論 文

Study on the Combined Melt Treatment to optimize Al-Si-Cast Alloys

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Abstract

공정계 및 공정계 조성에 가까운 주조용 AlSi합금은 자동차엔진 생산분야 등에서 광범위하게 사용되고 있다. 일반적으로 AlSi합금은 적용 분야에 따른 다양한 요구조건을 충족시키기 위하여 공정 조직 내 Si lamellar 상의 개량을 목적으로 종종 열처리를 행하나, 그들의 기계적 성질은 주로 응고 기간 중의 주조 조직 변화에 의해 결정되어진다. 본 연구는 1차 정출상들에 대한 미세화 첨가원소와 공정조직 내 Si의 형상 및 결정입 사이에서 나타날 수 있는 상호 작용에 대하여 관찰하였으며, 특히 AlSi9 및 AlSi14 합금에서의 인장 및 마모 특성은 물론 그들의 미세 조직 변화에 대한 P와 Sr의 동시 첨가 효과에 대하여 조사하였다. 동시 첨가한 경우 공정 조직 내 Si의 개량화는 물론 1차 정출상의 미세화를 통하여 단일 첨가에 비하여 상기 합금의 인장 및 마모 특성을 동시에 증가시켰다.

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Key words : Phosphorus, Strontium, Al-Si alloy, Mechanical properties, Grain size

1. Introduction

Cast aluminum silicon alloys with composition of eutectic and near eutectic are extensively used in a variety of applications, for example in engine manufacturing of automotives. Consequently, attention has been paid to optimize their structure and mechanical properties. Though aluminum silicon alloys are frequently subjected to heat treatments to modify the eutectic Si lamellar and to meet various application requirements, their mechanical properties are mainly determined, by the as cast structure developed during solidification.

It is well known that the shape, size and orientation of the solidified crystals affect the as cast structure. Cellular or dendritic structure develops not only during solidification of a single-phase system, but eutectic systems. The cast structure exhibits eutectic grains in which the Si crystals in the form of small lamellar grow interconnectedly with each other. Hypoeutectic or hypereutectic AlSi alloys are characterized by the amount, size and distribution of the primary phases (α-Al or Si). In these alloys, fine primary phases (α-Al or Si) and modified eutectic Si positively affect the foundry characteristics and mechanical properties of the cast products. Refining of primary aluminum [1-4] and silicon [5-8] phases has been extensively studied up to now. However, much less attention has been paid to emphasize the effect of eutectic Si grain size on the structure [9-11].

Accordingly, the present work was intensively undertaken to study the possible interactions between refining additives for primary phases and the eutectic Si morphology and grain size. Moreover, the effect of the combined additions on tensile and wear properties of AlSi9 and AlSi14 alloys was investigated.

2. Experimentals

The tests were carried out on AlSi9 and AlSi14 alloys that were prepared from pure starting materials, Table 1.

To determinate the influences of different additives on the alloy structures, batches (100 g) of AlSi9 or AlSi14 were placed in coated oxide-ceramics and melted using

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Table 1. Compositions of the starting materials(wt%)

Alloy AlSi9										
Si	Fe	Cu	Mn	Mg	Zn	Ti	B	P	Sr	Na
8,93	0,059	0,0017	0,0021	0,0035	0,0112	0,0024	0,0004	-	<0,0001	<0,0001
Alloy AlSi14										
Si	Fe	Cu	Mn	Mg	Zn	Ti	B	P	Sr	Na
14,0	0,076	0,0016	0,0029	0,0040	0,0054	0,0058	0,0012	0,0011	<0,0001	0,0002

electric resistance furnace. When the melt temperature reached the pouring temperature, P- and Sr- containing master alloys were individually or simultaneously added by means of a dipping bell. During the addition, the melt was stirred by coated graphite stirrer or steel rod to get a homogeneous distribution of the additives in the melt. After holding time of 10 minutes, the melt was poured into a coated thick-wall steel mould by room temperature (∅: 35 mm, thickness of the wall: 7.5 mm, height: 45 mm). Subsequently, the specimens were cut 20 mm from the bottom and metallographically prepared for examination under optical and scanning electron microscope.

3. Results and discussion

3.1 Refining of the primary phases

The AlTiB and newly developed AlTiC master alloys, which are commercially available at present, can be successfully used to grain refine Al and wrought Al alloys. However, due to higher Si content in hypoeutectic AlSi casting-alloys (e.g. 6 to 9% Si), these refiners are to a great extent ineffective. On the other hand, only boron-containing master alloys have ability to achieve an efficient refining effect. In case of grain refinement with AlB master alloys, AlB_2 or TiB_2 particles, which spontaneously form if the melt contains titanium, with or without crystallized Si particles act as nucleus. Also, partially grown clusters containing both particle types have ability to favour crystallization of α-aluminium. Fig. 1 shows some examples of the crystallization centers. It can be seen that several particles contribute to the formation of crystallization centers. Refining of the primary Si phase in hypereutectic alloys using phosphorus has been well established for many years.

However, the addition of phosphorus into the melt is very difficult and has some disadvantages. In practice, the addition of binary CuP master alloys into the melt has been successfully used where the required AlP particles for refining the primary Si form first in the melt. In such case, high melt temperatures (approx. 850°C) and long holding times of at least 40 minutes are necessary. In such refining method, the master alloy is added directly into the casting furnace that may be contaminated with phosphorus[12]. To achieve a significant refining effect using CuP master alloys, the amount of phosphorus added has to be as high as 200 ppm. Moreover, a relatively higher master alloy amount must be added since the possibility of phosphorus burning is very high (up to 80%)[13,14].

For some years, the refining of primary Si with a ternary AlCuP master alloy has been applied in practice. This master alloy is prepared by powder metallurgy route where powders of aluminum, copper and phosphorus are mixed and extruded to rods. Subsequently, the master alloy rods can be continuously added into the spruce system. The advantage of this master alloy with approx. 20 wt% Cu and 1.4 wt% phosphorus is, that the active refiner AlP phase is already present in this alloy. In this way, the melt temperatures and holding times necessary for formation of the AlP drop down remarkably. Previous investigations by Vogel and Schneider[12], and Schneider et al.[15] have shown that AlCuP master alloy is extremely effective and free from emission during addition into the melt. Furthermore, it has not been shown essential disadvantages up to now. In the present work, the ternary AlCuP master alloy was used. The results show in Fig. 1 that regardless of the alloy Si content, small amount of phosphorus (10-20 ppm) is sufficient to achieve an optimum refining of the primary

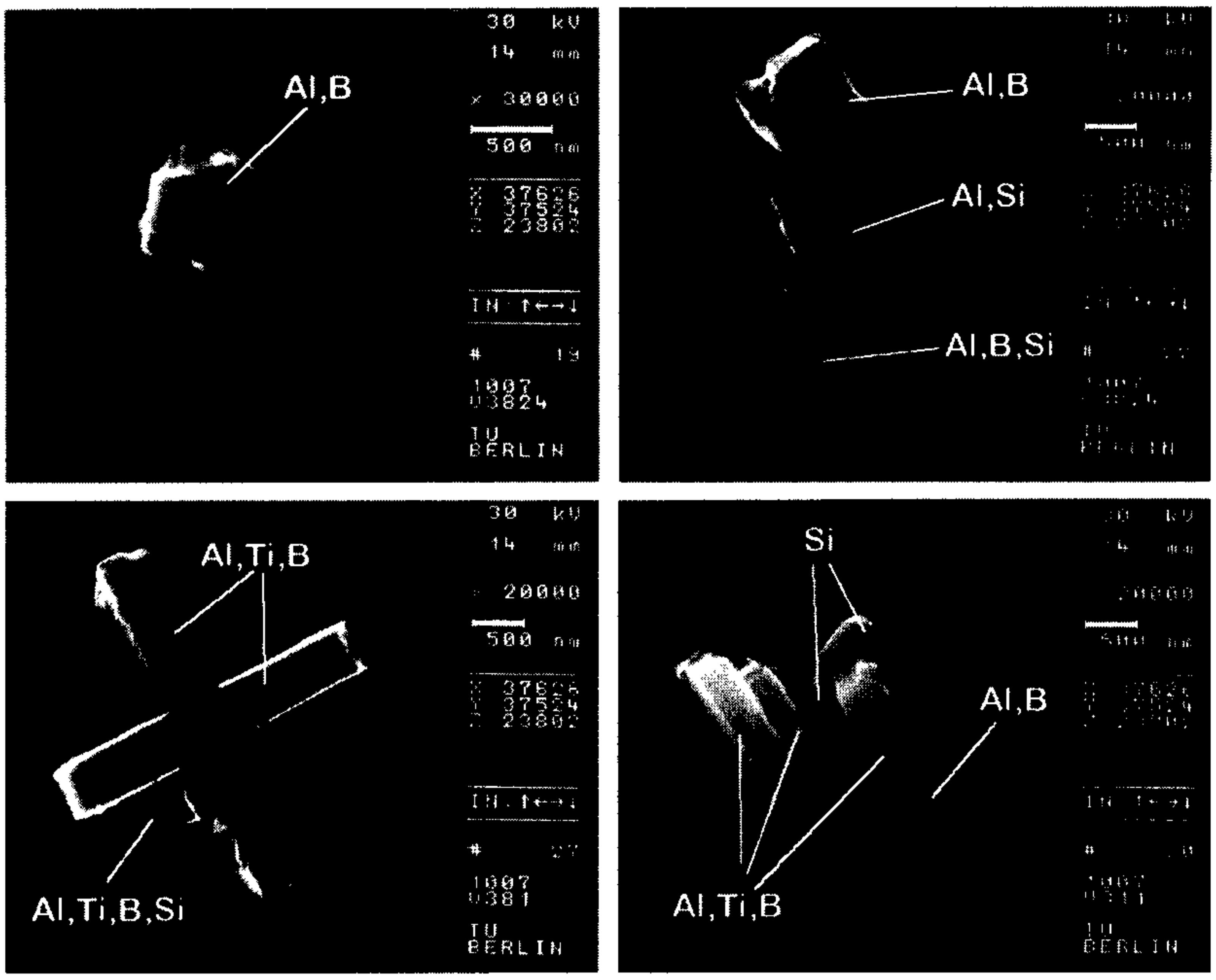


Fig. 1. Crystallization centers of primary α-aluminum; alloy: AlSi9.

phase (20 to 30 μm). In addition, the eutectic grain size of AlSi14 alloy is significantly decreased through relatively small amount of phosphorus addition. Like the case of the primary α-Al grain refinement, as the nuclei number linearly increases, the particle size of primary Si exponentially decreases. Furthermore, phosphorus dissolves in the melt, consequently, the solubility of Si in the melt increases, i.e. the eutectic point is displaced to higher Si concentration. It should be mentioned that the AlCuP master alloy produced by powder metallurgy method is added directly into the melt, Fig. 2. In such melt, the AlP particles have the ability to act as nucleus for both primary Si and eutectic Si grain.

3.2. Modification of eutectic silicon

In case of hypereutectic AlSi alloys, the largely required amount of strontium addition depends essentially on the volume fraction of the eutectic in the structure. As the volume fraction of the eutectic increases, the amount of strontium added must be increased at a constant cooling rate. In case of chill casting, the amount of strontium, which is required for complete modification of the eutectic Si in hypoeutectic cast alloy, is approx. 80 to a maximum of

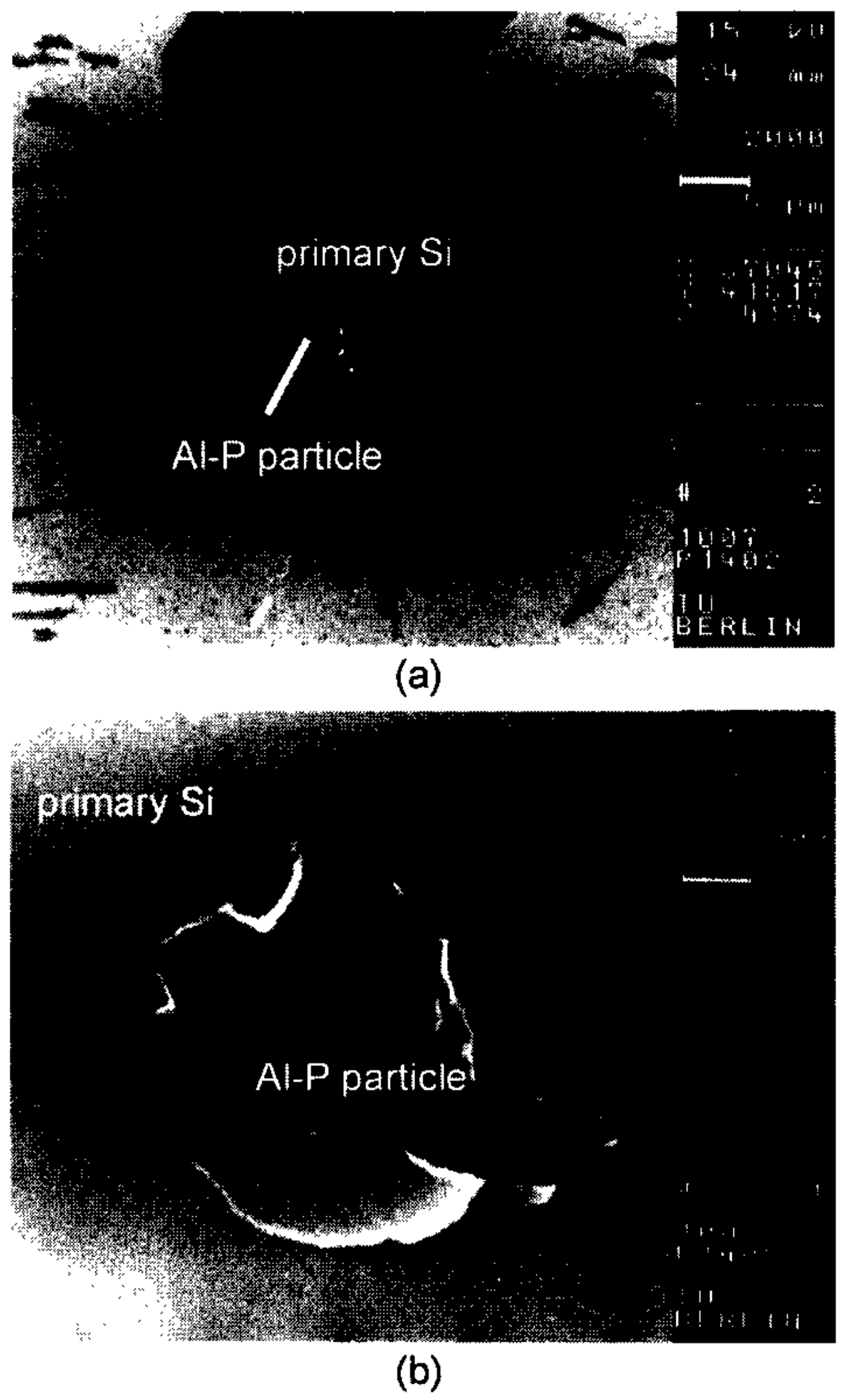


Fig. 2. AlP-Crystallization centers of primary Si. (a: overview, b: magnified view, alloy: AlSi14)

150 ppm. The addition of strontium to hypereutectic cast alloy to modify eutectic Si results also in reducing the particle size of primary Si (from 160 to 80 μm). This refining effect is lesser than that the case of phosphorus addition. Also, in case of hypoeutectic alloys, the amount of strontium required for complete modification of the eutectic Si depends on the volume fraction of the eutectic in the structure. The alloys with composition of slightly hypereutectic exhibit nearly complete eutectic structure owing to displacing of the eutectic point through strontium addition to higher Si content. In this case, the amount of strontium added must be larger (approx. 150 to 200 ppm) than that the case of highly hypereutectic alloys (approx. 80 to 150 ppm). In spite of eutectic point displacing to higher Si content in highly hypereutectic alloys, a fraction of the Si forms as primary Si and, hence, the eutectic volume fraction is reduced in the structure. A further effect of strontium is the achievement of very fine eutectic grain size compared with phosphorus at the complete modification.

3.3. Refining of the primary phases and modification of eutectic silicon (combined melt treatment)

The main aim of the combined melt treatment for hypoeutectic alloys is to grain refine the primary α-Al and achieve a complete modification of the eutectic Si at the same time. As it can be seen in Fig. 3, the produced microstructure reveals fine grains of α-Al. And also - belonging to the addition of 150 ppm Sr - the samples show a complete modification of the eutectic Si, compare Fig. 4a. One of the advantages of the combined melt treatment is the significant reduction in the amount of refiner added to 50%, depending on the casting temperature, at approximately constant modifier addition, see Fig. 3. Concerning the casting temperature, optimum temperature was determined to be from 720 to 750°C based on the interaction between the two additives of boron and strontium. Indeed, the grain refining effect of B-containing master alloy increases with decreasing temperature.

In addition, the added amount of boron can be signifi-cantly reduced by simultaneous addition of strontium at low casting temperatures. On the other hand, the modi-fication effect of strontium deteriorates with decreasing casting temperature at a constant

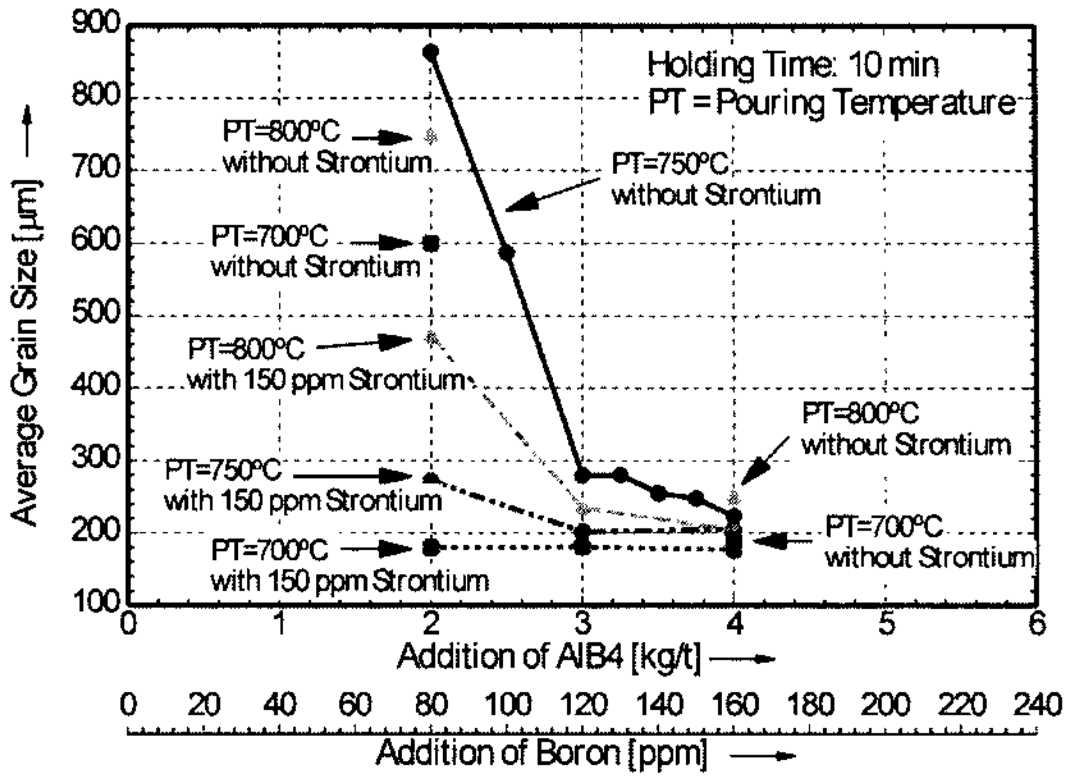


Fig. 3. Influence of the strontium modifier addition on the grain refining effect (primary Al) of the AlB4 master alloy rod; alloy: AlSi9.

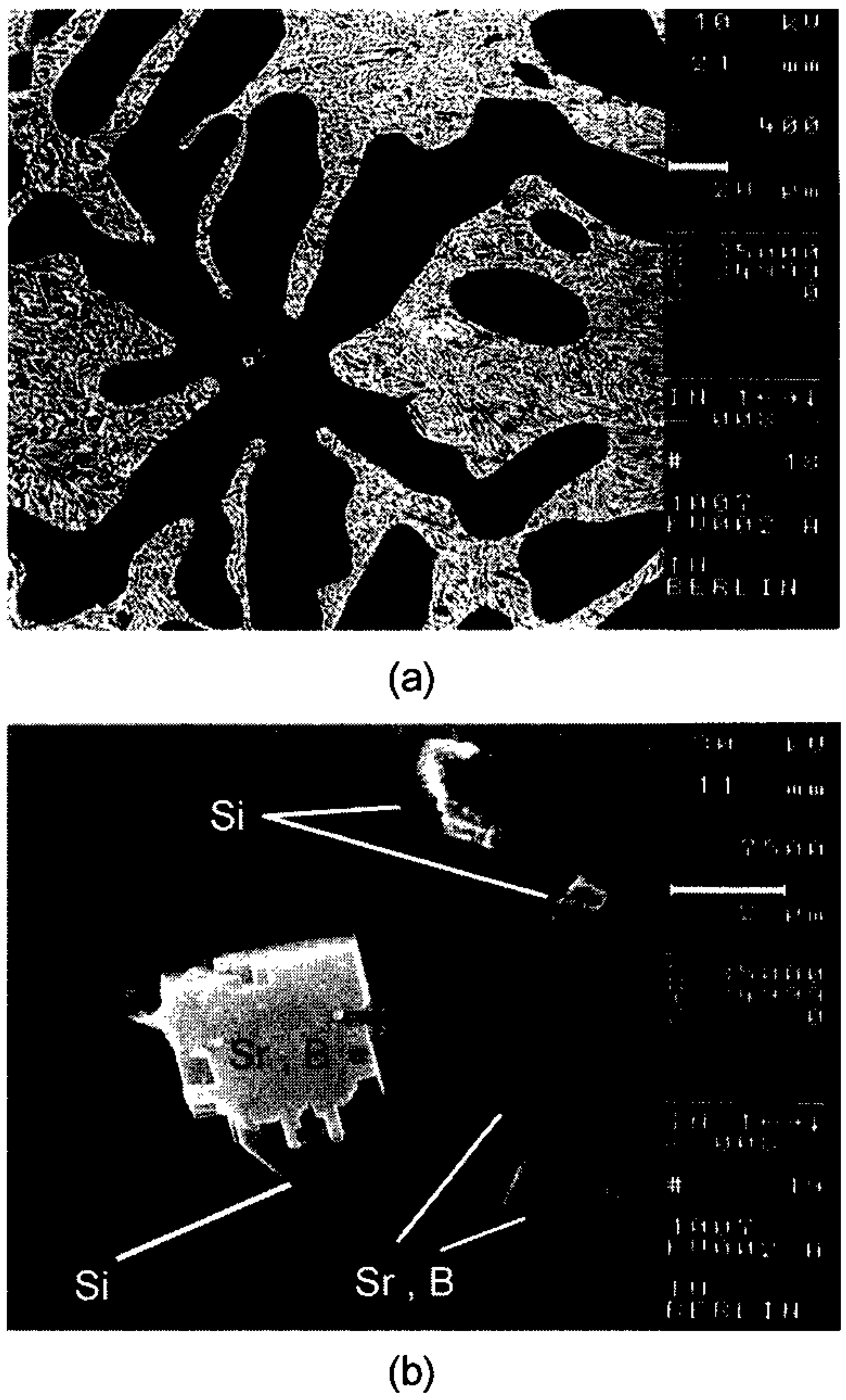
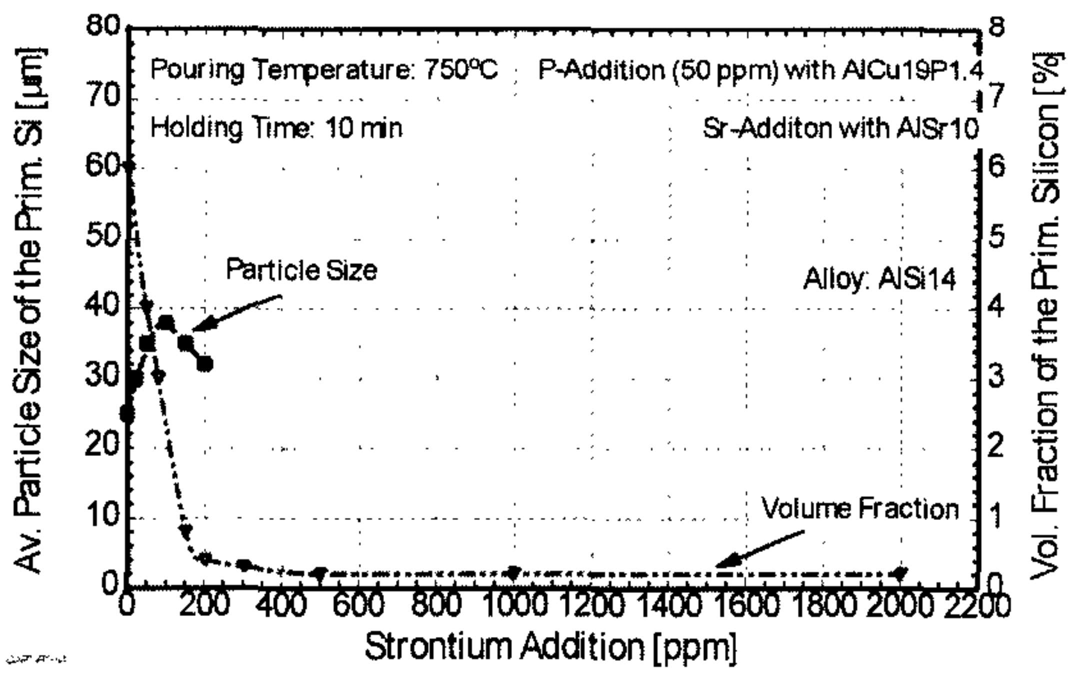
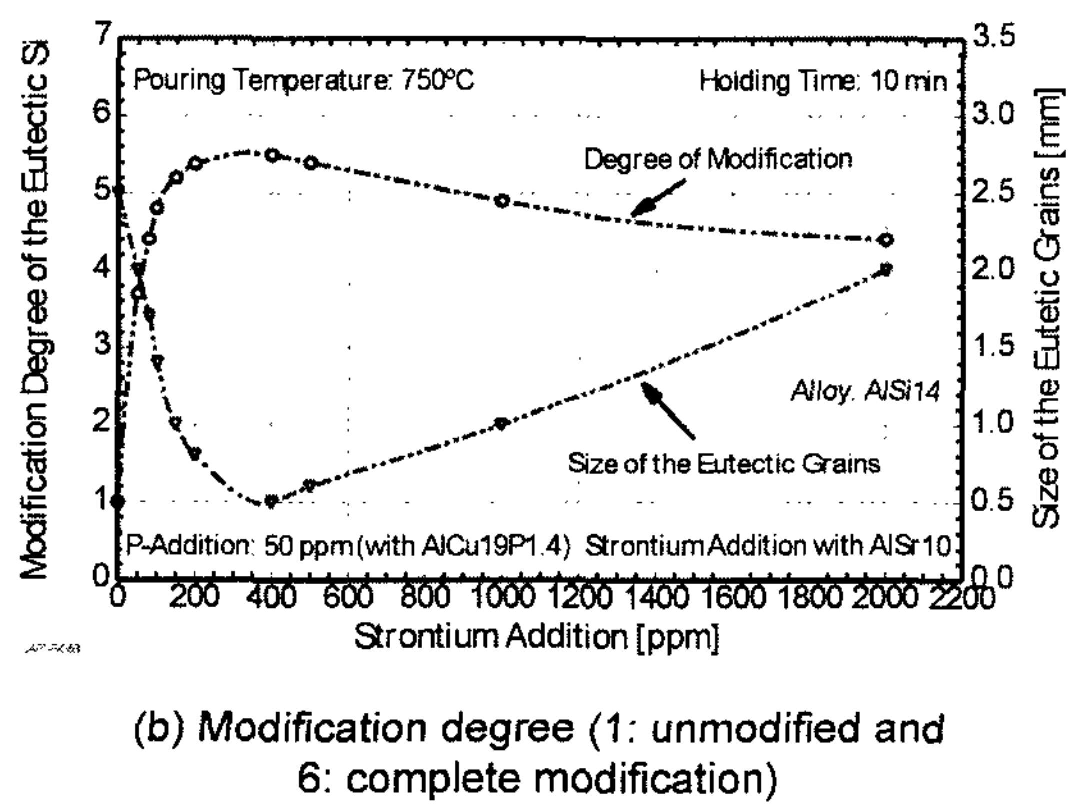


Fig. 4. Crystallization centers of the primary α-Al using combined melt treatment (a: overview, b: magnified view).

holding time. Through combined addition of AlB4 and strontium, both strontium-boron containing particles (SrB_6) and B-containing particles, which are also active nucleus in case of boron addition alone, promote crystallization centers, Fig. 4. For the combined melt treatment of the AlSi14 hypereutectic alloy, phosphorus content was maintained constant in the samples and the amount of strontium added was varied. Then the influence of melt treatment on the structure parameters was determined, Fig. 5. Concerning the particle size of primary silicon, a statement can be only made if the amount of strontium added is small (a maximum of 200 ppm strontium). However, through the combined addition of phosphorus and strontium (from approx. 200 ppm of strontium) into the slightly hypereutectic alloy (AlSi14), the formation of the primary Si is depressed because of displacing the eutectic point to higher Si content, i.e. the volume fraction of the primary Si may be about zero. On the other hand, small amount of strontium with simultaneous addition of phosphorus results in formation of primary silicon having average particle size in the range of approx. 30 to 40 μm. The present investigation clearly shows that even the phosphorus concentration is larger in the melt, modification of eutectic Si by using strontium is possible. In such case, the added amount of strontium must be adapted to the phosphorus concent-ration. The addition of phosphorus and strontium into AlSi14 alloy leads to a more pronounced reduction in the grain size of the eutectic, comparing to the case when only one of the two elements is added. Depending on the melt treatment route, small Si clusters (in absence of phosphorus) or small primary Si particles (in presence of phosphorus) act as crystallization centers for the eutectic grain, Fig. 6a and b. As in case of primary α-



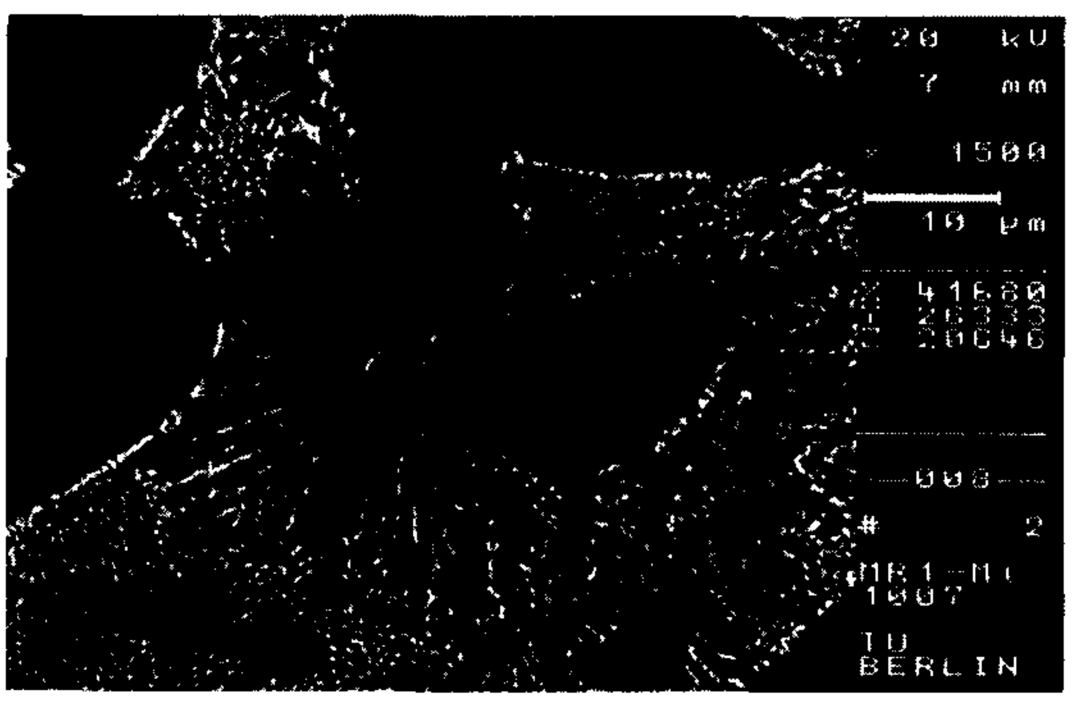
(a) Average particle size and volume fraction of primary Si



(b) Modification degree (1: unmodified and 6: complete modification)

Fig. 5. Influence of the amount strontium addition on the structure parameters using combined melt treatment.

(a)



(b)

Fig. 6. Crystallization centers of eutectic grains (a : Si clusters, b : Si particles)

(a)

(b)

Fig. 7. Morphology of eutectic grains. (a: columnar crystals - unidirectional temperature gradient, b: globular crystals - radial temperature gradient)

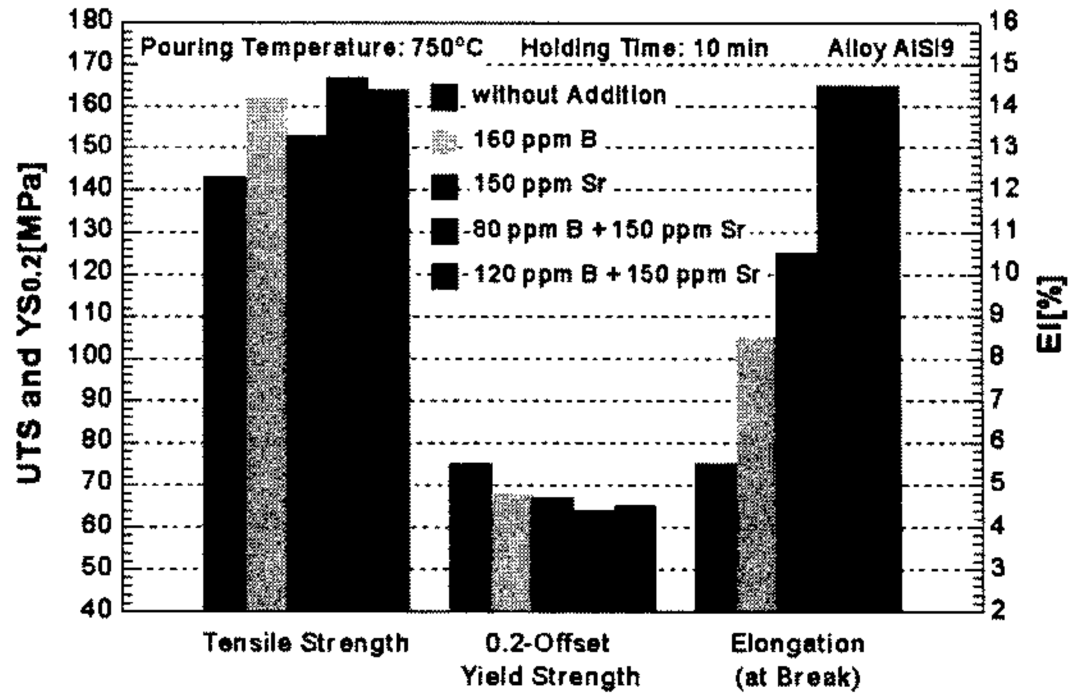


Fig. 8. Tensile properties of the AlSi9 alloy.

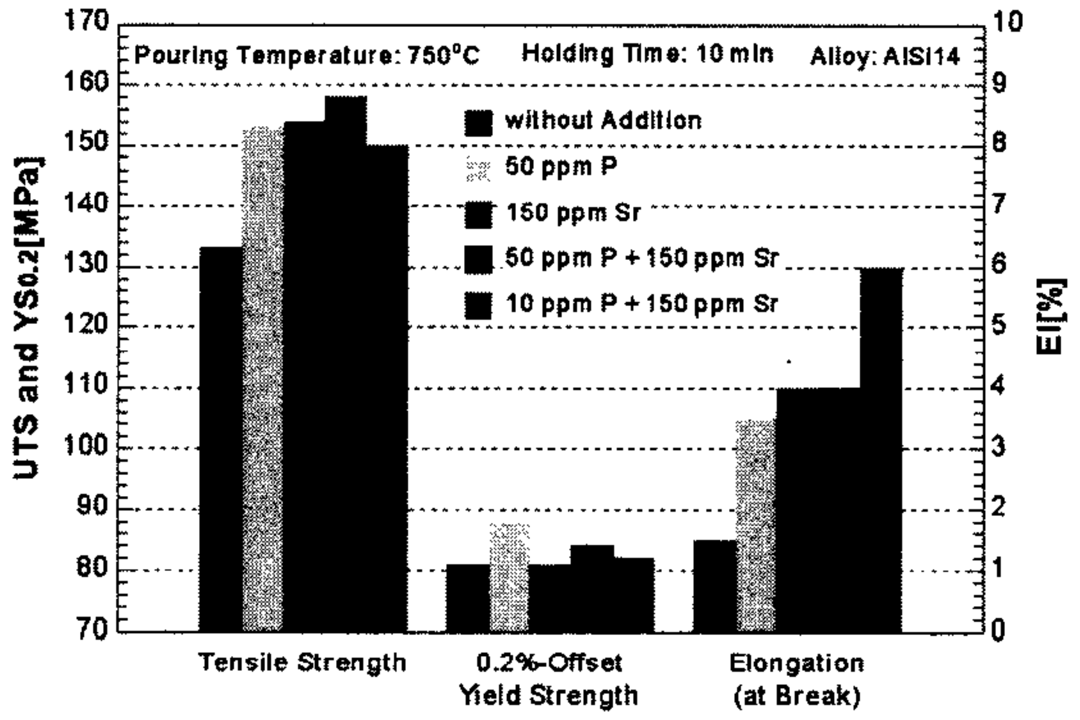


Fig. 9. Tensile properties of the AlSi14 alloy.

Al structure, the eutectic grains may develop in the form of columns and/or equiaxed. The formed grain morphology is based on different growth mechanisms, which, in turn, depending upon the corresponding temperature gradient, Fig. 7 a and b.

3.4. Tensile and wear properties

The influence of the melt treatment on the tensile and wear properties of AlSi14 was examined. Since the tensile and wear properties showed a comparable dependence upon the melt treatment during the experimental work, wear tests of AlSi9 hypoeutectic alloy were discarded and a comparable dependence as in the case of AlSi14 alloy was formulated. Concerning the tensile properties of the AlSi9 alloy, it was found that grain refinement of α-Al or modification of eutectic Si enhances both the tensile strength and elongation. By using combined treatment, the tensile strength insignificantly increases; however, the elongation increases by approx. 40% com-paring to the conventional modification, Fig. 8. Generally, the addition of only strontium or phosphorus to the AlSi14 alloy attributes significantly to its tensile strength and elongation compared to the normal alloy. Through controlling the combined additive of both phosphorus and strontium, tensile strength and elongation of the hypereutectic alloy can be enhanced to a level com-parable to those of the hypoeutectic alloy, Fig. 9. On the other hand, the yield strength remains relatively unaffected. The effect of the melt treatment on the total wear coefficient under two different conditions is represented in Fig. 10. Virtually, the addition of phos-phorus or strontium causes a reduction in the total wear coefficient, but the lowest one is achieved by the combined treatment. The improvement in tensile and wear properties is attributed to the structure

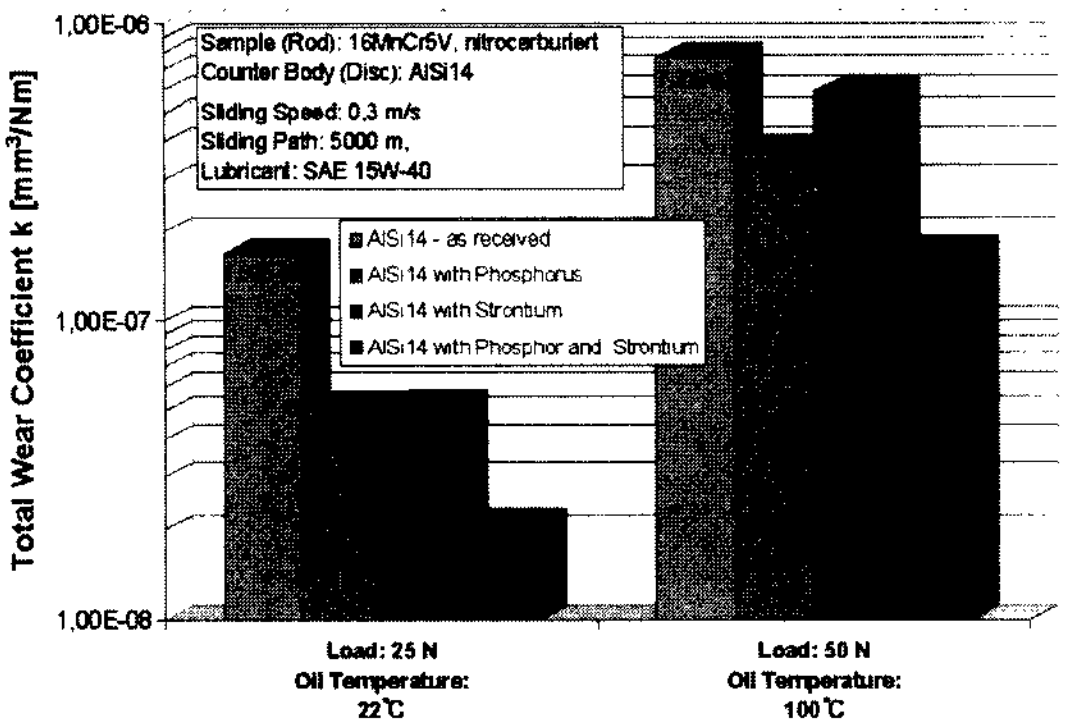


Fig. 10. Total wear coefficient of the AlSil4 alloy.
phosphorous addition: 50 ppm, strontium addition: 200 ppm; phosphorous-and strontium addition (together):50 ppm P + 200 ppm Sr

parameters (namely, refining of the eutectic grain and primary Si as well as modification degree of the eutectic Si) that are optimized by the combined melt treatment.

4. Conclusions

1) A combined melt treatment route of Al-Si cast alloys was developed to grain refine primary phases(α-Al or Si) and achieve complete modification of the eutectic Si simultaneously.

2) The amount of boron added to grain refine the primary phase can be significantly reduced by simultaneous addition of strontium for modification the eutectic Si at low casting temperatures.

3) The addition of phosphorus and strontium into AlSil4 alloy leads to a more pronounced reduction in the grain size of the eutectic, comparing to the case when only one of the two elements is added.

4) The tensile elongation increases by approx. 40% through combined treatment compared to the conventional modification.

5) The addition of phosphorus or strontium causes a reduction in the total wear coefficient, but the lowest one is achieved by the combined treatment.

6) The improvement in the tensile and wear properties is attributed to the structure parameters that are optimized by the combined melt treatment.

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