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MODIFICATION OF HYPEREUTECTIC SILUMINS WITH PHOSPHORUS AND SODIUM

P. A. Parkhutik, L. D. Kalashnik, and M. Z. Lubenskii

UDC 669.71;621.74

The structure of unmodified aluminum–silicon alloys consists of crystals of primary silicon and large needles of α Si eutectic (Fig. 1a). To refine the primary silicon, phosphorus in pure form (red phosphorus) or in the form of various phosphorus-containing compounds is added to the melt before pouring. The modifying influence of phosphorus is explained mainly by the formation of high-melting particles of AlP, isomorphous with silicon, which serve as additional centers for solidification of silicon [1, 2]. The presence of nuclei in the silicon crystals has not been demonstrated experimentally.

However, phosphorus additions have no effect on refining of the eutectic component, which, as is known, is achieved by microadditions of alkali metals, particularly sodium. It is assumed that the combined addition of phosphorus and sodium to Al–Si alloys is inexpedient due to their mutually exclusive modifying effects [3, 4].

We investigated the structure and mechanical properties of binary Al–Si alloys with 12.0, 16.0, and 20% Si modified with phosphorus and sodium separately and together at different concentrations, varying the modification and casting temperatures, holding time, and so forth. The alloys were prepared from A99 aluminum and KrO silicon. Heats weighing 150 g were prepared in graphite–fireclay crucibles in an electric resistance furnace. Phosphorus (0.005-0.6% of the charge) was added to the melt at 800-850°C in the form of pure phosphorus, a copper–phosphorus master alloy (~10% P), and sodium phosphates ($NaPO_3$, $Na_4P_2O_7$, Na_3PO_4).

The heats were cast in sand and metal molds either directly after modification or after standing 15-30 min. Metallic sodium and also in the form of salts (0.01-0.8% of the charge) was added to the melt at 770-850°. Combined alloying with phosphorus and sodium was carried out by two methods – both modifiers in different proportions were added simultaneously at 800 and 850°, the melt was stirred and cast at 770 and 880°, respectively; phosphorus was added at the same temperatures, the melt was allowed to stand 15-20 min, the temperature was lowered to 770-780°, sodium was added, and the melt was cast at this temperature.

Figure 1b-d shows the microstructure of Al + 20% Si modified with the different elements.

With the addition of phosphorus alone (in pure form or master alloy) the primary silicon was refined and evenly distributed in the ingots in all cases (Fig. 1b). The structure of the eutectic remained coarse in this case. Sodium phosphate $NaPO_3$ (0.2-0.5%) had a similar effect. The addition of sodium alone (0.03-0.1%) ensures modification of the eutectic, but primary silicon is not refined, the particles becoming only more compact (Fig. 1c). Larger silicon concentrations lead to "overmodification" of the eutectic and rounding of the grains of primary silicon; in this case the toughness increases considerably and the flowability of the alloy is impaired.

Physicotechnical Institute, Academy of Sciences of the Belorussian SSR. Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No. 8, pp. 67-69, August, 1977.

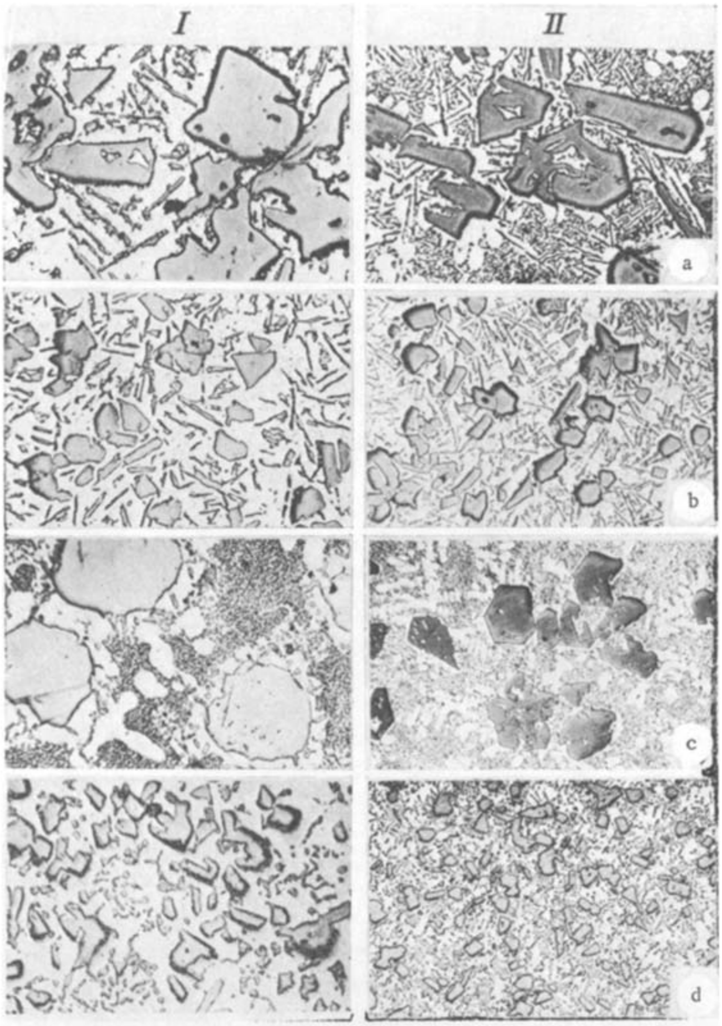

Fig. 1. Microstructure of Al + 20% Si not modified (a), modified with phosphorus (b), with phosphorus and sodium together (c), and with phosphorus and sodium in succession (d) (×100). I) Cast in sand molds; II) cast in chill molds.

With combined addition of phosphorus and sodium (first variation) the particles of eutectic silicon are slightly refined and rounded and the crystals of primary silicon are also broken up and are unevenly distributed in the casting.

Addition of the modifiers in succession (second variation) leads to a stable structure with evenly distributed particles of primary silicon and modified fine-grained eutectic. An especially favorable structure is formed in chill molds (Fig. 1d, II). With combined addition of the optimal quantity of phosphorus (0.05-0.1%) and sodium (0.02-0.03%) the strength and ductility of hypereutectic Silumins increase substantially [5]. Similar results were obtained by modification of high-silicon Al–Si alloys with sodium phosphate ($NaPO_3$) and subsequent treatment with universal triple flux (45% NaCl + 40% NaF + 15% NaAlF) [6].

The positive effect of combined modification with phosphorus and sodium was also confirmed in production tests of the complex-alloyed piston alloy VKZhLS-2.

Differing explanations of the separate effect of phosphorus and sodium on the structure of Silumins were offered in [1-5, 7]. However, the combined effect of these elements was not considered. The mechanism of combined modification is assumed to be as follows.

With simultaneous addition of both elements they may react with each other and form Na_3P, which has little or no effect on primary or eutectic silicon [3, 4]. After addition of phosphorus alone, high-melting phosphide AlP is formed before the beginning of solidification, the particles of which serve as nuclei for primary

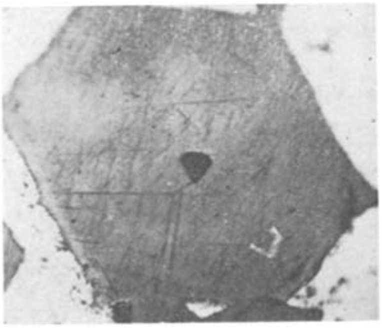

Fig. 2. Microstructure of Al + 20% Si with 0.6% P (×1000).

silicon. This is indicated by the smaller supercooling of the heat with primary solidification of silicon in the presence of phosphorus [5, 7] and also by inclusions of regular shape within silicon crystals observed in separate cases (Fig. 2). However, AlP is formed slowly and the heat must be left standing for completion of the reaction. It is not excluded that not all the phosphorus added participates in the reaction but is partially burned, and some of it may exist in free form. With subsequent addition of sodium, a partial interaction with the remaining phosphorus is possible. Therefore, the quantity of sodium should be sufficient to ensure possible reaction with phosphorus and to modify the eutectic [5, 7]. The treatment of hypereutectic melts with sodium phosphates is characteristic in this respect. The larger the sodium concentration in the phosphate, the better the modification of the eutectic and the weaker the effect of phosphorus on the refining of primary crystals of silicon [6].

Metallographic and thermal analysis confirmed this mechanism of the effect of phosphorus and sodium on the structure of hypereutectic Silumins with successive addition of the modifiers in the proportion P : Na = 3-5 : 1.

CONCLUSIONS

1. The nucleation theory of the refining of primary silicon crystals in hypereutectic Silumins microalloyed with phosphorus was verified by experiments. Particles were observed in silicon crystals (possible AlP) which served as additional centers of nucleation of primary silicon crystals.

2. Combined modification of high-silicon Silumins with phosphorus and sodium leads to refining of primary and eutectic silicon.

3. Modification with phosphorus is most expedient with phosphorus-containing salts, especially sodium phosphates.

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