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EFFECT OF Sb-MODIFICATION ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF SECONDARY ALLOY 319

319 alloy has been selected for the study in the present work due to its wide use in many applications. 319 alloy is used in automotive and aerospace industry for the complicated castings which must comply high strength requirements. In practice, the most common elements with the modifying effect are strontium, sodium and antimony. The addition of these elements leads to a change in the shape of eutectic silicon, resulting in an increase of the mechanical characteristics and the microstructure. An experimental program has been undertaken to explore the effect of antimony on chosen mechanical properties and the microstructure of investigated alloy. An analysis of the results of these experimental works is made in order to determine an optimum Sb (Al-10% Sb) addition to produce material exhibiting desirable properties. Experimental works have showed that the addition of the Al-10% Sb results in similar or even higher mechanical properties than the conventional 319 alloy. Based on the carried out experiments the best combination of mechanical properties has been achieved by the addition of 2 000 ppm Al-10% Sb.

Keywords: Alloy 319, secondary alloy, Microstructure, Mechanical Properties, Modification, Antimony

1. Introduction:

The factor determining the properties of the casting is the size of grain zones with different morphology. To make a casting with isotropic properties it is necessary to obtain the fine-grained straight axis structure. Modification is one of the possible interventions in the crystallization process confirmed by many scientific papers; e.g. Gruzleski and Closset (1990), Dahle et al. (2005), Tavitas et al (2008) etc. It is well known that the (chemical) modification is the intentional treatment of the melt with different suitable elements or alloys to alter the shape of structural components. Modifiers are appropriate in the melt-soluble additives which reduce the surface tension of the melt-crystal interface, reducing the work needed for the production of large supercritical nucleus. During crystallization modifier atoms are concentrated on the surface of growing nucleuses, limiting their growth and induce hypothermia concentration, thus creating favorable conditions before nucleating crystallization front as demonstrated by Dinnis et al. (2005). In the aluminium alloys they influence the shape of the eutectic phase. The modification process is still not completely scientifically explained. Despite of some advantages, Sb as modifier is not frequently used comparing to Sr and Na. Kube et al. (1998) mentioned that the general advantage of Sb as a modifier is the fact that the melt does not oxidize and therefore it does not create conditions for the formation of pores and it does not participate in the decrease of pressure tightness.

319-type alloys are used for castings of complicated shapes with different wall thicknesses. Most commonly, they are used for castings, which are moderately highly stressed. (Engine blocks, cylinder heads and pistons, clutch housings, exhaust ends, die-cast chassis).

Despite their specificities, the usage of the secondary alloys for the production of automotive castings has a great perspective in the consideration of the most effective efforts to reduce prices of castings. The impact of Sb on the mechanical properties of secondary 319 alloy that is used to produce cylinder heads is discussed in the present paper.

2. Experimental procedures

Experiments were carried out in the foundry laboratory of the Department of Technological engineering, University of Žilina, where aluminium alloy 319 was used as the experimental material. Chemical composition of the chosen elements of 319 alloy is listed in the Table 1.

TABLE 1

Chemical composition of 319 alloy

Elements	Si	Fe	Cu	Mn	Mg	Cr
(wt. %)	6,52	0,435	3,88	0,459	0,291	0,01
Elements	Ni	Zn	Pb	Sn	Ti	Zn
(wt. %)	0,01	0,465	0,031	0,003	0,163	0,398

The modification process using antimony in the form of master alloy Al-10% Sb has been carried out while overheating the metal bath to 730 ± 5°C.

Castings for the production of the test samples were cast into permanent molds preheated to 300 ± 10°C. Ready castings were collected after 40 seconds in order to keep the same

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solidification conditions and then, test bars for mechanical tests were made from them.

There were 11 melts made, in each there were 10 castings for test bars made for tensile testing according to EN 10002-1. These melts vary by the different amount of antimony. The amount of antimony chosen for each cast is listed in the Table 2.

3. Results and discussions

3.1. Mechanical properties

Test bars have been subjected to selected mechanical tests - Tensile testing, Brinell hardness.

3.1.1 Tensile test

The tensile test was performed on a tensile machine WDW – 20 in the laboratory of mechanical tests, University of Žilina at 22°C.

Fig. 1 shows that the most appropriate amount of Sb alloy is 1 000 to 2 500 ppm Al-10% Sb when the tensile strength and elongation reached the highest values (UTS = 229 MPa, elongation = 1,5%). Modified alloy achieved higher values of ultimate tensile strength, because of a growing proportion of antimony in it, expanding UTS values ranging from 216 to 229 MPa. Medlen and Bolibruchová (2011) have recently pointed out that antimony over-modified alloy results in a decrease of tensile strength.

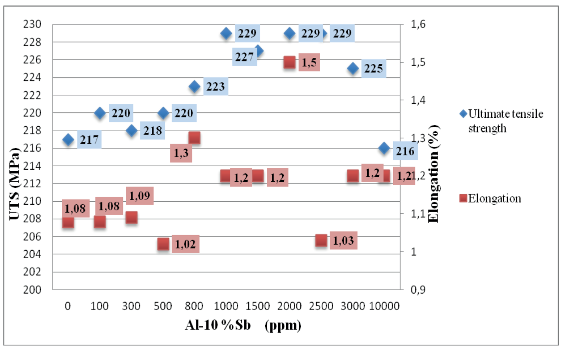


Fig.1. Relation between UTS, elongation and amount of antimony (ppm)

The maximum value has been reached for the sample with the addition of 2 000 ppm Al-10% Sb.

3.1.2 Brinell hardness test

Brinell hardness measurement has been performed at 22°C. Processed results of measurements are shown in the Fig. 2.

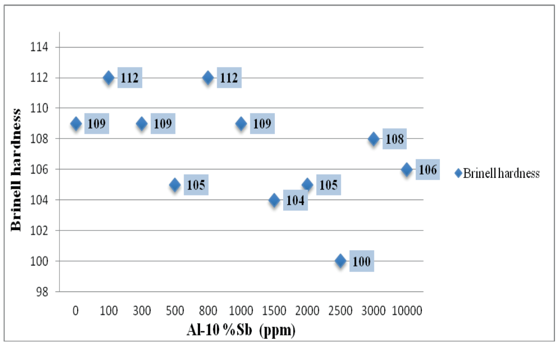


Fig. 2. Relation between Brinell hardness and amount of antimony (ppm)

3.2. Microstructure analysis

The microstructures were analyzed according to EN – STN 42 0491. Microstructure and morphology of silicon of 319 alloy from each cast are shown in Fig. 3a to Fig. 9a. In all samples, the structure consists of α-Al dendrites, in which the plane metallographic sample is observed in the form of the white bodies, eutectic silicon excreted in the form of black bodies and red and grey bodies are intermetallic phases based on copper.

Based on the alloy microstructure observation in Fig. 3a to Fig. 9a and comparing them with each other, it can be concluded that the microstructure of the investigated alloy using 250x magnification has not essentially changed. This fact has been recently confirmed by Medlen and Bolibruchová (2012). It can be observed slightly changing α-Al dendrites while silicon shape is not noticeable. For better recognition of the eutectic silicon shape observation has been carried out at 1600× magnification (Fig. 3b and 9b). The values in brackets give the antimony content of the sample in wt. %, according to the chemical analysis.

TABLE 2

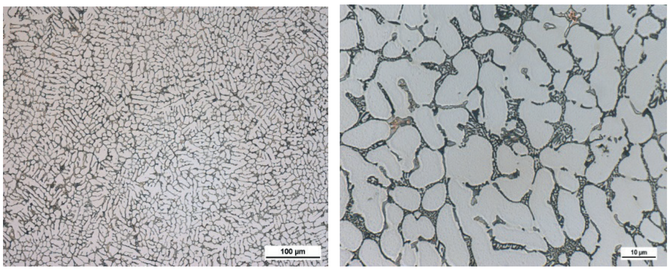
Amount of antimony for each cast of 319 alloy used in the present work

Number of cast	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Amount of Sb (ppm Al-10 %Sb)	0	100	300	500	800	1000	1500	2000	2500	3000	10000

TABLE 3

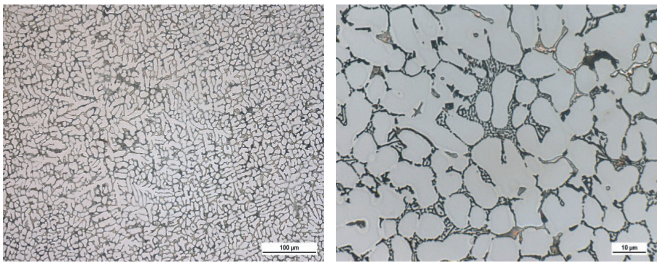
Survey of the optimal addition of 2 000 ppm Al-10 %Sb (0.017 wt. % Sb) effect on the selected properties of alloy 319

Effect of the addition of 2 000 ppm Al10Sb on 319 alloy properties compared with non-modified alloy (<100 ppm Al-10 %Sb)			
	< 100 ppm Al-10 %Sb	2 000 ppm Al-10 %Sb	The change of alloy characteristics
Ultimate tensile strength [MPa]	218	229	5 % increase
Elongation [%]	1,08	1,5	39 % increase
Brinell hardness HBS	109	105	4 % decrease



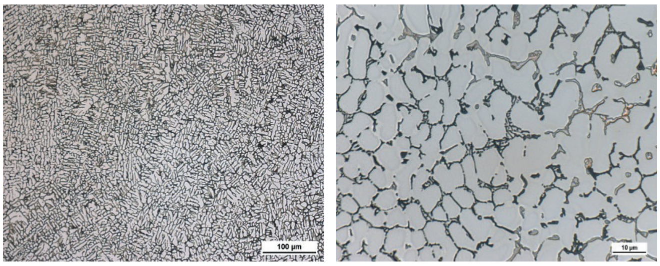
a) mag. 250× etch. 0.5 % HF b) mag. 1600× etch. 0.5 % HF

Fig. 3. Micrographs showing the microstructure of as-cast 319 alloy (0.0038 wt. % Sb)



a) mag. 250× etch. 0.5 % HF b) mag. 1600× etch. 0.5 % HF

Fig. 4. Micrographs showing the microstructure of 319 alloy with the addition of 500 ppm Al-10 %Sb (0.0055 wt. % Sb



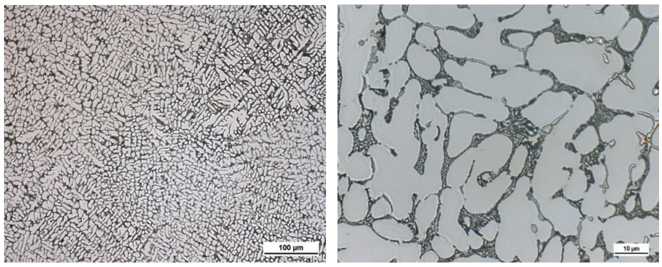
a) mag. 250× etch. 0.5 % HF b) mag. 1600× etch. 0.5 % HF

Fig. 5. Micrographs showing the microstructure of 319 alloy with the addition of 1 000 ppm Al-10 %Sb (0.0094 wt. % Sb)

Adding of Al-10% Sb the sharp shape of acicular eutectic silicon was transformed into many areas of stick-like shaped crystals, e.g. Fig. 3b to 4b. In Fig. 3b it is possible to observe clusters of perfectly rounded grains of eutectic Si excluded on the edges of dendritic cells. Imperfectly rounded grains can be seen in Fig. 4b, where the mechanical characteristics began to increase. Reducing the distance of Si particles and size of dendritic cells are visible in Fig. 5a to Fig. 6a. The smaller the distance between dendritic cells is, the higher the strength characteristics of 319 alloy gets. This is confirmed in Fig. 1 and Fig. 2, where high values of UTS, elongation and Brinell hardness have been achieved. Figure 5b shows the microstructure of alloy containing 0.0094 wt. % Sb, comparing with previous samples it began to create a large number of smaller areas of eutectic silicon crystals with perfectly rounded grains. A sample of material with such a microstructure showed the highest mechanical properties.

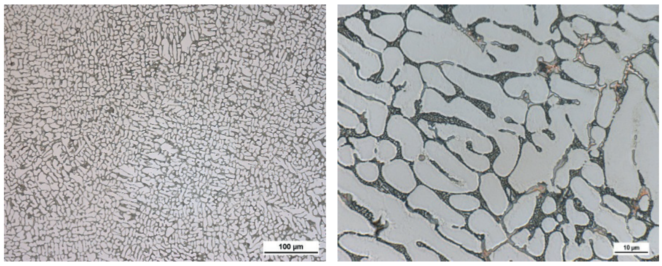
Fig. 6b shows a microstructure containing 0.017 wt. % Sb. Where perfectly rounded grains of eutectic Si can be seen. These as the sample at the concentration of 0.0094 wt. % Sb increase the ultimate tensile strength of the investigated alloy. Dahle et al. (2005) have recently shown that perfectly rounded grains of eutectic Si causes the increase of UTS in Al-Si alloys.

In the sample containing 0.019 wt. % Sb (Fig. 7b) the change of the eutectic silicon shape into the fiber-like form can be seen. The highest ultimate tensile strength values are achieved while elongation and Brinell hardness decrease rapidly.



a) mag. 250× etch. 0.5 % HF b) mag. 1600× etch. 0.5 % HF

Fig. 6. Micrographs showing the microstructure of 319 alloy with the addition of 2 000 ppm Al-10 %Sb (0.017 wt. % Sb

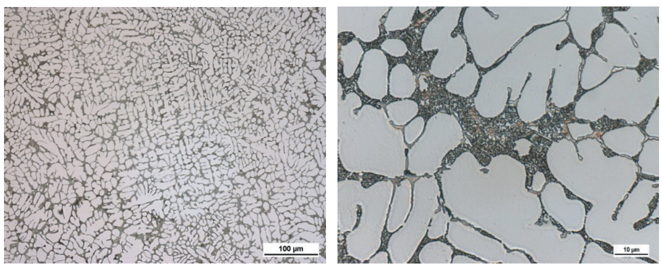


a) mag. 250× etch. 0.5 % HF b) mag. 1600× etch. 0.5 % HF

Fig. 7. Micrographs showing the microstructure of 319 alloy with the addition of 2 500 ppm Al-10 %Sb (0,019 wt. % -+

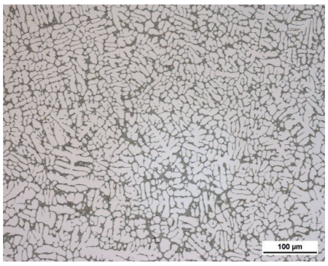
The microstructures in Fig. 8b and Fig. 9b, where the high concentration of antimony is, can be seen even more eutectic silicon in fiber-like form as shown in Fig. 7b, increased spacing of dendritic cells causes a decrease in mechanical properties.

From the perspective of mechanical characteristics and eutectic Si shape the optimal amount of Sb for 319 alloy is from 1 000 to 2 000 ppm Al-10 %Sb, representing the concentration of Sb in the alloy from 0.0094 wt. % Sb to 0.017 wt. % Sb. Given amounts of Sb caused that the imperfectly rounded Si particles develop up to perfectly rounded in the microstructure, where the ultimate tensile strength UTS reaches values from 227 to 229 MPa. Brinell hardness reaches from 104 to 109 HBS. Antimony over-modified 319 alloys (> 2000 ppm Al-10 %Sb) has got negative effect on the mechanical properties of the investigated alloy.



a) mag. 250× etch. 0.5 % HF b) mag. 1600× etch. 0.5 % HF

Fig. 8 Micrographs showing the microstructure of 319 alloy with the addition of 3 000 ppm Al-10 %Sb (0.026 wt. % Sb)



9

a) mag. 250× etch. 0.5 % HF b) mag. 1600× etch. 0.5 % HF

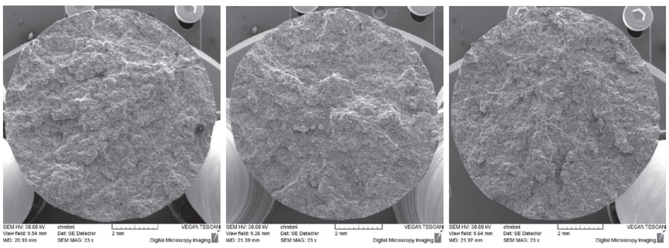
Fig. 9 Micrographs showing the microstructure of 319 alloy with the addition of 10 000 ppm Al-10 %Sb (0.08 wt. % Sb)

3.3. Fractography evaluation of fracture surface

Samples subjected to a tensile test have been used for the fractographic evaluation of fracture surfaces. At the collected breakage of the samples fractography of fracture surfaces have been evaluated. Three samples have been observed, namely the non-modified sample, the sample with the highest achieved ultimate tensile strength and lastly the sample with the highest achieved elongation. Based on the macroscopic observations of the fracture surfaces, it can be claimed that in all cases the combination of fractures has been achieved.

In Fig. 10a macrograph shows fracture surfaces of the non-modified 319 alloy which already contains 0.0038 wt. % Sb. In Fig. 10a, showing fracture surface of investigated alloy, a brittle fracture can be observed, resulting in a very low elongation of the obtained samples 1.08%. This sample achieved an ultimate tensile strength UTS = 217 MPa, and Brinell hardness 109 HBS. Fig. 10b shows a macrograph of the fracture surface 319 alloy with the addition of 1 000 ppm Al-10 %Sb (0.0094 wt.% Sb). Compared to Fig. 10a more subtle structure can be observed, what probably caused the highest measured ultimate tensile strength UTS = 229 MPa. Elongation achieved the average value of the observed and compared samples i.e. 1.2%, with unchanged values of Brinell hardness 109 HBS compared to the base alloy.

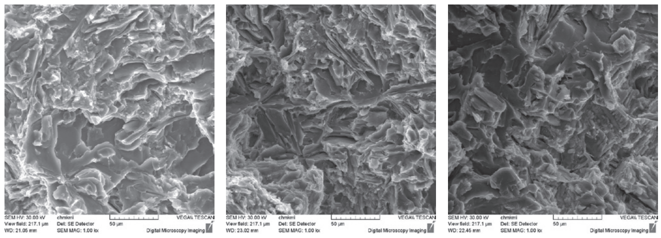
Macrograph showing fracture surfaces of 319 alloy with addition of the Sb with highest measured elongation (1.5 %) is shown in Fig. 10c. The Fig.10c shows more ductile fracture surface. This sample contains 2 000 ppm Al-10 %Sb (0.0170 wt. % Sb). As the sample with the addition of 1 000 ppm Al-10 % Sb has reached the same ultimate tensile strength UTS = 229 MPa where the reason is probably the same rounded shape of eutectic silicon in both samples. Brinell hardness value has dropped to 105 HBS.



a) 0.0038 wt. % Sb b) 0.0094 wt. % Sb c) 0.0170 wt. % Sb

Fig.10 Macrographs showing the fracture surfaces of 319 alloy with the addition of the Sb

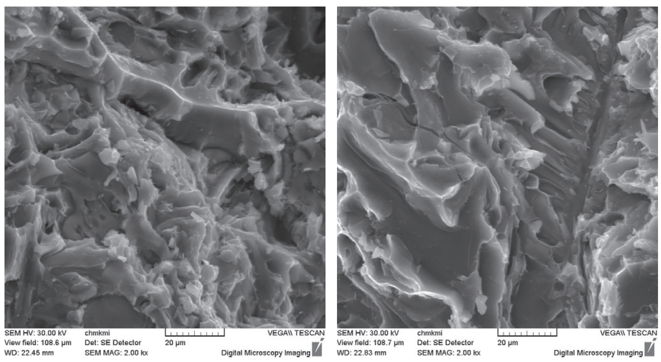
Detail at 1000 × magnification examined fracture surfaces is shown in Fig. 11. Microstructure of 319 alloy consists of α-Al dendrites and eutectic silicon. According to Warmuzek (2004) silicon creates clusters of rounded particles which on the fracture surface developed transgranular brittle fracture with pit morphology and remodeling plastic ridge of α-Al phase only with local occurrence of cleavage facets. The shape and size of holes caused by transgranular brittle fracture is determined by the shape and size of eutectic silicon.



a) 0.0038 wt. % Sb b) 0.0094 wt. % Sb c) 0.0170 wt. % Sb

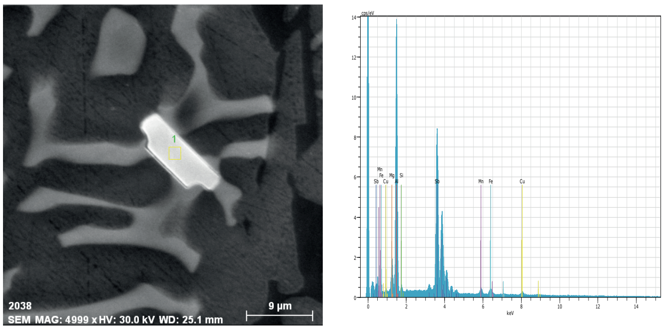
Fig.11 Micrographs showing the fracture surfaces of 319 alloy with the addition of the Sb, TEM, mag. 1 000×

In Fig. 12 intermetallic phases present in the investigated alloy with 0.0170 wt. % Sb at 2 000 × magnification can be observed. Intermetallic phases of the alloy with different shapes may be easier recognized on the fracture surface. Fig. 12a shows the Cu-based intermetallic phase as well as pulled matrix ridge. Phases based on copper consist of many tiny particles creating compact oval bodies on the fracture surface. Intermetallic phases based on copper are involved in heat treatment. The intermetallic phase based on Fe can be experienced in Fig. 12b. These phases create relatively large branched skeletal bodies, where this shape involves tension in the alloy, thereby reduces the ultimate tensile strength and elongation.



a) detail of the Cu based phase b) detail of the Fe based phase

Fig. 12 Micrographs showing the fracture surfaces of 319 alloy with the addition of 0.0170 wt. % Sb, TEM, mag. 2 000×



a) Detail of Al-Sb type of phase   b) EDX analysis of the chemical composition

Fig. 13 Sb-based intermetallic phase of alloy 319

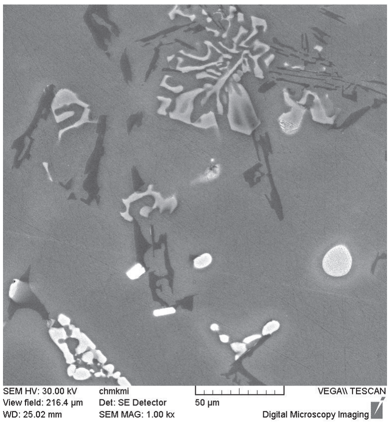


Fig. 14 Intermetallic phases present in alloy 319, mag. 1 000×

These intermetallic phases based on Cu and Fe are hard but brittle what is reflected in the increasing of the hardness of the alloy.

3.4. Analysis of intermetallic phases

The analysis of the intermetallic phases was made due to effort to see how antimony reacts in the investigated alloy; if it does or does not create any intermetallic phases. Further aim of the investigation was to clarify the shape and color of Sb in 319 alloy. The mechanical properties and foundry properties do not affect only the α-Al phase with the eutectic silicon, but also the presence of intermetallic phases contained in the alloy, their type, size and shape as demonstrated by Tenekedjiev and Closset (1990). These intermetallic phases are generally characterized by higher values of hardness and very low plastic properties such as hard but brittle phases based on iron. Fig. 13 show intermetallic phases.

The aim of the intermetallic phases investigation of various shapes was to determine in which form antimony in the alloy is excreted, if it is excreted in the solid solution α-Al phase or if it is eliminated as an individual intermetallic phase. A rectangular shape bright to radiant light gray intermetallic phase can be observed in Fig. 13. EDX analysis revealed high concentration of antimony. Intermetallic phase based on antimony (Fig. 13a) is excluded on the edge of skeletal Fe-phase. Based on the EDX analysis and comparison with the shape and composition of intermetallic phases specified by Dimayuga (1991) can be claimed that it is $AlSb_2$ type of phase.

Fig. 14 shows the intermetallic phases present in 319 alloy microstructure with the addition of antimony using 1 000× magnification.

In all investigated samples regardless of the amount of Al-10% Sb the identical intermetallic phases have been observed probably Fe-based Al_5FeSi in the form of fine needles, and possibly Cu-based phase of compact oval-shaped bodies of Al_2Cu.

4. Conclusions

Based on experimental works it can be claimed that the increasing amount of antimony increases ultimate tensile strength of investigated alloy up to a certain point and after that comes to the over-modification leading to decrease of UTS. The optimal amount of Sb for 319 alloy is between 1 000 to 2 500 ppm Al-10 %Sb (0.009 to 0.019 wt. % Sb), where the ultimate tensile strength reached the maximum. 229 MPa. The optimal addition increases the elongation of investigated alloy nearly up to 39%, where the elongation reached 1.5 % and non-modified alloy reached 1.08 %.

The optimal amount of antimony in the structure of the alloy creates imperfectly and perfectly rounded particles of eutectic silicon, forming many small clusters. The size of dendritic cells was decreased resulting in higher strength characteristics of alloys. High concentration of Sb creates large clusters of fiber-like eutectic silicon shape, it increases the size of dendritic cells which leads to mechanical properties lowering.

From the set of the experimental works the optimal amount of antimony for alloy 319 is 2 000 ppm Al-10 %Sb (0.017 wt. % Sb). Ultimate tensile strength reached the highest value 229 MPa at the maximum reached 1.5 % elongation. Brinell hardness reached 105 HBS, which is a very high value for as-cast alloy (Table 3).

The present work deals with antimony influence on 319 alloy to determine its influence on selected mechanical properties and on the microstructure. Based on the results of experimental work the following conclusions and benefits can be made:

The addition of antimony (Al-10% Sb)

- It increases the mechanical properties of as-cast alloy 319 using permanent molds, the optimal amount of Sb changes the shape of eutectic Si from the imperfectly up to the perfectly rounded particles which results in the improvement of the mechanical characteristics.
- Alloy 319 with the addition of 2 000 ppm Al-10% Sb reached best combination of strength properties (Ultimate tensile strength, Elongation, Brinell Hardness).

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