# INFLUENCE OF PERITECTIC ELEMENTS ON MICROSEGREGATION, HOMOGENIZATION AND PRECIPITATION IN CAST ALUMINUM ALLOYS

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## Abstract

The microsegregation and homogenization of two groups of alloying elements in cast aluminum alloys, one is Cu and Mg of eutectic elements and the other is Ti and Zr of peritectic elements , were studied and the influence of them on the precipitation behavior in the aged aluminum alloys was also clarified. The extreme microsegregation of these alloying elements in the cast aluminum alloys formed the cored structure in cellular dendrites of the aluminum alloys. Cu and Mg were enriched in the outside region of the cored structure and Ti and Zr were enriched in the inside one. The Mg-cored and Cu-cored structures were eliminated by the homogenization at 703K for 20h and 803K for 100h, respectively , but the cored segregations of Ti and Zr were not eliminated at all under the same homogenization conditions. The homogenization of Cu and Mg solutes delayed in the aluminum alloys with Ti and/or Zr, and the complete elimination of these coring segregations was hardly achieved in the alloys with Ti. In the alloys aged after the solution treatment the distinctive precipitation behavior was observed in the inside and the outside regions of the cored structure in dendrite cells. No precipitates were formed in the inside region of the Ti enriched cored structure in Al-Mg-Ti alloys. The growth of the precipitates became slower in Al-Cu-Ti alloys and faster in Al-Cu-Zr alloys in the inside region of the cored structure than in the outside region of the cored structure.

## Introduction

In aluminum alloys for cast and wrought materials, small amount of transition elements such as Cr,Ti,V and Zr is added for the grain refinement of cast or recrystallized materials and for the prevention of stress corrosion cracking or casting cracking.
These elements compose the phase diagrams of the peritectic reaction system at the aluminum

rich corner, and their equilibrium distribution coefficients are larger than unity. Therefore, the initially solidified regions are enriched with these elements and the cored structure forms in the dendrite cell of cast ingots [1,2]. Complete elimination of the cored segregation structure with high Cr,Ti and/or V content requires long thermal exposure more than 2~3 weeks at 923K [3], and the cored structures remain even in materials 95% heavily rolled and homogenized at 723K of the conventional homogenization temperature for eutectic alloying elements such as Cu,Mg,etc [4,5]. It has been clarified that the microsegregation of alloying elements in Al-Cu alloys and Al-Mg alloys is accelerated and their homogenization is retarded by the addition of V and Ti [4] and Cr [5].

In the present work,the microsegregation,homogenization and precipitation behavior in cast Al-Cu-Ti,Al-Cu-Zr and Al-Mg-Ti alloys were investigated.

## Experimental Procedures

The aluminum alloy ingots were prepared from 99.99% purity aluminum ingot,99.9% purity magnesium ingot, 99.9% purity copper plate, Al-5%Ti and Al-5%Zr master alloys. The alloys were melted in an electric resistance furnace ,using a clay-bonded graphite crucible dressed with high purity alumina,under an argon atmosphere at 100K above the liquidus temperature. The molten alloys were degassed by adding $C_2Cl_6$ and were poured into permanent molds heated at 423K . Specimens were homogenized in a salt bath ($NaNO_3$:$KNO_3$=1:1), quenched into water and were heated in an oil bath for the precipitation treatments. The microsegregation and homogenization of solute elements were measured by means of EPMA. For microstructural observations the specimens were polished and etched with dilute Tucker's reagent. For TEM observation of precipitation structures the specimens were polished electrolytically at 248K using nitric acid 1 and methanol 4 mixed solution.

## Results and Discussion

### Microsegregation

The microstructures and the line analysis of the solute elements by EPMA in an as-cast and homogenized Al-9.45%Mg-0.13%Ti alloy are shown in Fig. 1. The marked microsegregation , that is, the crystallization of the non-equilibrium eutectic $Mg_2Al_3$ at the grain boundary and interdendrite cells and the nonuniform distribution of Mg and Ti concentration in the dendrite cells is found. At the center of the dendrite cell, the minimum Mg concentration was indicated as 3.6%Mg and the maximum Ti concentration was indicated as 0.7%Ti of about 5 times as high as the initial Ti contents. The concentration of Mg increased and that of Ti decreased from the center toward the cell wall of dendrite, and these solute distribution results in Mg and Ti cored structures . On the other hand, the minimum concentration of Mg at the center of dendrite cells in Al-9.4%Mg alloy was 4.7% . The amount of non-equilibrium eutectic $Mg_2Al_3$ crystallized was 6.2 vol% in Al-9.4%Mg alloy and was 7.4vol% in Al-9.45%Mg-0.13%Ti alloy.

The amount of non-equilibrium eutectic $Al_2Cu$ and the minimum Cu concentration were indicated as 2.4 vol% and 0.7%Cu in Al-4.7%Cu alloy respectively, and they were indicated as 2.5 vol% and 0.64%Cu in Al-4.5%Cu-0.16%Ti alloy respectively. The maximum Ti concentration was indicated as 0.7% , which is about 4.5 times as high as the initial Ti content.

In Al-6.7%Cu-0.31%Zr alloy,the amount of non-equilibrium eutectic $Al_2Cu$ and the minimum Cu concentration were indicated as 1 vol% greater and 1%Cu lower than in Zr free alloy. The maximum Zr concentration was about 3 times as high as the minimum Zr concentration in the outside region of the cored structure. Thus, the degree of microsegregation in the cast aluminum alloys increase with addition of the peritectic elements Ti and Zr, and the peritectic elements themselves form the marked cored segregation .

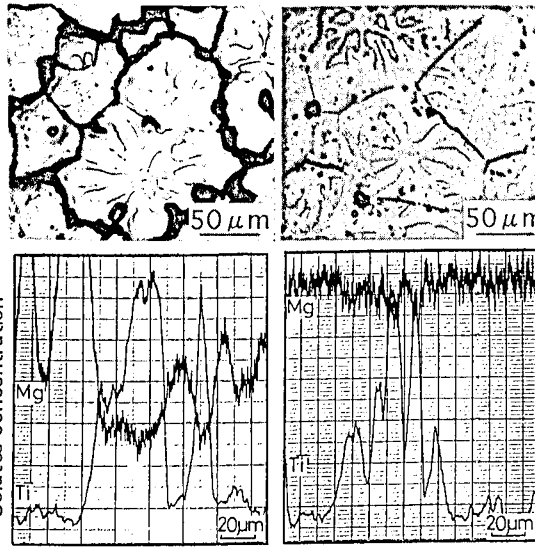


Fig.1 Line analysis of solute distribution in as-cast and homogenized Al-9.45%Mg-0.13%Ti alloy.

## Homogenization

By the homogenization at 703K for 18h,the Mg cored structure was eliminated , but the Ti cored segregation did not eliminate at all, as shown in Fig. 1. The homogenization behavior in Al-9.4%Mg and Al-9.45%Mg-0.13%Ti alloys is shown in Figs. 2 and 3. The dissolution of non-equilibrium eutectic $Mg_2Al_3$ was retarded slightly in the Ti added alloys comparing with that in the Ti free alloys, but the complete dissolution was obtained by thermal exposure at 703K for 1h. However, the complete homogenization of Mg in Al-9.45%Mg-0.13%Ti alloy was hardly achieved even by thermal exposure at 703K for 100h, and the minimum Mg concentration in the inside region of the Ti cored structure could not increase more than 8.9%Mg , which is about 0.92 times as small as the initial Mg contents. In Al-4.5%Cu-0.16%Ti alloy, the

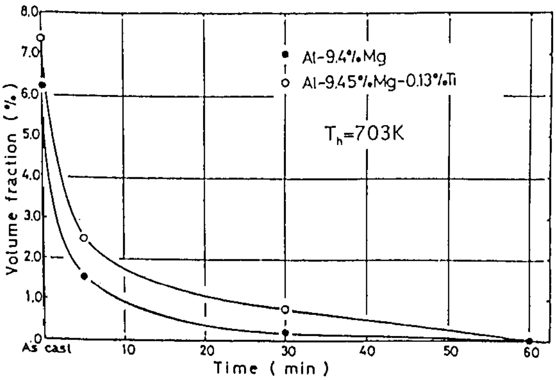


Fig.2 Dissolution behavior of non-equilibrium eutectic $Mg_2Al_3$ during thermal exposure at 703K in Al-9.4%Mg and Al-9.45%Mg-0.13%Ti alloys.

dissolution of non-equilibrium eutectic $Al_2Cu$ was completed by thermal exposure at 803K for 5h. Although the complete homogenization of Cu was achieved by thermal exposure at 803K for 100h in Al-4.7%Cu alloy, but the complete homogenization of Cu in Al-4.5%Cu-0.16%Ti alloy was not achieved and the Cu concentration at the center dendrite cell was only 93% of the initial Cu contents.

The homogenization behavior in Al-6.5%Cu and Al-6.7%Cu-0.31%Zr alloys is shown in Figs. 4 and 5. The dissolution of non-equiliblium eutectic $Al_2Cu$ was almostly completed by thermal exposure at 803K for 5h and the equiliblium eutectic $Al_2Cu$ remained about 2 vol%. The complete homogenization of Cu was almostly achieved by thermal exposure at 803K for 100h in Al-6.7%Cu-0.31%Zr alloy as same as in Al-6.5%Cu alloy, in spite of remaining the Zr cored segregation. The progress of the homogenization in Al-6.7%Cu-0.31%Zr alloy was slower than in Al-6.5%Cu alloy. The homogenization in the cast aluminum alloys progresses rapidly on the early stage of the thermal exposure until the complete dissolution of non-equilibrium eutectic phases, and it was achieved more than 80% of the initial content of eutectic

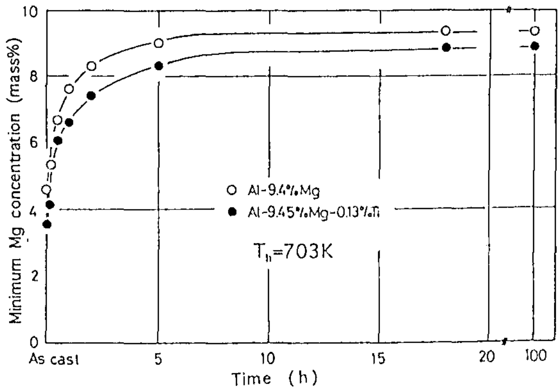


Fig.3 Homogenization behavior of minimum Mg concentration in dendrite cells during thermal exposure in Al-9.4%Mg and Al-9.45%Mg-0.13%Ti alloys.

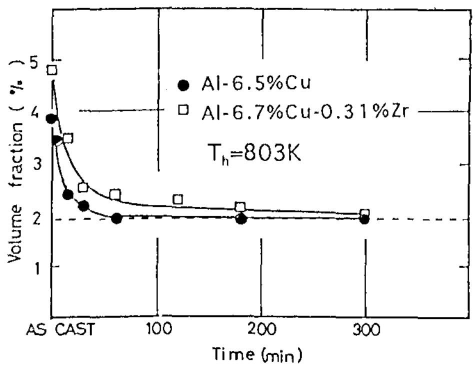


Fig.4 Dissolution behavior of non-equilibrium eutectic $Al_2Cu$ during thermal exposure at 803K in Al-6.5%Cu and Al-6.7%Cu-0.31%Zr alloys.

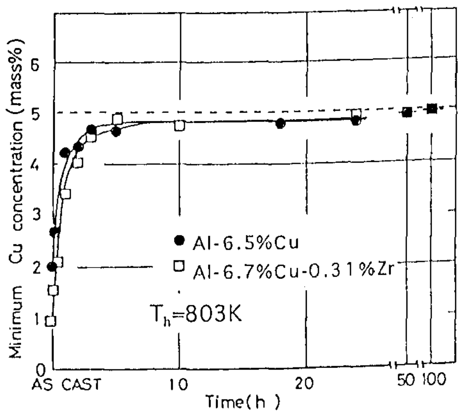


Fig.5 Homogenization behavior of minimum Cu concentration in dendrite cells during thermal exposure at 803K of Al-6.5%Cu and Al-6.7%Cu-0.31%Zr alloys.

elements and thereafter the homogenization progresses slowly. In the cast aluminum alloys with the peritectic elements Ti and Zr , the complete homogenization of the eutectic elements Cu and Mg delayed , and was hardly achieved in the alloys with Ti.

In order to clarify the phenomenon that the homogenization of Cu and Mg was hardly achieved in the Ti cored segregated region , the diffusion behavior of Mg and Ti in aluminum alloys was examined by use of a diffusion couple of Al-2%Mg/Al-2%Mg-0.15%Ti alloys. The change of Mg and Ti concentration profiles at the vicinity of the interface in the diffusion couple exposed at 703K is shown in Fig. 6. In all specimens treated by thermal exposure, the Ti concentration profile in the dendrite cells did not changed, because the Ti could hardly diffuse at 703K in aluminum alloy. The large difference of Ti concentration remained clearly in the both sides at the interface. However, the Mg concentration profile changed remarkably. In the side of the Ti added alloy the Mg concentration at the vicinity of the interface decreased and in the opposite side the Mg concentration increased with increasing the thermal exposure time. In the alloy containing both the high diffusion rate and the very low diffusion rate elements, the high diffusion rate element diffuses firstly to achieve the chemical potential equilibrium. This phenomenon is called as the up hill diffusion. It has also presented by Darken[6] and Kirkaldy[7]. The Ti concentration in the inside region of the cored structure in cast Al-9.45%Mg-0.13%Ti alloy was about 0.7% and that in the outside of the cored structure was nearly 0%. The Ti cored structure was hardly eliminated by thermal exposure at 703K. On the final stage of the homogenization treatment, the low Mg concentration in the inside region of the cored structure is equilibrated with the high Mg concentration in the outside of the cored structure due to the chemical potential equilibrium. The further homogenization of Mg hardly progresses unless the progress of the diffusion of Ti.

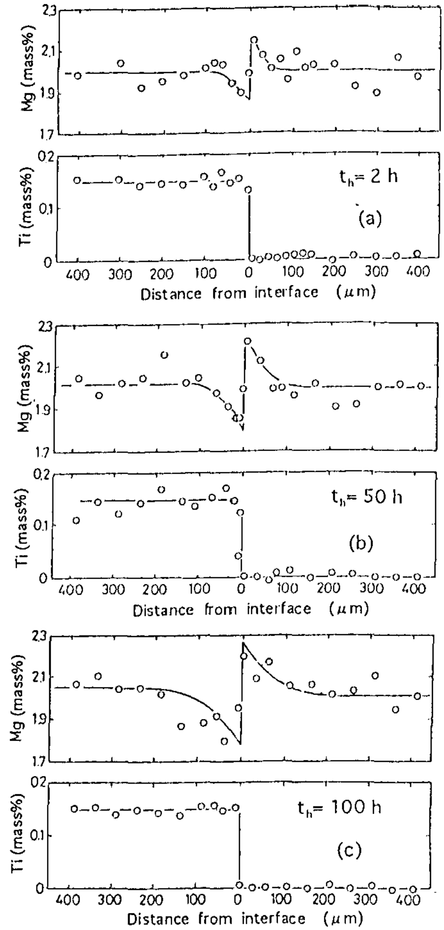


Fig.6 Mg and Ti distribution in welded Al-2%Mg/Al-2%Mg-0.15%Ti alloys specimen homogenized at 703K for 2h (a) and 50h (b) and 100h (c).

## Precipitation

The precipitation did not occurred during the homogenization treatment inside the cored


Fig.7 Nonuniform precipitation structure in Al-9.45%Mg-0.13%Ti alloy aged at 453K for 25h.

structure of Al-9.45%Mg-0.13%Ti and Al-4.5%Cu-0.16%Ti alloys. The microstructure in the cast Al-9.5%Mg-0.13%Ti alloy aged at 453K for 25h after the solution treatment at 703K is shown in Fig. 7. The marked nonuniform precipitation structure was found . The precipitation of the intermediate phase $\beta'$ occurred in the outside region of the Ti cored structure . The precipitation of the $\beta'$ phase did not occurred at all in the inside of the Ti cored structure at 453K aging.

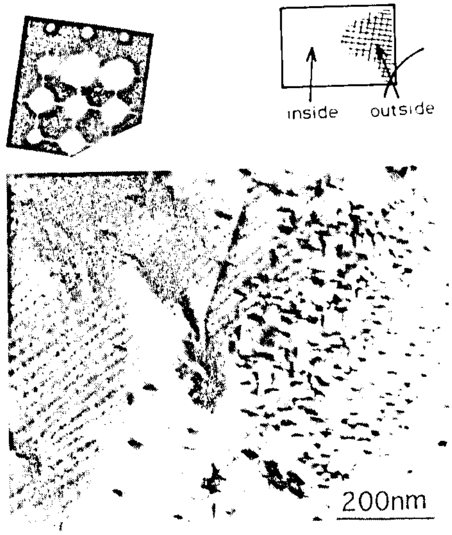


Fig.8 TEM structure of Al-4.5%Cu-0.16%Ti alloy aged at 453K for 6ks.

The TEM structures of Al-4.5%Cu-0.16%Ti alloy aged at 453K are shown in Figs.8 and 9.

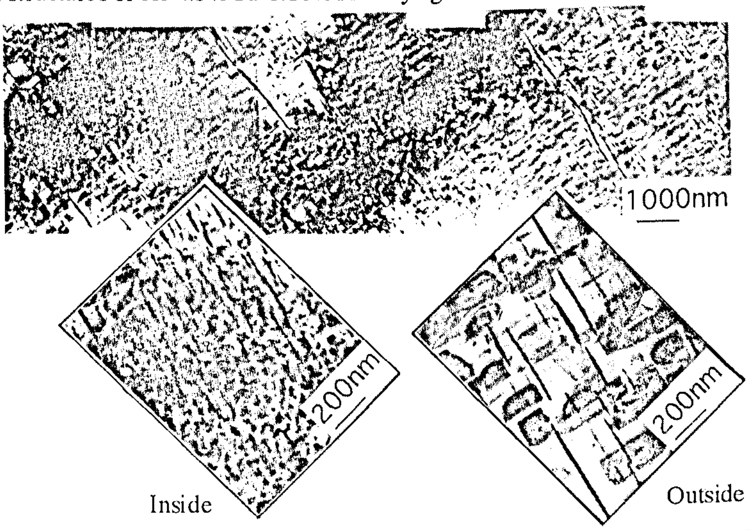


Fig.9 TEM structures of Al-4.5%Cu-0.16%Ti alloy aged at 453K for 240h.

Although the formation of the G.P.(2) zone occurred in the outside region of the Ti cored structure ,but no precipitates were formed in the inside of the cored structure in the early stage of the aging for 6ks. In the further aging for 240h, the fine intermediate phase $\theta$' precipitated in the inside of the cored structure and the $\theta$' phase grow coarsened sufficiently in the outside of the cored structure. The formation and growth of the precipitates in Al-4.5%Cu - 0.16%Ti alloy become slower in the inside of the Ti cored structure than in the outside of the Ti cored structure.

The precipitation of metastable cubic $Al_3Zr$ phase $\beta$'in the inside of the Zr cored structure occurred during the homogenization treatment at 803K for 10h in Al-6.7%Cu-0.31%Zr alloy , as shown in Fig.10. The complete homogenization of the Cu concentration was achieved because of the decrease of the Zr concentration in the inside of the Zr cored structure due to the precipitation of $\beta$' phase. The very fine spherical metastable $Al_3Zr$ with the strain field precipitate during thermal exposure at 803K for 10h after annealing at 723K for 50h , as shown in Fig. 11. The fine spherical precipitates

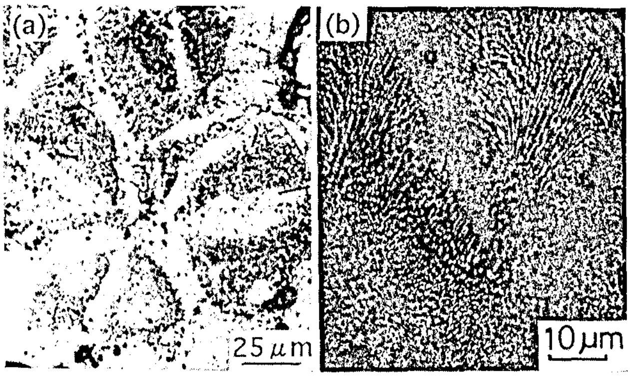


Fig.10 Precipitation structure in the inside region of Zr cored structure in Al-6.7%Cu-0.31%Zr alloy homogenized at 803K for 10h.
(a)Optical image (b) SEM image

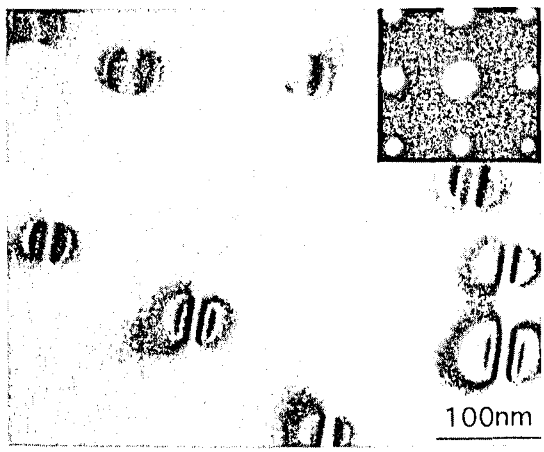


Fig.11 Precipitation of fine metastable $Al_3Zr$ in Al-6.7%Cu-0.31%Zr alloy homogenization treated at 803K for10h after annealing at 723K for 50h.

affect the precipitation of the θ 'phase and G.P.zone as shown in Fig. 12. The coarse θ ' phase formed at the vicinity of the fine $Al_3Zr$ phase with the strain fields and the formation of the fine G.P.zone was found in the matrix farfrom $Al_3Zr$ phase. The phase transformation from G.P.zone to θ ' phase and the formation and growth of the θ ' phase were accelerated in the inside of the Zr cored structure rather than in the outside of the Zr cored structure.

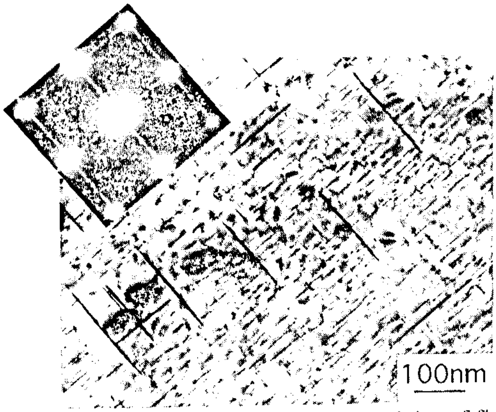


Fig.12 Precipitation behavior at vicinity of fine $Al_3Zr$ Phase in Al-6.7%Cu-0.31%Zr alloy aged at 453K for 12ks.

## Conclusions

(1) The degree of microsegregation in the cast aluminum alloys increase with addition of Ti and Zr, and the peritectic elements themselves form the marked cored segregation .

(2) In the cast aluminum alloys with Ti and Zr , the complete homogenization of the eutectic elements Cu and Mg delays , and is hardly achieved in the alloys with Ti . The further homogenization progresses unless the progress of the diffusion of Ti due to the chemical potential equilibrium..

(3)The complete homogenization of Cu concentration in Al-Cu-Zr alloy is achieved because of the decrease of the Zr concentration in the inside of the Zr cored structure due to the precipitation of β ' phase.

(4) The intermediate phase β ' in Al-Mg-Ti alloy precipitates in the outside region of the Ti cored structure .The growth of the precipitates in Al-Cu -Ti alloy become slower in the inside of the Ti cored structure than in the outside of the Ti cored structure.

(5)The θ ' phase in Al-Cu-Zr alloy nucleates preferentially at the vicinity of the fine metastable $Al_3Zr$ phase with the strain fields and the growth of the θ ' phase is accelerated in the inside of the Zr cored structure rather than in the outside of the Zr cored structure.

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