INVESTIGATION OF THE DISTRIBUTION OF SOME ELEMENTS IN ALUMINUM – SILICON ALLOYS
BY LIMITED-AREA X-RAY SPECTRAL ANALYSIS*

V. S. Grebenkin and I. Ya. Dzykovich

Limited-area x-ray spectral analysis was used to determine the distributions of lead, tin, magnesium, zirconium, titanium, and cerium (as rare earth metal) in Al–Si alloys containing 4.0% Si. It was necessary to study the distribution of low-melting components (lead or tin) in the aluminum alloys in connection with the "neutralizing" element. The selection of this element was based on the substantial chemical affinity of some alkali earth, transition, and rare earth elements for elements of group IV B – silicon, tin, and lead.

The alloys were prepared in the TÉP-1 laboratory crucible furnace in painted cast iron crucibles or graphite–refractory crucibles. The charge materials were A000 aluminum, SIL-0 silumin, alloys of Al + 10% Mg; Al + 5% Ti; Al + 10% Ce; Al + 2% Zr; Al + 8% Sn, and pure lead.

To the liquid Al–Si alloys were added 1.0% (nominal amount) of Sn and Pb and 1.0% of the additional element – magnesium, cerium (as rare earth metal), zirconium, titanium, etc.

The ratio of the additional element to tin or lead was taken as 1:1 by weight, which was sufficient for the formation of chemical compounds of stoichiometric composition. The silicon concentration of the alloys was 4–6% (nominal).

Samples 30 mm in diameter and 70 mm long were cast in sand molds. Cubes 7 × 7 × 7 mm were cut from the samples, the center of the cube coinciding with the middle of the radius of the casting. This made it possible to obtain microsections with a small number of casting defects and large inclusions of the structural components suitable both for metallographic analysis and examination in the Camec microanalyzer. The microsections were polished but not etched in the case of alloys with titanium and zirconium and were electropolished in the case of alloys with magnesium and cerium. The electrolyte was 65% nitric acid (30%) and methyl alcohol (70%). The distribution of the elements in the structural components of the alloys is given in Table 1; the microstructures are shown in Fig. 1.

Crystallizing intermetallic compounds are formed primarily in the alloys containing titanium, zirconium, and cerium, and eutectics in alloys with magnesium (see Fig. 1). Crystallizing intermetallic compounds are absent in the alloys with magnesium.

It is interesting to note that the intermetallic compounds of titanium, zirconium, and cerium do not match the stoichiometric composition and always contain relatively small amounts of silicon (see Table 1).

Thus, our investigation confirms the fact that the intermetallic compounds of transition metals formed in Al–Si alloys can contain silicon, which replaces part of the aluminum in these compounds, probably because of the similar electronic configurations of aluminum (S2P1) and silicon (S2P1). Such elements as tin and lead, with an electronic configuration similar to silicon (S2P2) also enter into the composition of intermetallic compounds and, depending on their concentrations in the alloy, replace aluminum and silicon in the intermetallic compound.

Tin or lead entering into the composition of the intermetallic compound is partially neutralized and its concentration in the aluminum–silicon eutectic is reduced. However, the neutralization of tin or lead

*This work was done under the direction of Corresponding Member of the Academy of Sciences UkrSSR Professor A. A. Gorshkov and with the participation of T. V. Sil'chenko.

Institute of Casting Problems of the Academy of Sciences of the Ukrainian SSR. Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No. 10, pp. 28–30, October, 1968.
Fig. 1. Microstructure of Al-Si alloys (×500). a) Al-Si-Mg-Sn; b) Al-Si-Mg-Pb; c) Al-Si-Zr-Sn; d) Al-Si-Zn-Pb; e) Al-Ce-Sn; f) Al-Si-Ce-Pb; g) Al-Si-Ti.

is slight, since the eutectic adjoining the intermetallic compound is enriched in low-melting components. Isolated eutectic also contains a certain small amount of tin or lead.

The concentration of lead in the eutectic and in the grain boundaries was lower than that of tin in all cases, which apparently is explained by the finer and more even distribution of lead throughout the alloy in the form of an emulsion; the diameter of the lead particles was somewhat smaller than the diameter of the electron beam, which made the analysis difficult.

The alloys with magnesium, tin, and lead contained complex eutectics: $\alpha + Mg_2Si + Mg_2Sn + Si$, $\alpha + Mg_2Si + Mg_2Pb + Si$ or $\alpha + Mg_2(Si, Sn) + Si$, $\alpha + Mg_2(Si, Pb) + Si$. This may be due to the identical electronic configurations of silicon, tin, and lead ($S^2P^2$) and the similar heats of formation of $Mg_2Si$, $Mg_2Sn$, and $Mg_2Pb$: $\Delta H Mg_2Si = 6.3$ kcal/g-atom, $\Delta H Mg_2Sn = 6.1$ kcal/g-atom, and $\Delta H Mg_2Pb = 4.2$ kcal/g-atom. Thus, it can be assumed that tin or lead replaces silicon in complex chemical compounds with magnesium in the eutectic because of the almost identical chemical activity with respect to magnesium.

The metallographic examination of Al-Si-Sn alloys revealed a lighter field (light gray) surrounded by a darker field in the eutectic. According to the data from microanalysis, the light inclusions contained 6.1, 3.41, and 2.16% Sn; 16.6, 15.25, and 12.3% Si; and 7.95, 6.2, and 2.72% Mg. No low-melting eutectic with 99.5% Sn was found. The magnesium concentration was sufficient to combine the tin. This was confirmed by the ratios of the tin, silicon, and magnesium concentrations in complex eutectics and the stoichiometric compositions of $Mg_2Si$ (36 wt.% Mg) and $Mg_2Sn$ (28.5 wt.% Mg).