# Influence of Sn, Pb, Bi and Sb on the Microstructure and Mechanical Properties of Commercial AlSi8Cu2 Alloy

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In this work the influence of selected elements (Sn, Pb, Bi and Sb) on microstructure and mechanical properties of commercial AlSi8Cu2 alloy at four different temperatures (20, 100, 200, 300 and 350 ° C) was studied. The influence of individual elements and their combinations was studied. The content of elements in the range of 0.1-1 wt% was studied. Significant influence of these elements was found from 0.5% content especially at elevated temperatures.

Keywords: aluminum alloys, microstructure, mechanical properties, impurities

#### 1 Introduction

In this work, the influence of relatively low melting elements (Sn, Pb, Sb and Bi) on microstructure and selected mechanical properties of commercial AlSi8Cu2Mn alloy (ČSN 42 4339) is studied. It is a hypoeutectic aluminum alloy with silicon and other alloying elements used for general purposes and also for die casting. This alloy is used to produce dynamically stressed and complex castings of larger sizes, such as engine blocks or automotive gearboxes. This alloy has very good castability. Due to the very fine microstructure of this alloy, it does not undergo otherwise usual heat treatment, which would not lead to a significant increase in mechanical properties as in most other aluminum alloys. This alloy is an example of an "environmentally friendly alloy" which, when processed by die casting technology, may contain significantly higher amounts of some elements than conventional gravity alloys. A typical example is iron, which is present in the form of extremely fine intermediary phases, which do not disturb the structural homogeneity of the alloy under rapid solidification conditions during die casting to such an extent as in the case of gravity casting technology [1]. Iron is a typical element which is is practically always present in the recycled aluminum alloys. As a result of efforts to maximize recycling, aluminum alloys may also contain a number of other elements which, even in small quantities, can significantly influence the properties of aluminum alloys.

There are a number of chemical elements that significantly affect the properties of aluminum alloys in amounts significantly below 0.1 wt%. These are especially refining (especially P, Ti, B, Zr) and modifying (especially Na and Sr) additives, which even in such low amount significantly influence the microstructure of the alloy and the properties of the final castings [1-2]. Other elements in such a small amount usually do not have a significant effect on the microstructure, but they can significantly affect the mechanical properties of the alloy. Such elements also include metals with relatively low melting points such as Sn (232 °C), Pb (327 °C), Sb (630 °C) and Bi (271 °C). In addition to the lower melting point compared to aluminum, these elements also have a

significantly higher density. With the exception of antimony, these elements do not form intermediary phases with aluminum. In the case of gravity casting, it is practically impossible to achieve an uniform distribution of the elements over the entire casting volume, which may also result in inhomogeneity of the mechanical properties. At elevated temperatures, instability of the microstructure regions containing these elements becomes apparent, where the formation and development of cracks during mechanical stress is greatly facilitated. This problem should not occur to a significant extent in die casting technology.

If we do not take into account the special aluminum alloys that purposelly contain Sn, Pb, Sb and Bi, then these elements may be present in small amounts already in the master alloys from which the foundries produce commercial alloys. However, the main source of these elements in aluminum alloys is just recycled alloys. These elements are still used in some cases as soft solders for joining aluminum alloys. At present, solders of the Zn and Al alloys are preferred for soldering aluminum alloys. Due to the said properties of Sn, Pb, Sb and Bi in most commercial aluminum alloys, the content of these elements in the material standards is strictly limited.

## 1.1 Influence of Sn, Pb, Bi and Sb on the properties of aluminum alloys

#### Influence of tin

Tin is not a very important alloying element in aluminum alloys. it was previously used to improve of casting properties of Al-Si alloys. Al-Sn alloys use their self-lubricating property as well as Al-Pb alloys. For environmental reasons, tin alloys are preffered today. The addition of copper or silicon to aluminum alloys containing tin improves the alloy's mechanical properties and wear resistance. The microstructure consists of an aluminum dendritic matrix and tin phases in the interdendritic space [3-5]. The Al-Sn phase diagram (Fig. 1) is a binary eutectic system with low mutual solubility of both elements. The eutectic point is at a temperature of 228 ° C and a eutectic tin content of 99.4 wt.% [5].

In the case of Al-Si tin alloying, there is a partial or almost complete replacement of silicon in the  $Mg_2Si$  and

Al<sub>x</sub>Mg<sub>5</sub>Cu<sub>4</sub>Si<sub>4</sub> phases by tin. In the case of the co-presence of tin together with magnesium in Al-Si alloys, the Mg<sub>2</sub>Si phase formation is affected and enter the intermediate phases as Mg<sub>2</sub>Sn phase, or form a new Mg<sub>2</sub>Si<sub>0.2</sub>Sn<sub>0.8</sub> phase. These phases are most often present in the morphology of Chinese script, tin negatively affects toughness in these phases. Coarse phases are formed and mechanical properties are greatly reduced with higher tin content in alloy [6].

## Influence of lead

The mutual solubility of aluminum and lead is extremely low, the maximum solubility of lead in aluminum is 0.025 wt.% at 659 °C [7], see phase diagram in Fig.1.

Lead is added to some aluminum alloys to improve machinability, often lead is added with bismuth to improve machinability more effectively [7-9]. The resulting lead phase has a lower melting point than aluminum, and so at the cut point, these phases melt and reduce the friction, making it impossible to forming build up. However, lead does not only have this positive influence for aluminum alloys, it is also referred to as an impurity and its content is given by standard for particular alloys. Lead reduces toughness, ductility, thermal conductivity and promotes intergranular corrosion. Tin, which also improves machinability [10-11], is now used as a substitute for problematic toxic lead.

Special foundry methods are used for Al-Pb alloys because there is very high density difference between the aluminum melt and lead, which complicates the achievement of uniform phase distribution by conventional casting techniques [11-14].

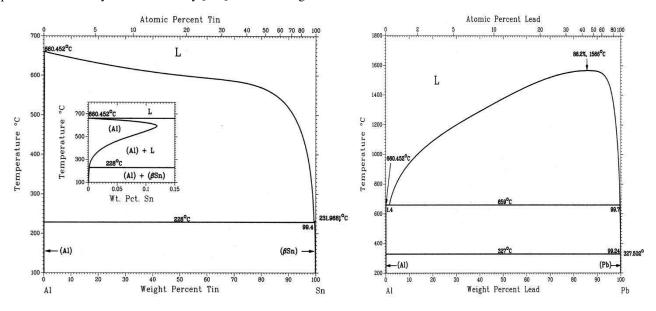


Fig. 1 Al-Sn and Al-Pb phase diagrams [7]

#### Influence of antimony

Antimony is an element that is not intentionally added to aluminum alloys. Al-Sb phase diagram is eutectic system (Fig. 2) with very little solid solubility, as in the case of the Al-Sn system. There are two eutectic reactions in the system [14-15]. Antimony in Al-Si alloys affects the crystallization of the eutectic phase. It has a modifying effect. Antimony modifies eutectic Si into lamellar morphology as well as strontium or bismuth. For this effect an order of magnitude higher antimony content in the alloy is required, than in the case of Na or Sr. However, before casting, the Al-Si alloy melt must not contain, in addition to antimony, also Sr or Na, with which the antimony preferably forms the intermediary phases (SrSb<sub>3</sub>, Sr<sub>3</sub>Sb<sub>2</sub>, SrSb, Sr<sub>2</sub>Sb, Na<sub>3</sub>Sb<sub>2</sub> and NaSb). This would cancel the modification effect. Furthermore, antimony significantly deteriorates oxidation resistance of Al-Si alloys and decrease the castability [12]. Therefore, its content in

commercial alloys is strictly limited by their material standards.

## Influence of bismuth

Bismuth is an element with properties generally very similar to antimony. Therefore, its similar effect on the properties of Al-Si alloys is not surprising. [12,16]. Unlike antimony, bismuth do not form intermediary phases with aluminum. Like antimony, it shows a slight modification effect during the crystallization of eutectic silicon. With sodium or strontium, bismuth form similar intermediary phases to antimony, and here too the modification effect is lost as a result of this interaction. Bismuth also significantly deteriorates oxidation resistance of Al-Si alloys and decrease the castability [16]. When magnesium is present in the alloy, bismuth reacts with it to form the Bi<sub>2</sub>Mg<sub>3</sub> phase, which is characterized by a high melting point. In Fig.2 is a phase diagram of Al-Bi.

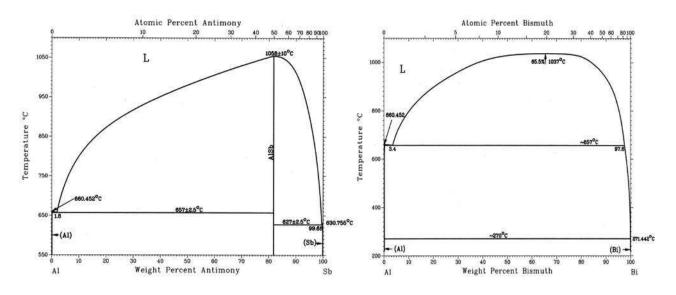


Fig. 2 Al-Sb and Al-Bi phase diagrams [7]

Therefore, it is very important to know the influence of these elements on the properties of aluminum alloys at normal temperature and especially at elevated temperatures, where differences in the properties of the aluminum phase and the phases formed by Sn, Pb, Sb and Bi can be expected [16-18].

## 2 Experiment

The influence of Pb, Sn, Sb and Bi on the microstructure and mechanical properties – hardness and compressive yield strength at normal and enhanced temperatures

(20, 100, 200, 300 and 300°C), thermal stability of AlSi8Cu2 commercial alloy (ČSN 42 4339) was studied in this work. Chemical composition of base AlSi8Cu2 alloy is in the Table 1.

The studied alloys were prepared from basic alloy to which elements of 99.99 wt.% purity were added. All alloys were prepared in an electric induction furnace in an Ar atmosphere. The melts were cast into a massive brass mold (cooling rate approx. 10 Ks<sup>-1</sup>). Cylindrical samples with a diameter of 20 mm were used for experiments.

**Tab. 1** Chemical composition of base commercial AlSi8Cu2 alloy (ČSN 42 4339), wt%

Si	Cu	Mn	Fe	Mg	Ni	Sn	Zn	Ti	Pb	Sb	Bi	Sr	Al
8.11	2.05	0.32	0.62	0.14	0.07	0.01	0.34	0.06	0.02	0.01	0.01	≤ 0.01	bal.

The following alloys were prepared. 12 alloys were alloyed with only 0.1, 0.5 and 1 wt% additions of each one element. Furthermore, 6 alloys with binary additions Sn + Pb and Sb + Bi were prepared with the same contents as in the previous case. The last 3 alloys contained additions of all elements simultaneously with the same contents. The overview of prepared alloys together with the results of mechanical properties is clearly shown in Table 2. The chemical composition of the samples was determined by x-ray fluorescence spectrometry. The analysis confirmed that the intended alloy content corresponds to the measured values. The maximum deviation was negligible 6% relative to the addition. Similarly, the content of the main alloying elements in AlSi8Cu2 alloy has not been significantly affected.

Metallographic samples were made by conventional metallographic technique. The microstructure of the samples was studied by light microscope Olympus PME 3 and by scanning electron microscope TESCAN VEGA 3 LMU with EDS analyzer. Brinell hardness measurements were carried out using a Heckert WPM machine according to ČSN EN ISO 6506-1. Hardness of each sample was determined three times. Mechanical testing of alloys in uniaxial pressure was performed using a universal tensile

machine LabTest 5.250SP1. Uniaxial pressure test was performed at the temperatures of 20, 100, 200, 300 and 300° C. The sample was tempered at the appropriate temperature for 20 min. before each test.

## 3 Results and discussion

## 3.1 Microstructure

The microstructure of all studied alloys is practically identical. It consists of a primary  $\alpha$ -Al solid solution, Al-Si euectic and other phases excluded in the interdendritic space (phase containing Cu, Fe, Mg as well as studied elements). Microstructure of base alloy is in the Fig.3. Only in the case of alloys with maximum contents of Sn, Pb, Sb and Bi is a significantly higher proportion of the phases containing the studied elements (Fig.4). Alloys containing more than 0.5% Sb or Bi also had a noticeable modifying effect.

Due to the fine character of the microstructure, the intermediary phases containing the studied elements were distributed uniformly. Significant segregation effect can be expected for alloys cast gravitationally into sand moulds.

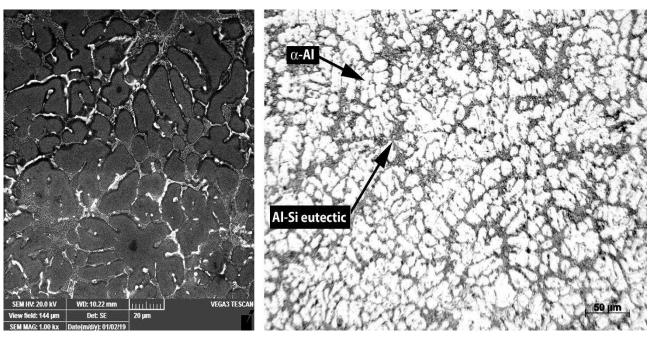


Fig. 3 Microstructure of base AlSi8Cu2 alloy (SEM – left, LM – right)

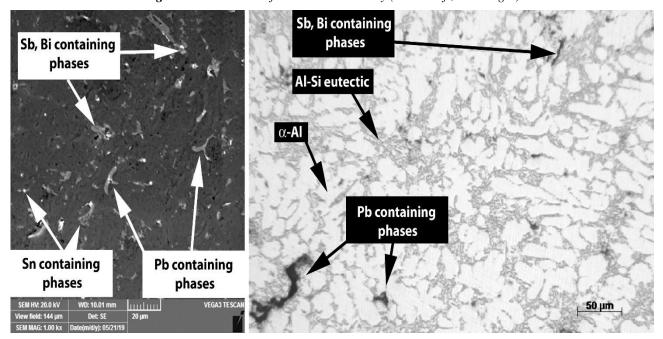


Fig. 4 Microstructure of AlSi8Cu2 Sn1Pb1Sb1Bi1alloy (SEM – left, LM – right)

## **Mechanical properties**

Mechanical properties at uniaxial pressure at temperatures of 20, 100, 200, 300 and 350 °C were studied. Due to the high plasticity of the alloys, it was not possible to determine the compressive strength. For this reason, only the values of compressive yield stress were computed. The results are shown in Table 2.

It is evident that at the lowest content of 0.1 wt.% the influence of the studied elements is not significant. Since the addition of 0.5 wt.%, the influence of the studied additives is already apparent. Alloys with antimony additi-

ons showed the highest compressive yield stress at normal temperature. This is probably related to the stability of the phases produced by antimony and also to its modifying effect. For tests at 100 and 200 °C, there is an apparent increase in the yield point values of most alloys, which is probably related to the phase precipitation from the supersaturated aluminum solid solution during the test. The compressive yield stress at the temperatures of 300 and 350 °C was significantly lower for all alloys, which is probably due to the ageing of the solid aluminum solution. Plastic deformation at 350 °C can be facilitated by the presence of liquid phases consisting of Pb, Sn or Bi.

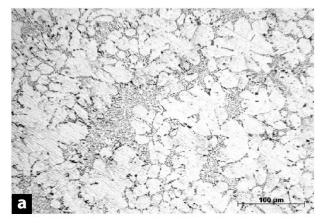
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	Alloy	ing elements	R <sub>pd0.2</sub> [MPa]						
	Sn	Pb	Sb	Bi	20°C	100°C	200°C	300°C	350°C
AlSi8Cu2					214	211	224	111	92
AlSi8Cu2	0.1				194	195	194	72	75
AlSi8Cu2		0.1			199	206	209	89	88
AlSi8Cu2			0.1		224	228	234	101	88
AlSi8Cu2				0.1	194	209	225	81	89
AlSi8Cu2	0.5				209	205	227	71	66
AlSi8Cu2		0.5			228	227	239	73	69
AlSi8Cu2			0.5		257	258	259	79	83
AlSi8Cu2				0.5	233	241	244	72	75
AlSi8Cu2	1				196	221	218	57	58
AlSi8Cu2		1			251	222	231	89	81
AlSi8Cu2			1		257	267	259	75	72
AlSi8Cu2				1	206	220	249	81	81
AlSi8Cu2	0.1	0.1			196	198	200	77	71
AlSi8Cu2	0.5	0.5			195	227	224	72	69
AlSi8Cu2	1	1			221	221	231	83	71
AlSi8Cu2			0.1	0.1	226	241	232	89	88
AlSi8Cu2			0.5	0.5	251	259	266	87	85
AlSi8Cu2			1	1	207	206	218	77	65
AlSi8Cu2	0.1	0.1	0.1	0.1	212	229	231	62	62
AlSi8Cu2	0.5	0.5	0.5	0.5	206	241	243	58	59
AlSi8Cu2	1	1	1	1	229	261	262	56	57

## Temperature stability

The hardness values of alloys show similar tendencies as in the case of compressive yield strength. The highest hardness values are achieved with alloys with higher antimony or bismuth content. Further, the hardness was measured after 1, 2, 4 and 100h annealing at 350 ° C, which

is already the extreme temperature for these alloys. During annealing, the microstructure of the alloys produces the effects described above. They are also added to the silicon phase roughing effect. This is illustrated in Figure 5, which shows the microstructures of the base alloy and the alloys alloyed with the maximum contents of the elements studied.



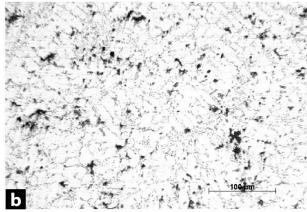


Fig. 5 Microstructure of base alloy AlSi8Cu2 (a) and AlSi8Cu2 Sn1Pb1Sb1Bi1alloy (b) after tempering at 350°C for 100 h, LM

Already after 1h of annealing, there was a visible decrease in hardness of all alloys, which continued even after further annealing. After 100h annealing of all alloys,

the hardness dropped by one third or more, see Table 3.

**Tab.3** Brinell hardness of studied alloys at 20°C and during the tempering at 350°C

	Alloy	ing elements	s, addition in	HBW 2.5/62.5					
					Tempering time at 350°C				
	Sn	Pb	Sb	Bi	20°C	1 h	2 h	4 h	100 h
AlSi8Cu2					87	69	64	63	57
AlSi8Cu2	0.1				86	68	69	64	55
AlSi8Cu2		0.1			86	73	69	67	58
AlSi8Cu2			0.1		95	73	71	66	60
AlSi8Cu2				0.1	92	65	64	67	58
AlSi8Cu2	1				85	64	64	60	48
AlSi8Cu2		1			85	65	64	65	56
AlSi8Cu2			1		89	70	70	65	57
AlSi8Cu2				1	91	73	72	67	57
AlSi8Cu2	0.1	0.1			91	75	74	65	57
AlSi8Cu2	1	1			85	65	65	60	51
AlSi8Cu2			0.1	0.1	84	75	77	61	62
AlSi8Cu2			1	1	92	68	67	65	58
AlSi8Cu2	0.1	0.1	0.1	0.1	88	74	75	69	62
AlSi8Cu2	1	1	1	1	76	65	65	59	53

#### 4 Conclusion

The influence of Sn, Pb, Sb and Bi on the microstructure and mechanical properties of the commercial AlSi8Cu2 alloy was documented. With a content of 0.1 wt.%, the effect is practically negligible. Most material standards of commercial aluminum alloys allow this maximum element content. At higher contents, antimony and bismuth in most cases slightly increase the hardness and compressive yield strength, which can be attributed to the modifying effect of these elements. Lead and tin slightly deteriorate these properties. The compressive yield strength of most alloys slightly increased at 200°C. At temperatures of 300 and 350°C, there was already a significant decrease in compressive yield strength. The microstructure of all studied alloys was very similar. A noticeable increase in the phase content containing the elements was only observed at their maximum content. Furthermore, a significant decrease in hardness of all alloys during annealing at 350°C was found already after 1h.

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#### References

- [1] MICHNA, Š., LUKÁČ, I., OČENÁŠEK, V., KOŘENÝ, R., DRÁPALA, J., SCHNEIDER, H., MIŠKUFOVÁ, A. et. al. (2005). *Encyklopedie hli-níku*, Adin, s. r. o., Prešov, ISBN 80-89041-88-4.
- [2] SVOBODOVÁ, J., HAJDÚCH, P. (2017). Quality Analysis of AlTi5B1 Master Alloy. *Manufacturing Technology*, Vol. 17, No. 5, 2017, pp. 858-863. J.E. Purkyne University in Usti and Labem. Czech Republic.
- [3] DOLEŽAL, J., BRYKSÍ STUNOVÁ, B., KUČERA, V. (2015). Současné poznatky o vlivu doprovodných prvků ve slitinách Al-Si. Vol. LXIII. 2015. pp.345-348.
- [4] ZEDAN, Y., SAMUEL, H.W. (2011). Doty Effects of Sn, Bi, and Pb Additions on the Mechanical Properties and Machinability of Al-11%Si-2.25%Cu-0.3%Mg Casting Alloys, 2011. pp. 11-71. American Foundry Society.
- [5] BERTELLI, F., et al. (2017). Microstructure, tensile properties and wear resistance correlations on directionally solidified Al-Sn-(Cu; Si) alloys. *Journal of Alloys and Compounds*, 2017. 695. pp. 3621-3631.

- [6] PILOTE, L., GHERIBI, A.E., CHARTRAND, P. (2018). Study of the solubility of Pb, Bi and Sn in aluminum by mixed CALPHAD/DFT methods. In: Applicability to aluminum machining alloys. 2018. 61. pp. 275-287. Calphad.
- [7] BAKER, H., (1992). ASM Handbook, Vol. 3 Alloy Phase Diagrams, ASM International
- [8] MA, Z., et al. (2010). Parameters controlling the microstructure of Al–11Si–2.5Cu–Mg alloys. *Materials & Design*, 2010. 31(2) pp. 902-912.
- [9] ZHU, J.N., et al. (2018), Microstructure and wear behaviour of Al-20Mg2Si alloy with combined Zr and Sb additions. *Journal of Alloys and Com*pounds, 2018. 767 pp. 1109-1116
- [10] FANG, X. AND FAN, Z. (2006). Rheo-diecasting of Al–Si–Pb immiscible alloys. *Scripta Materialia*, 2006. 54(5). pp. 789-793.
- [11] PALIWAL, M. AND JUNG, I.-H. (2010). *Thermodynamic modeling of the Al–Bi, Al–Sb, Mg–Al–Bi and Mg–Al–Sb systems.*, 2010. 34(1) pp. 51-63. Calphad.
- [12] FARAHANY, S., et al. (2013). Evaluation of the effect of Bi, Sb, Sr and cooling condition on eutectic phases in an Al–Si–Cu alloy (ADC12) by in situ thermal analysis. In: *Thermochimica Acta*, 2013. 559. pp. 59-68.
- [13] FARAHANY, S., OURDJINI, A., BAKHSHESHI-RAD, H.R. (2016). Microstruc-

- ture, mechanical properties and corrosion behavior of Al–Si–Cu–Zn–X (X=Bi, Sb, Sr) die cast alloy. In: *Transactions of Nonferrous Metals Society of China*, 2016. 26(1): pp. 28-38.
- [14] SOO, V.K., et al. (2018). Sustainable aluminium recycling of end-of-life products: A joining techniques perspective. In: *Journal of Cleaner Production*, 2018. 178. pp. 119-132.
- [15] GRIMAUD, G., PERRY, N., LARATTE, B. (2018). Aluminium cables recycling process: Environmental impacts identification and reduction. In: *Resources, Conservation and Recycling*, 2018. 135. pp. 150-162.
- [16] GRONOSTAJSKI, J., A. MATUSZAK, A. (2000). New methods of aluminium and aluminium-alloy chips recycling. In: *Journal of Materials Processing Technology*, 2000: pp. 34-39
- [17] ŠERÁK, J., VODĚROVÁ, M., VOJTĚCH, D., NOVÁK, P. (2014). Microstructure and Properties of Magnesium Alloys Working at Elevated Temperatures, *Manufacturing Technology*, Vol. 14, No. 2, 2014, pp. 238-244. J.E. Purkyne University in Usti and Labem. Czech Republic.
- [18] ŠERÁK, J., VOJTĚCH, D. (2017). Dispersion of Mechanical Properties of Commercial Aluminium Alloys within Their Material Standards. *Manufacturing Technology*, Vol. 17, No. 5, 2017, pp. 831-837. J.E. Purkyne University in Usti and Labem. Czech Republic.

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