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Assessment of Impact of Nickel Additions on Tin Bronzes

J. Kozana [a], A. Garbacz-Klempka [a, *], M. Piękoś [a], E. Czekaj [b], M. Perek-Nowak [c]
[a] AGH-University of Science and Technology, Faculty of Foundry Engineering, Reymonta 23, 30-059 Kraków, Poland
[b] Foundry Research Institute, Zakopiańska 73, Kraków, Poland
[c] AGH-University of Science and Technology, Faculty of Non-Ferrous Metals, Mickiewicza 30, 30-059 Kraków, Poland
* Corresponding author. E-mail address: agarbacz@agh.edu.pl

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Abstract

High prices of tin and its limited resources, as well as several valuable properties characterising Cu-Sn alloys, cause searching for materials of similar or better properties at lower production costs. The influence of various nickel additions to CuSn10 casting bronze and to CuSn8 bronze of a decreased tin content was tested. Investigations comprised melting processes and casting of tin bronzes containing various nickel additions (up to 5%). The applied variable conditions of solidification and cooling of castings (metal and ceramic moulds) allowed to assess these alloys sensitivity in forming macro and microstructures. In order to determine the direction of changes in the analysed Cu-Sn-Ni alloys, the metallographic and strength tests were performed. In addition, the solidification character was analysed on the basis of the thermal analysis tests. The obtained results indicated the influence of nickel in the solidification and cooling ways of the analysed alloys (significantly increased temperatures of the solidification beginning along with increased nickel fractions in Cu-Sn alloys) as well as in the microstructure pattern (clearly visible grain size changes). The hardness and tensile strength values were also changed.
It was found, that decreasing of the tin content in the analysed bronzes to which approximately 3% of nickel was added, was possible, while maintaining the same ultimate tensile strength (UTS) and hardness (HB) and improved plasticity (A_5).

Keywords: Wear resistant alloys, Tin bronze, Microstructure, Alloy additives, Cu–Sn–Ni

1. Introduction

Tin bronzes are one of the oldest groups of non-ferrous metal alloys amongst numerous copper alloys for casting. Indeed, the use of different and certainly valuable properties of the material obtained by smelting copper with tin and other elements, was amongst the factors that significantly contributed to the development of civilisation in the Bronze Age. Then, either intentionally or by chance, in a more or less controlled manner, tin and other elements are present in bronze products of the time at various and varied levels [1]. In modern times, also tin bronzes with a varied tin content, and with additions of other elements such as phosphorous, iron, lead, zinc, etc. can be found in standards, references or product ranges of smelting plants manufacturing copper and copper alloys. No doubt, thanks to their valuable properties tin bronzes are applied in many areas of the economy, i.e. including heavy-duty parts of machines and devices, such as plain bearings, bearing bushings, components of drives and steam accessories – resistant to the impact of some acids. The high price of tin bronzes, arising largely from the deficit of their main alloy addition – tin, contributes to the limitation of a broad application of these alloys. If we look for alternative solutions to substitute for this alloy addition, nickel seems interesting. Due to specific properties of this element and its effect in other – not only copper - alloys, combined with a slightly lower price than tin, its application seems justified.

Hence, solving the problem of maintaining or increasing the mechanical properties of tin bronzes, when substituting tin by nickel or other elements, can contribute to an increase in use and application of these alloys. [2-7]

The unlimited solubility of nickel in copper in the solid state (Fig. 1) shows that this element can considerably strengthen copper by solution hardening [8-10].

The issues concerning obtaining copper, purifying and refining copper based alloys, including tin bronzes [11-14] are widely discussed in the literature. These bronzes are characterized by good castability and machinability, and high resistance to static and dynamic loads. They are also characterised by the corrosion and abrasion resistances and can be used at increased temperatures (up to 280°C). Apart from these advantages, tin bronzes show a relatively wide range of solidification temperature, which is related to their tendency to the shrinkage porosity, and the dendritic segregation [12].

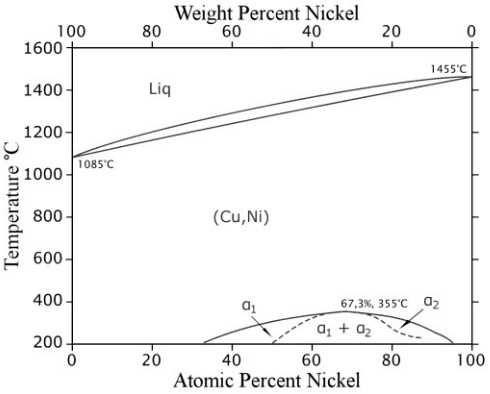

Fig. 1. Cu-Ni equilibrium diagram [9]

As a result of these considerations, and on the basis of research on developing properties, purifying and refining non-ferrous metal alloys, including tin and multi-component bronzes [1, 15-16], carried out in the Laboratory of Foundry of Non-Ferrous Metals of the Faculty of Foundry Engineering of AGH University of Science and Technology for many years, a number of experiments has been planned, and a selected part of the research is presented in this paper.

2. Methodology and conditions of research

The research on developing properties of tin-nickel bronzes was carried out using metal charge in the form of bronze CuSn10 according to EN 1982 (PN-91/H87026), electrolytic nickel and electrolytic, cathode copper designated MOK (acc. PN-77/H-82120). Melts were made in a medium frequency induction furnace, in a chamotte-graphite crucible. During the investigations the protective coat of a slag mixture was applied on the charge and metal bath surface, and deoxidizing additions in the form of phosphorous copper CuP8 were introduced. At the same time stable and repeatable conditions of the conducted melts were ensured. During the research eight alloys with varied chemical compositions were obtained; primarily in terms of the content of tin and nickel, and thus also of the copper content. Other metallic elements were considered impurities. The obtained alloys were cast to metal and ceramic moulds, characterized by substantially different heat discharging from solidifying castings.

During the research the following was analysed:

- the chemical composition of the obtained alloys according to the design of experiments, using the Spectro Midex energy dispersion X-ray fluorescence spectrometer;
- the nature of the solidification and cooling of the alloys – in ceramic moulds characterised by a slow heat discharge, and in metal moulds, ensuring a fast solidification of a casting. A sheathed thermocouple type K with a diameter of 0.5 [mm], along with an analogue-digital converter and a recorder coupled with a computer, was used to record the nature of solidification. As a result of the tests, curves dT/dτ at a time step of 0.319 [s] were obtained:
- the grain size of samples solidifying in metal and ceramic moulds on the casting cross-section;
- the impact of varied amounts of additions, mainly tin and nickel in alloys Cu-Sn-Ni on forming the microstructure of the alloys analysed;
- the selected mechanical properties: tensile strength (UTS), hardness (HB) and elongation (A_5) of bronzes solidifying in metal moulds.

3. Results of chemical tests and their analysis

The chemical composition of the alloys was analysed with a Spectro Midex X-ray fluorescence spectrometer. The test samples were taken from castings from metal moulds. The surface for tests was prepared by rolling the cylindrical sample face. The average test results are presented in Table 1.

Table 1.
Results of the chemical composition analysis of alloy CuSn10 with a Ni addition

Alloy designation	**CuSn10**	**CuSn10Ni1**	**CuSn10Ni3**	**CuSn10Ni5**
Sample No.	No. 01	No. 02	No. 03	No. 04
Cu	88.03	87.08	84.9	83.18
Sn	11.12	11.07	10.71	10.36
Ni	0.09	1.14	3.26	5.42
Pb	0.43	0.42	0.41	0.49
residue:	0.33	0.29	0.72	0.55

Table 2.
Results of the chemical composition analysis of alloy CuSn8 with a Ni addition

Alloy designation	**CuSn8**	**CuSn8Ni1**	**CuSn8Ni3**	**CuSn8Ni5**
Sample No.	**No. 11**	**No. 12**	**No. 13**	**No. 14**
Cu	91.41	90.94	88.03	86.17
Sn	7.542	7.417	7.621	7.297
Ni	0.0868	1.157	3.239	5.253
Pb	0.5549	0.1947	0.2682	0.4516
residue:	0.4063	0.2913	0.8418	0.8284

The obtained results indicate that the planned and completed tests were correct. Slight deviations from the intended chemical composition and impurities were insignificant from the point of view of the experiment conducted.

4. Analysis of the crystallisation process of Cu-Sn-Ni alloys

The results of the crystallisation process analysis provide a lot of interesting information concerning the development of structure and properties of alloys. However, the accuracy of analysis depends on many factors, i.e. the sensitivity and inertia of the thermocouple, the recorder accuracy, and also the heat discharge rate from the solidifying casting through the mould. Therefore, a ceramic mould of a rectangular prism shape, having a cylindrical cavity with a diameter of 30 [mm] and a height of 50 [mm], with a thermocouple placed from the top, in the centre of the mould cavity, was used to investigate the nature of alloy solidification and cooling. The recorded findings of the conducted tests are presented in Figs. 2-3 and Tables 3-4.

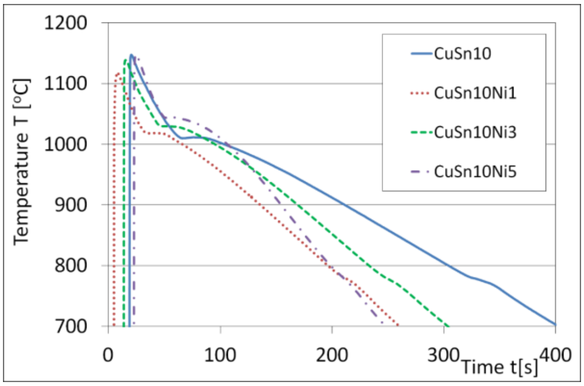

Fig. 2. The course of cooling of the CuSn10 alloy with a Ni addition

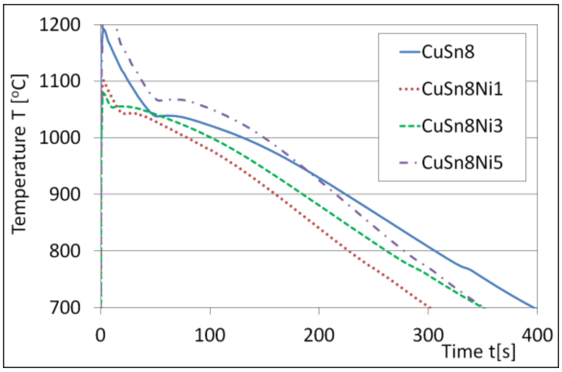

Fig. 3. The course of cooling of the CuSn8 alloy with a Ni addition

Analysing the curves of alloys Cu-Sn-Ni presented in Figures 2 and 3 one can observe, first of all, a varied nature of alloy solidification with a very clear difference in the temperature of the solidification start, designated as T_2, as well as an explicit transformation occurring within the range of 750 – 800°C, designated as T_3 in Figure 4.

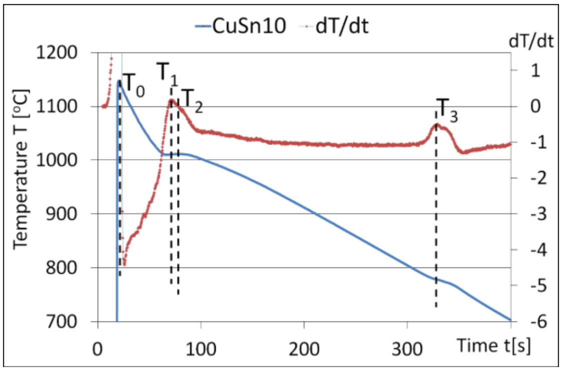

Fig. 4. An example of the cooling curve T(t) and the crystallisation curve dT/dt(t) of the CuSn10 alloy

Parameters of characteristic transformation points: T_1 – the metastable temperature of maximum supercooling, T_2 – the crystallisation temperature and T_3 – the temperature of the occurring transformation and the pouring temperature T_0 of the alloys analysed are compared in Tables 3-4.

Table 3.
Comparison of characteristic data read from the analysis of crystallisation of alloys CuSn10, CuSn10Ni1, CuSn10Ni3 and CuSn10Ni5 (Fig. 2)

CuSn10				**CuSn10Ni1**		
T	t [s]	T [°C]	dT/dt [°C/s]	t [s]	T [°C]	dT/dt [°C/s]
T_0	20.4	1147.4	0.932602	8.3	1118.5	-0.87774
T_1	66.1	1009.6	0.039185	34.8	1018.4	0.00000
T_2	75.9	1011.3	0.000000	43.4	1018.7	0.00000
T_3	326.9	779.1	-0.19592	211.2	779.9	-0.75235
CuSn10Ni3				**CuSn10Ni5**		
T	t [s]	T [°C]	dT/dt[°C/s]	t [s]	T [°C]	dT/dt[°C/s]
T_0	15.3	1138.7	-0.18809	25.2	1148.1	-1.5674
T_1	49.1	1029.8	0.00000	51.1	1043.7	-0.18025
T_2	50.7	1029.8	0.00000	55.2	1045.6	0.00000
T_3	248.8	779.4	-0.7837	201.9	794.2	-1.53605

Table 4.
Comparison of characteristic data read from the graphs of crystallisation of alloys CuSn8, CuSn8Ni1, CuSn8Ni3 and CuSn8Ni5 (Fig. 3)

CuSn8				**CuSn8Ni1**		
T	t [s]	T [°C]	dT/dt [°C/s]	t [s]	T [°C]	dT/dt [°C/s]
T_0	2.9	1191.8	0.454545	2.9	1101.2	0.250784
T_1	51.7	1037.5	-0.18025	20.7	1042.4	0.031348
T_2	58.1	1038.7	0.00000	25.8	1043.3	0.00000
T_3	333.9	770.1	-0.39185	249.5	769.8	-0.94044
CuSn8Ni3				**CuSn8Ni5**		
T	t [s]	T [°C]	dT/dt [°C/s]	t [s]	T [°C]	dT/dt [°C/s]
T_0	3.2	1077.5	-1.05016	3.2	1245.6	0.0000
T_1	11.2	1053.3	0.000000	53.6	1066.2	0.0000
T_2	16.9	1055.2	0.250784	66.7	1068.2	0.0000
T_3	282.6	775.0	-0.75235	293.8	778.3	-0.9404

It was observed that a Ni addition caused an increase of the crystallisation start temperature T_2 (Fig. 5), thus explicitly extending the crystallisation range of the Cu-Sn-Ni alloys tested within the range of the occurring transformations.

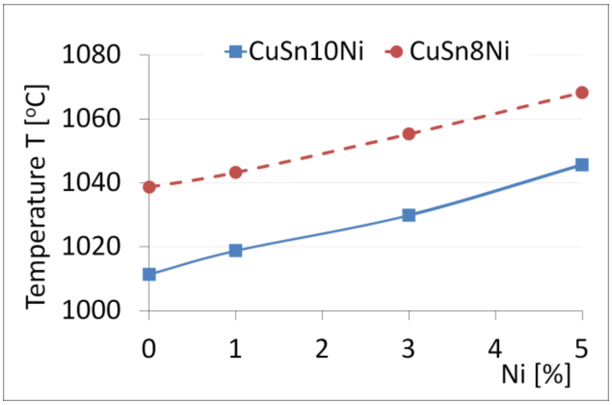

Fig. 5. Influence of Ni on the crystallisation start temperature T_2 of the investigated alloys CuSn8Ni and CuSn10Ni

5. Results of macrostructure examinations

The obtained samples of alloys Cu-Sn-Ni cast into metal moulds were analysed for the impact of varied nickel additions on the macrostructure. The examinations were carried out on the basis of commonly used methodology of preparing and etching samples of Cu-Sn alloys. A NIKON SMZ 745 stereoscopic microscope with a camera and a system for image analysis Nis-Elements was applied for observations of sample surfaces. Photos of metallographic specimens were made at magnification 6.7x.

Examples of macrostructures of alloys solidifying in a metal mould are presented in Figs. 6-13.

The analysis of macroscopic examinations showed a very intensive impact of the varied chemical composition of alloys on the size, shape, and grain orientation on the transverse surface of the cylindrical samples observed. The macrostructure revealed in the alloys shows the existence of wall crystals oriented radially from the mould wall to the centre of the casting, equiaxed crystals with a varied grain size at the edge and in the centre of the casting. Regardless of the tin content in the bronzes analysed, the nickel addition is crucial for the macrostructure, i.e. the type and size of grains.

Due to the presence of varied nickel additions in alloy CuSn10, for a nickel addition of 3% equiaxed crystals with the smallest grains form almost on the whole metallographic specimen surface. In alloy CuSn8Ni, the coarse crystal macrostructure, primarily with visible wall crystals, becomes intensively refined and transformed into equiaxed crystals already for a nickel addition of 1%. An increase in the nickel addition to 3% causes a new directional crystallisation with clearly marked edge zone in the casting, and fine equiaxed crystals in this area and in the centre of the casting. A macrostructure image like this indicates a very strong impact of heat discharge conditions of the solidifying and cooling casting on the type and size of grains in alloys Cu-Sn-Ni.

An increase in the nickel addition to 5% leads to a growth of wall crystals, with a small area in the centre of the sample surface with large equiaxed crystals.

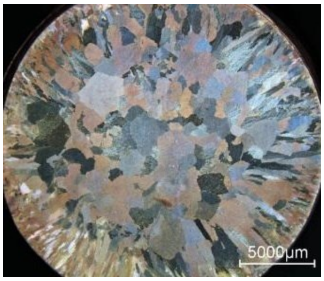

Fig. 6. Alloy CuSn10, metal mould

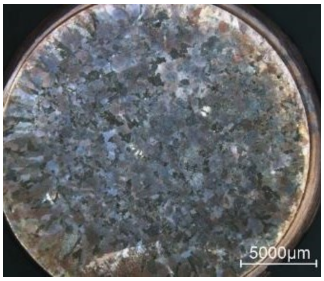

Fig. 7. Alloy CuSn10Ni1, metal mould

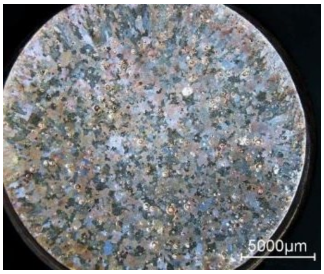

Fig. 8. Alloy CuSn10Ni3, metal mould

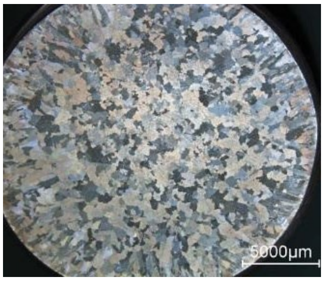

Fig. 9. Alloy CuSn10Ni5, metal mould

Fig. 10. Alloy CuSn8, metal mould

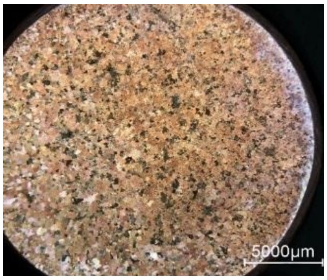

Fig. 11. Alloy CuSn8Ni1, metal mould

Fig. 12. Alloy CuSn8Ni3, metal mould

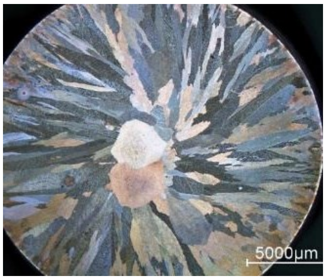

Fig. 13. Alloy CuSn8Ni5, metal mould

6. Analysis and results of microstructure examinations

Surfaces of castings were observed to find out changes in the microstructure of samples, cast into metal and ceramic moulds. To this end, a Nikon Eclipse microscope was used, and the observations were carried out at magnifications of 100 and 500x. The findings are compared in Figs.14-31.

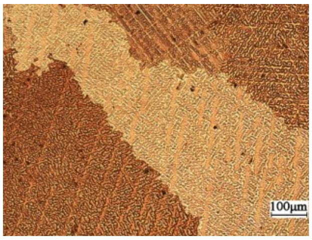

Fig. 14. Alloy CuSn10, metal mould, 100x

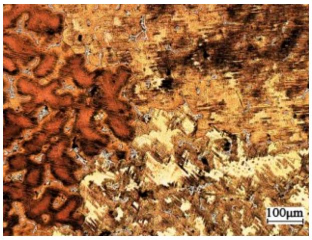

Fig. 15. Alloy CuSn10, ceramic mould, 100x

Fig. 16. Alloy CuSn10Ni1, metal mould, 100x

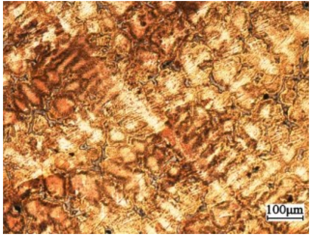

Fig. 17. Alloy CuSn10Ni1, ceramic mould, 100x

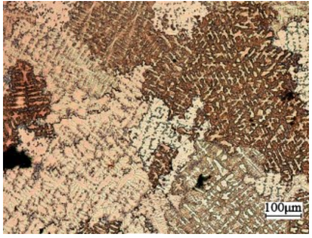

Fig. 18. Alloy CuSn10Ni3, metal mould, 100x

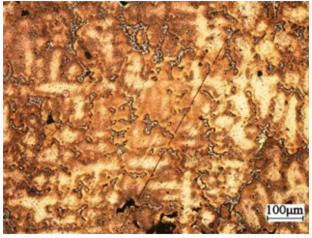

Fig. 19. Alloy CuSn10Ni3, ceramic mould, 100x

Fig. 20. Alloy CuSn10 Ni5, metal mould, 100x

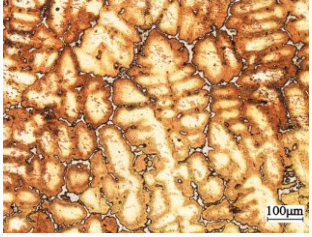

Fig. 21. Alloy CuSn10 Ni5, ceramic mould, 100x

By investigating changes in the microstructure, one can find that nickel additions not only influence the macro scale, but the microstructure as well. The distinct dendritic structure of α-Cu changes to form precipitates in the dendrite area and in interdendritic spaces.

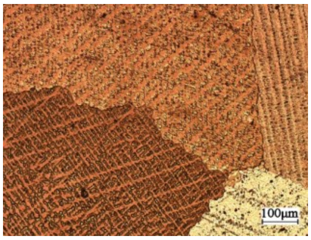

Fig. 22. Alloy CuSn8, metal mould, 100x

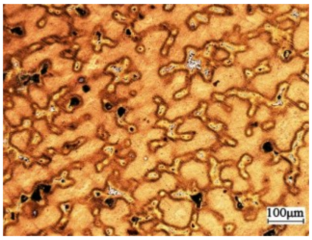

Fig. 23. Alloy CuSn8, ceramic mould, 100x

Fig. 24. Alloy CuSn8Ni1, metal mould, 100x

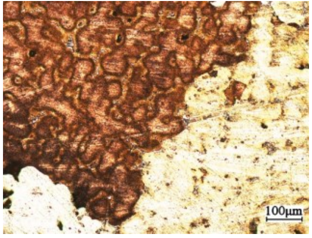

Fig. 25. Alloy CuSn8Ni1, ceramic mould, 100x

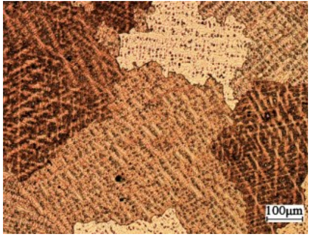

Fig. 26. Alloy CuSn8Ni3, metal mould, 100x

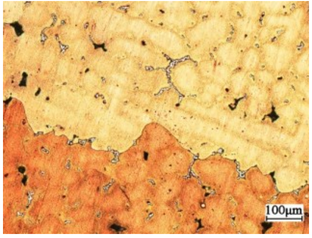

Fig. 27. Alloy CuSn8Ni3, ceramic mould, 100x

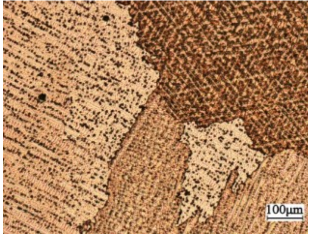

Fig. 28. Alloy CuSn8Ni5, metal mould, 100x

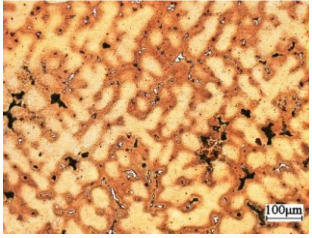

Fig. 29. Alloy CuSn8Ni5, ceramic mould, 100x

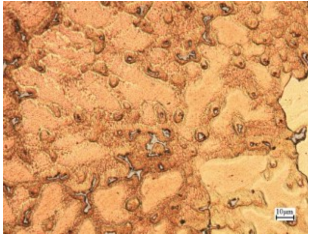

Fig. 30. Alloy CuSn8Ni3, metal mould, 500x

Fig. 31. Alloy CuSn8Ni3, ceramic mould, 500x

Changes in the microstructure can also be observed when comparing the surfaces of castings solidifying in metal moulds and in ceramic moulds. In castings solidifying in a ceramic mould, apart from the obvious dendrite growth, also a more complete process of residual liquid crystallisation in interdendritic spaces can be observed.

A detailed investigation of this area requires an in-depth analysis, which will be the subject of further research. Continuing metallographic investigations, selected samples of the alloys analysed were examined with SEM-EDS scanning microscopy with microanalysis performed in selected points. The selected findings of the examinations are presented in Fig. 32 and Table 5 for CuSn10Ni3 alloy, and in Fig. 34 and Table 6 for CuSn8Ni3 alloy. Distributions of Cu, Sn and Ni is presented in a chart form in Fig. 33 and 35.

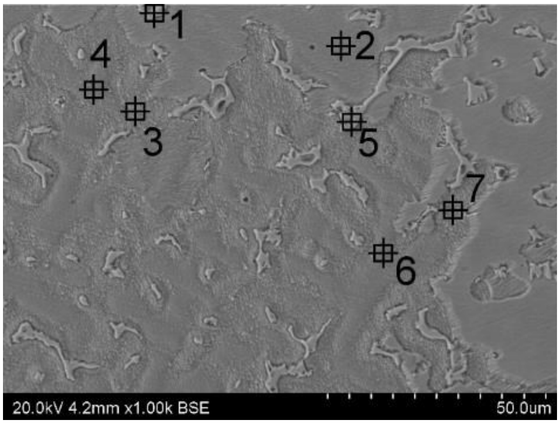

Fig. 32. The SEM-EDS image of the surface of alloy CuSn10Ni3 (metal mould) with indicated microanalysis points (Table 5)

Table 5.
The results of microanalysis in microareas of Fig. 32

	Wt %			Atom %		
pt	**Ni**	**Cu**	**Sn**	**Ni**	**Cu**	**Sn**
pt 1	5.89	59.44	34.67	7.56	70.45	22.00
pt 2	3.53	92.29	4.18	3.89	93.84	2.28
pt 3	2.93	84.12	12.96	3.36	89.27	7.36
pt 4	3.38	93.81	2.81	3.70	94.78	1.52
pt 5	5.41	62.71	31.88	6.84	73.23	19.93
pt 6	3.58	93.25	3.17	3.92	94.36	1.72
pt 7	2.99	83.40	13.61	3.44	88.80	7.76

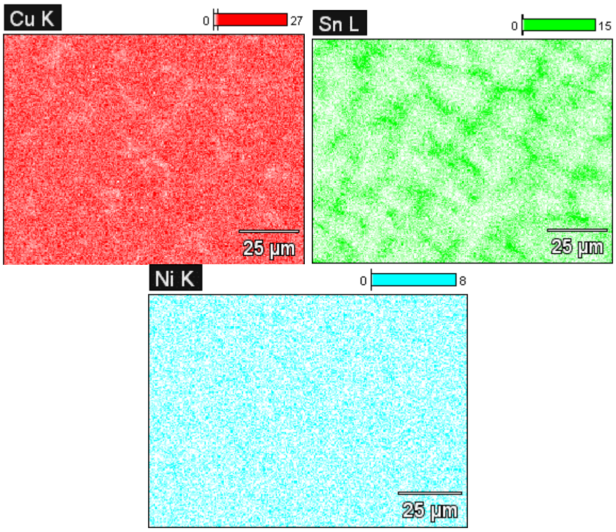

Fig. 33. The SEM-EDS image of the surface of alloy CuSn10Ni3. Maps of main constituents: Cu, Sn, Ni

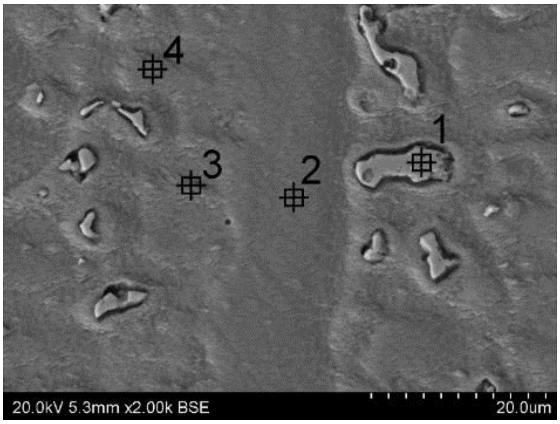

Fig. 34. The SEM-EDS image of the surface of alloy CuSn8Ni3 (metal mould) with indicated microanalysis points (Table 6)

Table 6.
The results of microanalysis in microareas of Fig. 34

	Wt %			Atom %		
pt	**Ni**	**Cu**	**Sn**	**Ni**	**Cu**	**Sn**
pt 1	5.92	57.47	36.61	7.67	68.85	23.48
pt 2	3.60	96.40	-	3.89	96.11	-
pt 3	2.79	90.65	6.60	3.07	93.29	3.64
pt 4	3.25	91.38	5.37	3.60	93.47	2.94

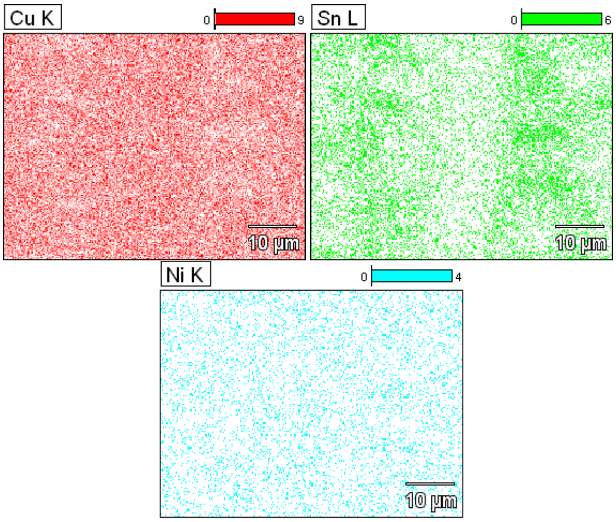

Fig. 35. The SEM-EDS image of the surface of alloy CuSn8Ni3. Maps of main constituents: Cu, Sn, Ni

It should be concluded from the chemical composition analysis of visible precipitates that nickel added to alloys Cu-Sn-Ni occurs both in the metallic matrix i.e. in the solution of tin in α-copper, and in precipitates seen on the background of the solution. These precipitates can be identified, on the basis of the obtained results and analysis of the literature [17], as intermetallic phases Cu_9Sn_3Ni. Tin - as usually in bronzes - indicates a tendency for segregation. The obtained results confirm this tendency, since the lowest tin concentration is observed in dendrite axes and successive increase in interdendritic spaces. The presented charts are visualising the distribution of alloy components.

Generally the influence of Ni with Sn is stronger than of Cu [18]. It results, from thermodynamic calculations of the Cu-Sn-Ni system, that Ni indicates strongly controlled diffusional increase of phases: $(Cu,Ni)_6Sn_5$ and $(Cu,Ni)_3Sn$, by joining various solutions of Cu(Ni) with Sn in a solid state [5, 18].

7. Results of tests of mechanical properties of alloys Cu-Sn-Ni

The observed changes in the solidification and cooling of the alloys analysed should result in changes of their mechanical properties. At this stage of research, changes in tensile strength, elongation A_5 and hardness of castings of alloys CuSn10Ni and CuSn8Ni made in a metal mould were chosen to be evaluated. After preparing the samples, hardness was tested with the Brinell method and the static tensile test of round samples in the as-cast state was carried out. The test results are shown in Figs. 36-37.

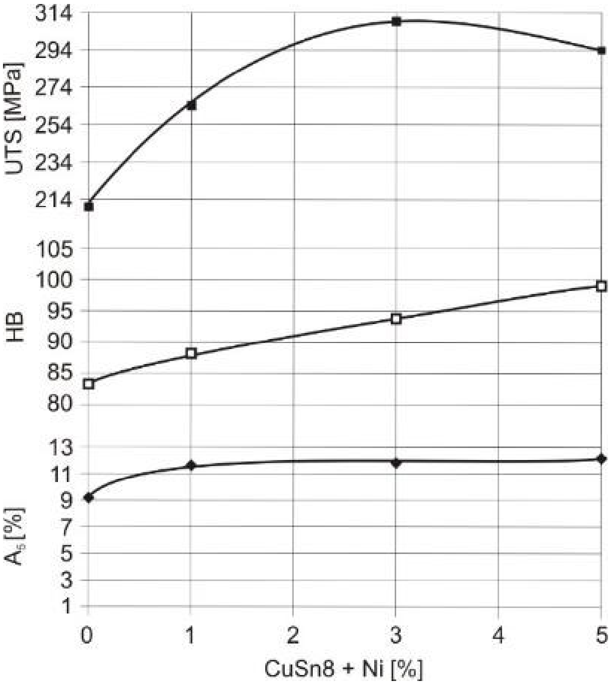

Fig. 36. Impact of nickel on mechanical properties of alloy CuSn8Ni

The data presented in Figs. 23 and 24 show that the nature of impact of nickel in the alloys analysed is similar, regardless of the tin share in the bronze. An increase in mechanical properties was obtained at a nickel addition of 3 %. Above this value, nickel does not show any increase in strength UTS and elongation A_5, it only causes an increase in hardness.. 3% addition of nickel allows to decrease the tin content to 8% without worsening the alloy properties.

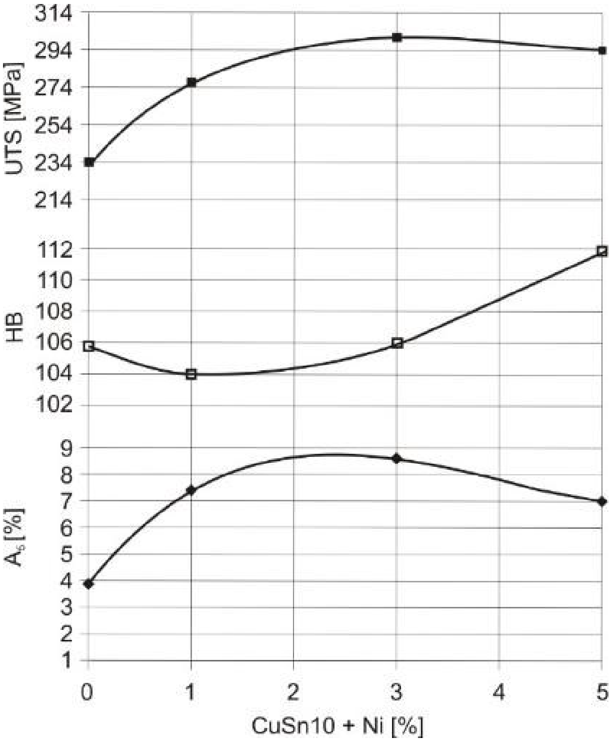

Fig. 37. Impact of nickel on mechanical properties of alloy CuSn10Ni

8. Conclusions

The conducted tests of tin bronzes with varied additions of nickel showed a number of changes concerning crystallisation, developing the macro- and microstructure and mechanical properties. Nickel added within a range from 1 to 3 % causes a linear increase in the crystallisation start temperature of alloys Cu-Sn-Ni. The revealed macrostructure of alloys shows the sensitivity of this group of alloys to impact conditions of the mould walls, as well as to varied nickel additions. Depending on the alloy composition within the casting, the formation of wall crystals with the radial orientation and equiaxed crystals with a varied grain size on the casting cross section was revealed. However, the nickel addition is crucial to the macrostructure, i.e. the grain type and size. The obtained results indicate a strong correlation of the nickel addition with the tin share in the alloy. For bronze CuSn10 the most favourable macrostructure occurs for a nickel addition of 3 %, whereas for alloy CuSn8 for 1 % of Ni. For higher values a grain growth occurs in the alloys analysed. Not only cause nickel additions an intensive impact in the macro, but also in the microscale. The distinct dendritic structure of α-Cu with a nickel addition changes to form precipitates in the dendrite area and in interdendritic spaces. Also changes in the microstructure occur at significantly varied conditions of the solidification and cooling of the castings (metal mould versus ceramic mould). Not only a growth of dendrites was observed in castings from ceramic moulds but also a more complete crystallisation process of the residual liquid in interdendritic spaces. The test results indicate that in the tin bronzes analysed, nickel causes a tendency to form intermetallic phases type Cu_9Sn_3Ni.

Generally, the influence of Ni with Sn is stronger than of Cu [18]. Nickel indicates strongly controlled diffusional increase of intermetallic phases in the Cu-Sn-Ni system, by joining various solutions of Cu(Ni) with Sn in the solid state.

The strength test results indicate a similar nature of impact of nickel in alloys analysed, regardless of the tin share in the bronze. At nickel additions of 3 % the UTS, A_5 and HB increase, while above this value only hardness increases. Applying the nickel addition in amount of approximately 3% it is possible to decrease the tin content from 10% to 8%, not worsening significantly properties of the alloy.

Taking the high price of tin into account, it seems appropriate from the standpoint of economy and the aim of optimisation of mechanical properties, to restrict the nickel addition to tin bronzes to the range from 2 to 4 %.

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