Technology of obtaining REM-containing master alloy for silumins modification

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Abstract. The technology of producing ligatures containing rear earth metals (REM) for modification of silumins has been developed. The optimum content ratio of yttrium, cerium and lanthanum 2: 1: 0.5 (15-20 wt.% Y, 7-10 wt.% Ce, 3.5-5.0 wt.% La) for the synthesis of REM aluminides has been established. The peculiarities of the REM aluminides synthesis is studied using the methods of optical and electron microscopy and X-ray microanalysis, followed by the identification of the structural components of the Al-REM alloy. The microstructure of the master alloy is proved to consists of: REM aluminides (yttrium-containing and cerium-containing), metal base (Al), Al eutectic + REM aluminide and $\alpha + Si$.

1 Introduction

There are very few publications on the development of compositions of master alloys from rare-earth metals for the silumins modification [1–4]. In the majority of works aluminum master alloys containing Ti, C, B, Ca, REM, P, and others are used [5].

Today Ce, La, Nd, Y etc. metals as well as mischmetals and transition metals or REM master alloys are widely used for modifying aluminum alloys, silumins in particular [6-19]. For example, the modification of the alloy Al-20 wt.% Si [7] with cerium (0.3-1.0 wt.%) contributes to the transformation of primary silicon of a large star-like shape to a small block shape, and the eutectic silicon of a needle-shape to a thin fibrous shape. In this case, the tensile strength $\sigma_b$ and relative elongation $\delta$ are increased by 68% and 53.7%, respectively. The combined effect of Ce and Pr (0.6 wt.%) [8], Ce and La (2.0 wt.%) in A356 and A413 alloys with and without strontium [10-11], mischmetals based on La, Y and other alloys in Al-21 wt.% Si [12-14] and ligatures from Ce and Mn [16] significantly change the silumin fractography and its mechanical properties.

The literature review provides no information on the problem of technology development of the Al-Y-Ce-La master alloy synthesis. In this regard the present work gives a detailed identification of the structural components of this master alloy and determines their micro- and nanohardness values.

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2 Research methods

Aluminum of A95 grade was superheated to 900°C in the pure argon atmosphere and pure yttrium, cerium and lanthanum were introduced in the ratio - 2: 1: 0.5 (wt.%: 15-20 Y; 7-10 Ce; 3.5-5.0 La) [1,2].

Micro X-ray spectral analysis was performed to determine the content of elements on an analytical research complex based on FE-SEM Hitachi Su-70 (Japan) with attachments for energy dispersive (Thermo Scientific Ultra Dry) and wave X-ray microscopic analysis.

The microhardness test was carried out according to the standard procedure on a Vickers instrument of Shimadzu HMV-G brand [20]. Nanohardness was measured on an Integra Prima atomic force microscope [21]. Local analysis was carried out on 3-5 points of sample sections, and the average chemical composition of the structural components - α-solid solution, eutectic and intermetallic compounds AlxSiyFezREMz - was determined.

3 Results and discussion

Table 1 shows the stoichiometry of the synthesized aluminides (yttrium-containing and cerium-containing) in Al-Y-Ce-La master alloy.

According to the state diagrams, yttrium forms Al3Y aluminide, but cerium and lanthanum - Al11Ce3 and Al11La3 (respectively Al3.66Ce and Al3.66La). The synthesized REM aluminide containing yttrium corresponds to the formula Al3.11REM, but the standard one according to the state diagram - Al3Y. The discrepancy between these values is insignificant (0.11 at.% Al).

Table 1. Stoichiometry of REM aluminide.

| Aluminide REM | Element composition, at.% | Eutectic                      |
|---------------|---------------------------|-------------------------------|
| Yttrium-      |                           |                               |
| containing REM|                           |                               |
| Y 17.2        | Ce 5.38                   | Al 100%                       |
| La 1.71       | ∑REM 24.29                | Al17.71 REM 24.29=Al3.11REM  |
| cerium-       |                           |                               |
| containing REM|                           |                               |
| Y 6.44        | Ce 8.62                   | Al 100%                       |
| La 6.26       | ∑REM 21.32                | Al7.86 REM 21.32=Al3.69REM    |

The resulting cerium-containing REM aluminide has a stoichiometry of Al3.69REM, slightly different from Al3.66REM. The discrepancy in stoichiometry is 0.03 at.% Al. From table 1 it follows that Al, Fe, Si and REM are present in the eutectic in certain amounts, the estimated structure of the eutectic corresponds to: Al+Al3.66REM+Al3Y+Si+FeAl3. The iron-silicon compounds of variable composition AlxSiyFez are also supposed to present.

The results of microhardness measurements showed that the yttrium-containing REM aluminate has a higher microhardness value (on the average 6547 MPa) than the microhardness of cerium-containing REM aluminate (the average 4695 MPa). The microhardness of pure aluminate is 254 MPa, and the microhardness of eutectic (Al + REM aluminate) is 423 MPa.

Fig. 1 shows the microstructure and location points of nanohardness measurement of structural components Al-Ce-La-Y of master alloy.

It was established that nanohardness value of cerium-containing REM aluminate is 8560 MPa. Nanohardness of yttrium-containing REM aluminate is 9627 MPa. Accordingly, the nanohardness - and microhardness of yttrium-containing REM aluminate is significantly higher than that of eutectic-containing REM aluminate. The average value of aluminum...
nanohardness corresponds to 1500 MPa. The average nanohardness value of the eutectic is 4650 MPa.

![Image](https://example.com/image.jpg)

**Fig. 1.** Microstructure and location points of nanohardness measurement of Al-Ce-La-Y structural components of master alloy: 1 - light crystal of REM aluminide (cerium-containing); 2 - darker crystal of REM aluminide (yttrium-containing); 3 - eutectic (Al + REM aluminide of variable concentration).

### 4 Conclusions

Micro X-ray analysis identified the structural components of the synthesized master alloy Al-Y-Ce-La:

- metal base consists of pure aluminum and eutectic (Al+Al$_x$REM$_y$); microhardness of pure aluminum is 254 MPa, and nanohardness - 1500 MPa;
- yttrium-containing REM aluminide has the Al3Y stoichiometry; microhardness is 6547 MPa, and nanohardness is 9627 MPa;
- cerium-containing REM aluminide has the stoichiometry Al$_{11}$REM = Al$_{3.66}$REM (Al$_{3.66}$Ce, Al$_{3.66}$La); Microhardness - 4695 MPa, and nanohardness - 8560 MPa.
1) The increase in the addition of master alloy up to 0.5 wt.% contributes to the grinding of structural components - $\alpha$-solid solution and eutectic, and to crystallization of highly solid complex-doped aluminide Al$_x$Si$_y$Fe$_z$ with and without REM (in the original alloy).
2) Structural components of the AK7ch alloy are identified at the addition of the increasing amount of Al-Y-Ce-La master alloy ($\alpha$-Si solid solution in aluminum, $\alpha$+Si eutectic and complex-doped REM aluminides - Al$_x$Si$_y$Fe$_z$ and Al$_x$Si$_y$Fe$_z$REM$_v$).
3) Regularities of changes in the element solubility and microhardness values of the structural components depending on the addition amount of master alloy Al-Y-Ce-La are revealed. Correlations between the silicon solubility in the $\alpha$-solid solution and its microhardness are found. The hardness of the HB alloy is stated to depend on the values of microhardness of the $\alpha$-solid solution and eutectic.

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