J Mater Sci (2010) 45:2233–2238
DOI 10.1007/s10853-009-3908-7

HTC2009

An experimental study on the influence of particles on grain boundary migration

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Received: 2 June 2009 / Accepted: 17 September 2009 / Published online: 1 October 2009

Abstract The pinning effect of particles on grain boundary migration was studied in a Fe–20 mass% Cr alloy deoxidised with Ti and Zr. The different nitrogen contents (65, 248 and 490 ppm) were used to vary the number of precipitated inclusions. The specimens from equiaxed zones of metal samples with different particle densities were examined by in situ observations during a 60-min holding time at 1200 and 1400 °C in a Confocal Scanning Laser Microscope. The change of particles pinning effect on the grain growth was described by an average grain size, $\bar{D}_A$, and the ratio between the perimeter and area of grains, P_{GB}/A_G. It was found that the pinning effect of particles (mostly complex Ti–Zr oxynitrides) on grain growth decreased with a decreased nitrogen content in the metal. Furthermore, the effect of particles decreased with an increased temperature of treatment, due to the reduction of the number of particles on the grain boundaries.

Introduction

It is well-known that the final properties of steel are dependent on the microstructure. In addition, that the grain size is one of the basic parameters that defines the metal microstructure. Therefore, grain growth and different means of grain size control have been extensively studied for both fundamental and technological reasons. One of the perspective methods for pinning of grain growth is the use of inclusion particles precipitated in the metal during deoxidation, solidification and cooling. These particles restrict the growth of grains at high temperatures during heating or welding of a solid metal. Therefore, numerous investigations have discussed the influence of different inclusions on the grain growth in various steels and alloys [1–9].

A migration of grain boundaries is significantly initiated by heat treatment of metals at high temperatures due to an increased grain boundary mobility which is increasing with increasing temperature, and thus accelerates the grain growth process. Until recent time, most of the data on grain growth during heat treatment were obtained by comparing the microstructures before and after heating [2–4, 7–9]. An alternative method is an in situ observation of the grain boundary migration by using a Confocal Scanning Laser Microscope (CSLM), since it can provide more accurate and dynamic data for the determination of the pinning effect of different particles on grain growth at high temperature [5, 6, 10–12].

In the present study, the effect of nitride–oxide particles on the migration of grain boundaries has been studied for a Fe–20 mass% Cr alloy during heat treatment at 1200 and 1400 °C. The number and composition of the inclusions in the metal were changed by varying the nitrogen content in the samples. The change of the grain boundary curvature and pinning effect of particles were determined based on the in situ observations by using a CSLM.

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Experimental

Electrolytic Fe and pure Cr metal were used for the making/preparation of a Fe–20 mass% Cr mother alloy in an arc furnace under an Ar atmosphere. Then, 150 g of this alloy was melted at 1600 °C in an MgO crucible under an Ar gas atmosphere (500 mL/min) in a high-frequency induction furnace (100 kHz, 20 kW). In order to exclude the strong induction stirring of the melt, a graphite susceptor was inserted between the furnace wall and the crucible. Initially, the melt was held at 1600 °C to ensure a uniform chemical composition the melt. Thereafter, Ti and Zr were added as deoxidants. After deoxidation, the melt was stirred and held at 1600 °C for 30 s. This was followed by cooling to 1400 °C with a cooling rate of 0.8 °C/s and then finally water quenching. The final nitrogen content in the metal was 65, 248 and 490 ppm in Samples 1, 2 and 3, respectively. In addition, the oxygen content was approximately 150 ppm in all samples.

The as-cast ingot samples were cut vertically and horizontally and etched for a detection of the equiaxed zone. The number of particles per unit volume was estimated in an equiaxed zone for each sample. The inclusions on film filter after electrolytic extraction of metal specimen were analysed by using a Scanning Electron Microscope (SEM).

For in situ observation of grain growth and pinning effect of particles during heat treatment at different temperatures, cylindrical specimens (Ø4.2 × 1.5 mm) were cut from the equiaxed zone of Samples 1, 2 and 3 (Fig. 1a). Each specimen was polished and then placed in an alumina crucible to be used in the CSLM for magnified examination during heating up to 1200 and 1400 °C. The actual surface temperature was calibrated using a blank sample with Pt–PtRh thermocouple attached to the surface. The surface temperature of the specimen was found to vary about 20–40 °C from the control temperature at the bottom of crucible. The temperature was measured at the bottom of the crucible by using a Pt–PtRh thermocouple. Thus, by using this data, the surface temperature of the specimen, 1200 and 1400 °C, was controlled. The atmosphere in the CSLM was pure Ar. The heating rate of the specimen was 100 °C/min.

First, the sample was heated to 200 °C and held for 10 min in order to remove possible water vapour being present. Thereafter, the specimen was heated to the experimental temperature. A detailed description of the CSLM method and its capabilities can be found in the pioneering work [13]. The grain boundary, which is revealed by thermal etching (thermal groove) [14, 15] at high temperature, starts to be visible after approximately 800 °C and becomes clearer with an increased temperature. During an experiment, each specimen was kept at the experimental temperature for 60 min and then cooled down to room temperature by switching of the heating element.

The specimen surface during heat treatment in CSLM was observed in situ with objective glasses of 10, 20 and 40 times. The observation area with a ×10 objective represented roughly 1/20th of the total area of the specimen. In this case, these projection images consisted of a frame of 640 × 480 pixels; the frame resolution was 1.36 μm/pixel [16]. Therefore, the observation of the migration of grain boundaries and pinning effect of particles during holding at a given temperature was video recorded at a 1/30 second interval [16]. A sweeping sequence was initiated at 2, 5, 10, 15, 30, 45 and 60 min (Fig. 1b). The recorded sequence was later transferred to the computer. By using a snapshot tool to retrieve overlapping images from a scanning sequence for combining pictures makes the total specimen surface visible. When the surface was visible, the grain boundaries could be analysed by a software program (Winroof©). The area, A_G, diameter, D_A and perimeter, P_{GB}, of each grain were measured. The size of each grain, D_A, was determined as the equivalent diameter of a circle, which has the same area as the measured grain. These examinations were combined with local observations of grain growth on a specimen surface at objective glasses of 40 times between the times for the scanning procedure.

After the heat experiment, the samples were analysed in a SEM equipped with an EPMA for a characterisation of the pinning particles. Determination of the chemical composition of pinning particles was performed with focus on the composition differences between O and N in particles acting as pinning sites.

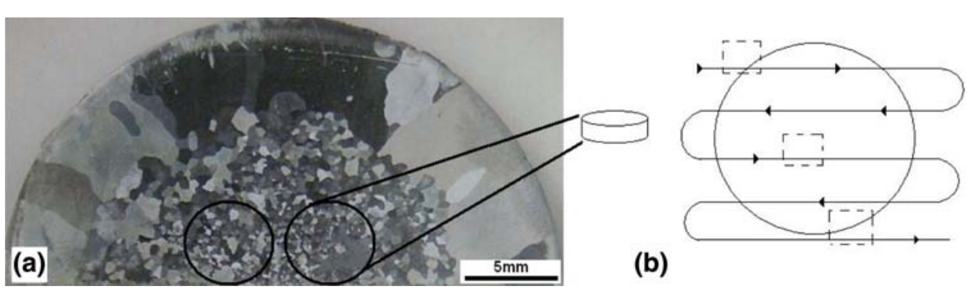


Fig. 1 Schematic illustrations of cut specimens for in situ observation of pinning effect of particles on grain growth (**a**) and scanning procedure in CSLM during heat treatment (**b**)

Results and discussion

The results for measurement of an average grain size, $\bar{D}_A$, in samples with different N contents (65, 248 and 490 ppm) are presented in Fig. 2 as a function of the holding time at 1200 and 1400 °C. It is apparent that the $\bar{D}_A$ values decrease with an increased nitrogen content in the samples. This is due to an increased number of precipitated inclusions. More specifically, the numbers were 0.7×10^6 mm^{-3}, 1.5×10^6 mm^{-3} and 5.3×10^6 mm^{-3} in Sample 1 (65 ppm N), Sample 2 (248 ppm N) and Sample 3 (490 ppm N), respectively. In addition, it was found that most of the inclusions in samples with high nitrogen content (248 and 490 ppm) are nitrides and oxynitrides. These were precipitated during solidification and were mainly located on grain boundaries; the authors recognised them as "secondary particles". As a result, the pinning effect of these particles on grain growth increases due to an increased number of precipitated inclusions on grain boundaries. This, in turn, is caused by increased nitrogen content in the sample.

The $\bar{D}_A$ values increase during holding of Sample 1 (65 ppm N) at 1200 °C, due to the low number of inclusions on grain boundaries. The average sizes of grains in Samples 2 and 3 were found to be almost constant during all times of heat treatment at 1200 °C. This is due to the high number of inclusions on the grain surface, which fixed the grain boundaries and pinned the grain growth. However, the $\bar{D}_A$ value increases significantly with an increased holding time at 1400 °C in all experiments. This can be explained by a reduced pinning effect of particles due to dissolution of some nitrides during heat treatment at 1400 °C, as will be discussed below.

It also should be pointed out that the grains grow rapidly during heating and the initial 15 min holding time of the samples at 1400 °C, particularly in Sample 1 with 65 ppm nitrogen content. The difference between $\bar{D}_A$ values obtained at 1400 and 1200 °C, ΔD_A $\left(=\bar{D}_{A(1400)}-\bar{D}_{A(1200)}\right)$, for a 2 min of holding time decreases significantly with an increased nitrogen content as well as with an increased number of inclusions. Thus, the ΔD_A value for a 2-min holding time decreases from about 200 μm for Sample 1 (65 ppm N) to 100 μm for Sample 2 (248 ppm N) and to almost 0 μm for Sample 3 (490 ppm N), see Fig. 2. It can be said from these results that the number of particles on the grain surface in Sample 1 is very low. Furthermore, that these particles cannot stop or decrease the grain growth. In this case, the grain size increases very quickly during the initial time of heat treatment at 1400 °C (before 2 min). Thereafter, the rate of grain growth decreases. In Samples 2 and 3, the number of inclusions on grain boundaries increases with an increased nitrogen content in the metal. Therefore, the pinning effect of these particles on grain growth also increases. As a result, the ΔD_A value at a 2 min of holding time of heat treatment decreases significantly.

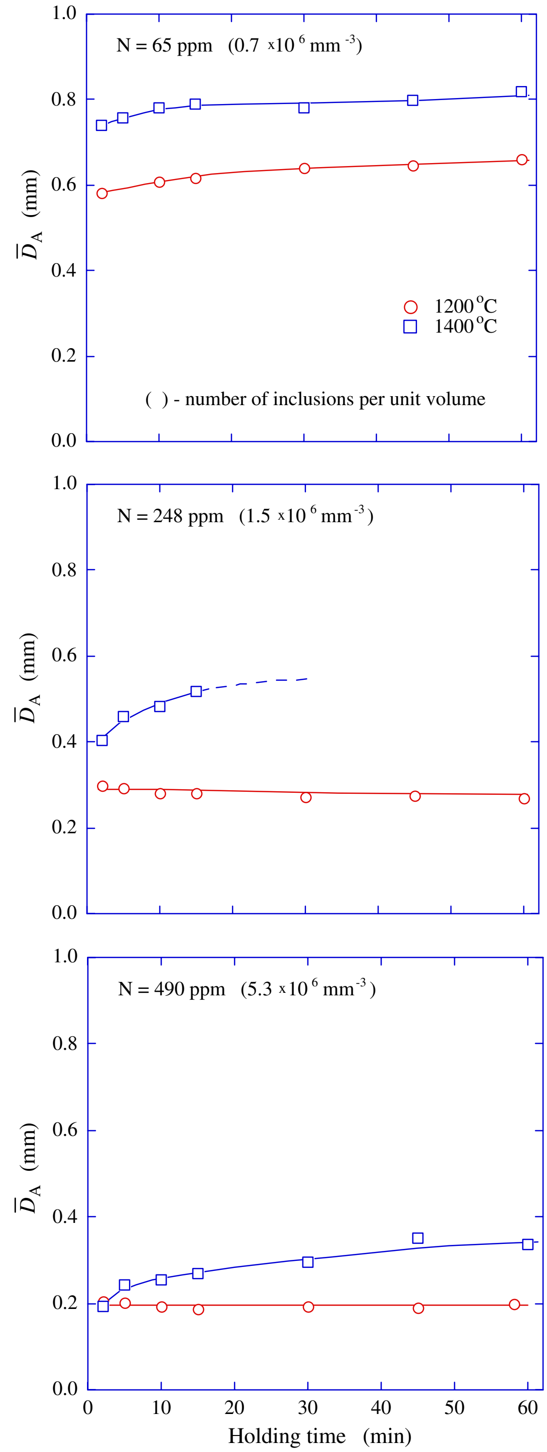


Fig. 2 Average grain size in samples with different N content as a function of holding time at 1200 and 1400 °C

Another grain parameter which correlates directly with grain growth and pinning effect of particles is the ratio between the perimeter (or length) of the grain boundary, P_{GB}, and the grain area, A_G. It can be expected that a larger value of the P_{GB}/A_G corresponds to a smaller grain size. Moreover, a change of the grain perimeter describes the pinning effect of particles on the grain growth and the change of grain boundary curvature during heat treatment. Therefore, a determination of the time and temperature dependence of the P_{GB}/A_G on the particle pinning effect on the grain growth during heat treatment was made to achieve a better understanding.

The change of the average value of the P_{GB}/A_G during heat treatment at 1200 and 1400 °C is shown in Fig. 3 for samples with different nitrogen contents. It can be seen that the P_{GB}/A_G values increase with an increased nitrogen content in the samples. This is due to that the pinning effect of particles increases with an increased number of precipitated inclusions on the grain boundaries.

In Sample 1, in which the nitrogen content is low, the pinning effect of inclusions is very low. Therefore, the P_{GB}/A_G value in this sample decreases significantly after a 15-min holding time at 1200 °C. However, after 30 min the P_{GB}/A_G value is almost constant and the average grain size hardly changes during the following heat treatment.

In Samples 2 and 3 with medium and high nitrogen contents, the P_{GB}/A_G value at 1200 °C increases during 15 and 30 min of holding times, respectively. In these periods, the curvatures of the grain boundary between particles increase, as shown in Table 1. This is due to the high value of the driving force for grain growth. As a result, the average perimeter of grain increases, but the average grain area practically does not change. When the driving force for grain growth equals the pinning force of particles on the grain boundary, the grain growth is stopped. Therefore, the values of the P_{GB}/A_G ratio and $\bar{D}_A$ are almost constant during the following holding period at 1200 °C. From this moment, the equilibrium between grain growth and the pinning effect of particles on grain boundaries is reached.

It is apparent from Fig. 3 that the P_{GB}/A_G values obtained during heat treatment at 1400 °C are significantly lower than those at 1200 °C. It can be explained by the dissolution of most nitride particles during holding at 1400 °C, as discussed below. In Sample 1, which contains low nitrogen content, the number of nitride inclusions is very low. Therefore, the pinning effect of these particles on the grain growth is negligible. Thus, the P_{GB}/A_G value is very low during all time of heat treatment. In Samples 2 and 3 with medium and high N contents, the P_{GB}/A_G values decreases rapidly during 15 min of holding and then remain almost constant. It follows from these results that most of the nitride inclusions on grain boundaries are dissolved during this period. Therefore, the pinning effect of these particles decreases. In this case, a curvature of grain boundaries between the remaining inclusions decreases

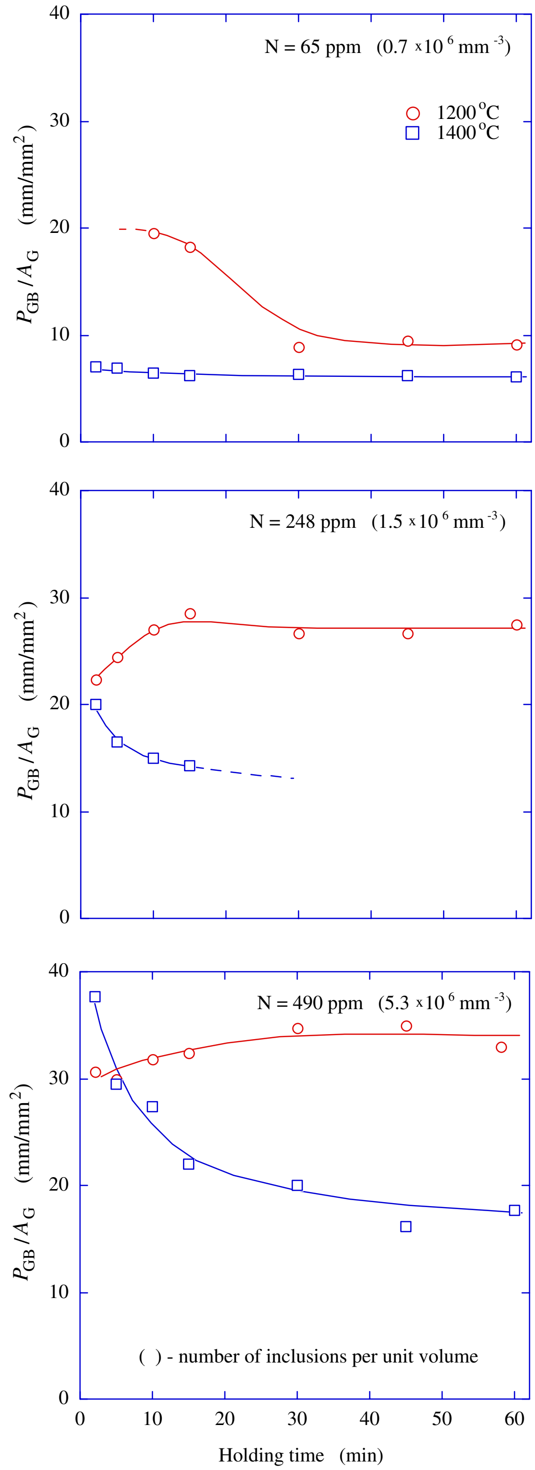
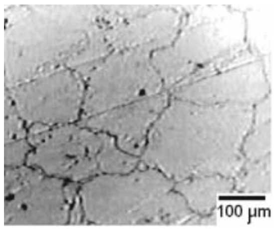
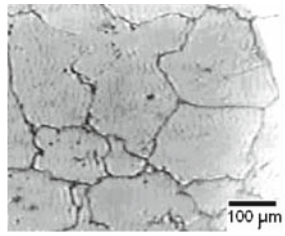
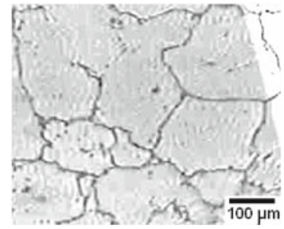
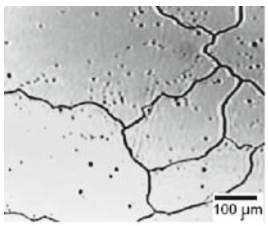
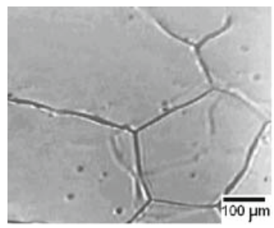
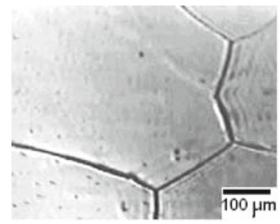


Fig. 3 Ratio between grain boundary perimeter and grain area in samples with different N content as a function of holding time at 1200 and 1400 °C

visibly, as shown in Table 1. Thereafter the equilibrium between grain growth and pinning effect of remaining particles is reached and the $\bar{D}_A$ and P_{GB}/A_G values change slightly (Figs. 2, 3). However, it should be pointed out that

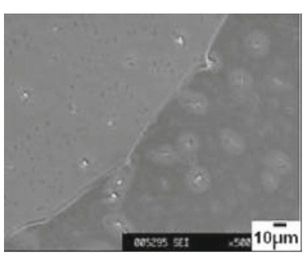
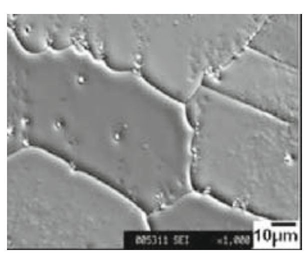
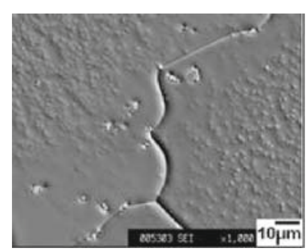
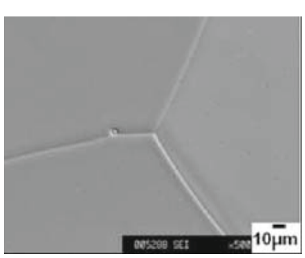
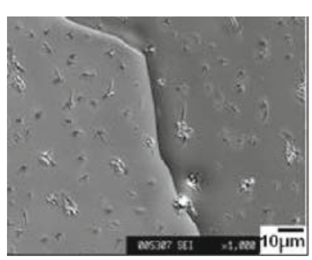
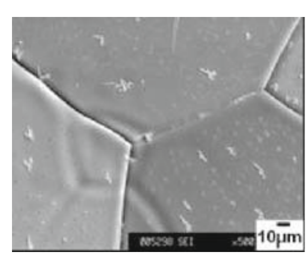
Table 1 Typical snapshots from CSLM showing changes in grain boundary structure of same grain during heating of Sample 3 (490 ppm N)

T (°C)	Holding time (min)		
	2	15	60
1200			
1400			

the final values of the P_{GB}/A_G after 60 min of heat treatment considerable increase. Accordingly, the $\bar{D}_A$ value, decreases with an increased N content.

Typical photographs of the pinning effect of inclusions on grain growth, after 60 min heat treatment at 1200 and 1400 °C, are given in Table 2 for samples with different nitrogen contents. According to analysis of composition for typical inclusions by EPMA, the particles acting as pinning sites on grain boundaries are in most cases nitrides for samples with high nitrogen contents (248 and 490 ppm). The composition of these inclusions is varied in the following ranges: 38–64 mass% Ti, 9–27 mass% Zr, 24–43 mass% N and 0–12 mass% O. The numbers of these nitrides on grain boundaries of Samples 2 and 3 are enough for an effective pinning of grain growth to occur during heat treatment. In this case, the grain boundaries between particles have a significant curvature. In Sample 1 with 65 ppm nitrogen content, the inclusions on surface of

Table 2 Typical photographs of grain boundaries with inclusions after 60 min heat treatment

T (°C)	Nitrogen content (ppm)		
	65	248	490
1200			
1400			

grains are mostly oxides and oxynitrides with a lower content of N and Ti (0–31 mass% Ti, 35–66 mass% Zr, 0–26 mass% N and 8–33 mass% O). The number of these particles on grain boundaries is very low. Therefore, these inclusions do not have any substantial effect on the grain growth.

It can be seen in the photographs given in Table 2 that most nitride particles on the grain surface have been dissolved during holding at 1400 °C. As a result, the remaining inclusions do not affect grain growth and the grain boundaries do not have the visible curvature between particles.

As a consequence, the secondary particles which precipitated near grain boundaries are effective at temperatures up to at least 1200 °C. Therefore, for an increased pinning effect at higher temperature it is suggested to create more stable secondary particles.

Conclusions

The pinning effect of particles on grain boundaries and grain growth phenomena were investigated in a Fe–20 mass% Cr alloy deoxidised with Ti and Zr. This was done at different nitrogen contents in the metal samples. The grain boundary migration during holding at 1200 and 1400 °C has been studied by combination of total and local in situ observations in a CSLM.

It was found that the average grain size, $\bar{D}_A$, decreases with increasing nitrogen content in the samples due to an increased number of nitride inclusions precipitated during solidification. The change of pinning effect for particles on grain growth during heat treatment can be described more detailed by using a ratio between the perimeter and area of grains, P_{GB}/A_G, than that by using average size of grain. This is because the grain perimeter corresponds directly with the change of grain boundary curvature during heat treatment due to the pinning effect of particles.

The P_{GB}/A_G ratio values at 1200 °C for samples with higher nitrogen contents (248 and 490 ppm) increase during 15 and 30 min of holding time, respectively. This is due to the significant increase of the curvatures of the grain boundary between particles. Thereafter, the equilibrium between grain growth and pinning effect of particles is obtained and thereby the P_{GB}/A_G value does not change.

In the case of heat treatment at 1400 °C, the P_{GB}/A_G values for samples with higher nitrogen contents decreases rapidly during a 15-min holding time. This is due to that most of the nitride inclusions dissolve and that the curvature of the grain boundaries between the remaining inclusions decreases. After 15 min, the equilibrium between grain growth and pinning effect of remaining particles is obtained and thereby the P_{GB}/A_G ratio values only change slightly.

Acknowledgements The authors would like to thank Professor Mats Hillert and Professor Stefan Jonsson at the Royal Institute of Technology (Sweden) for fruitful discussions during preparation of this paper. Some parts of this work has been carried out with a financial grant from the Research Fund for Coal and Steel of the European Community.

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