Study of the influence of both a modifier P and a nanomodifier ND on the structure of a hypereutectic aluminium-silicon alloy AlSi18

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Abstract. The process of hardening a hypereutectic aluminium-silicon alloy AlSi18 in unmodified, modified and nano-modified state has been studied. Two types of modifiers have been used - a standard modifier P, introduced into the melt by means of the ligature CuP 0,4wt.%, and a nanomodifier (nanodiamonds - ND) 0,1wt.%.

1. Exposition

Experiments with new types of modifiers of aluminium alloys, namely nanomodifiers (NM), have been carried out in the past years. The nanomodifiers are ultradisperse nanopowders with particles sizing 4-100 nm, having high melting temperature (~ 2273 – 3273 K depending on the composition), which are usually obtained either in result of a self-propagating high-temperature synthesis (SPHTS) [1] or by plasma-chemical synthesis (PCS) – for producing nitrides, carbides, oxides, oxi-carbides etc. [1, 2, 3].

The nanomodifier-nanodiamond (ND) is produced by detonation technology [4]. These nanoparticles, used as modifiers, have physical-chemical properties, influencing the structure of the alloys and therefore they can be used for obtaining new promising materials.

Most of the existing studies have been carried out on hypoeutectic and eutectic aluminium-silicon alloys, as well as on certain types of cast iron and steel [8, 9, 10, 11, 12, and 13]. We could not find any data about studies of the influence of nanomodifiers on the structure and the properties of hypereutectic aluminium-silicon alloys in the literature, studied by us.
Aim: The present paper aims at studying the influence of both a standard modifier – P, and a nanomodifier – ND, on the process of hardening the hypereutectic aluminum-silicon alloy AlSi18, as well as on the size of the primary Si crystals and their distribution.

2. Production and preparation of nanomodifiers
Explosive technology research, started in the Department “Space Materials Science and Nano-technologies” at SRTI-BAS, has led to creating and patenting an industrial technology and an installation for nanodiamonds (ND) synthesis [14]. The detonation technology for nanodiamonds synthesis is based on blasting powerful explosive materials (EM) or mixtures of them with a negative oxygen balance, whereas the freed carbon transforms into a diamond. Both the pressure and the temperature in the detonation wave (P – T parameters) correspond to the thermo-dynamic stability of the diamond (P ≥10 GPa; T ≥ 3000 K). The main characteristics of the nanodiamond are given in [13].

The nanosized and hard-to-melt particles are difficult to wet (or they do not get wet at all) by liquid metals or alloys. Therefore, their homogeneous distribution when introduced into a melted metal is a very difficult task [1]. The decision to pre-coat nanoparticles has helped to solve this problem. One way to obtain active and melt-wetting NMs is the method of their mechanical-chemical treatment with pre-cladding metals in centrifugal planetary mills [2]. When introduced into the melt, the pre-cladding layer dissolves and facilitates the process of wetting, while the activated surface of the nanoparticles serves as a substrate for primary crystals formation (nucleation) [5].

Another way to prepare and activate the surface of the nanoparticles is to pre-treat them chemically until an appropriate metal coating from different metals is obtained (Ag, Ni, Cu) [6, 7].

3. Studied alloy
Hypereutectic aluminium-silicon alloy – AlSi18 – was studied. Its chemical composition is shown in table 1.

| Si | Fe | Cu | Mn | Mg | Cr | Ni | Zn | Pb | Al |
|----|----|----|----|----|----|----|----|----|----|
| 17,55 | 0,120 | 0,025 | 0,047 | 0,001 | 0,001 | 0,005 | 0,102 | 0,01 | rest |

The nanomodifier ND 0,1 wt.%, used for better wetting by the melt, was Ni-coated by means of a currentless deposition method.

The used standard modifier P 0,4 wt.% was introduced into the melt by the ligature CuP10.

4. Methodology of study
The study of the hypereutectic aluminium-silicon alloy AlSi18 consisted in conducting experiments with unmodified, modified with a modifier P, and modified with a nanomodifier ND versions of the alloy.

The melting of the alloy is carried out in an electrosurgical laboratory furnace by using preliminary cleaned and dry stock materials. The melting process is carried out under a layer of roof-refining flux in an amount of 0.5 wt.% from the amount of the stock material. After melting, the melt is stirred vigorously for removing non-metallic inclusions, then the slag is removed, and the process of degassing the alloy is started. Degassing is performed at a temperature of 760 °C by purging with argon for 3minutes, then cleaning the metal mirror and casting samples.

When a modified by P alloy is used, the modification is carried out before degassing at a temperature of 770°C. The alloy is degassed by purging with argon for 3minutes at a temperature of 760°C. The metal mirror is cleaned and the process of samples casting is started.

Typical in the preparation of the hypereutectic aluminium-silicon alloy AlSi18, modified by a nanomodifier ND, is that the modification of the alloy is carried out at a temperature of 760°C after its refining and degassing. The calculated amount of nanomodifier (ND) is mounted on the titanium
stirrer of a stirring device. The nanomodifier is introduced close to the bottom of the crucible. Then mechanical stirring is started for 3 minutes at a low number of revolutions per minute – 120 – 130 min – 1, which is done to evenly disperse the nanomodifier particles throughout the melt volume.

Figure 1 presents the structure of the device for producing a sample for obtaining time-temperature curves. The thermocouple has Ni-CrNi electrodes with diameter of 0.25 mm and unprotected hot solder. Thus the thermal resistance at the border between the thermocouple and the metal is reduced, i.e., the inertness of the thermocouple decreases. The electrodes of the thermocouple are prevented from touching the melt by mounting them in a thin-walled stainless tube. The bottom is protected by a heat-insulating substrate of pre-coated sand. Thus conditions for heat exchange only through the walls of the container and through the upper free surface are ensured.

The temperature recording is performed using an archiver, allowing to record the discrete temperature readings for the corresponding sample over an interval of 0.2 s. A fast-running USB FLASH ARCHIVER MS DL-F2 v-2.0 is used.

5. Results

From the obtained time-temperature curve for unmodified alloy AlSi18 (figure 2) the temperature interval of alloy crystallization is defined (630°C-578°C). The characteristic change in the slope of the curve due to the solid phase separation is observed and the cooling rate decreases. The curve shows a degree of overcooling during the eutectic crystallization at 1 °C for 5 seconds, and, consequently, the free energy of the solid phase is less than the free energy of the liquid phase, i.e. there are energy conditions for the crystallization process to occur. Due to the radiation of the hidden heat of crystallization, the temperature goes up again to the theoretical temperature of alloy crystallization (578°C) and stays at that level until the melt is completely hard. Straight liquation is observed under conditions of equilibrium cooling of the AlSi18 alloy, i.e. the hard-to-melt component pushes the fusible component to the center of the cast samples, figure 3.
Figure 2. Time-temperature curve AlSi18

Figure 3. Distribution of Si crystals AlSi18

Figure 4 presents the time-temperature curve of a modified by a standard modifier P alloy AlSi18. Unlike the time-temperature curve of the unmodified alloy AlSi18, this time the curve does not register any level of overcooling during crystallization, which is explained by the formation of crystallization centers by the introduced into the melt modifier. A more even distribution of the primary Si crystals in the volume of the sample is observed for this type of alloy, which can be explained by the modifying effect of P, figure 5.

Figure 4. Time-temperature curve for AlSi18(P)

Figure 5. Distribution of Si-crystals AlSi18(P)

Figure 6 shows the time-temperature curve for a modified by a nanomodifier ND alloy. For this type of alloy a horizontal curve section at the liquidus line is observed, as well as an unregistered
degree of overcooling during crystallization at the solidus line. This is explained by the big number of crystallization centers formed by the nanomodifier ND and the intense separation of the primary Si crystals. The most even distribution of Si crystals in the volume of the sample is observed for the type of alloy, modified by a nanomodifier ND, what is explained by the greater extent of refinement of the silicon crystals and the registered area of intense silicon crystal separation at the liquidus line area of the alloy, figure 7.

Figure 6. Time-temperature curve AlSi18ND

Figure 7. Distribution of Si crystals AlSi18ND

Figure 8.

From the micro-structural analysis it has been established that the primary silicon crystals are different in shape for the unmodified version of the alloy AlSi18: they are right-walled polygons, well-formed plates that resemble needles or plate-type crystals of irregular shape in the plane of the microscopic observation, figure 8. The arbitrary average diameter of the primary silicon crystals in the unmodified AlSi18 alloy ranges from 87.2 to 97.6 μm.

Figure 9.

The primary silicon crystals in the structure of the modified by P version of the alloy differ in shape and size from the ones, in the unmodified version, figure 9. Their arbitrary average diameter ranges from 59.2 to 52.1 μm. Right-walled polygonal crystals prevail and plate-type primary crystals are not observed.
Figure 10.
Primary silicon crystals of polygonal shape predominate in the modified by a nanodiamond version of the AlSi18 alloy, while the amount of primary crystals of irregular shape is insignificant, figure 10. The arbitrary average diameter of the primary silicon crystals in a modified by a nanodiamond modifier AlSi18 alloy is 54 µm.

Table 2 illustrates the change in the value of the arbitrary average diameter of the primary Si crystals in the three versions of the AlSi18B alloy: unmodified; modified by P; and modified by ND nanomodifier.

| Alloy   | Modifier | Arbitrary average diameter of the grains D [µm] |
|---------|----------|-----------------------------------------------|
| AlSi18  | -        | 92,4                                          |
| AlSi18  | P        | 55,7                                          |
| AlSi18  | ND       | 54                                            |

In an AlSi18 alloy, modified by phosphorus, reduction of the arbitrary average diameter of the primary Si crystals by 34,1% is observed.
In an AlSi18 alloy, modified by ND nanomodifier, reduction of the arbitrary average diameter of the primary Si crystals by 41,6% is registered.

6. Conclusions
From the conducted study it has been established that:
- The primary Si crystals in a hypereutectic aluminium-silicon alloy AlSi18 are successfully modified by means of a nanomodifier ND.
- The modification of the AlSi18 alloy by a nanomodifier ND can replace its modification by a standard P modifier.
- The replacement of the standard P modifier by a nanomodifier ND in AlSi18 alloy modification will also have ecological effect in addition.
- The conducted study confirms the positive influence of the nanomodifier ND on the size of the primary Si crystals and their distribution in the structure of the AlSi18 alloy.

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