JMEPEG (2009) 18:32–37
DOI: 10.1007/s11665-008-9259-8

1059-9495/$19.00

Processing Effects on Grain Refinement of AZ31 Magnesium Alloy Treated with a Commercial Al-10Sr Master Alloy

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(Submitted September 14, 2007; in revised form April 19, 2008)

The effects of Sr amount and melt holding time on the grain refinement of AZ31 magnesium alloy treated with a commercial Al-10Sr master alloy are investigated. The effects of solutionizing, rolling, and remelting of commercial Al-10Sr master alloy on the grain refinement of AZ31 magnesium alloy are also investigated. An increase in Sr amount from 0.01 to 0.1 wt.% or melt holding time from 20 to 80 min causes the grain size of AZ31 alloy treated with the commercial Al-10Sr master alloy to gradually decrease. In addition, the solutionizing, rolling, or remelting of commercial Al-10Sr master alloy can improve the refinement efficiency of the master alloy to AZ31 alloy, and the improvement resulting from the remelting is best obvious, followed by rolling and solutionizing, respectively.

Keywords Al_4Sr phase, AZ31 magnesium alloy, commercial Al-10Sr master alloy, grain refinement

1. Introduction

At present, the Mg-Al-based alloys are widely applied in industrial production, but their mechanical properties and performance still do not meet the needs of some important parts in vehicles and other applications. Therefore, many ways are being investigated in order to further improve the mechanical properties and performance of Mg-Al-based alloys (Ref 1-4). It is well known that the grain refinement is an important method of elevating the properties and improving the formability for magnesium alloys. Recent investigations indicated that the Sr in the form of Al-Sr master alloys, which have been widely used in industrial practice especially for the modification of Al-Si alloys, is an effective grain refiner of Mg-Al-based alloys (Ref 5-7). Srinivasan et al. (Ref 8) and Nam et al. (Ref 9) reported that adding an Al-10Sr master alloy to a Si-containing AZ91 magnesium alloy appeared to refine the microstructure by promoting a smaller grain size, and similar results in AM50 magnesium alloy were also reported by Zhao et al. (Ref 10) and Hirai et al. (Ref 11). In addition, Zeng et al. (Ref 12) and Cheng et al. (Ref 13) reported that adding pure Sr and Al-10Sr master alloy to AZ31 magnesium alloy effectively reduced the grain size of the alloy.

In spite of the above studies, the effects of Sr amount and melt holding time on the grain refinement of Mg-Al-based alloys treated with a commercial Al-10Sr master alloy are still not clear. In addition, according to the established practice of Al-Sr master alloys for the modification and refinement of aluminum alloys, a high dissolution rate can be obtained for the finer Al_4Sr phases in Al-Sr master alloys, thereby enhancing the efficiency of modifiers. This refinement of Al_4Sr phase may be achieved by deformation, rapid solidification, or heat treatment (Ref 14-16). But up to now, the type of Al-Sr master alloys used to refine magnesium alloys mainly focuses on the untreated commercial Al-Sr master alloys. The investigation about the effects of rolled, heat-treated, and remelted commercial Al-Sr master alloys on the grain refinement of Mg-Al-based alloys is very rare. Due to the above-mentioned reasons, the present work investigates the effects of Sr amount and melt holding time on the grain refinement of AZ31 magnesium alloy treated with an untreated initial commercial Al-10Sr master alloy. In addition, the effects of solutionized, rolled, and remelted commercial Al-10Sr master alloy on the grain refinement of AZ31 magnesium alloy are also investigated.

2. Experimental

The initial commercial Al-10Sr master alloy, which was prepared by traditional casting and subsequent extrusion at Changzhou Metal Materials Company Limited in China, was first used to refine AZ31 alloy. The refinement treatment was carried out in an electrical resistance furnace by using a graphite crucible with a capacity of 2 kg and protected by 2 wt.% RJ-2 flux additions (45 wt.% MgCl + 37 wt.% KCl + 8 wt.% NaCl, 4 wt.% CaF + 6 wt.% BaCl). When the melt temperature of AZ31 alloy reached approximately 1013 K, the melts were respectively treated with 0.01, 0.05, and 0.1 wt.% Sr using the initial commercial Al-10Sr master alloy. After the initial commercial Al-10Sr master alloy was added to the melt, the melts were homogenized by mechanical stirring. After mixed completely, the melts were held at 1013 K for 20, 40, 60,

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and 80 min, respectively, and then poured into a permanent mould with a cavity of size Φ20 × 90 mm in order to obtain the samples for microstructural analysis. Furthermore, the samples of AZ31 alloy treated with the initial commercial Al-10Sr master alloy were subjected to an annealing treatment (688 K/12 h, water cooled) in order to clearly reveal the crystal grains.

In addition, in order to alter the size of Al_4Sr phases in the initial commercial Al-10Sr master alloy, the initial commercial Al-10Sr master alloy was solutionized, rolled, and remelted, respectively, and then these treated Al-10Sr master alloys were respectively used to refine AZ31 alloy under the same conditions as the initial commercial Al-10Sr master alloy. The solutionizing, rolling, and remelting processes of initial commercial Al-10Sr master alloy were respectively described as followings: (1) the solid solution treatment was carried out at 773 K for 4 h and followed by water quenching; (2) the rolling was carried out at 573 K for a total reduction level of 50%, and the rolling process included an 20% reduction level at the beginning at a predetermined temperature. For further reduction levels, the sample was again heated to the same temperature and rolled; and (3) the remelting was carried out in an electrical resistance furnace using a graphite crucible with a capacity of 2 kg. After holding at 1013 K for 60 min, the melts of initial commercial Al-10Sr master alloy were poured into a water-cooled permanent mould with a cavity of size 50 × 0.5 × 60 cm, to permit rapid solidification. Table 1 and 2 respectively list the chemical compositions of untreated and remelted commercial Al-10Sr master alloys and the chemical compositions of as-cast AZ31 alloy treated with the different Al-10Sr master alloys.

The samples of Al-10Sr master alloy and AZ31 alloy were mechanically polished and etched in a solution of 1.5 g picric acid, 25 mL ethanol, 5 mL acetic acid, and 10 mL distilled water, and then examined by an Olympus Optical microscope. The grain size of AZ31 alloy was measured by the standard linear intercept method using an Olympus stereomicroscope. The phases in the Al-10Sr master alloy and AZ31 alloy were also analyzed by D/Max-1200X type analyzer operated at 40 kV and 30 mA.

Table 1 Chemical compositions of the untreated and remelted commercial Al-10Sr master alloys (wt.%)

Types of commercial Al-10Sr alloy	Sr	Fe	Si	Mg
Untreated	10.5	0.29	0.20	Bal.
Remelted	10.1	0.18	0.12	Bal.

3. Results and Discussion

3.1 Effects of Sr Amount and Melt Holding Time

Table 3 and 4 respectively list the average grain size of AZ31 alloy modified with the untreated commercial Al-10Sr master alloy for different Sr amounts and melt holding times. It is found from Table 3 and 4 that adding small amounts of Sr to AZ31 alloy can effectively reduce the grain size of the alloy.

Table 3 Average grain size of AZ31 alloy treated with the untreated commercial Al-10Sr master alloy for different Sr amounts and 60 min melt holding time

Nominal alloys	Melt holding time, min	Average grain size, μm	Standard error of grain size measurement, μm
AZ31	60	200	4.30
AZ31 + 0.01 wt.% Sr	60	125	3.10
AZ31 + 0.05 wt.% Sr	60	118	3.64
AZ31 + 0.1 wt.% Sr	60	111	3.17

Table 4 Average grain size of AZ31 alloy treated with the untreated commercial Al-10Sr master alloy for 0.1 wt.% Sr and different melt holding times

Nominal alloys	Melt holding time, min	Average grain size, μm	Standard error of grain size measurement, μm
AZ31 + 0.1 wt.% Sr	20	127	3.67
AZ31 + 0.1 wt.% Sr	40	117	3.02
AZ31 + 0.1 wt.% Sr	60	111	3.17
AZ31 + 0.1 wt.% Sr	80	90	4.48

Table 2 Chemical compositions of the as-cast AZ31 alloy treated with different Al-10Sr master alloys for different Sr amounts and melt holding times

			Elements, wt.%				
Nominal alloys	Melt holding time, min	Types of commercial Al-10Sr alloy	Al	Zn	Mn	Sr	Mg
AZ31	60	Without Sr modification	2.85	0.76	0.17	…	Bal.
AZ31 + 0.01 wt.% Sr	60	Untreated	2.87	0.77	0.18	<0.01 (a)	Bal.
AZ31 + 0.05 wt.% Sr	60	Untreated	2.87	0.78	0.17	0.031	Bal.
AZ31 + 0.1 wt.% Sr	60	Untreated	2.88	0.77	0.16	0.087	Bal.
AZ31 + 0.1 wt.% Sr	20	Untreated	2.88	0.78	0.17	0.086	Bal.
AZ31 + 0.1 wt.% Sr	40	Untreated	2.86	0.77	0.17	0.087	Bal.
AZ31 + 0.1 wt.% Sr	80	Untreated	2.87	0.76	0.18	0.087	Bal.
AZ31 + 0.1 wt.% Sr	60	Solutionized	2.87	0.75	0.17	0.086	Bal.
AZ31 + 0.1 wt.% Sr	60	Rolled	2.87	0.76	0.16	0.086	Bal.
AZ31 + 0.1 wt.% Sr	60	Remelted	2.88	0.75	0.16	0.087	Bal.

(a) The real Sr-content is not identified due to low Sr adding rate

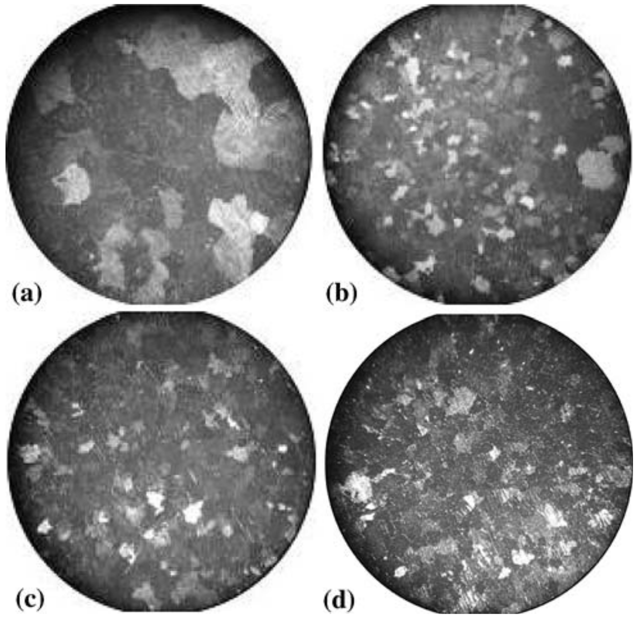

Fig. 1 Grain refinement of AZ31 alloy treated with the untreated commercial Al-10Sr master alloy for different Sr amounts and 60 min melt holding time: (a) without Sr modification, (b) 0.01% Sr; (c) 0.05% Sr; and (d) 0.1% Sr. The diameter of each polished section is $\sim$25 mm

Table 5 Average grain size of AZ31 alloy treated with the various commercial Al-10Sr master alloys for 0.1% Sr and 60 min melt holding time

Nominal alloys	Types of commercial Al-10Sr alloy	Average grain size, µm	Standard error of grain size measurement, µm
AZ31 + 0.1 wt.% Sr	Untreated	111	3.17
AZ31 + 0.1 wt.% Sr	Solutionized	103	3.13
AZ31 + 0.1 wt.% Sr	Rolled	91	4.85
AZ31 + 0.1 wt.% Sr	Remelted	68	4.62

Furthermore, it is found from Table 3 that for a given 60 min melt holding time, an increase in Sr amount from 0.01 to 0.1 wt.% causes the average grain size of AZ31 alloy to gradually decrease. In addition, it is also observed from Table 4 that for a given Sr amount of 0.1 wt.%, an increase in melt holding time from 20 to 80 min causes the average grain size of AZ31 alloy to gradually decrease. Figure 1 presents an overview of AZ31 alloy modified with the untreated commercial Al-10Sr master alloy for different Sr amounts and 60 melt holding time, corresponding to the observations shown in Table 3.

3.2 Effect of Processing of Commercial Al-10Sr Master Alloy

Table 5 lists the average grain size of AZ31 alloy treated with the various commercial Al-10Sr master alloys for 0.1 wt.% Sr and 60 min melt holding time. Obviously, the conclusion that adding small amounts of Sr to AZ31 alloy can effectively reduce the grain size of the alloy is further confirmed by Table 5. In addition, it is further found from Table 5 that the refinement efficiency of remelted commercial Al-10Sr master alloys is best, followed by the rolled, solutionized, and untreated commercial Al-10Sr master alloys, respectively. Based on the above results, it is inferred that the processing (solutionizing, rolling, or remelting) of commercial Al-10Sr master alloy can improve the refinement efficiency of the master alloy to AZ31 alloy, and the improvement resulting from remelting and rolling is best obvious.

4. Discussion

As listed in Table 1, the Fe element is detected in the untreated and remelted commercial Al-10Sr master alloys. The previous investigations (Ref 17) indicated that the Fe addition is an effective grain refiner for Mg-Al-based alloys. Therefore, one problem arises whether the grain refinement of AZ31 alloy treated with the various commercial Al-10Sr master alloys is related to the Fe element. According to the above information from Table 2, the Fe element is not detected in the AZ31 alloy treated with the various commercial Al-10Sr master alloys, which might be related to the manganese in the experimental alloys since the Fe can be removed by the precipitation and setting of intermetatallic particles containing iron and manganese during the melting. Therefore, in the present investigations the effect of Fe on the grain refinement of AZ31 alloy treated with the various commercial Al-10Sr master alloys may be neglected.

In general, the grain refinement in industrial applications usually involves adding nucleants and/or solute elements into a melt before casting, and the effect of a solute element may be explained in terms of the growth restriction factor GRF (Eq 1) (Ref 5, 6, 12). In addition, the grain refinement is also related to the heterogeneous nucleation during solidification. One criterion of heterogeneous nucleation is that the disregistry of nucleant planes is less than 6% (Ref 18). Figure 2 shows the XRD results of untreated and remelted commercial Al-10Sr master alloys. It is found from Fig. 2 that the two master alloys are composed of α-Al and Al_4Sr phases. Since under the experimental conditions of this work the solutionizing and rolling did not cause the formation of any new phases, it is believed that the various commercial Al-10Sr master alloys are composed of α-Al and Al_4Sr phases. It is well known that the Al_4Sr phase is a body centered tetragonal structure with $a = 4.46$ nm and $c = 11.07$ nm (Ref 19). The α-Mg phase is a Hexagonal Close-Packed crystal structure with $a = 0.320$ nm and $c = 0.520$ nm (Ref 19). Obviously, the lattice disregistry between Al_4Sr and α-Mg phases is larger than 6%, indicating that the Al_4Sr phase cannot act as the heterogenerous nucleus for the α-Mg phases. Therefore, the Al_4Sr phases in the various commercial Al-10Sr master alloys could not directly influence the grain refinement unless the free Sr was obtained by the dissolution of Al_4Sr phase. It is well known that the solid solubility of Sr in magnesium is relatively limited (about 0.11 pct) (Ref 12); thus after the Al_4Sr phase is gradually dissolved into the melt of AZ31 alloy, the free Sr will rapidly enrich in the liquid ahead of growing interface and then restrict the grain growth during solidification (Ref 5, 6). Therefore, the grain refinement of AZ31 alloy treated with the various commercial Al-10Sr master alloys is possibly related to the GRF mechanism. According to the GRF mechanism, larger the

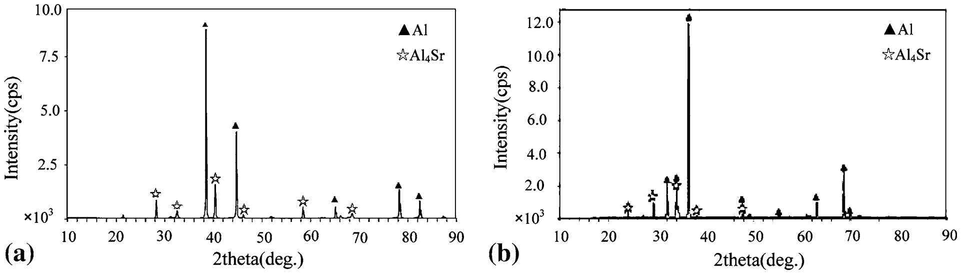

Fig. 2 XRD results of the (a) untreated and (b) remelted commercial Al-10Sr master alloys

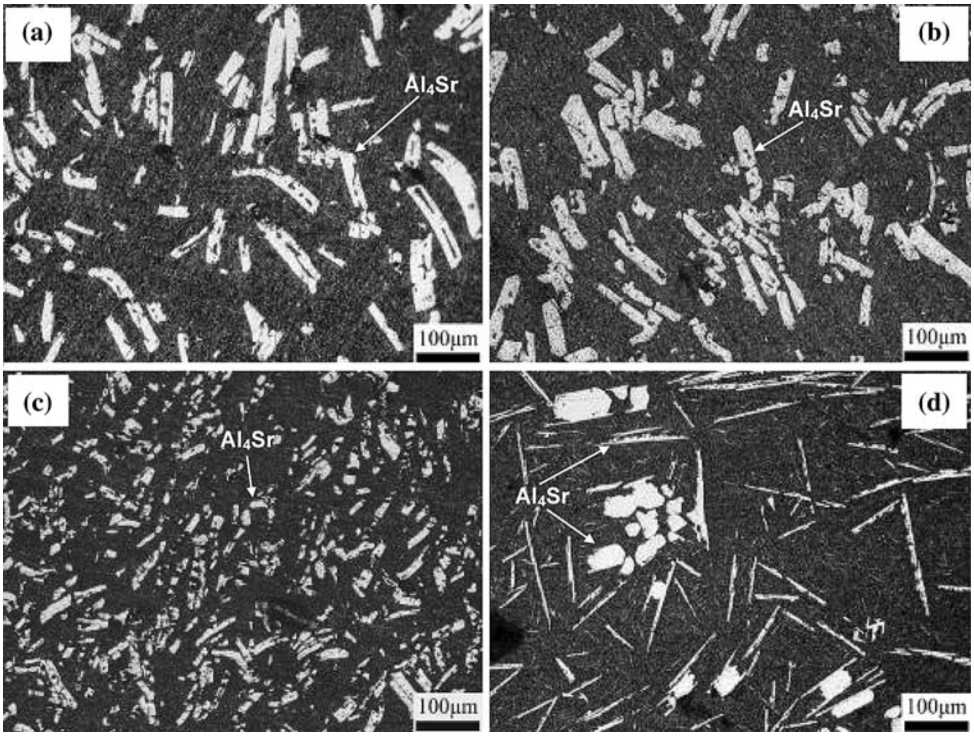

Fig. 3 Microstructures of the various commercial Al-10Sr master alloys: (a) untreated, (b) solutionized, (c) rolled, and (d) remelted

value of GRF, higher will be the refinement efficiency. GRF is defined from:

$$\mathrm{GRF} = \sum_i m_i c_{0i}(k_i - 1) \qquad \text{(Eq 1)}$$

where m_i is the slope of the liquidus line, c_{0i} is the initial concentration of element i and k_i is the partition coefficient. Under the experimental condition of this work, i denotes Al, Zn, and Sr elements, respectively. For the AZ31 alloy modified with the untreated commercial Al-10Sr master alloy for different Sr amounts and 60 min melt holding time, the increase in Sr amount from 0.01 to 0.1 wt.% will cause the amount of Al_4Sr phase in the melt of AZ31 alloy to increase. Accordingly, the concentration of free Sr will increase. As a result, the GRF value increases according to Eq 1. Obviously, the effect of Sr amount on the grain refinement of AZ31 alloy modified with the untreated commercial Al-10Sr master alloy may be easily explained according to the GRF mechanism. In addition, the GRF mechanism is also suitable for the effect of melt holding time on the grain refinement of AZ31 alloy modified with the untreated commercial Al-10Sr master alloy, because the increase in melt holding time from 20 to 80 min will cause the dissolution time of Al_4Sr phase to increase and then a relatively high concentration of free Sr and a large GRF value will be obtained.

Furthermore, the GRF mechanism may be also used to explain the effects of solutionized, rolled, and remelted commercial Al-10Sr master alloy on the grain refinement of AZ31 alloy. Figure 3 shows the microstructures of various commercial Al-10Sr master alloys. As shown in Fig. 3, the morphology and size of Al_4Sr phase in the various commercial Al-10Sr master alloys are of great difference. It is found from Fig. 3(a) and (b) that, although the Al_4Sr phases in the untreated and solutionized commercial Al-10Sr master alloys mainly exhibit particles, the Al_4Sr phase in the solutionized commercial Al-10Sr master alloy is relatively finer than the Al_4Sr phase in the untreated commercial Al-10Sr master alloy. In addition, it is also observed from Fig. 3(c) and (d) that the Al_4Sr phases in the rolled and remelted commercial Al-10Sr

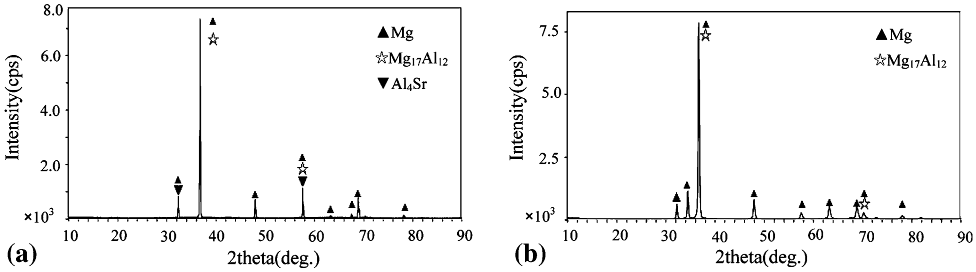

Fig. 4 XRD results of AZ31 alloy treated with the (a) untreated and (b) remelted commercial Al-10Sr master alloys for 0.1% Sr and 60 min melt holding time

master alloys mainly exhibit fine granular and fiberous shapes. According to the established practice of Al-Sr master alloys for the modification and refinement of aluminum alloys, a high dissolution rate can be obtained for the finer Al_4Sr phase in Al-Sr master alloys (Ref 14-16). Therefore, it is inferred that the Al_4Sr phases in the rolled and remelted commercial Al-10Sr master alloys possibly have higher dissolution rates than the Al_4Sr phases in the untreated and solutionized commercial and Al-10Sr master alloys. This conclusion may be indirectly confirmed by Fig. 4. As shown in Fig. 4, the Al_4Sr phase is detected in the AZ31 alloy modified with the untreated commercial Al-10Sr master alloy but not detected in the AZ31 alloy modified with the remelted commercial Al-10Sr master alloy. Since adding small amounts of Sr (<0.1 wt.%) to magnesium alloys usually does not cause the formation of any new phases (Ref 10), it is inferred that the Al_4Sr phase does not completely dissolve into the melt of AZ31 alloy thus is detected in the AZ31 alloy modified with the untreated commercial Al-10Sr master alloy. Obviously, the incomplete dissolution of Al_4Sr phase in the melt of AZ31 alloy modified with the untreated commercial Al-10Sr master alloy is possibly related to the relatively low dissolution rate of Al_4Sr phase. Based on the above analysis, it is further inferred that for a given Sr amount of 0.1 wt.% and 60 min melt holding time, the concentration of free Sr in the melt of AZ31 alloy modified with the remelted or rolled commercial Al-10Sr master alloys is higher than that of the free Sr in the melt of AZ31 alloy modified with the solutionized or untreated commercial Al-10Sr master alloys. As a result, the remelted and rolled commercial Al-10Sr master alloys exhibit higher refinement efficiency than the solutionized and untreated commercial and Al-10Sr master alloys according to the GRF mechanism. In spite of the above discussions, the exact mechanism to explain the effect of processing of commercial Al-10Sr master alloy on the refinement efficiency of the master alloy is not completely clear. It is a subject for further study in our group.

5. Conclusions

1. The effects of Sr amount and melt holding time on the grain refinement of AZ31 alloy modified with the commercial Al-10Sr master alloy are very obvious. Under the experimental conditions of this work, an increase in the Sr amount from 0.01 to 0.1 wt.% or melt holding time from 20 to 80 min causes the grain size of AZ31 alloy treated with the commercial Al-10Sr master alloy to gradually decrease.
2. The solutionizing, rolling, or remelting of commercial Al-10Sr master alloy can improve the refinement efficiency of the master alloy to AZ31 magnesium alloy, and the improvement resulting from the remelting is best obvious, followed by rolling and solutionizing, respectively.

Acknowledgments

The present work was supported by the National Natural Science Funds for Distinguished Young Scholar in China (No. 50725413), the Major State Basic Research Development Program of China (973) (No. 2007CB613704), and Chongqing Science and Technology Commission in China (No. 2006AA4012-9-6 and No. 2007BB4400).

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