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Effect of Modification on Characteristic Values of TDA Curves

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Abstract

The work presents the examination results of the effect of strontium and antimony modification on the microstructure of a cast and the characteristic values of the TDA curves. Strontium and antimony modifiers were added to silumin 226 in a melting crucible furnace, separately, in the amounts of 0.1; 0.2 and 0.3% of the mass of the modified metal. After modification, the silumin was refined with the solid refiner ECOSAL-Al 113 in the amount of 0.5% of the charge mass.

Keywords: Theoretical basics of casting processes, Silumin 226, Modification

1. Introduction

Modification of silumins aims at reducing the size or changing the morphology of eutectic or primary silicon precipitations. In hypoeutectic silumins, an effect of modification is a change in the morphology of eutectic silicon from the lamellar one into the fibrous one or a reduction of the interfacial distance in the eutectic α+β. The change of the lamellar silicon into the fibrous one is obtained by way of sodium or strontium modification [1÷3]. The current industrial practice involves the use of Sr, which, contrary to Na, is not a long-term modifier, which means that the effect of modification is maintained after successive silumin remelts. The Sr modification causes an increase of R_m, A and HB of the silumins, whereas it also reduces their impact resistance and increases the gassing degree [1÷5]. The reduction of the distance between the Si lamellae in the eutectic α+β is obtained by way of Sb modification [1÷3].This modifier also causes intense precipitation of phosphorus from silumin in the form of gas [1]. The examined silumin 226 belongs to the group of hypoeutectic silumins, in which the classic eutectic α+β does not exist [6]. Due to the high content of iron and copper, it involves the crystallization of the following: the ternary eutectic α + $Al_9Fe_3Si_2$ + β and the quaternary eutectic α + Al_2Cu + AlSiCuFeMgMnNi + β [1]. In those eutectics, in non-modified silumins, Si (phase β) has the lamellar form. Applying the modification of the examined silumin should cause analogical effects of the silicon lamella changes to those in the classic eutectic α+β of silumin without alloy additions.

2. Test methodology

The silumin was melted in a gas shaft furnace. The silumin chemical composition range is presented in Table 1.

Table 1.
Chemical composition range of silumin 226

Chemical composition, %							
Si	Cu	Zn	Fe	Mg	Mn	Ni	Al
9.27 ÷ 9.54	1.96 ÷ 2.32	0.84 ÷ 0.97	0.70 ÷ 0.87	0.30 ÷ 0.33	0.20 ÷ 0.23	0.06 ÷ 0.10	rest

The recording of the TDA curves involved the use of the thermocouple PtRh10-Pt placed in the standard tester ATD10m-PŁ [7].

The silumin microstructure was examined on metallographic microsections etched with a 4% aqueous solution HF with the magnification of ×100 and ×500 of the metallographic microscope Eclipse MA200 by Nikon.

3. Test results

Figure 1 shows the representative TDA curves of silumin 226 after Sr modification, whereas Table 2 presents the coordinate values of the characteristic points on the curves obtained for the non-modified silumin and the one after modification with different amounts of Sr.

a)

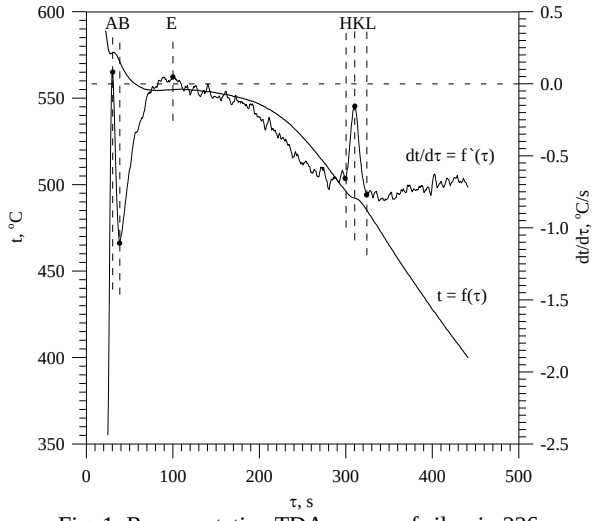


Fig. 1. Representative TDA curves of silumin 226 after Sr modification

The TDA curves presented in Fig. 1 illustrate the crystallization process of the examined silumin, which is analogical to the description for non-modified silumins. You may have noticed there three thermal effects associated with the crystallization of subsequent phases: the primary phase α (effect AB), the ternary eutectic α + $Al_9Fe_3Si_2$ + β (effect BEH) and the quaternary eutectic α + Al_2Cu + AlSiCuFeMgMnNi + β (effect HKL). The successive points determined on the curves denote the following:

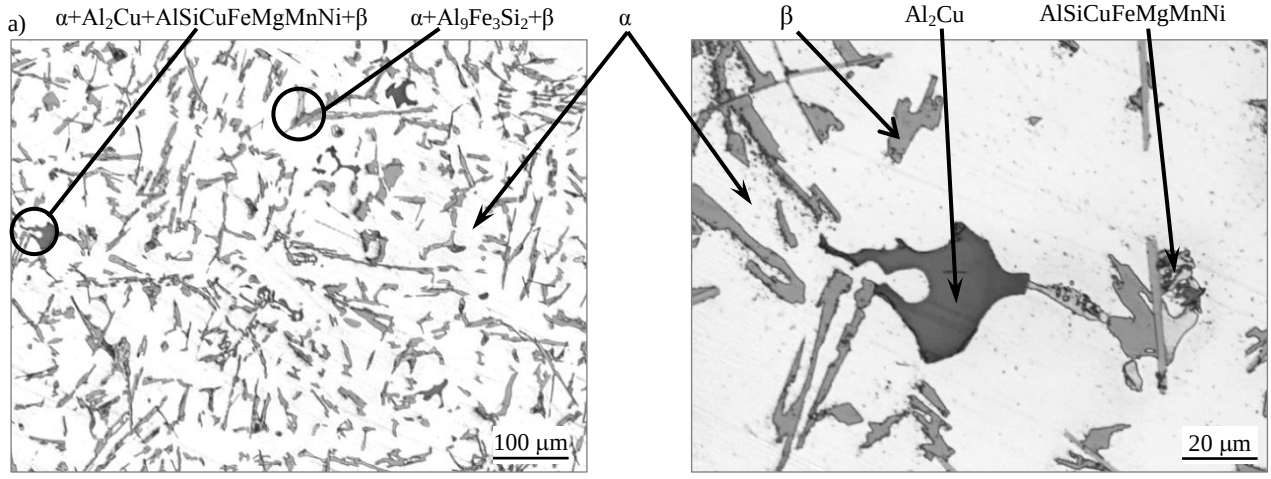
- A – maximal thermal effect of crystallization of phase α,
- B – crystallization end of phase α and crystallization beginning of eutectic α + $Al_9Fe_3Si_2$ + β,
- E – maximal thermal effect of crystallization of eutectic α + $Al_9Fe_3Si_2$ + β,
- H – crystallization end of eutectic α + $Al_9Fe_3Si_2$ + β and crystallization beginning of eutectic α + Al_2Cu + AlSiCuFeMgMnNi + β,
- K – maximal thermal effect of crystallization of eutectic α + Al_2Cu + AlSiCuFeMgMnNi + β,
- L – crystallization end of eutectic α + Al_2Cu + AlSiCuFeMgMnNi + β and of the whole alloy.

From the data shown in Table 2 we can infer a slight drop in the crystallization beginning temperatures of the eutectics present in the alloy: „tB" – temperature of crystallization beginning of eutectic α + $Al_9Fe_3Si_2$ + β i „tH" – temperature of crystallization beginning of eutectic α + Al_2Cu + AlSiCuFeMgMnNi + β. We cannot be talk about tendencies for temperature or cooling rate „K" changes in the remaining analyzed points are observed.

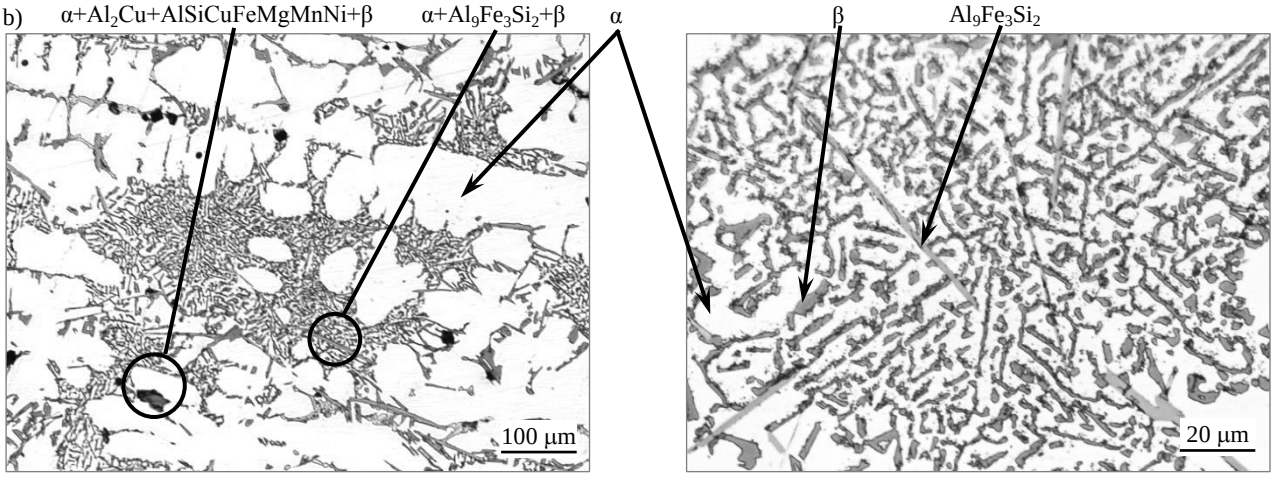
Figure 2 presents the microstructure of silumin 226 cast into the TDA tester – without modification and after modification with different Sr addition.

Table 2.
Values of the quantities describing the TDA curves of silumin 226 – non-modified and after Sr modification

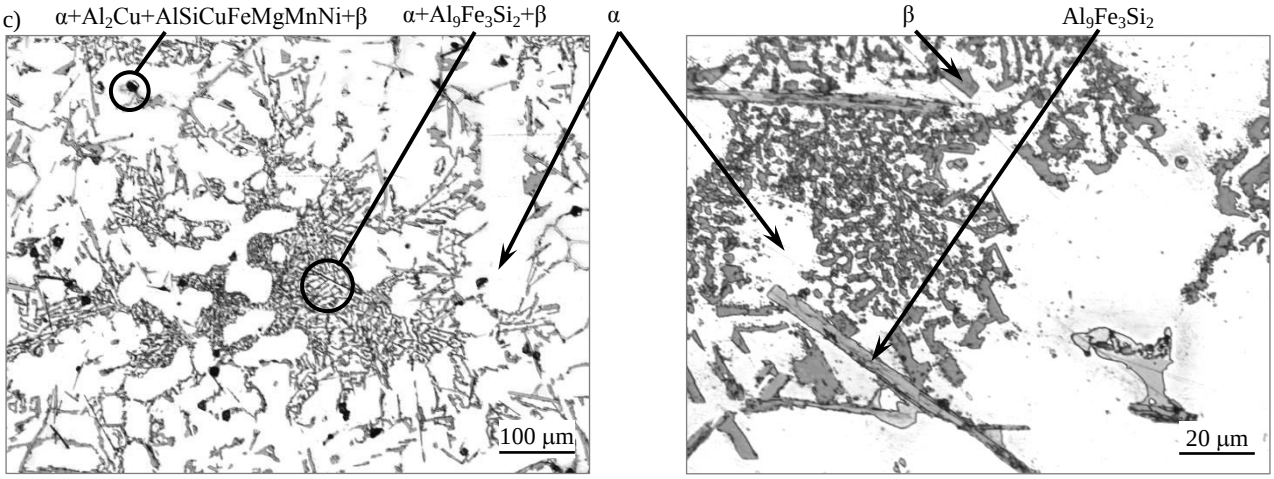
No.	Sr addition, %	t, °C						dt/dτ, °C/s					
		tA	tB	tE	tH	tK	tL	KA	KB	KE	KH	KK	KL
1	0.0	582.0	576.4	558.6	502.5	493.0	482.7	0.13	-1.03	0.10	-0.67	-0.17	-0.68
2	0.1	582.3	575.2	555.3	499.5	491.7	487.6	0.08	-0.96	0.09	-0.68	-0.12	-0.69
3	0.2	577.5	574.4	565.1	497.2	492.1	478.7	0.55	-1.05	0.11	-0.67	-0.35	-0.76
4	0.3	576.3	571.4	554.6	496.2	492.1	485.3	0.08	-1.11	0.05	-0.66	-0.16	-0.77



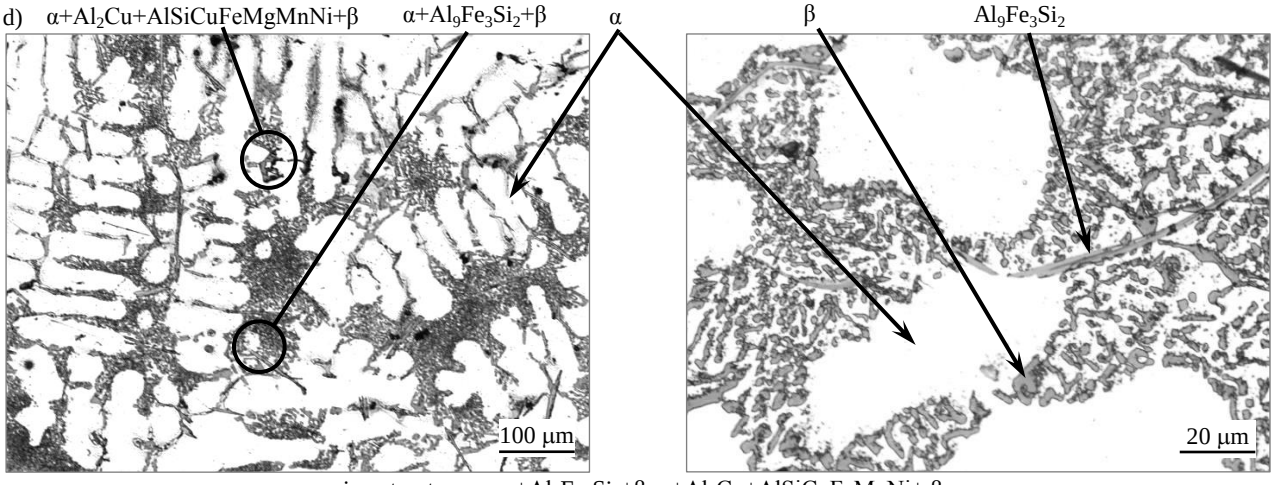
microstructure: α, α+$Al_9Fe_3Si_2$+β, α+Al_2Cu+AlSiCuFeMgNi+ β



microstructure: α, α+$Al_9Fe_3Si_2$+β, α+Al_2Cu+AlSiCuFeMgNi+ β



microstrcuture: α, α+$Al_9Fe_3Si_2$+β, α+Al_2Cu+AlSiCuFeMgNi+ β



microstructure: α, α+$Al_9Fe_3Si_2$+β, α+Al_2Cu+AlSiCuFeMgNi+ β

Fig. 2 (a÷d). Microstructure of a cast, made on an TDA tester, of non-modified silumin 226 (a) and silumin after modification with different amounts of strontium: 0.1% (b), 0.2% (c) and 0.3% (d)

From the data presented in Fig. 2 we can infer an agreement of the microstructure of silumin 226, both the non-modified and the modified one, with the crystallization process resulting from the TDA curves.

Strontium introduced into silicon forms the compound Sr_3P_2, which binds phosphorus. The phosphorus present in silumins forms, in turn, the compound AlP, which constitutes an active base for silicon crystallization. After the Sr introduction, the liquid metal is deprived of AlP crystallization bases, and thus, in order to cause eutectic crystallization in the silumin, the latter needs higher overcooling. This causes the reduction of the temperature of the crystallization beginning of the particular eutectics present in the examined silumin 226. This remains in accordance with the data included in Table 2. The temperature of the crystallization beginning of the ternary eutectic $\alpha+Al_9Fe_3Si_2+\beta$ of the silumin without the Sr addition equals tB = 576.4°C. After the introduction of 0.1% Sr, it is reduced to tB = 575.2°C. An increase in the Sr concentration in the silumin up to 0.2 and 0.3% causes a further reduction of the „tB" temperature to 574.4 and 571.4°C, respectively. In general, introducing 0.3% Sr into the examined silumin causes the reduction of the „tB" temperature by 5.0°C in respect to the silumin not containing strontium. A similar situation is observed also for the quaternary eutectic $\alpha+Al_2Cu+AlSiCuFeMgNi+\beta$. As a result of the introduction of 0.3% Sr into the silumin, the temperature of the crystallization beginning of this eutectic, „tH", was reduced from 502.5°C (for silumin without Sr) to 496.2°C. This gives the temperature reduction of the crystallization beginning of the quaternary eutectic by 6.3°C. Together with the increase of the Sr addition in the silumin, the morphology of the eutectic precipitations of phase β (Si) changes as well. This results from Fig. 2 (a÷d). In the microstructure of the silumin 226 without the Sr addition (Fig. 2a) we can observe the presence of only lamellar Si precipitations. Introducing 0.1% Sr causes the reduction of the Si lamella size in the eutectics as well as the reduction of the interlamellar distance. An increase of the Sr addition to 0.2% (Fig. 2c) causes a partial change of the lamellar morphology of Si into the fibrous one. Beside the fibrous precipitations, also present is a certain amount of Si lamellae of a relatively short length. An increase of the modifier addition (Sr) to 0.3% causes a significant increase in the fraction of the fibrous precipitations of the eutectic silicon and the degree of their dispersion (Fig. 2d).

Figure 3 presents the representative TDA curves of silumin 226 after antimony modification, whereas Table 3 shows the coordinate values of the characteristic points on the curves obtained for the non-modified silumin and the silumin after modification with different amounts of Sb. On the curves presented in Fig. 3 we can see analogical thermal effects to those in the case of curves for silumin 226 – non-modified and modified with Sr. These effects correspond to the crystallization of the primary phase α (effect AB) and the eutectics $\alpha + Al_9Fe_3Si_2 + \beta$ (effect BEH) and $\alpha + Al_2Cu + AlSiCuFeMgMnNi + \beta$.

From the data presented in Table 3 we can only infer a slight increase of the „tH" temperature of the crystallization end of the ternary eutectic $\alpha + Al_9Fe_3Si_2 + \beta$. From the literature data it is known that the introduction of Sb into the silumin causes an intense release of phosphorus in the form of gas. Antimony also causes the formation of the compound AlSb, whose density equals 4.34 g/cm^3. The high density of the AlSb compound in respect to that of silumin (~2.70 g/cm^3) causes it to drop down to the floor of the crucible, as well as gas cavities and the Al_2O_3 oxide depositing onto mirror of the liquid metal. It can be generally assumed that the introduction of Sb into silumin causes its degassing and purifying, which, in consequence, can cause the increase of the „tH" temperature of the crystallization end of the ternary eutectic. Figure 4 (a÷d) shows the microstructure of silumin 226, cast into the TDA, without modification and after the modification with Sb in different amount.

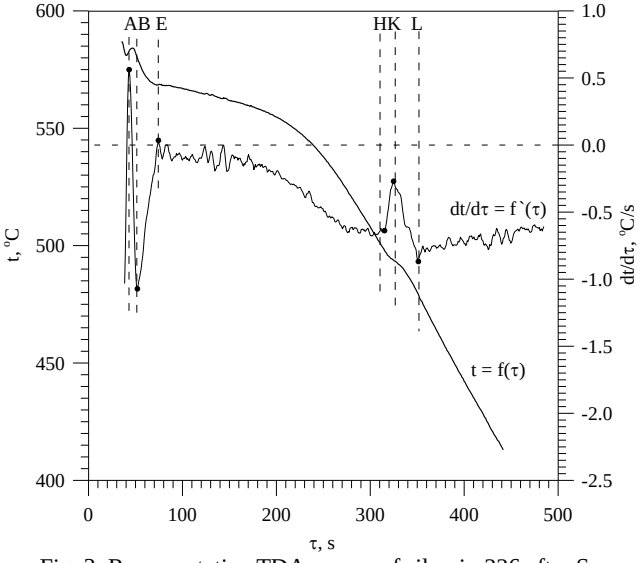
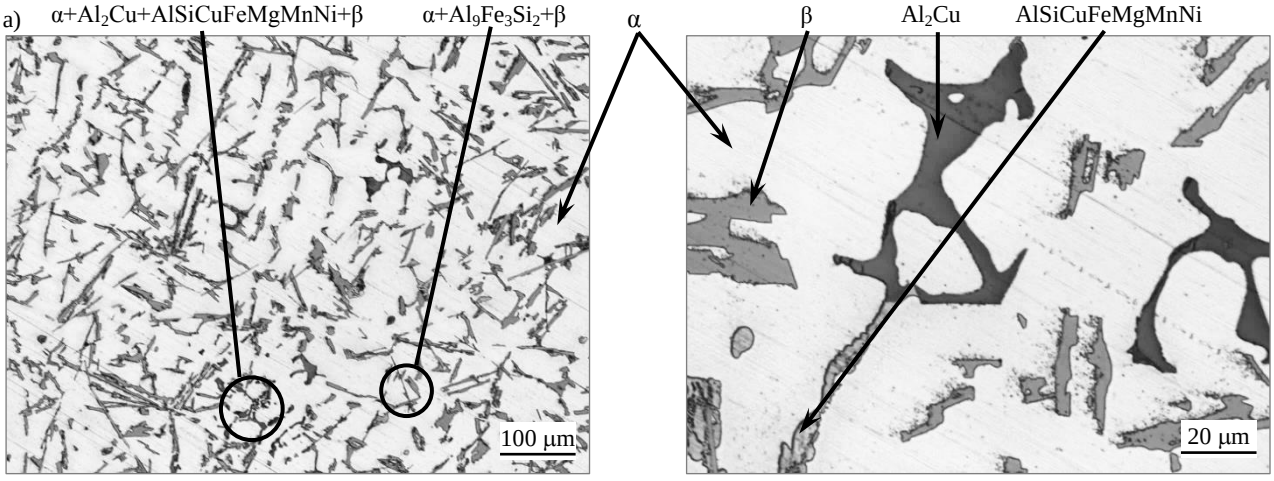


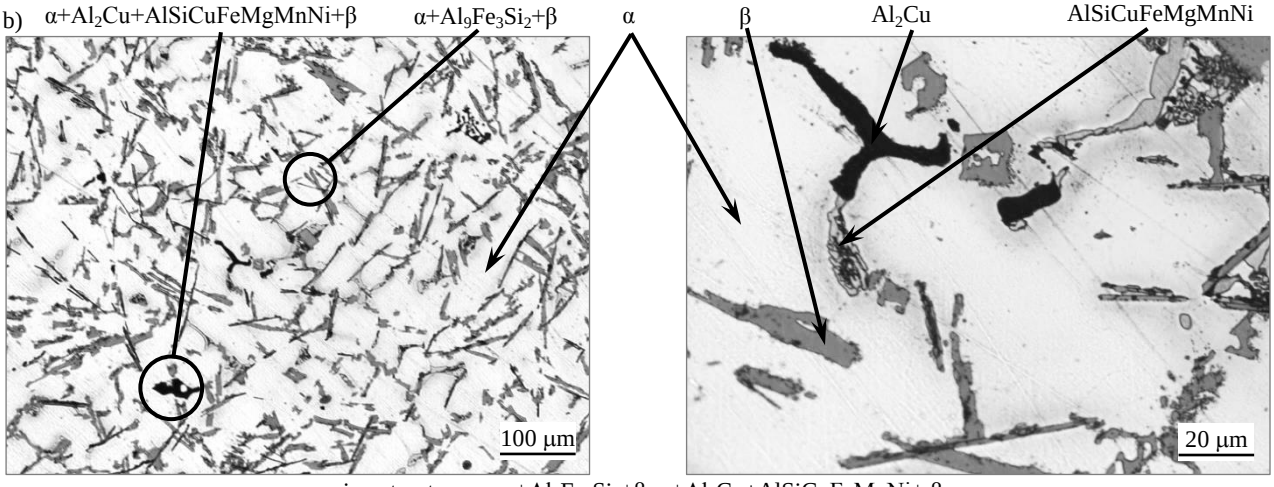
Fig. 3. Representative TDA curves of silumin 226 after Sr modification

Table 3.
Values of the quantities describing the TDA curves of silumin 226 – non-modified and after Sb modification

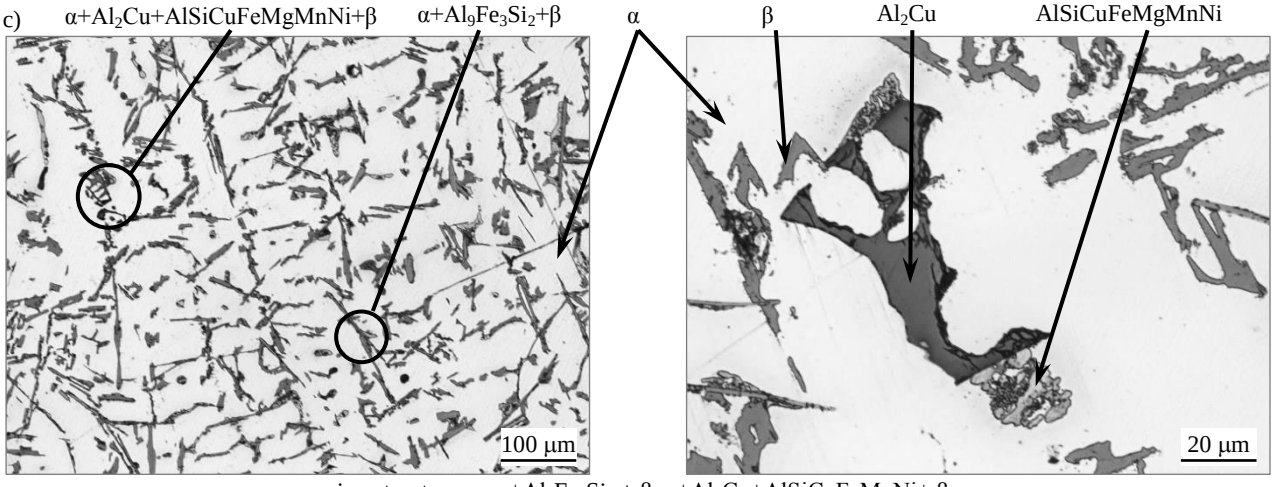
No.	Sb addition, %	t, °C						dt/dτ, °C/s					
		tA	tB	tE	tH	tK	tL	KA	KB	KE	KH	KK	KL
1	0.0	582.1	574.5	565.3	497.5	493.4	480.1	0.45	-1.01	0.12	-0.63	-0.17	-0.78
2	0.1	582.8	579.9	568.5	497.9	493.9	479.3	0.56	-1.07	0.03	-0.64	-0.27	-0.87
3	0.2	577.1	573.9	566.2	499.6	493.8	479.0	0.24	-0.84	0.14	-0.68	-0.23	-0.79
4	0.3	580.7	575.8	566.7	501.6	495.3	479.9	0.32	-1.04	0.12	-0.65	-0.32	-0.77



microstructure: α, α+$Al_9Fe_3Si_2$+β, α+Al_2Cu+AlSiCuFeMgNi+ β



microstructure: α, α+$Al_9Fe_3Si_2$+β, α+Al_2Cu+AlSiCuFeMgNi+ β



microstructure: α, α+$Al_9Fe_3Si_2$ + β, α+Al_2Cu+AlSiCuFeMgNi+ β

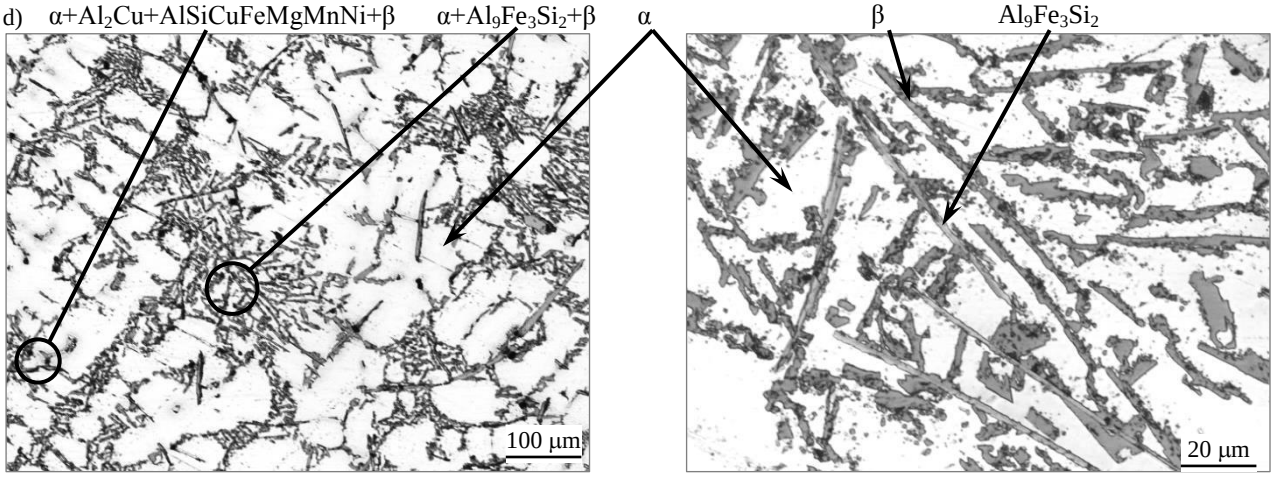


Fig. 4 (a÷d). Microstructure of a cast, made in an TDA tester, of a non-modified silumin 226 (a) and silumin modified with different amounts of antimony: 0.1% (b), 0.2% (c) and 0.3% (d)

From Fig. 4 it can be inferred that the microstructure of the silumin 226 after the introduction of 0.1 and 0.2 % Sb does not, in fact, undergo any change. Only after the introducing of 0.3% Sb we can observe a microstructure change, which consists in a refinement of the silicon lamellae and the reduction of the distance between them. Presumably, the introduction of Sb into the silumin does not cause a complete elimination of the phosphorus from it. Probably, the remaining phosphorus forms active AlP nuclei. The role of active nuclei of the Si crystallization may also be played the precipitations of the phase AlSb. Due to the above, the overcooling during the crystallization of the eutectic phases in this case is not as strong as in the case of the Sr modification and the morphology does not change into the fibrous one. A large number of active AlSb bases present when 0.3% Sb is introduced causes the reduction of the interlamellar distance of Si in the eutectics.

4. Conclusions

The following conclusions can be drawn from the performed examinations:

- introducing strontium into 226 silumin causes the reduction of the values of the temperatures „tB" and „tH" of the crystallization beginnings of the eutectics present in the examined silumin,
- introducing strontium causes a change in the morphology of the eutectic silicon into the fibrous one,
- the antimony modification causes an increase of the temperature of the crystallization end of the ternary eutectic „tH",
- for 0.3% antimony, significant refinement and reduction of the distance between the Si lamellae was observed.

Acknowledgements

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