

Oxidation Behavior and Surface Tension of Mg-1.2Ca Alloy with Ce Addition

Qin Lin, Ding Jian, Zhao Weimin, Fang Zheng

Hebei University of Technology, Tianjin 300132, China

Abstract: The effects of alloying element Ce on the oxidation behavior and the surface tension of Mg-1.2Ca alloy were investigated in order to further develop the burn resistant magnesium alloys. Results show that with the increase of Ce content from 0 wt% to 1.5 wt%, the ignition point of Mg-1.2Ca alloy increases rapidly while the surface tension declines. The ignition point of Mg-1.2Ca-1.2Ce alloy can reach 780 °C. It can be melted in atmosphere without any protection method. The oxidation film of Mg-1.2Ca melt becomes smooth and dense with the increase of Ce addition, which can prevent magnesium alloys from further oxidation and burning. According to the test and analysis, the oxide film of Mg-1.2Ca-1.2Ce alloy consists of three layers, that is, loose MgO in the outer layer, MgO-CaO composite oxide film in the middle layer and MgO-Ce₂O₃ composite oxide film in the inner layer.

Key words: magnesium alloy; oxidation; surface tension; calcium; cerium

Magnesium alloys are widely used in aerospace, electronic technology and automotive industry due to their good properties such as low density, high specific strength and stiffness, as well as good processability. However, magnesium alloys are prone to oxidate or even burn as they have high chemical activity and loose oxide film. So fluxes or protective gas methods should be taken to prevent oxidation during melting and casting processes^[1]. However, both of two methods would lead to many problems, such as inclusion, environmental pollution and complication of melting process and equipment. So it is necessary to investigate a better burn resistant method.

Alloying is an effective method to improve the burn resistant performance of magnesium alloys. Recently, the effect of rare earth (RE) on properties of magnesium alloys has been investigated. RE is usually used as addition element to enhance the oxidation resistance^[2]. It was revealed that Ce content in the solid solution will influence the burn resistant performance of magnesium alloys together with other elements in the alloys, such as Ca. The interactive effect on the oxidation resistance is much more complicated than that of

the single element in the solid solution. Sakamoto et al.^[3] studied the oxidation of Mg-Ca alloy. The results indicated that the ignition temperature could increase by 250 °C after 5 wt% Ca was added into pure magnesium. They also found that the burn resistant performance was improved at the cost of the decrease of tensile properties, so the content of Ca should be controlled in about 1 wt% for the pure magnesium.

Surface tension is both a fundamental property and an important technological parameter to high temperature alloy^[4], which is related to the concentration of active element, the internal stress and the wettability. And above mentioned parameters have a great influence on the formation and the morphology of oxide film of magnesium alloys. However, the surface tension of the magnesium alloy melt was rarely studied. The structure of the oxide film on the molten alloy and its thermodynamic and kinetic mechanisms were far from being understood. In the present paper, the author also studied the oxidation behavior of magnesium alloys by means of surface tension testing.

1 Experiment

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Corresponding author: Ding Jian, Ph. D., Associate Professor, School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300132, P. R. China, E-mail: djian@126.com

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Mg-1.2Ca-xCe alloys used in the present investigation was smelted from commercial pure Mg (99.95%), Mg-29.7%Ca and Mg-30.0%Ce master alloys in an SG2-1.5-12 electric resistance furnace under the protection of 99.5vol%CO₂-0.5vol% SF₆ gases. The raw materials were first cut and mixed in a proper ratio, melted and then cast into mould, finally the ingots with composition of Mg-1.2Ca-xCe (x=0, 0.3, 0.6, 0.9, 1.2, 1.5) were obtained.

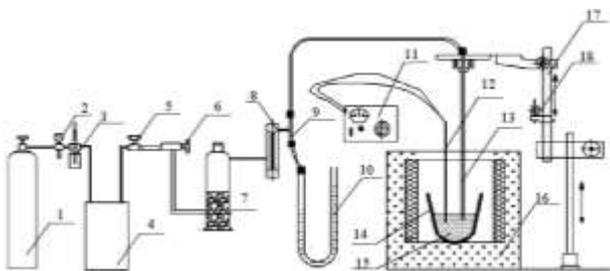
The samples were taken from the central section of the ingots, and then they were machined to cylindrical shape with the dimension of Φ12 mm×15 mm for testing ignition points. Upon testing the ignition points, the samples were continuously heated in the electric resistance furnace at a constant heating rate of 4 °C/min until the ignition occurrence^[5]. And the temperature during heating was measured with a multi-channel data acquisition system (with an accuracy of ±2 °C). It is worthy mentioning that neither flux nor gas protection were used in this process. For each alloy, the ignition point was tested for three times and then the average value of ignition point was calculated.

The surface tension of molten Mg-1.2Ca-xCe alloys were measured at the temperature of 730 °C in open air using the maximum bubble pressure method (MBPM)^[6], as shown in Fig.1. The maximum bubble pressure method proposed by Simon^[7] is based on the use of a single capillary immersed into the studied liquid. Mg-29.7%Ca and Mg-30.0%Ce interalloys were added after commercially pure Mg melted completely at the temperature of 730 °C, removing the impurities of melt surface. The surface tension were tested after maintaining the melt at the temperature of 730 °C for 15 min.

The surface tension σ can be calculated from the measured maximum capillary pressure P and the known capillary radius r by the Laplace equation^[8]:

$$\sigma = Pr/2 \tag{1}$$

The measured capillary pressure P can be expressed via the excess maximum pressure in the measuring system $P_s = \rho_1 g H_{max}$, where H_{max} represent the maximum difference of liquid level between U-tube manometer, and ρ_1 is the density of liquid;



1-argon gas, 2-pressure reducer, 3-flowmeter, 4-pressure stabilizer, 5-needle valve, 6-fine needle valve, 7-drying bottle, 8-flowmeter, 9-three-limb tube, 10-U-tube, 11-temperature controller, 12-thermocouple, 13-capillary, 14-graphite crucible, 15-melt, 16-furnace, 17-bracket, 18-dial gage

Fig.1 MBPM surface tension testing schematic

hydrostatic melt pressure $P_h = \rho_2 gh$, where h is the immersion depth of the capillary into the melt, and ρ_2 is the density of melt. Hence the capillary pressure is given as follows:

$$P = P_s - P_h \tag{2}$$

Together with Eq.(1) we obtained:

$$\sigma = (\rho_1 H_{max} - \rho_2 h) gr/2 \tag{3}$$

The analyses of composition and microstructure of oxidation film were conducted by a Hitachi S4800 scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). The phase of oxidation film was examined by an X-ray diffraction (XRD) system (SmartLab, Rigaku) with Cu K α radiation.

2 Results and Discussion

2.1 Ignition point testing

A typical temperature-time curve of ignition point testing of pure magnesium is shown in Fig.2. The combustion heat of the samples is large enough to cause a steep rise in the temperature-time curve. The temperature-time curves display a rapid oscillation of rising in burning process and the first inflection point is defined as the ignition point of the sample in the present research^[9].

The results of the ignition point testing are shown in Fig.3. And the fitted curve is also drawn up in the figure, which complied with Gaussian function. As can be seen from the graph, the ignition point of Mg-1.2Ca increases rapidly when the content of Ce is in the range from 0 wt% to 1.2 wt%. However, when the content of Ce is more than 1.2 wt%, the ignition point is almost invariable. The average ignition point of Mg-1.2Ca-1.2Ce can reach 780 °C, which is about 77 °C higher than that of Mg-1.2Ca. The data of ignition point of Mg-1.2Ca-xCe alloys can be fitted as the following equation:

$$T = 702.21 + 80.80 \exp\left[-2\left(\frac{x - 1.39}{1.03}\right)^2\right] \tag{4}$$

where, T is the ignition point (°C) and x is analyzed content of Ce (wt%) in Mg-1.2Ca.

2.2 Oxide film analysis

The oxide films of Mg-1.2Ca and Mg-1.2Ca-1.2Ce can be vividly seen in Fig.4. Both of them are cooled under natural condition from magnesium melt. As can be seen, the oxide

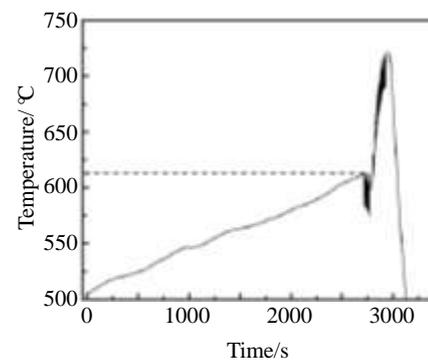


Fig.2 Typical ignition point test of pure magnesium

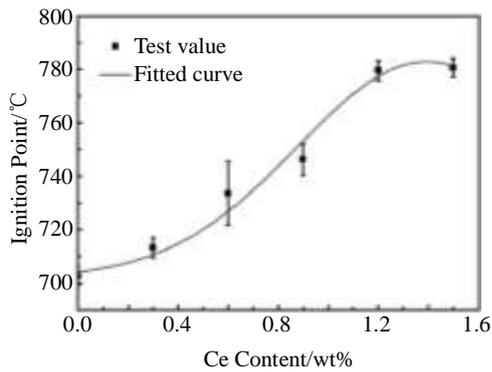


Fig.3 Effect of Ce content on the ignition point of Mg-1.2Ca alloy

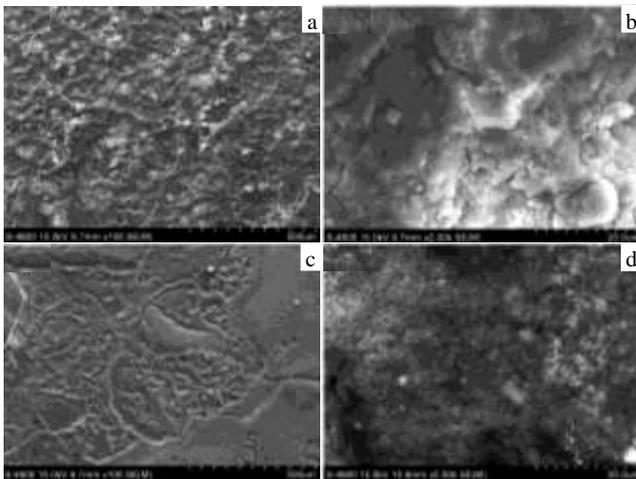


Fig.4 Oxide film morphologies of magnesium alloys with different Ce content: (a, b) the oxide film of Mg-1.2Ca and (c, d) the oxide film of Mg-1.2Ca-1.2Ce

film of Mg-1.2Ca-1.2Ce is dense and bonds with the matrix very well. On the contrary, the oxide film of Mg-1.2Ca is thin and contains many micro-pores and cracks, which can well explain the difference of burn resistance performance between the two alloys.

The phase of Mg-1.2Ca-1.2Ce oxide film is composed of Mg, MgO, CaO and Ce₂O₃, which is confirmed by the XRD

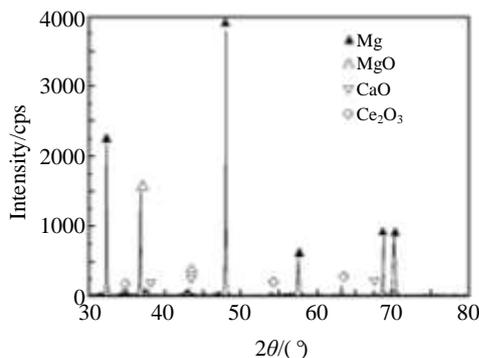


Fig.5 XRD pattern of Mg-1.2Ca-1.2Ce oxide film

analysis in Fig.5. And the main reason of the improvement of the ignition point is that the oxide film tightness increases. The tightness is always expressed by P-B ratio (ratio of the volume of the oxide to the consumed metal volume). When the P-B ratio is larger than 1, the oxide film has the function to protect the matrix; while the P-B ratio is smaller than 1, the oxide film is loose. The P-B ratio of pure magnesium equals to 0.81 for MgO^[10], and thus the surface oxide film cannot prevent the proliferation of oxygen and the oxidation of inner magnesium. However, the P-B ratio of Ce₂O₃ is 1.16, the addition of Ce₂O₃ in the oxide film can make it more compact.

The cross section morphology of Mg-1.2Ca-1.2Ce oxide film with thickness of 2~3 μm, is shown in Fig.6. When Ca and Ce are added to magnesium alloys, because the P-B ratio is larger than 1, the filling of Ca and Ce oxide into the holes of magnesium results in the formation of a composite and compact coherent oxide film which can prevent the penetration of oxygen during heating. From the elements distribution, we can see that Ca and Ce are mainly located at the surface of magnesium melt. The oxide film can be divided into three layers. Due to the magnesium vapor pressure, the outer layer are mainly composed of loose MgO. The middle layer and inner layer are mainly composed of MgO-CaO and MgO-Ce₂O₃ composite oxide film, respectively.

2.3 Surface tension testing

Rare earths are surface active elements, as they are prone to gather on melt surface, and this gathering phenomenon will greatly affect the oxide film of magnesium and its burn resistant performance. Surface tension is an important parameter to high temperature melt, which is a perfect way to reflect the value of Ce concentration. The surface tension of Mg-1.2Ca-xCe alloys were tested at 700 °C, using MBP method. As can be seen in

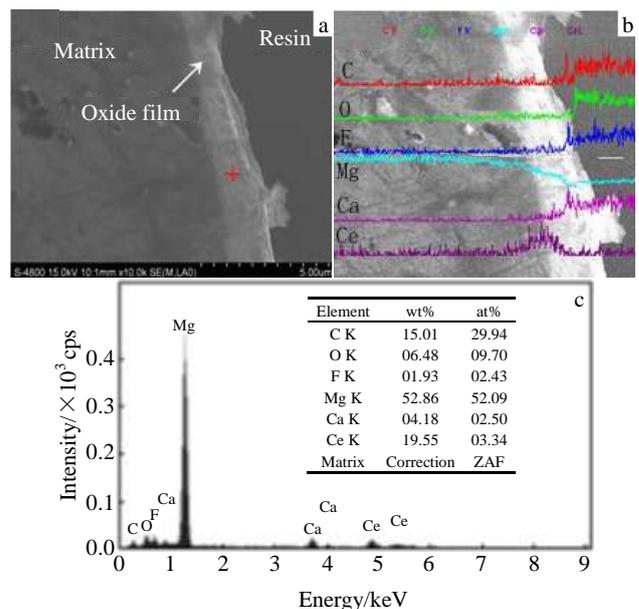


Fig.6 Morphology (a), EDS line analysis (b), and EDS spot analysis (c) for cross section oxide film of Mg-1.2Ca-1.2Ce

Fig.7, the surface tension of Mg-1.2Ca decreases rapidly with the increase of Ce content. The data of surface tension of Mg-1.2Ca-xCe alloys can be fitted as a parabola equation,

$$\sigma = 0.567 - 0.079x + 0.017x^2 \quad (5)$$

where σ represents surface tension, and x is the content of Ce.

The relationship between surface tension and ignition point is illustrated in Fig.8. It can be seen that the ignition point increases with the decreasing of Mg-1.2Ca-xCe melt surface tension.

The gathering of Ce on the surface of magnesium alloy melt makes the surface tension reduce and greatly improves the burn resistance performance, resulting in forming a composite oxide film on melt surface. Internal stress is another factor to the burn resistant of magnesium alloys, which prompts the forming of wrinkle and crack. Hence, the internal stress should be controlled at a proper level. Ce is a surface active element, which can decline the surface tension and the internal stress. So this is another reason why oxidation resistant of Mg-1.2Ca is improved with Ce addition.

2.4 Transformation in solid-state

In order to understand the mechanism of burn resistance of magnesium alloy, the transformation of Mg-1.2Ca and Mg-1.2Ca-1.2Ce solid-state samples during continuous heating in the atmosphere were investigated. In the present study, the heating temperature was maintained at 730 °C. And the evident changes of the samples were caught with the increasing of time. All the samples were polished before heating process.

Fig.9 shows the surface morphologies transformation of

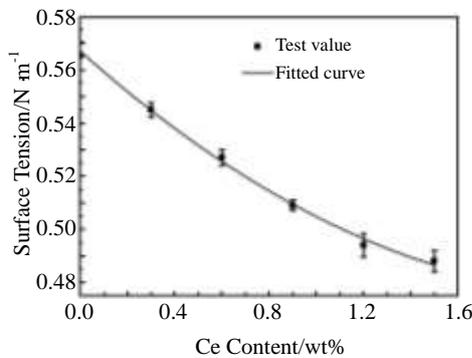


Fig.7 Effect of Ce content on the surface tension of Mg-1.2Ca

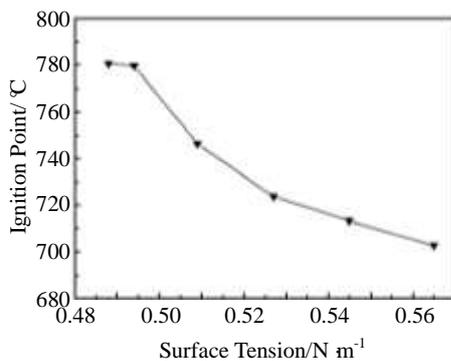


Fig.8 Relationship between surface tension and ignition point

Mg-1.2Ca solid-state at 730 °C for different heating time under atmosphere situation. After 10 min heating, a thin oxide film is generated on the surface of Mg-1.2Ca solid-state. From Fig.9a, Fig.9b, it can be seen that some wrinkles exist around the phase boundaries due to the unbalanced internal stress. When the time increases to 20 min, the oxide film continues to grow, as seen in Fig.9c, Fig.9d). The increase of the thickness and the expansion of oxide film exacerbates the internal stress and the intensity of wrinkle. When the internal stress is large enough, the micro-pores or even obviously cracks may be produced at the edges of wrinkles. Owing to rapid transport rate of oxygen in external scale, the oxygen pressure at the scale/substrate interface is very high. Therefore, solid-state reactions among oxygen may occur, giving rise to complex oxides. The morphology of the oxide resembles some cauliflower, which can be seen in Fig.9e and Fig.9f.

The particularly high burn resistance of Mg-1.2Ca-1.2Ce can be again deduced from its solid-state transformation, as can be seen in Fig.10. Fig.10a, 10c and 10e images represent the morphologies of solid-state transformation, at 730 °C for different heating time. And the Fig.10b, 10d, and 10f are their high magnification images. The thin oxide film is formed after 10 min oxidation, which is very smooth. Then, many cracks appear on the surface of oxide film. The fracture mode of crack joint is ductile fracture which is full of dimples. With time and temperature increasing, some parts in the film collapse from the matrix. Fortunately, the surface of the magnesium alloy is packaged by a new dense oxide film, which completely isolates magnesium matrix from atmosphere.

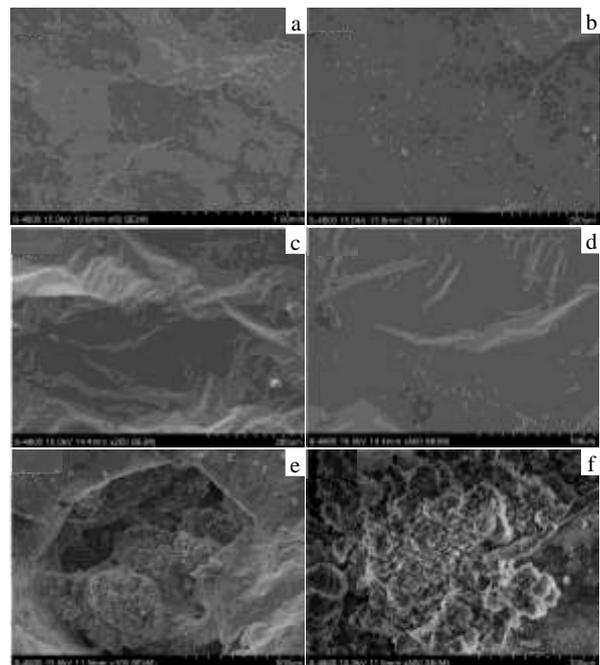


Fig.9 Morphologies transformation of Mg-1.2Ca solid-state at 730 °C with different heating time: (a, b) 10 min, (c, d) 20 min, and (e, f) 40 min

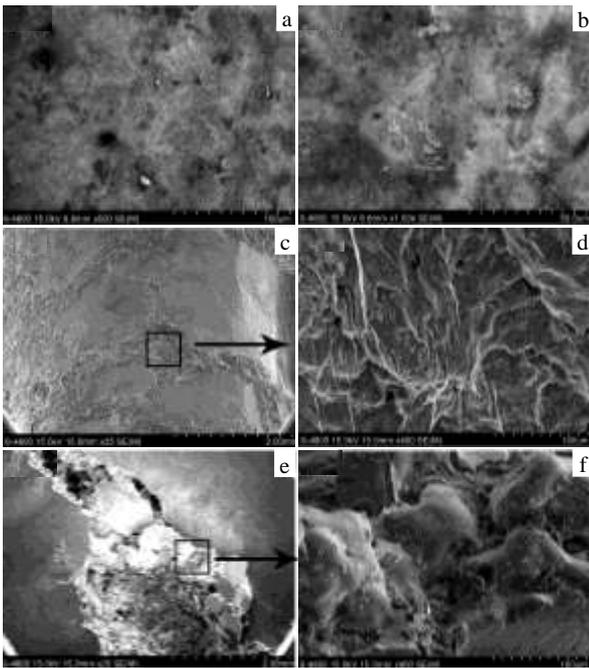


Fig.10 Morphologies transformation of Mg-1.2Ca-1.2Ce solid-state at 730 °C with different heating time: (a, b) 10 min, (c, d) 20 min, and (e, f) 40 min

The effect of Ce on oxidation resistance in the present study should be attributed to the oxidation mechanism different from Mg-1.2Ca at 730 °C. During the exposure at 730 °C, both alloys exhibit different oxidation behaviors between the matrix and eutectic regions. This is associated with the difference of compositions in individual phases due to microsegregation during solidification. What is more, the huge difference in oxide film tightness is the most important reason for the appearance of the discrepancy of solid-state transformation between two alloys.

3 Conclusions

1) For the Mg-1.2Ca-xCe magnesium alloys, the ignition point

increases rapidly with increasing of Ce content from 0 wt% to 1.2 wt%; however, the ignition point almost has no change when the Ce content is in the range from 1.2 wt% to 1.5 wt%. The ignition point of Mg-1.2Ca-1.2Ce alloy can reach 780 °C, which increases by 80 °C compared with that of Mg-1.2Ca alloy.

2) The surface oxide film structure of magnesium alloy turns into the composite dense one from the porous by adding Ce, which is composed of three layers: MgO outer layer, MgO-CaO middle layer and MgO-Ce₂O₃ inner layer.

3) The surface tension of Mg-1.2Ca inclines with the addition of Ce. And the ignition point increases with the decreasing of surface tension of Mg-1.2Ca-xCe melt.

4) In the respect of the oxide film tightness, there exists a huge difference between Mg-1.2Ca and Mg-1.2Ca-xCe. The ignition of Mg-1.2Ca is attributed to the wrinkles and cracks on oxide film. The Mg-1.2Ca-xCe have tight and dense oxide film which will package the alloys completely at high temperature resulting in isolating magnesium matrix from atmosphere, so the burn resistant performance of the alloys are improved greatly.

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Ce 元素的添加对 Mg-1.2Ca 合金氧化行为和表面张力的影响

秦 林, 丁 俭, 赵维民, 方 正
(河北工业大学, 天津 300132)

摘 要: 为了发展高性能阻燃镁合金, 对工业纯镁在添加元素 Ca 和 Ce 的氧化性能进行了研究。结果表明, 随着 Ce 含量从 0% 到 1.5% (质量分数) 的增加, Mg-1.2Ca 合金的燃点不断提高, 熔体表面张力不断下降。Mg-1.2Ca-1.2Ce 燃点可以达到 780 °C, 而且可在大气中不添加任何保护的情况下进行熔炼。随着 Ce 含量的增加, Mg-1.2Ca 熔体氧化膜变得光滑而致密, 可以很好地起到阻止氧化、燃烧的效果。通过检测和分析, Mg-1.2Ca-1.2Ce 的氧化膜可以分成 3 层: 外层是疏松的 MgO, 中间层是 MgO-CaO 复合氧化膜, 内层是 MgO-Ce₂O₃ 复合氧化膜。

关键词: 镁合金; 氧化; 表面张力; 钙; 铈

作者简介: 秦 林, 男, 1988 年生, 硕士, 河北工业大学材料科学与工程学院, 天津 300132, E-mail: qlin_hbut@163.com