Evolution of Black Cauliflower-like Precipitates on the Surface of AA5083 Slab during Homogenizing

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Black cauliflower-like precipitates were discovered at the remelting points and cold shuts of the surface of AA5083 slab. Most of the precipitates were composed of several small black precipitates and pores, with MgO and αAl as the major phases. The melting and evaporating of the Al-Mg eutectic phases at the grain boundaries had to be responsible for this phenomenon. The concentration of magnesium is obviously higher at the remelting points than at the other flat surfaces of the slab. Most of the magnesium was concentrated at the grain boundaries in the form of Al-Mg eutectic. As a result of the rapid solidification on the surfaces of the remelting points, most of the surfaces could not melt after homogenization due to no eutectic precipitating at the grain boundaries. However, a few grain boundaries containing eutectics could melt to be the paths for the evolution of eutectic vapor and give rise to the black cauliflower-like precipitates on the surface. Moreover, gas pores beneath and pits on the original surfaces could be found for most black cauliflower-like precipitates. Either the gas pores or the pits could gather considerable eutectic vapor and result in the coarse black cauliflower-like precipitates. However, black cauliflower-like precipitates could be suppressed by the addition of 2.6ppm of beryllium.

Keywords: AA5083, Cauliflower-like precipitate, Evaporation of eutectic

1. INTRODUCTION

The chemical activity and oxidizing capability of magnesium is well known. However, the magnesium oxide film is not so continuous and dense as the aluminum oxide that is able to protect the melt from oxidizing, and high magnesium content aluminum alloys, such as AA5083 and AA5182 (Mg＞4%), are prone to produce a considerable amount of slag during smelting. Consequently a trace amount of beryllium is usually added while smelting these alloys to form a thin dense film on the surface of the melt to protect against any reduction due to oxidizing[1, 2, 3, 4].

However, beryllium is poisonous; most aluminum smelters in advanced countries have discarded the addition of beryllium. For the health of workers, China Steel Aluminum Corporation (CSAC) have also tried to smelt AA5083 and AA5182 alloys without beryllium. As a result, the problem was not only the increase of slag amount but also the unexpected and tremendous amount of black cauliflower-like precipitates observed on the surface of slab after homogenizing. Since the black cauliflower-like precipitates were very hard, they must be removed before surface planing of slab to prevent fracture of the planer tool. Besides, the deterioration of the surface quality of the slab was also a con-

cern. Therefore, the mechanism and solution for the evolution of black cauliflower-like precipitates were studied.

2. EXPERIMENTAL METHOD

Two different beryllium content AA5083 slabs produced by CSAC were examined in this study. The chemical compositions of the slabs are shown in Table 1. Slab A was smelted without any beryllium addition but there remained a 0.7ppm trace amount. Slab B was smelted with intentional addition and contained 2.6ppm beryllium.

The study included analyses of the chemical composition and phase components of the black cauliflower-like precipitates, observations of their forming process and phase transforming during the heating process. In order to observe the microstructure of the black cauliflower-like precipitates, samples were cut from the surface layer of slabs which included the cross sections of cauliflower-like precipitates and the alloy beneath. The microstructures of the cauliflower-like precipitates were observed by SEM, and the chemical compositions of the different phases in them were subsequently analysed by EDS. Also, the cauliflower-like precipitates were removed from the

Table 1 Chemical compositions of AA5083 slabs in this study (wt.%)

Slab \ Element	Mg	Mn	Fe	Si	Cu	Cr	Be	Al
A	4.40	0.873	0.282	0.104	0.027	0.092	0.7ppm	Bal.
B	4.89	0.660	0.316	0.125	0.028	0.085	2.6ppm	Bal.

surfaces of slabs and ground into powders. With the powders, the phases included were identified by XRD and the average chemical composition of precipitates was analysed by ICP.

In order to observe the evolution process of the cauliflower-like precipitates, the surface layers of slabs were homogenized at 520°C for 2hours to 12hours in the laboratory. Pictures of the surfaces of the slabs were taken before and after homogenizing to compare the differences between them. In addition, the original surface conditions of those slabs where black cauliflower-like precipitates evolved were also observed with the naked eye.

DSC with a temperature increasing rate of 3°C/min were used to analyse the eutectic point. Comparisons of the differences in heating between Alloy A and Alloy B, and the locations at surface and inside of slabs were also conducted with DSC. Since the specimens heated in DSC were protected with argon, they could be considered as homogenized in a protected atmosphere and compared with the specimens heated in the normal atmosphere.

3. RESULTS AND DISCUSSION

3.1 Appearance and Component of Cauliflower-like Precipitates

Observed by the naked eye, it could be easily found that the cauliflower-like precipitates evolved only at the remelting spots and cold shuts of the slab surface. The precipitates evolved at the remelting spots could even be observed surrounded by an area as dark as ink, as shown in Fig.1(a). Their magnified appearance, observed by stereomicroscope, indicated that they were really uneven on the surface and looked like cauliflowers. Furthermore, part of them seemed to be composed of many tiny spots as shown in Fig.1(b).
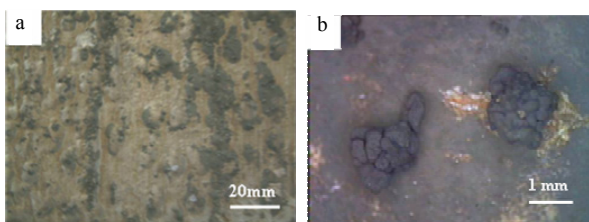

Fig.1. (a)Appearance of AA5083 slab after 520°C homogenizing; and (b)Magnified appearance of cauliflower-like precipitates observed by stereomicroscope.

In order to observe the microstructure of the cauliflower-like precipitates, the cross sections of the cauliflower-like precipitates and the matrix beneath them were observed by SEM. The SEM observations indicated that the cauliflower-like precipitate was composed of not only one particle but also contained very close and numerous black spots in them as shown in Fig.2(a). The chemical compositions of the particles analyzed by EDS showed that the regions with close and numerous black spots contained magnesium, aluminum and oxygen as shown in Fig.2(b)~(d), while the remaining white regions mainly contained pure aluminum and rare magnesium as compared with the matrix beneath. Besides, it deserves to be mentioned that a big hole could be found at all times in the center of the bigger particles. Holes surrounded by oxides could also be found at the matrix beneath.
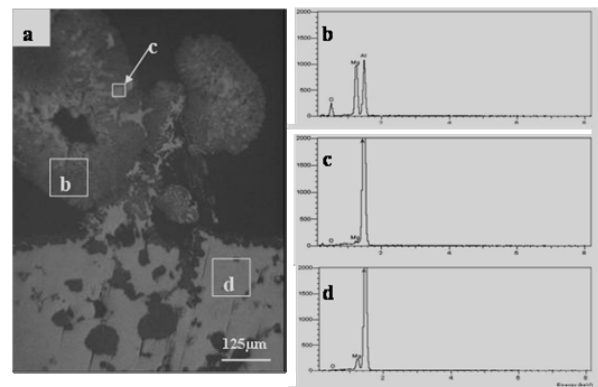

Fig.2. (a)Microstructure of cauliflower-like precipitate; (b) and (c)Chemical compositions of black region and white region respectively of cauliflower-like precipitate; and (d)Chemical composition of matrix beneath.

For a further study of the phase components and chemical composition of cauliflower-like precipitates, powders ground from removed precipitates were analyzed by XRD and ICP respectively. The result of the XRD analysis indicated that there were only two components in the precipitates as shown in Fig.3. The major component was αAl, the other one, MgO, was minor in comparison. The results of the ICP analysis indicated that while the aluminum content was as high as 60.3%, the magnesium and oxygen contents were only 19.1% and 20.6% respectively.
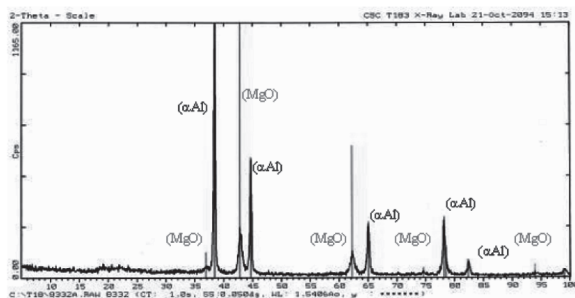
Fig.3. X-Ray diffraction(XRD) pattern of cauliflower-like precipitates removed from slab surface of AA5083 alloy.

3.2 Simulation of Homogenizing Treatment in Laboratory

Since the cauliflower-like precipitates evolved during the homogenizing of the slab, homogenizing treatments at 520°C for 2~12hours for two AA5083 alloys with different beryllium contents were conducted to observe the evolution process. The results are shown in Fig.4. After 520°C×2hours homogenizing treatment, the slab surfaces of Alloy A, with low beryllium content, turned completely black. However, cauliflower-like precipitates were not found until 520°C×4 hours homogenizing treatment, and then evolved everywhere on the surface of the slab, yet did not increase in size and number even after longer homogenizing treatment. On the other hand, Alloy B, with high beryllium content, showed quite different results. The slab surfaces of Alloy B turned golden after homogenizing treatment; besides, cauliflower-like precipitates were rarely found even after homogenizing for 12hours. This showed that the evolution of cauliflower-like precipitates could indeed be suppressed by the addition of beryllium. However, a similar and very interesting phenomenon was observed in both alloys after the homogenizing treatment. The phenomenon was that the cauliflower-like precipitates were frequently observed on the sawing planes right beneath the slab surfaces as shown in Fig.5.
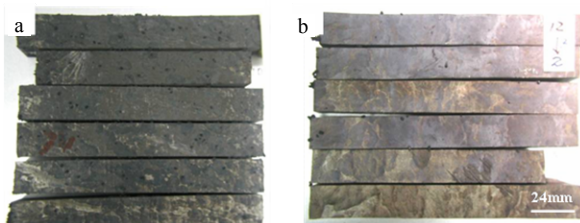

Fig.4. Surface appearances of AA5083 Slabs with (a) low beryllium, and (b)high beryllium after homogenization at 520°C for 2, 4, 6, 8, 10, 12 hours. The specimens were put from bottom to top in order of the homogenized time, with 12hours at the top.

3.3 Study of the Evolution of Cauliflower-like Precipitate

3.3.1 The Influence of Slab Appearance on Cauliflower-like Precipitate Evolution

According to the observation in Fig.5, cauliflower-like precipitates were prone to evolve from sawing planes immediately beneath the slab surface. It was observed that there were many gas pores in the sawing plane when this lay just beneath the slab surface before homogenizing. In order to investigate the relationship between cauliflower-like precipitate evolution and these pores, we took pictures of the sawing plane of a specimen before and after homogenizing for a contrast. The results indicated that wherever a gas pore existed before homogenizing, there would be a cauliflower-like precipitate evolving during homogenizing as shown in Fig.6. However, little and small precipitates were also observed evolving from some pore-free surfaces. That proved that while gas pores were really prone to induce cauliflower-like precipitates, they were not necessary.
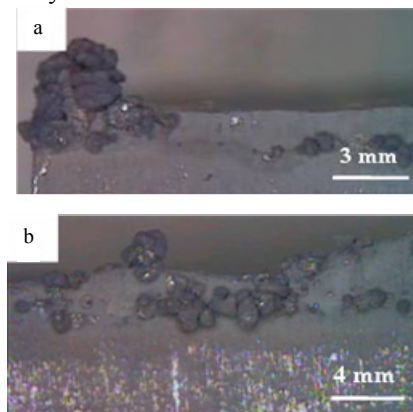

Fig.5. Cauliflower-like precipitates evolving around intersection lines of slab surfaces and sawing planes: (a) Precipitates evolving at sawing plane and intersection point of slab surface and two perpendicular sawing planes; and (b)Numerous precipitates evolving at sawing plane right beneath slab surface.
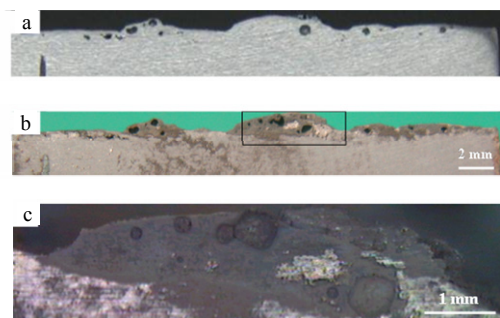

Fig.6. (a)Appearance of sawing plane before homogenizing; (b)Appearance of sawing plane after homogenizing at 520°C for 12hours; and (c)Magnified image in square frame of (b).

For a further study of the relationship between the specimen appearance and the cauliflower-like precipitate evolution, we took pictures of the slab surface showing a specimen before and after homogenizing for a contrast as shown in Fig.7. The pictures showed that where most cauliflower-like precipitates evolved, there were tiny bulges before homogenizing, and still pits were also observed. As we observed the cross section of the tiny bulges and pits, it was seen that the tiny bulges contained pores while the pits were deep and narrow. It was thus clear that the pores and the pits provided precisely the right conditions to induce cauliflower-like precipitates. However, not all the tiny bulges and pits would evolve into cauliflower-like precipitates, especially those located outside the remelting spots.
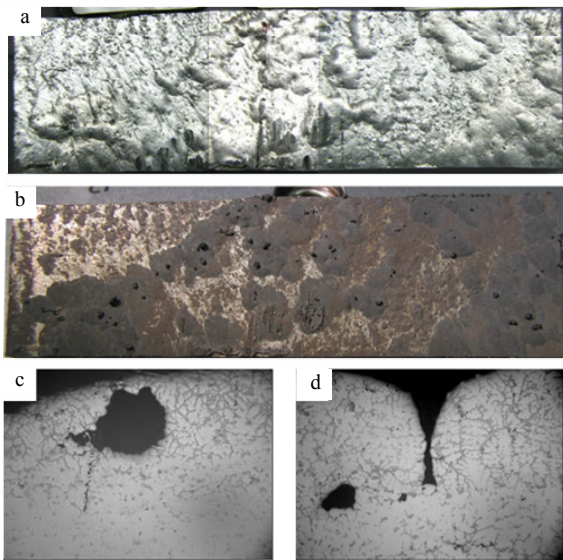

Fig.7. (a) and (b)Slab surface of a specimen before and after homogenizing at 520°C for 12hours; (c) and (d) Microstructures of a tiny bulge and a pit before homogenizing.

3.3.2 Relationship between Cauliflower-like Precipitate and Matrix

As described in the previous section, whenever there was a cauliflower-like precipitate, there was a bulge containing a pore or a deep narrow pit before the homogenizing treatment. However, the pores or the pits were not necessarily observed beneath the cauliflower-like precipitates after homogenizing. A comprehensive survey showed that the cauliflower-like precipitates could be categorized into three types according to their microstructures. The first type was small and looked like a hollow cauliflower as shown in Fig.8(a), but no information revealed their growth history. The second type was quite different from the first type in appearance. According to the cross section

observation of this precipitate, it looked like a tree growing from the matrix. Furthermore, there were many irregular pores inside the precipitate and small pores in trunk and root as shown in Fig.8(b). The third type, however, had a big gas pore in the matrix beneath the precipitate, as shown in Fig.8(c). Generally speaking, the second and the third type of cauliflower-like precipitates were much bigger than the first one.
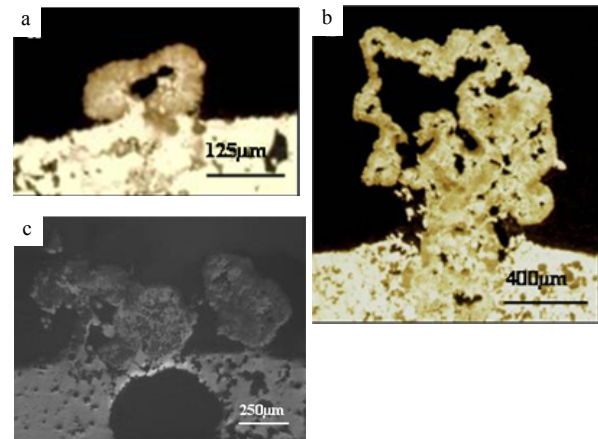

Fig.8. (a)The 1st type, (b)The 2nd type, and (c)The 3rd type cauliflower-like precipitates evolving after homogenized at 520°C for 12hours.

3.3.3 Mechanism Study for the Evolution of Cauliflower-like Precipitate

3.3.3.1 Distribution Difference of Magnesium Element

Since the cauliflower-like precipitates were composed of MgO and αAl and bulged out from the slab, the magnesium and aluminum certainly came from the matrix. It was observed that there used to be numerous gas pores in the matrix beneath the cauliflower-like precipitates. Furthermore, the bigger the cauliflower-like precipitates, the more the gas pores. Therefore, it is suggested that the magnesium and aluminum elements of the cauliflower-like precipitates evolved from the gas pores during homogenizing treatment.

For a further study on the different microstructure and magnesium element distribution between the surface and interior of the slab, SEM and magnesium mapping were conducted. The results, as exhibited in Fig.9, showed that the magnesium content was much higher in the grain boundary for the surface layer as compared with the interior. DSC analysis revealed that the surface layer with a remelting point had a heat absorption peak at around 450°C, while such a peak was absent in the interior of the slab as shown in Fig.10.

According to the phase diagram of Al-Mg alloy[5], the absorption peak at around 450°C was due to the

melting of the Al-Mg eutectic phase. It indicated that the surface layer with remelting point not only contained higher magnesium, but also had an eutectic phase. The magnesium content at the grain boundary in the interior of the slab was also higher than average; however, it was too low to form a eutectic phase. The reason for the magnesium content being higher at the remelting point will be discussed in a later section.
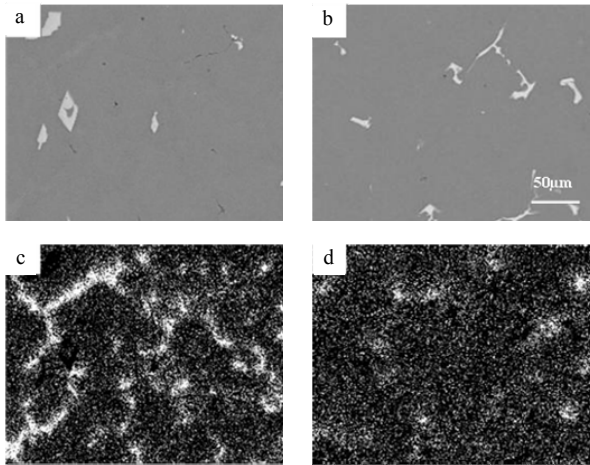

Fig.9.   (a) and (b)microstructures of surface layer and interior of slab respectively observed by SEM; (c) and (d) magnesium element mapping for (a) and (b)respectively.
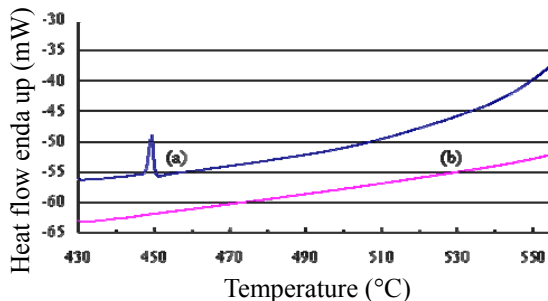

Fig.10. Specimen analyzed by DSC sampled at (a)surface layer of slab, and (b)interior of slab.

3.3.3.2   The Influence of Homogenization on Al-Mg Eutectic phases

As DSC analysis was heated up to over 500°C, it could simulate homogenization to a certain extent. It was observed that part of the grain boundaries at the surface layer of the remelting point were replaced by cavities after DSC analysis as shown in Fig.11(a) and (b). According to the comparison between DSC and magnesium mapping, it was easy to perceive that the formation of these cavities was due to evaporation of Al-Mg eutectics. In the regions where cavities did not form, the magnesium element was still concentrated at

the grain boundaries according to the magnesium mapping. The reason that the cavities could be observed so clearly after DSC analysis was because the analysis was conducted in an argon atmosphere that protected the specimen from oxidizing.

Based on the result mentioned above, the grain boundary structure on the surface should be related to the cavity formation. As the temperature reached 450°C, the eutectics began to melt. Since magnesium is prone to evaporate in a liquid state, the molten eutectics then evaporated away from the grain boundaries and left cavities behind. However, the vapors in grain boundaries had to leave by way of the surface; cavity formation therefore became dependent on melted grain boundaries on the surface. If there was no melted grain boundary on the surface, no vapor could evaporate away even when there were molten eutectics beneath. The molten eutectics would solidify again as the temperature came down, and thus no cavity would form either. This explains why the result of Fig.11(c) does not show any cavity even though the Mg content was high near the surface.
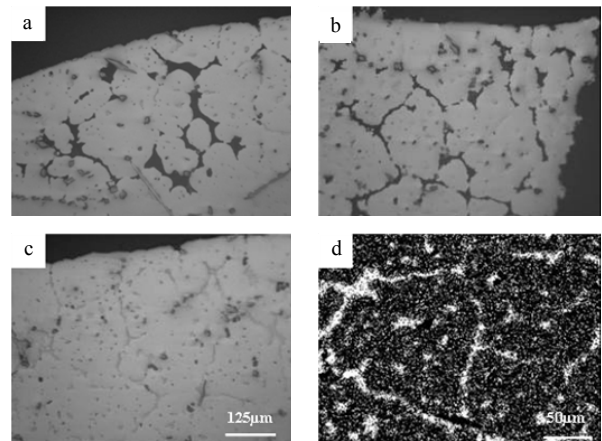

Fig.11.   (a), (b) and (c) show the microstructure at surface layer containing remelting point after DSC analysis; where (b) shows the microstructure at edge, and (c) shows the microstructure without cavity; (d) magnesium distribution analysis of (c) by mapping.

3.3.3.3   Influence of Al-Mg Eutectic Evaporation on the Evolution of Cauliflower-like Precipitate

To sum up the results above, it is clear that the evolution of cauliflower-like precipitates resulted from the evaporation of Al-Mg eutectics. However, it was observed that the cauliflower-like precipitate frequently evolved above a gas pore, as shown in Fig.8(c). This suggested that the pore was one of the reasons to induce the cauliflower-like precipitate. The reason for a pore to induce a cauliflower-like precipitate should be because it could act as a vapor sink and gather a large

number of aluminum and magnesium vapors from the grain boundaries around its inner surface. If the pore was just beneath the surface of slab, the vapors could find a way out through the surface to supply plenty of aluminum and magnesium for the growth of cauliflower-like precipitate above the pore.

On the other hand, a pit could also be a vapor sink and gather aluminum and magnesium vapors from the grain boundaries. The type of cauliflower-like precipitate evolving from a pit should be the 2nd one as shown in Fig.8(b). This 2nd type of precipitate looked like a tree growing from the matrix simply because the pit could gather vapors and oxidize in the pit. Furthermore, the numerous pores showing up on a sawing plane have the same function as a gas pore and a pit, therefore, it also becomes a favored location for cauliflower-like precipitates to evolve.

Another cauliflower-like precipitate that did not show any relation with the matrix, as Fig.8(a), must be supplied with vapors directly from the grain boundaries beneath the surface. As a result of the lack of a vapor sink like a gas pore or pit that gathered vapors from all directions around, this type of cauliflower-like precipitate appeared much smaller in size as compared with the other two types.

Besides, the reason for one to several holes frequently observed in a cauliflower-like precipitates must be due to the outward diffusion of magnesium atoms. According to Zayan's study[6] for Al-Mg alloy homogenized at 550°C, it is indicated that magnesium atoms diffuse outwards to compete in oxidation reaction with Al atoms due to their high oxidation potential. Then a hole could be left behind between the matrix and the MgO layer on the surface. After that, the magnesium atoms in the matrix evaporated through the hole to reach the oxide layer, then diffused through the oxide layer to the surface and oxidized. This phenomenon is very similar to the cauliflower-like precipitate evolution in our study. As the cauliflower-like precipitate also contained aluminum and magnesium atoms, the magnesium atoms could diffuse outwards and oxidize as in Zayan's study. Then, a bulge-out precipitate with a hole would form and aluminum with lower oxidation

potential would be left behind in the inner layer.

3.3.4 Difference between Remelting Point and Normal Region

According to the results discussed in the previous section, the formation of cauliflower-like precipitates result from the evaporation of eutectic and oxidation of the vapors. Line scanning analysis showed that the magnesium content of the remelting point was obviously higher in the bulge region and remained high until the flat region was reached as shown in Fig.12. Therefore almost all the grain boundaries in this region were occupied by eutectics which acted as the source and supplied aluminum and magnesium for cauliflower-like precipitate evolution. On the other hand, the magnesium content at the surface layer without remelting point was only higher at a small region beneath the surface; it was too little for a cauliflower-like precipitate to evolve, even though there were gas pores and pits to help vapor gathering in this region.
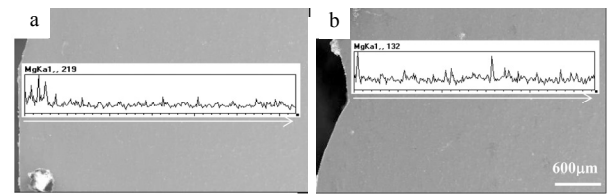

Fig.12. Line scanning inwards from slab surface for magnesium element at (a) remelting point, and (b) normal region.

The reason for the magnesium content being higher at the remelting point than at the flat surface is related to the remelting process of the solidification shell. For DC (direct chill) casting of aluminum alloys, the aluminum melt solidifies when it touches the top mold and forms a shell surrounding it. Since the shell shrinks due to solidification and separates with the mold immediately after it solidifies, an air-gap region forms before it is pulled into the water cooling zone. The cooling rate of the air-gap region is rather slow because it is just air being cooled, thus the shell in this region is prone to remelt. The remelting process, as shown in Fig.13, is considered to start from the grain
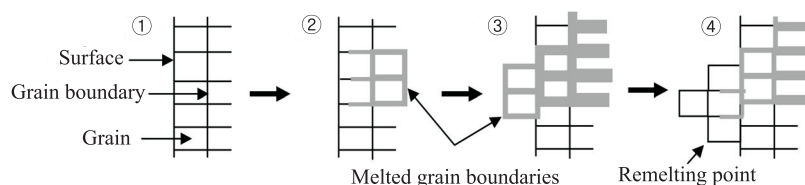

Fig.13. Diagram for the formation of remelting point during DC (direct chill) casting where:①Solidification shell has not remelted yet; ②Remelting in local region; ③Remelting region expands, the mixture of solid and melt flow out of slab surface due to hydraulic pressure effect; and ④The mixture solidifies again when it is pulled toward water cooling zone. Remelting point forms after it.

boundaries due to their high magnesium content and low melting point. As the remelting region expands, the mixture of solid and melt flows out of the slab surface due to the hydraulic pressure of the melt. Then, the mixture solidifies again when it is pulled toward the water cooling zone. After that, bulge-out remelting points form on the slab surface.

Since the temperature range for the solidification of Al-Mg alloy is really broad, severe shrinkage occurs during the solidification process. This solidification process allows the melt in the grain boundaries to flow to the shrinkage areas and replenish them. The melt in grain boundaries, however, has the highest magnesium content, thus higher magnesium content is found at the remelting point as compared with the flat surface of slab.

However, the solidification rate at the surface of the remelting point is fast, so that melt with a high magnesium content may not have the chance to replenish grain boundaries at the surface. Thus the magnesium content of grain boundaries at the surface should be lower than those beneath the surface. This means that the melting point of grain boundaries at the surface is higher than those beneath the surface. Although the grain boundaries beneath the surface have melted during homogenizing, solid grain boundaries may still remain at most surfaces. The vapors, then, cannot evolve from the melted grain boundaries if there are solid grain boundaries above it. On the contrary, if the grain boundaries at the surface are melted, they can allow the exit of vapors and the evolution of cauliflower-like precipitates.

The fact that the magnesium content of the grain boundaries beneath the surface is higher than those at the surface also explains the phenomena shown in Fig. 5 and in Fig.11(b). Due to the high magnesium content at grain boundaries beneath the surface, a higher magnesium plane can be exposed when a remelting point is sawn longitudinally. Therefore, it is undoubtedly much easier for the cauliflower-like precipitates to evolve at the exposed plane than at the original surface when the exposed gas pores after sawing are also taken into consideration.

Furthermore, the formations of cold shuts are quite similar to remelting points despite the fact that they are formed due to perturbation of melt during casting. The magnesium content at cold shut grain boundaries is also higher than at the normal flat surface of the slab. Therefore, cold shuts also become potential sites for cauliflower-like precipitates to evolve during homogenizing treatment.

The reason for gas pores to form beneath the surface of remelting point should be related to the steam. The steam comes from the cooling water and gets stuck above the solidification shell in the air-gap region.

Then, it forms gas pores when the remelting points were squeezed out of the solidification shell and to cover the original shell surface. A similar pore forming process also happens to a cold shut, which makes it prone to evolve cauliflower-like precipitates too. As to the pits, they must originate from some tiny unmelted spots that were relatively immobile compared with the melt around. The surrounding melt then flows out and almost covers the unmelted spots, but solidified before the spots were completely covered. Then, pits were left on the surface of the remelting point.

3.4 Mechanism for Beryllium to Prohibit Evolution of Cauliflower-like Precipitates

According to DSC analysis, there was an absorption peak around 450°C for the remelting point whose slab contained 2.6ppm beryllium as shown in Fig.14. It indicated that there was a melting with eutectics at 450°C for remelting point, whether beryllium was added to the alloy or not. That proved that the reason beryllium prohibits the evolution of cauliflower-like precipitates were not because it changes the microstructure or distribution of elements, but because it prohibits oxidizing.
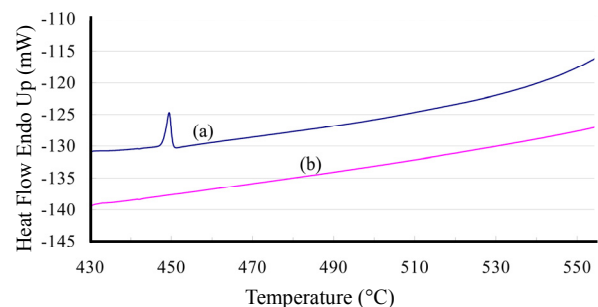

Fig.14. DSC analysis for the slab with 2.6ppm beryllium. The specimen was sampled at (a)slab surface with remelting point and (b)interior of slab.

Generally speaking, the reason for beryllium to be added into high magnesium aluminum alloys during smelting has been to prohibit the melt from oxidizing. Due to having a higher oxidation potential than aluminum, magnesium oxidizes easily to form a film on the surface of a melt during smelting. However, MgO film is not as continuous and dense as Al_2O_3 film so it cannot protect the melt from oxidizing. As a result, a considerable amount of magnesium is lost during smelting due to oxidation. However, the oxidation potential of beryllium is only slightly lower than that of magnesium, so a trace addition of beryllium can form a film of MgO+BeO mixture beneath the surface film of MgO[4]. The mixture film is more continuous and denser than MgO so it can protect the melt during smelting. Since the evolution of cauliflower-like pre-

cipitate during homogenizing treatment is quite similar to oxidation during smelting, the effect of beryllium to prohibit oxidation also works to prohibit the evolution of cauliflower-like precipitate during homogenizing.

According to smelter's experience[3], the addition of beryllium at a content of approximately 1/2000 of the magnesium could prohibit cauliflower-like precipitates effectively. A similar result was also observed in our study as homogenizing at 520°C for 12hours. However, cauliflower-like precipitates were frequently found at the intersection of sawn planes. Compared with the slab without beryllium addition, the cauliflower-like precipitates at the intersection of sawn planes were even bigger and showed different microstructure as Figure 15 shows. This suggested that the oxidation of magnesium was not prohibited on a sawn plane and that most magnesium moved around to the sawn plane if they could not find a way out at the slab surface. The reason why the addition of 2.6ppm beryllium could prohibit cauliflower-like precipitates on the surface effectively but failed to do so at the intersection of sawn planes should be because the film of MgO+BeO mixture there was not as dense as that formed on surface due to its high magnesium content.
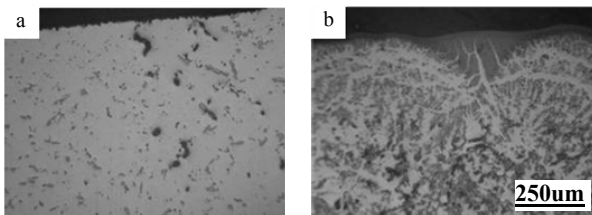

Fig.15. Microstructure of slab with 2.6ppm be homogenized at 520°C for 12hours: (a)cross section of slab surface layer at remelting point; and (b)cross section of cauliflower-like precipitate evolving from sawn plane at remelting point.

4. CONCLUSIONS

Based on observation by the naked eye, black cauliflower-like precipitates evolve at remelting points and cold shuts all the time. Therefore, the best solution for stopping the evolution of black cauliflower-like precipitates is to change the casting conditions to eliminate the remelting points and cold shuts, though addition of beryllium also works. The important conclusions from this study are summed up and stated as follows:

(1) According to XRD analysis, the cauliflower-like precipitates were composed of αAl and MgO.

(2) Magnesium content was higher at remelting points and concentrated at grain boundaries to form eutectics. The flat surface and inside of the slab did not show the same phenomenon.

(3) The cauliflower-like precipitate evolution was related to the melting and evaporating of Al-Mg eutectics. Most of them were induced by gas pores beneath surface or pits on surface as they could gather a large number of aluminum and magnesium vapors.

(4) The magnesium content of grain boundaries at the surface of the remelting point is lower than that beneath surface due to the fast solidification rate at the surface. Most grain boundaries at the surface could not provide an exit for vapors because they still remain solid during homogenizing treatment, while melted grain boundaries at the surface are prone to become the site for cauliflower-like precipitate evolution.

(5) The addition of 2.6ppm beryllium can suppress the evolution of cauliflower-like precipitates. The surface of slab remained glossy even after homogenizing treatment.

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