J Mater Sci (2012) 47:514–520
DOI 10.1007/s10853-011-5828-6

Effect of impurity reduction on rollability of AZ31 magnesium alloy

Xianhua Chen · Fusheng Pan · Jianjun Mao · Jiansheng Huang

Received: 26 March 2011 / Accepted: 26 July 2011 / Published online: 6 August 2011

Abstract The effect of impurity reduction on the hot rolling behavior of AZ31 magnesium alloy was systematically investigated in this study. In the as-cast alloys, the total content of main impurity elements such as Fe, Si, Cu, and Ni was varied from 0.0462 to 0.0163 wt% by changing the purity of used raw magnesium metals. The alloys after homogenization were subjected to hot rolling at 300 °C with a reduction of 20% per pass. It was found that the initiation of edge cracks is postponed with reducing impurity level in the alloys. And the maximum rolling reduction prior to edge cracking increases from 34 to 58% as the impurity content drops from 0.0462 to 0.0163 wt%. Microstructural observations showed that smaller grains are present in the alloy with lower impurity content in the cast and homogenization states. Moreover, decreasing impurity content leads to a reduced number of deformation twins and an enhanced volume fraction of small recrystallized grains in the as-rolled microstructure, which indicates that impurity reduction is beneficial to the recrystallization process and subsequent plastic deformation. Based on the results, the enhancement in hot rollability of the AZ31 sheet by impurity reduction should be due to finer grain size, the reduced number of deformation twins and the enhanced extent of recrystallization.

X. Chen · F. Pan · J. Mao · J. Huang
College of Materials Science and Engineering, Chongqing University, Chongqing 400044, People's Republic of China

X. Chen (✉) · F. Pan
National Engineering Research Center for Magnesium Alloys, Chongqing University, Chongqing 400044, People's Republic of China
e-mail: xhchen@cqu.edu.cn

Introduction

Magnesium alloys are quite attractive as lightweight structural materials particularly in some automotive applications due to their good properties, such as low density, good damping capacity, high specific strength, and excellent recyclability [1, 2]. However, magnesium alloys generally exhibit a significantly poor rollability accompanied with early edge cracking, which can be ascribed to their hexagonal crystal structure and the associated lack of sufficient independent slip systems to meet von Mises criteria for homogeneous plastic straining [3, 4]. This consequently leads to the very limited sheet applications of magnesium alloys as structural parts at present.

In order to improve the deformability of magnesium alloys, many studies have been carried out on the development of optimum rolling parameters, alloying additions, and processing techniques, as a result being able to modify texture, grain size, c/a ratio, and so on [3–8]. A decrease in the c/a ratio of magnesium alloys can enhance the glide of dislocations on non-basal planes. The strong basal texture forms in magnesium alloys during rolling process, which severely limits the basal slip. It is, therefore, true that weakening basal texture and reducing c/a ratio can improve the rollability of magnesium alloys. Mackenzie and Pekguleryuz have reported that lithium alloying additions improve the rollability of pure magnesium and AZ31 alloy due to increasing the activation of non-basal planes and also changing the texture [3]. Lim et al. [5] found that grain size of cross-rolled magnesium alloy is smaller than that of conventionally rolled alloy, which induces improved ductility and formability in the cross-rolled alloy.

Generally speaking, purity is an important factor affecting the development and application of high-quality magnesium alloys. In the past decades, some attention was paid on the influence of impurity elements (Fe, Si, etc.) on the microstructure and properties of magnesium and its alloys [9–12]. The results provided by Cao et al. [10] illustrated that Fe reduction induces an obvious grain refinement in as-cast Mg–Al alloy. The similar effect was observed in as-cast AZ91 alloy by Gao et al. [9], furthermore tensile testing showed that the strength and ductility increase with decreasing Fe content in the alloy. Very recently, the first author and his cooperators have investigated the microstructures, tensile properties, and damping capacity of ZK60 alloys with different impurity levels [13, 14]. The results showed that a reduction of impurities (Fe, Si, etc.) leads to finer dynamic-recrystallized grains after hot extrusion, resulting in that the alloy containing higher purity exhibits higher strength and damping capacity.

It is well known that grain size and dynamic recrystallization (DRX) play an important role in the process of hot rolling deformation of magnesium alloys [15]. Based on the results in the literature and our investigation on ZK60 alloy, it is expected that impurity content should have an evident effect on hot rolling behavior of magnesium alloys since impurity elements could change the grain size and DRX process. Whereas, the relationship between impurity reduction and hot rolling characteristics in magnesium alloys have been rarely investigated. In this study, twin-roll hot rolling processing was carried out on three AZ31 alloy sheets with various levels of impurity elements, and then their plastic forming capacities were compared. The microstructural factors that enhance rollability via impurity reduction are explored. The results of the present work are expected to be meaningful in the development of high performance magnesium with excellent deformability.

Experimental procedures

AZ31 alloys studied were prepared by semi-continuous casting. The raw materials used were pure aluminum, pure zinc, Al–Mn master alloy, and two different purity magnesium metals, i.e., high purity magnesium (99.98 wt%) and commercial purity magnesium (99.93 wt%). Three groups of AZ31 alloys were synthesized. The first group was made using high purity magnesium metal, and the second group using commercial purity magnesium metal. The alloy in the last group was made using a mixture of high purity (50 mass%) and commercial purity (50 mass%) magnesium metals. But the contents of Al, Zn, and Mn were controlled to be similar in these alloys. The chemical compositions measured by a photoelectricity spectrum analyzer (APL4460) are listed in Table 1, from which it is seen that the overall impurity contents are 0.0163 wt% (hereafter referred to as A1), 0.0249 wt% (A2), and 0.0462 wt% (A3), respectively.

The casting ingots were homogenized at 400 °C for 14 h in order to eliminate the dendrites and enhance the hot workability. $6.5 \times 50 \times 80$ mm^3 rolling specimens were machined from the homogenized alloys. Hot rolling of these AZ31 sheets was performed on a laboratory mill with a roll diameter of 300 mm at 300 °C. The specimens were heat treated at 300 °C for 8 min between passes to stabilize the rolling temperature. The thin sheets were reversed after each pass so that shear strain was introduced unidirectionally. The sheets were hot rolled from 6.5 to 1.7 mm in thickness with a reduction per pass of $\sim$20%, and the corresponding average strain rate is approximately 1.2–1.8/s.

Specimens for microstructure observations were prepared by mechanical grinding, polishing, and subsequent etching. The as-cast specimens were etched in a solution of 6 g picric acid, 2 mL acetic acid, 100 mL ethanol, 0.5 mL phosphoric acid, and 1 mL distilled water. The as-homogenized and rolled specimens were etched with a mixture of 5.5 g picric acid, 90 mL ethanol, 5 mL acetic acid, and 10 mL distilled water. All microstructures were observed in the rolling plane of the rolling plates. Microstructural examination was performed on optical microscope (OM, NEOPHOT-30) and scanning electron microscope (SEM, TESCAN VEGA II LMU) using an accelerating voltage of 20 kV. In order to clearly reveal grain structure and grain size, the as-cast etched specimens are examined using OM with polarized light; the polarizer and analyzer being perpendicular to each other. Analysis of second phase composition was carried out using energy dispersive spectroscopy (EDS), and grain size was measured by the linear intercept method.

Results

The evaluation of the hot rollability of AZ31 alloy can be demonstrated by the occurrence of cracks on the sheet surface or edge region [6, 8]. Macroscopic inspection of the rolled AZ31 sheets after the second pass rolling is shown in Fig. 1, which illustrates that impurity reduction can postpone the initiation of edge cracks in AZ31 alloys. In the case of A3 sheet, edge cracks began to occur after the second pass rolling and became more severe with increasing the accumulated reduction. On the other hand, edge cracks were not observed in A1 sheet until the fourth pass rolling. After the sixth pass rolling, A1 has significantly lower levels of edge cracking than A3. The maximum hot rolling reduction (ε_m) achievable in these sheets prior to the occurrence of edge cracking is given in Table 2. A1 sheet possesses a ε_m value of 58%, which is remarkably higher than that of A3 sheet (ε_m = 34%). The observations suggest that the reduction of impurity elements is beneficial to the improvement of hot rollability of

Table 1 Chemical compositions of AZ31 alloys (wt%)

Alloy	Al	Zn	Mn	Fe	Si	Cu	Ni	Mg
A1	2.89	0.93	0.30	0.0049	0.007	0.0040	0.00039	Bal.
A2	2.88	0.88	0.26	0.0103	0.010	0.0042	0.00037	Bal.
A3	2.92	0.89	0.24	0.0164	0.024	0.0051	0.00078	Bal.

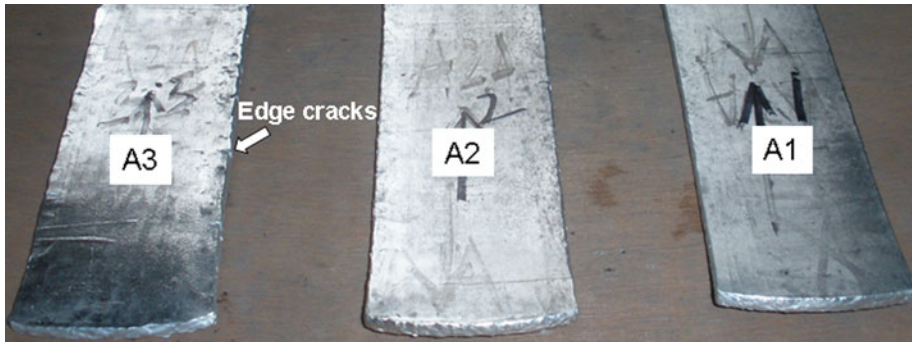

Fig. 1 Outward appearances of the AZ31 sheets after the second rolling pass

Table 2 Rolling properties of the AZ31 sheets with different impurity contents subjected to rolling deformation at 300 °C (ε_m denotes the maximum reduction prior to the occurrence of edge cracks)

Alloy	Impurity content (%)	Rolling pass of ε_m	ε_m (%)
A1	0.0163	4	58
A2	0.0249	3	50
A3	0.0462	2	34

AZ31 sheets, inducing a decrease of rolling production cost.

Figure 2 shows typical microstructures of the as-cast AZ31 alloys after etching using an optical microscope with polarized light. The granular structure is made visible by the color contrast between adjacent grains, and the dendritic structure enclosed within grains is also revealed by etching. It can be seen that the grain size is refined as the impurity level decreases in the alloys. Statistical measurements obtained that the average grain size of A1 alloy is approximately 410 μm, which much finer than those of A2 (600 μm) and A3 (920 μm) alloys. Grain refinement by impurity reduction can be explained with the hypotheses proposed by several researchers; that is, the presence of Fe interferes with the formation of Al_4C_3 or Mg–Al–C–O particles, which are the nucleation sites responsible for grain refinement in Mg–Al alloys [9, 10].

Typical optical micrographs of AZ31 alloy after homogenization at 400 °C for 14 h are displayed in Fig. 3. It is obvious that homogenization treatment has effectively eliminated dendrite structure, and grain boundaries are thus more clearly delineated. At the same time, a slight grain growth is found in the alloys, while the grain size still reduces with decreasing impurity level. Eutectic phases in AZ31 alloys were not fully dissolved in the matrix even after high-temperature homogenization. EDS analysis indicates that most of the second phase particles are $Mg_{17}Al_{12}$ in the as-homogenized condition, and a part of them contain impurity elements, such as Fe, Si, as revealed by Fig. 4. It is expected that some impurity elements should be solutionized in the matrix, however, the impurity content is too low to be detected using EDS measurement.

In order to reveal the mechanism that impurities affect the rolling behavior of AZ31 sheets, the microstructural evolution during hot rolling was investigated. Typical microstructural features in these AZ31 sheets subjected to the second pass rolling are highlighted by the optical and SEM images presented in Fig. 5. Obviously, the microstructural characteristics were changed significantly by rolling deformation. From Fig. 5a1, b1, and c1, it is observed that the microstructures tend to be rather heterogeneous and are characterized by the mixture of fine grains, coarse grains and deformation twins indicated by the arrows. A large amount of twins are present in as-rolled A3 alloy sheet, whereas the number of twins in as-rolled A1 alloy sheet is significantly reduced. The large grains in the order of several 100 μm, may be the remnants of as-homogenized grains that have not entirely been recrystallized. The newly formed fine grains should be dominantly induced by dynamic recrystallization due to strain accumulation during hot rolling, metadynamic recrystallization, and/or static recrystallization upon repeated pre-heating between passes [7, 16]. SEM micrographs in Fig. 5a2, b2, and c2 show the feature of the fine recrystallized grains more clearly, and the grain size is measured to be roughly 5–15 μm. It is evident that decreasing impurity content results in an enhanced volume fraction of small recrystallized grains. A1 sheet has the volume fraction of

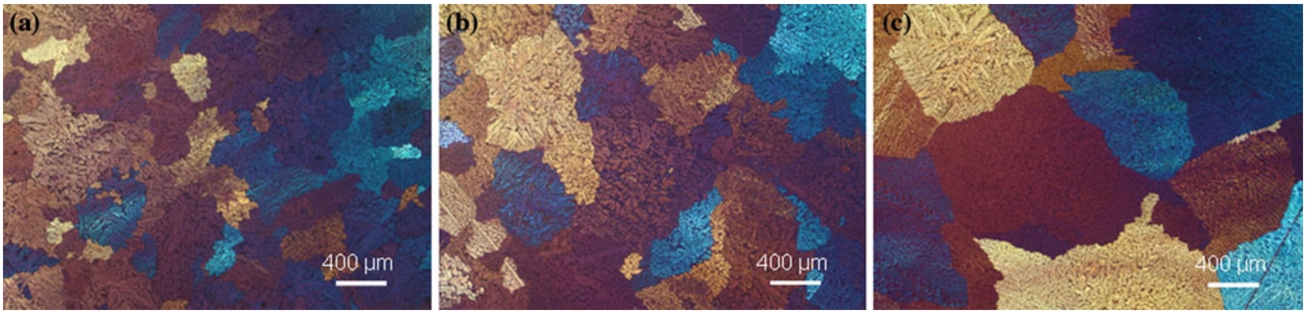

Fig. 2 Microstructures of as-cast AZ31 alloys with different impurity contents: **a** A1, **b** A2, and **c** A3

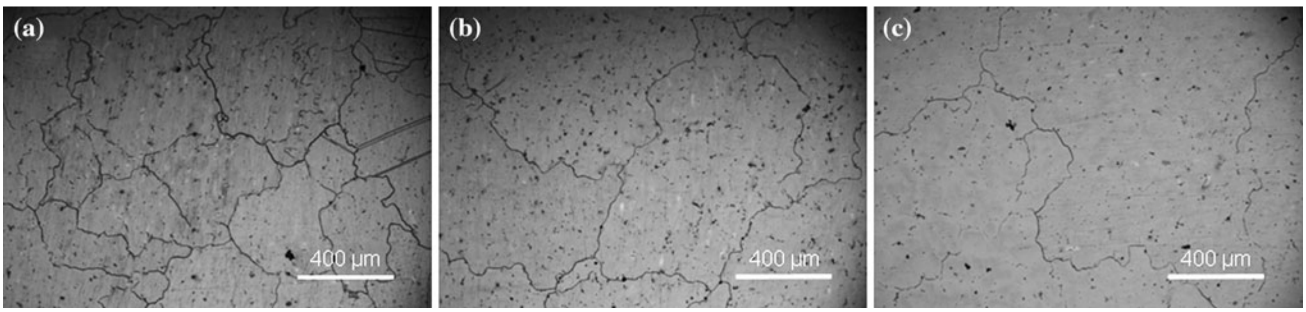

Fig. 3 Optical micrographs of the AZ31 alloys with different impurity contents in the homogenized condition: **a** A1, **b** A2, and **c** A3

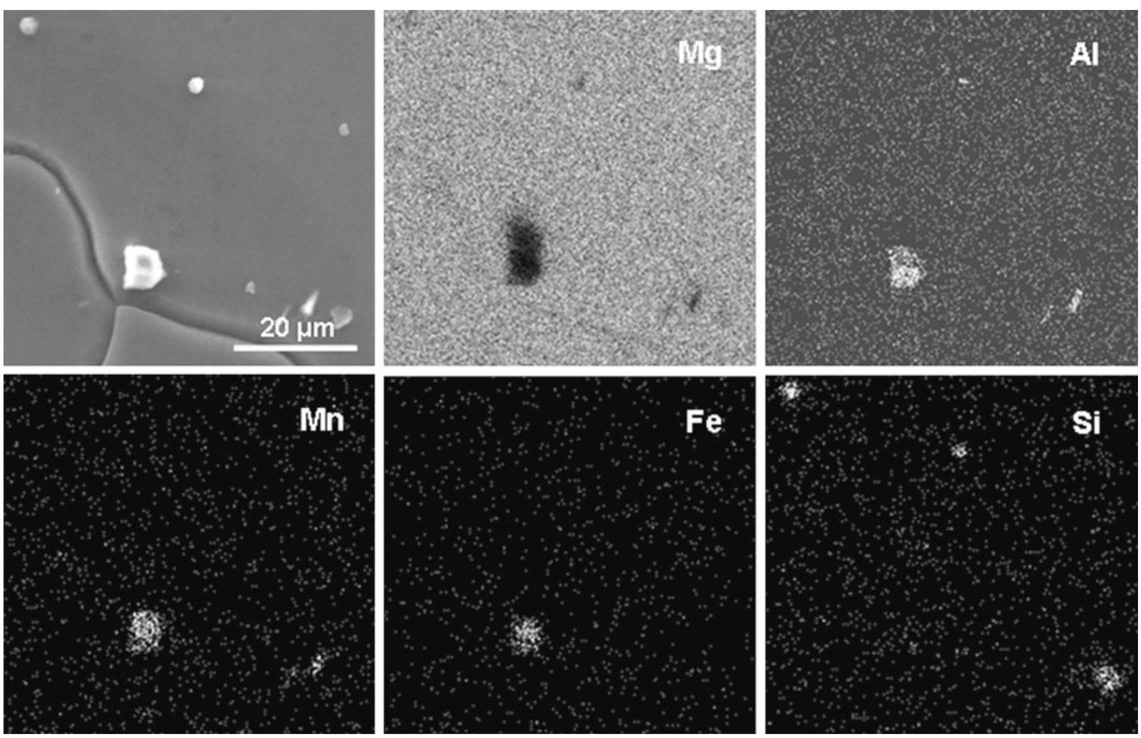

Fig. 4 EDS mapping of as-homogenized A3 alloy

small recrystallized grains of about 49%, however, the values are 33 and 20% for A2 and A3 sheets, respectively, indicating that an enhanced extent of recrystallization happened in the rolled sheet with lower impurity content. Figure 6 is optical micrographs illustrating the microstructures of the rolled sheets after the forth pass rolling at 300 °C. For each AZ31 rolled sheet, the microstructure becomes finer and more homogeneous with increasing

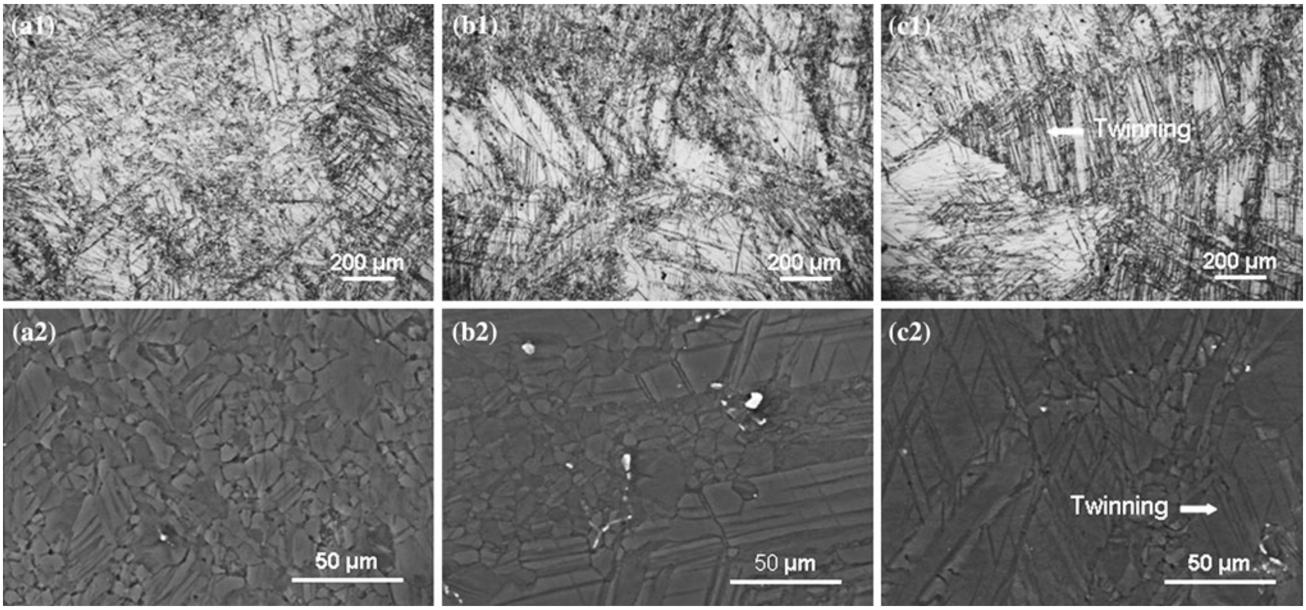

Fig. 5 Typical optical (**a1**, **b1**, and **c1**) and SEM (**a2**, **b2**, and **c2**) micrographs showing the microstructures of **a1** and **a2** A1, **b1** and **b2** A2, and **c1** and **c2** A3 sheets after the second pass rolling

rolling reduction. Some twins are still observed in the as-rolled microstructure. Dynamic and static recystallizations further lead to smaller grain size in the rolled sheets. It can be found the volume fraction of finer grains tends to be enhanced when the impurity level becomes lower.

Discussion

In general, alloying additions, processing parameter optimization, controlling the texture, grain refinement, and new rolling techniques are introduced to improve the rolling properties of magnesium alloys in the literature [3–8, 16]. According to our experimental results, impurity reduction has the similar effect on the rolling behavior of AZ31 magnesium alloy sheets, which could be intimately related to the changes of the size of α-Mg matrix phase in the cast and homogenized conditions, the amount of deformation twins and the recrystallization process during hot rolling.

For magnesium alloys, the symmetry of hexagonal close packed crystals has the effect of limiting the number of independent slip systems and making twinning a concernful deformation mechanism [15]. At room temperature, only basal slip can generally operate for plastic straining. When the temperature increases, critical resolved shear stress for non-basal systems decreases significantly, and then prismatic and pyramidal slip operation becomes possible [17, 18]. Hot rolling deformation consequently comes from the contributions of basal slip, non-basal slip, and twinning, which gives rise to a high density of twins presented in the rolled structure of AZ31 sheets, as shown in Figs. 5 and 6.

Compared to the AZ31 alloy with higher impurity content, the as-cast microstructure of the AZ31 alloy with lower impurity content has finer grains including a much larger area fraction of grain boundaries, which is also the case in the homogenization condition. Finer grain size is beneficial to the basal dislocation slip and the strain coordination between grains during rolling, making plastic deformation more uniform in the rolled sheets. It is well known that grain boundaries are able to prevent the localization of the externally applied stress and effectively absorb strain energy [8]. According to the results of Wang et al. [8], the grain boundaries provide high resistance against crack propagation, and more deformation energy is required to be applied for cracks to proceed through the boundaries. As a result, the finer grains in the cast and homogenized conditions provide important basis for the enhanced rollability in the AZ31 alloy containing lower impurity level.

According to our observation in Fig. 5, the AZ31 sheet with lower impurity content has a smaller number of deformation twins inside the α-Mg matrix after the second pass rolling, which should be attributed to the effect of grain refinement. Twin boundaries inside the matrix tend to act as crack nuclei [19, 20] at the same time they have low resistance against crack propagation that results in easy propagation of cracks along them [8]. It is believed that significantly reduced twin density is an important factor postponing the occurrence of edge cracks in A1 sheet.

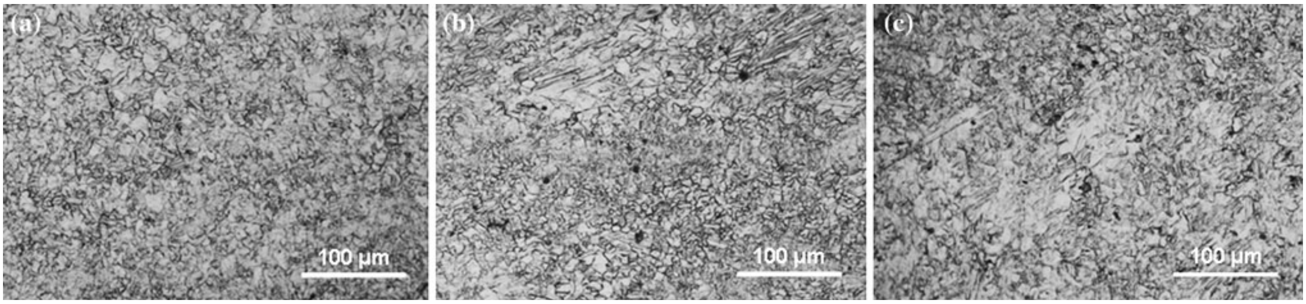

Fig. 6 Typical as-rolled microstructures of the AZ31 sheets after the forth pass rolling: **a** A1, **b** A2, and **c** A3

In the as-rolled microstructures, dislocations, twin boundaries, and grain boundaries can act as new nucleation sites for DRX during rolling and/or static recrystallization during the reheating between passes [21, 22], resulting in new fine grains with orientations more favorable for basal slip and assisting the subsequent deformation [15]. Nevertheless, the impurities could pin dislocations and prohibit dislocation climbing, which raises the difficulty of the formation of recrystallization nucleuses and reduces the nucleation ratio [13, 23]. Impurity reduction can lead to an increase in the volume fraction of fine recrystallized grains, as observed in Fig. 5. Besides refining grains, recrystallization plays an important role in eliminating strain hardening and releasing accumulated energy. Enhanced extent of recrystallization means weaker strain hardening that can be reflected by the results of hardness measurement. Therefore, the enhanced extent of recrystallization in the rolled sheet containing lower impurity content is helpful for the rolling deformation and prohibits the initiation of edge cracks.

The present experimental results shed light on edge cracking control in magnesium alloy sheets and are of much significance, since edge cracking is one of the main limiting factors on the preparation of high-quality magnesium alloy sheets for practical application [4].

Conclusions

1. The hot rollability of AZ31 magnesium alloys can be obviously affected by impurity content. Decreasing the impurity content from 0.0462 to 0.0163 wt% postpones the occurrence of edge cracks and increases the maximum rolling reduction prior to edge cracking from 34 to 58% during hot rolling.
2. Impurity reduction results in grain refinement of the as-cast microstructure in the AZ31 alloy. A smaller number of deformation twins and a larger volume fraction of fine recrystallized grains are observed in the as-rolled AZ31 sheet with lower impurity content.
3. The improved rollability in the AZ31 sheet by impurity reduction could be attributed to finer gains in the cast and homogenized conditions, less twin boundaries, and enhanced extent of recrystallization in the rolled condition, which may prohibit crack growth.

Acknowledgements The authors would like to thank the financial supports form National Natural Science Foundation of China (Grant No. 50725413), National Basic Research Program of China (Grant No. 2007CB613704), Ph.D. Programs Foundation of Ministry of Education of China (Grant No. 20090191120013), Fundamental Research Funds for the Central Universities (Grant No. CDJZR10130001), and Natural Science Foundation Project of CQ CSTC (Grant No. 2009BB4215).

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