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Purifying effect of new flux on magnesium alloy①

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Abstract: A new flux which can remove both Fe and non-metallic inclusions in magnesium alloy was introduced. The Fe content of the magnesium alloy can be decreased greatly from 0.062% to lower than 0.005% (degree of AZ91D) after being purified by this new flux. The optimum addition of B_2O_3 in the flux is 0.58 % by Gaussian Curve Fitting. Corrosion rate was measured after the specimen being immersed in 5% NaCl solution for 3 d. The results show that the corrosion rate of the magnesium alloy after purification by the new flux is only 0.3 $mg \cdot cm^{-2} \cdot d^{-1}$. On the other hand, non-metallic inclusions in the magnesium alloy decrease with increasing addition of JDMJ in the new flux. Average volume fraction of the non-metallic inclusions in the magnesium alloy decreases from 1.52% to 1.08%, which leads to improvement in the mechanical properties of the magnesium alloy by 30%. The mechanisms of Fe reduction and non-metallic inclusion-removing in magnesium melt by purification with the new flux were also revealed.

Key words: magnesium alloy; flux; purification; Fe; non-metallic inclusion
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1 INTRODUCTION

As one of the lightest structure materials, magnesium alloys offer light mass(ρ< 2 $g \cdot cm^{-3}$), specific strength (higher than that of the aluminum alloys and steels), specific stiffness, excellent machinability, superior damping and magnetic shielding capacities, which leads to a growing interest in magnesium and its alloys. In recent years, magnesium alloys have been widely used in aviation, spaceflight, automobile and electronics industries[1]. Since 1990's their application has steadily extended and it is predicted that it will increase by 25%-30% just in automobile industry in the coming years[2-4]. With the rapidly increasing demands for magnesium alloy in so many fields, the desire for its properties is becoming more critical. Therefore, a large number of methods and strategies are proposed to improve its properties including alloying, heat treatment and other techniques[5]. However, all these techniques are based on inherent quality of materials and only when the quality reaches a critical level the techniques such as modification process can take effects[6]. As for the magnesium alloy, impurity elements such as Fe and non-metallic inclusions such as MgO will destroy its inherent quality, thus greatly affect the later processing and treatments. Accordingly, it is necessary to reduce Fe content and remove non-metallic inclusions in magnesium melt for developing the properties of magnesium alloys.

The main impurity elements in magnesium alloys are Fe, Cu and Ni, of which Fe, even with a small amount, can remarkably impair the corrosion resistance of alloys because Fe, which is much nobler than Mg, has extremely low solubility in magnesium[7-9]. In addition, Fe is reported to influence grain refining process of super heat-treatment[10, 11]. The deleterious effect of Fe on corrosion behaviors has been attributed, on a microscopic scale, to the galvanic coupling between the magnesium substrate and Fe particle scattered in the matrix.

The non-metallic inclusions in magnesium alloy are mostly MgO, which destroy the continuity of the magnesium matrix and then reduce the mechanical properties of magnesium alloy.

At present almost magnesium fluxes can effectively remove the non-metallic inclusions. However, they have no effect on Fe reduction in magnesium alloy. It is reported that adding Mn in magnesium melt can reduce Fe content in magnesium alloy. The mechanism is that Mn combines with Fe and precipitates to the melt bottom or remains suspended in the metal during solidification[12]. Disadvantages of Mn addition are segregation of Mn and difficulty in controlling Fe/Mn ratio.

In order to remove both Fe and non-metallic inclusions in magnesium alloys and to avoid disadvantages of other methods, the authors propose a new method that can refine magnesium melt with the new flux containing B_2O_3 and JDMJ (developed by Shanghai Jiaotong University, China)[13]. It decreases the

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cost greatly and it is significant for both magnesium recycling and quality improving of raw magnesium alloys.

2 EXPERIMENTAL

The present experiment included two parts. One was to investigate the effect of B_2O_3 addition in the new flux on Fe-reducing and corrosion resistance of magnesium alloy; the other was to study the effect of JDMJ addition in the new flux on the non-metallic inclusions-removing and mechanical properties of magnesium alloy.

2.1 Experimental materials

Commercial magnesium alloy AZ91, which is the most widely used die casting magnesium alloy, was adopted in the present work. The new flux was prepared in QM-ISP pebble mill with JDMJ and chemical pure B_2O_3.

2.2 Experimental procedure

Magnesium alloy AZ91 was decontaminated and dried before being melted in crucible electric resistance furnace under the protection of a mixed gas atmosphere of SF_6 (1%, volume fraction) and CO_2 (bal.). The melt was refined by the new flux at the temperature range of 730−740 ℃, then was poured into permanent molds. Tensile specimens with a gauge size of 25 mm × 6 mm × 2 mm and corrosion specimens with a gauge size of d35 mm × 4 mm were cut by electric spark machining from the ingots. The sludge that precipitated at the crucible bottom was collected after pouring.

The chemical composition (Fe content) was ascertained with inductively coupled plasma spectrum machine (ICP, IRIS Advantage 1000) produced by Thermo Jarrell Ash Company. Tensile tests were carried out on a Zwick/Roell materials testing machine at a strain ratio of 0.5 mm/min. Metallographs, fractographs and corrosion photographs of specimens were observed by an optical microscopy (OM, OLYMPUS PME3) and a scanning electron microscope (SEM, PHILIP SEM515). The compositions of the inclusions were analyzed using an energy dispersive spectroscope (EDS) attached to the SEM. Statistical volume fractions of non-metallic inclusions in metallographic specimens were measured by using Leco image software. The phases in the sludge were ascertained with an X-ray diffractometer (XRD, Rigaku Dmax-rC).

Corrosion test specimens were grinded, then were washed in ethanol and acetone and dried by warm flowing air before the total surface area and the mass of specimens were measured. The specimens were immersed in 5% NaCl aqueous solution (pH10.5) saturated with $Mg(OH)_2$ that was exposed to ambient laboratory conditions at (25 ± 0.5) ℃ without stirring. Immersion period was 3 d. At the end of test, the corroded specimens were brushed and then cleaned by immersing and stirring in boiling chromic acid aqueous solution (180 g/L CrO_3 + 1% $AgNO_3$) for about 3 min. Consequently, specimens were rinsed by cleaning in boiling water and dried in a stream hot air. The measured mass of the corroded specimen was used to calculate the mass loss and the corrosion rate:

$$\Delta m = m_0 - m_c \quad (1)$$

$$R_c = \frac{\Delta m}{S_T \cdot t} \quad (2)$$

where Δm is the mass loss, mg; m_0 the mass of specimen before corrosion, mg; m_c the mass of corroded specimen, mg; R_c the corrosion rate, mg·cm^{-2}·d^{-1}; S_T the total surface area, cm^2; and t the immersion period, d.

3 RESULTS

3.1 Effect of B_2O_3 on Fe content and corrosion resistance of magnesium alloy

Fig. 1 shows B_2O_3 dependence of Fe content in magnesium alloy. With increasing B_2O_3 addition in the new flux, the Fe content in samples decreases sharply at the beginning and then remains almost unchanged when Fe content reaches 0.005%. The equation is obtained by Gaussian Curve Fitting:

$$y = 0.00476 + 0.27398\exp[-8.39725(x + 0.43487)^2] \quad (3)$$

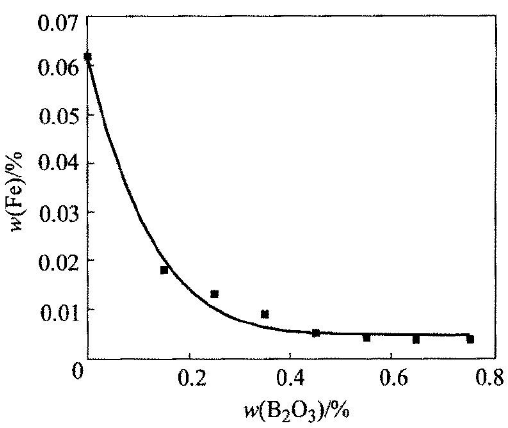

Fig. 1 B_2O_3 dependence of Fe content in samples

The limit value of y is 0.004 76, and that of x is 0.580 54 when the fit deviation is controlled within 1%. Therefore, in the experiment the limit value of Fe content in magnesium alloy is decided as 0.004 76% and the optimum addition of B_2O_3 in the new flux is about 0.58%.

There are complicated physical and chemical reactions between magnesium melt and the flux in the process of refinement for magnesium melt. During the reaction the thermodynamic potential becomes weak because the Fe content becomes less in magnesium melt till thermodynamic equilibrium. Then Fe content in magnesium melt does not change greatly even though more B_2O_3 is used in the flux. It accords with the result in Fig. 1. Corrosion rates of magnesium alloy samples with different Fe contents are illustrated in Fig. 2. It shows that there is a reasonably close correlation between Fe content and corrosion rate of magnesium alloy. The corrosion rate of the sample with 0.062% Fe before purification is 15 $mg \cdot cm^{-2} \cdot d^{-1}$, as contrast to 0.3 $mg \cdot cm^{-2} \cdot d^{-1}$ for the sample with 0.004% Fe after purification. The conclusion is that decreasing Fe content in magnesium alloy after purification by this new flux results in improvement in corrosion resistance of magnesium alloy.

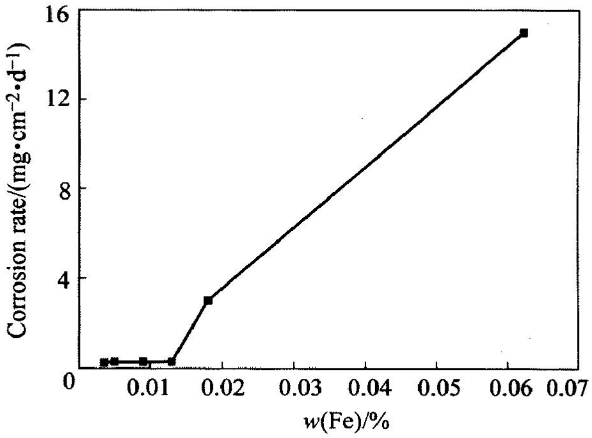

Fig. 2 Change of corrosion rate of samples with Fe content

Morphological characteristics of the corroded surfaces for the samples after being immersed in 5% NaCl aqueous solution for 3 d are shown in Fig. 3. It can be seen that there are corrosion pits homogeneously distributed on specimen surface, while the pits become sparse and small with decreasing Fe content in magnesium alloy. It accords with the results as mentioned above.

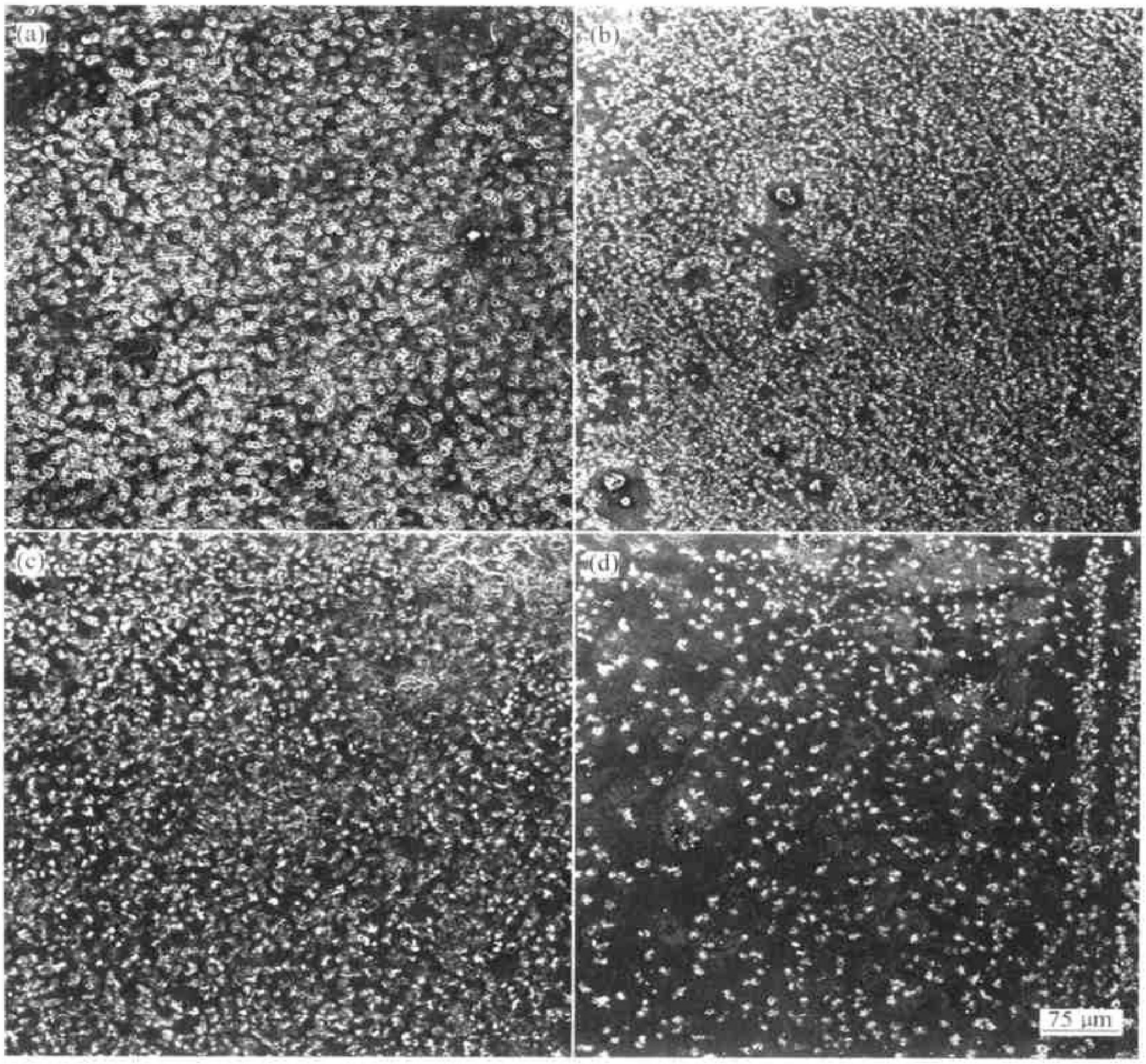

Fig. 3 Photographs of corroded surfaces for Fe-containing samples after immersion in NaCl aqueous solution (5 %) for 3 d

(a) —0.062% Fe; (b) —0.016% Fe; (c) —0.007% Fe; (d) —0.004% Fe

Because of low solubility in magnesium most Fe precipitates and scatters on magnesium matrix, which can remarkably impair corrosion resistance of magnesium alloy[14]. Reducing amount of Fe in magnesium, which is attributed to B_2O_3 in the new flux, leads to increasing corrosion resistance for magnesium alloy.

3.2 Effect of JDMJ on non-metallic inclusions and mechanical properties of magnesium alloy

Table 1 and Fig. 4 show statistical volume fraction of non-metallic inclusions in magnesium alloy. Average volume fraction of the non-metallic inclusions decreases from 1.52 % to 1.08 % after purification by this new flux, which lessens the disseverance effect on magnesium matrix.

Table 1 Statistical volume fraction of non-metallic inclusions in metallographic specimens using Leco image software

Sample	Number of fields	Total area of fields/ mm^2	Maximum volume fraction/ %	Minimum volume fraction/ %	Average volume fraction/ %
Before purification	100	0.61	6.53	0.95	1.52
After purification	100	0.61	1.26	0.94	1.08

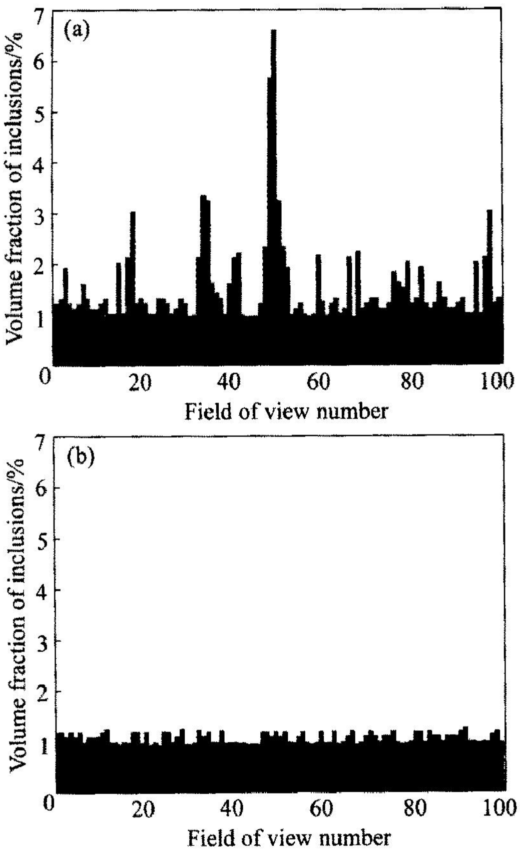

Fig. 4 Statistical distribution of non-metallic inclusions for metallographic samples
(a) —Before purification; (b) —After purification

Figs. 5(a), (c) and Figs. 5(b), (d) show the non-metallic inclusions in magnesium alloy before and after purification respectively. Fractographs of tensile samples, shown in Fig. 6, indicate that quasi-cleavage fracture mechanism is the main characteristic for samples. The difference is that more non-metallic inclusions exist in small and shallow dimples for samples before purification than that for samples after purification.

Fig. 7 illustrates the relation between the JDMJ addition and mechanical properties of magnesium alloy. It can be seen that tensile strength and elongation of samples can be improved significantly with increasing JDMJ addition in the new flux. Both tensile strength and elongation increases by 30% after purification by the new flux. The reason is that JDMJ in the new flux can effectively remove non-metallic inclusions, thus improves the mechanical properties of magnesium alloy.

From Fig. 7, it can also be seen that excessive addition of JDMJ in the flux leads to decrease of mechanical properties of magnesium alloy. It attributes to the presence of flux inclusions in case of excessive JDMJ addition in the flux. Fig. 8 shows morphology of flux inclusion in magnesium alloy and its EDS analysis.

4 DISCUSSION

4.1 Mechanism of Fe reduction in magnesium

As for reactions between magnesium melt and the flux, thermodynamic analysis is done as follows:

$$B_2O_3(s) = B_2O_3(l) \qquad (4)$$

$$\Delta G_1^{\ominus} = 24\,060 - 33.26T$$

$$2B(s) + 1.5O_2(g) = B_2O_3(l) \qquad (5)$$

$$\Delta G_2^{\ominus} = -1\,228\,800 - 210.14T$$

$$Mg(l) + 0.5O_2(g) = MgO(s) \qquad (6)$$

$$\Delta G_3^{\ominus} = -609\,570 + 116.52T$$

$$Fe(s) + B(s) = FeB(s) \qquad (7)$$

$$\Delta G_4^{\ominus} = -79\,500 + 10.46T$$

$$B_2O_3(s) + 3Mg(l) = 3MgO(s) + 2B(s) \qquad (8)$$

$$\Delta G_5^{\ominus} = -575\,850 + 526.44T$$

$$B_2O_3(s) + 3Mg(l) + 2Fe(s) = 3MgO(s) + 2FeB(s) \qquad (9)$$

The standard Gibbs free energy of reaction (9) is calculated using thermodynamic data[15]:

$$\Delta G_6^{\ominus} = -734\,850 + 547.36T = -180\,292 \text{ J/mol} \quad (T = 1\,013 \text{ K})$$

$\Delta G_6^{\ominus}$ is negative under practical condition (refining temperature $T = 1\,013$ K), therefore, there is a great thermodynamic potential in reaction (9). Furthermore, the reaction product FeB (its melting point is 1 650 ℃)[16] settles down in course of refining, which is confirmed by XRD result of the sludge shown in Fig. 9.

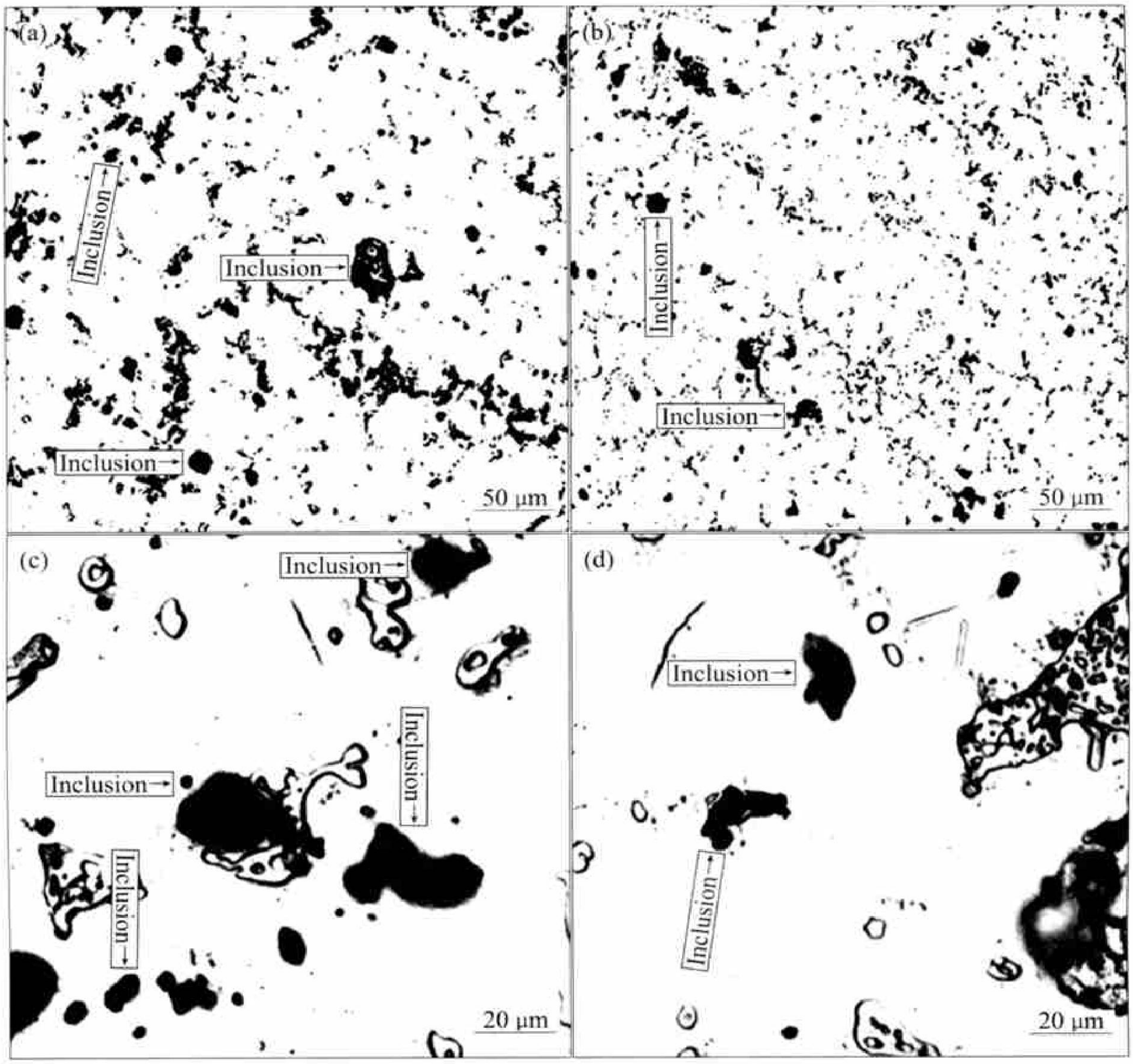

Fig. 5 Metallographic photographs of magnesium alloy
(a), (c) —Before purification; (b), (d) —After purification

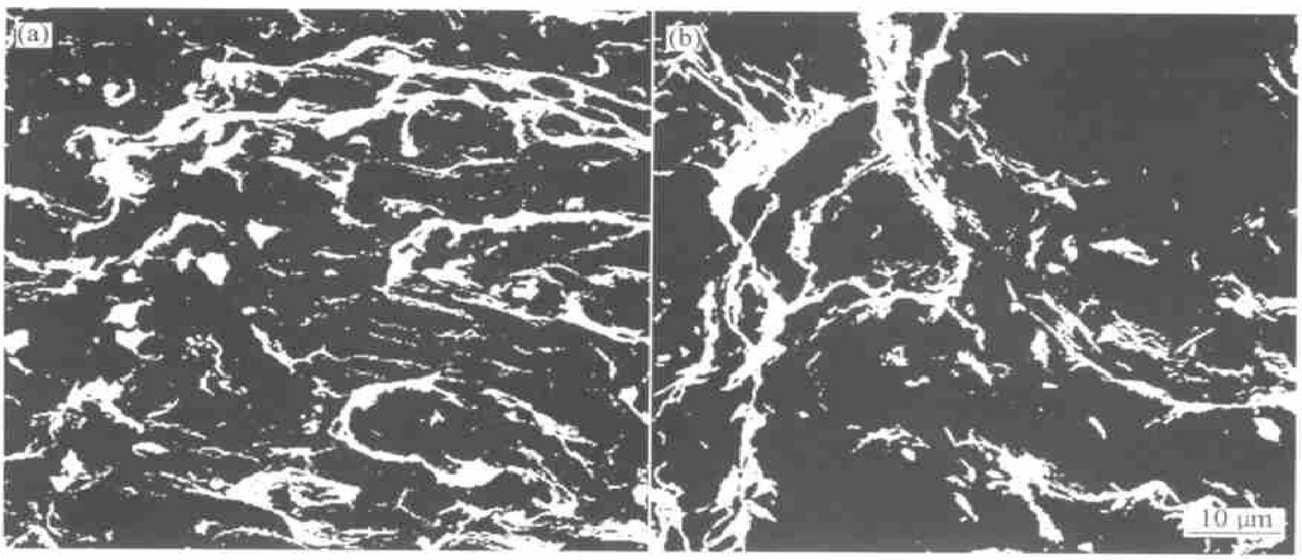

Fig. 6 Fractographs of tensile samples
(a) —Before purification; (b) —After purification

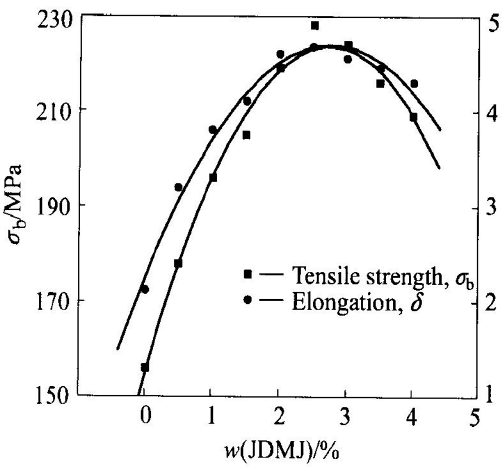

Fig. 7 Relationship between JDMJ addition and mechanical properties of samples

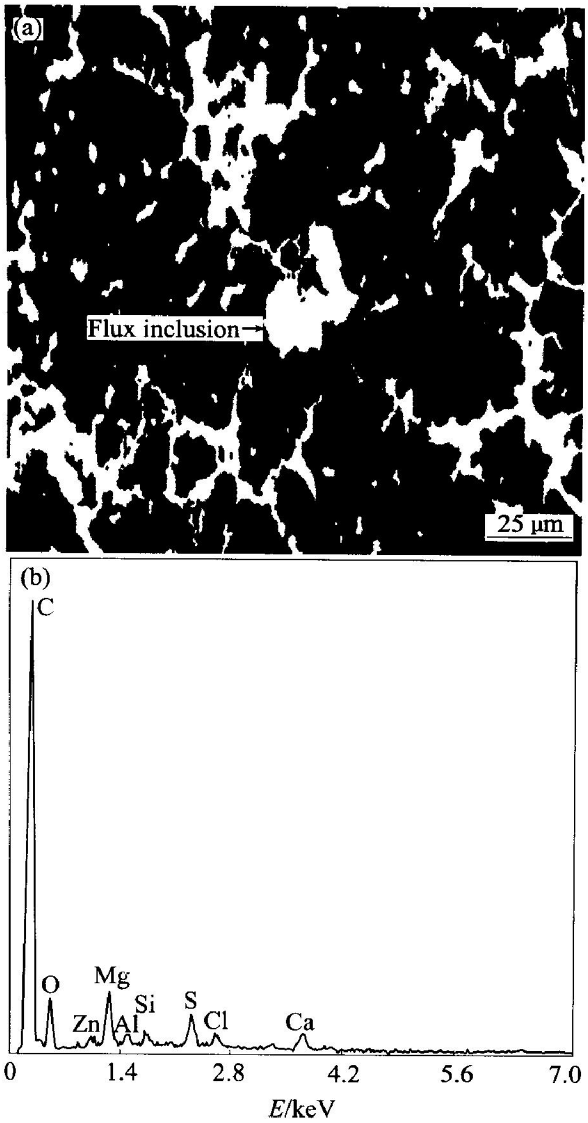

Fig. 8 SEM micrograph(a) of flux inclusion and its EDS result(b)

4.2 Mechanism of non-metallic inclusion-removing from magnesium alloys

There are many kinds of non-metallic inclusions in magnesium alloy in which MgO is in the majority.

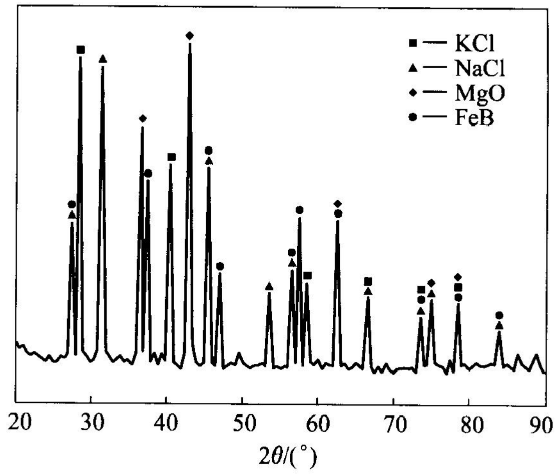

Fig. 9 X-ray diffraction pattern of sludge after purification

Most of them are wetted by $MgCl_2$ and KCl in the flux. And some of them might react with $MgCl_2$ and form stable or unstable complex substance illustrated as follows:

$$MgO + MgCl_2 \longrightarrow MgCl_2 \cdot MgO$$

$$5MgO + MgCl_2 \longrightarrow 5MgCl_2 \cdot MgO$$

The Gibbs free energy of non-metallic inclusions absorbed by the new flux from magnesium melt is expressed as

$$\Delta G = \sigma_{f-i} - \sigma_{m-i} = \sigma_m \cos\theta_{m-i} - \sigma_f \cos\theta_{f-i} = \sigma_{m-f} \cos\theta_f^{m-i} \quad (10)$$

where θ_{m-i} and θ_{f-i} are wetting angles of the non-metallic inclusion with magnesium melt and the flux, respectively; θ_f^{m-i} is the wetting angle between the non-metallic inclusion and magnesium melt in the flux.

As can be seen from Eqn.(10), ΔG will be more negative with decreasing σ_{m-f} and it means it is easy for non-metallic inclusions to transfer from magnesium melt to the flux. Fluoride addition in the new flux, which reduces the interfacial tension between magnesium melt and the flux, is helpful for non-metallic inclusions removing from magnesium alloy melt.

5 CONCLUSIONS

1) B_2O_3 addition in the new flux, which has an excellent effect on reducing Fe in magnesium alloy, makes Fe content in magnesium alloy decrease to lower than 0.005% (degree of AZ91D) and its optimum addition is 0.58%.

2) Lower Fe content in magnesium alloy after purification by the new flux improves corrosion resistance of magnesium alloy and the corrosion rate is only 0.3 $mg \cdot cm^{-2} \cdot d^{-1}$ after purification.

3) JDMJ in the new flux, which can effectively remove non-metallic inclusions in magnesium alloy, makes the volume fraction of non-metallic inclusions

in magnesium alloy greatly decrease from 1.52% to 1.08% after purification.

4) Less non-metallic inclusions in magnesium alloy after purification by the new flux cause improvement in mechanical properties of magnesium alloy by 30%.

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