medium cannot be used for the purification of magnesium alloys. Because the Gibbs free energy of MgO is very low, so it will react with oxide with high Gibbs energy, such as SiO_2. This reaction proceeds rapidly under the temperature range of 720 - 780 ℃. All foam ceramics containing SiO_2 will dissolve rapidly in the magnesium alloy melt under this temperature range. As a result, not only the Mg melt cannot be refined, but also more inclusions are brought into the melt. A new kind of MgO foam structure filter has been developed in our laboratory. One advantage of this kind of filter is its high temperature stability, which avoids the reaction between the filter and magnesium melt. The other advantage is the tiny wetting angle interface between MgO and the smelting flux. As a result, the filtration medium can easily absorb the flux drops.

References[12, 13] report that $TiCl_4$ is used to remove the Fe element in Mg melts. The mechanism is that $TiCl_4$ is reduced to form pure Ti by Mg in the melt at first. The reduced Ti has the same efficiency as that of adding pure Ti directly. Because $TiCl_4$ is in liquid state at the room temperature and has high volatility tendency, it is forbidden to be poured to the high temperature melt directly, in order to avoid splashing of melt drops. This leads to inconvenience in the refining operation because of uncontrolled operation of adding $TiCl_4$.

After TiO_2 is added to the melt, it reacts with $MgCl_2$ to form $TiCl_4$, then replacement reaction between $TiCl_4$ and Mg proceeds: $TiCl_4 + Mg = Ti + MgCl_2$. It can be understand that Ti can be obtained by adding TiO_2 to the melt and Ti reacts with Fe to form TiFe compound to deposit in the bottom of the melt. Therefore, the Fe element in the melt can be removed. Because TiO_2 is a solid powder, it has the advantages of easy adding and mixing with other ingredients in the flux evenly. These help the chemical reaction to proceed completely. According to the thermodynamic data, this reaction can proceed towards resultants direction at 700 ℃. Therefore, indirect adding Ti using the above method is also feasible on theory.

REFERENCES

[1] ZHAO Yun-hu, ZENG Xiao-qin, DING Wen-jiang. Effects of Be and Ca on surface oxidation behaviors of Mg-9Al-0.5Zn[J]. Trans Nonferrous Met Soc China, 2000, 10(6): 847 - 852.

[2] Mordike B L, Ebert T. Magnesium properties-applications-potential[J]. Materials Science and Engineering A, 2001, 302(1): 37 - 45.

[3] Robert B. Magnesium automotive meeting[J]. Light Metal Age, 1992, 50(6): 18 - 24.

[4] Cra R. Magnesium' s future in automotive components [J]. JOM, 1996, 48(4): 9 - 11.

[5] Byton B C. Magnesium industry review[J]. Advanced Materials and Processes, 1996(4): 33 - 34.

[6] Wang X Q, Li P J, Liu M X, et al. Review on recycling technique of magnesium alloy[J]. Foundry, 2001, 50 (8): 446 - 449. (in Chinese)

[7] Wardlow G D. Recycling must be carefully controlled [J]. Foundry Trade Journal, 1999, 170(2): 18 - 21.

[8] John C G. High-ductility recycled magnesium alloys[J]. Automotive Engineering, 1996, 29(8): 69 - 72.

[9] Holta O, Westengen H, Albright D. High purity magnesium die casting alloys: from ingot to cast product[J]. SAE, 1994, 103(1): 221 - 225.

[10] Wang Y S. Study on Hot Tearing Behavior of Magnesium Alloys[D]. Shanghai: Shanghai Jiaotong University, 2002: 35 - 36.

[11] Zhai C Q, Ding W J, Xu X P, et al. Development of new type hazardless fluxes used in the melting of Mg-alloys[J]. Special Casting and Nonferrous Alloys, 1997 (4): 48 - 50. (in Chinese)

[12] Xu R Y, Zhu T B. Study on refining fluxes for crystallizing magnesium(Ⅰ)[J]. Light Metals, 1994(6): 38 - 42.

[13] Xu R Y. Metallurgy of Magnesium[M]. Beijing: Metallurgical Industry Press, 1981.

(Edited by YANG Bing)