ARCHIVES OF METALLURGY AND MATERIALS
Volume 56 2011 Issue 1
DOI: 10.2478/v10172-011-0017-9

Ł.J. WIERZBICKI*, W. MALEC*, J. STOBRAWA*, B. CWOLEK*, B. JUSZCZYK*

STUDIES INTO NEW, ENVIRONMENTALLY FRIENDLY Ag-Cu-Zn-Sn BRAZING ALLOYS OF LOW SILVER CONTENT

BADANIA NOWYCH, EKOLOGICZNYCH SPOIW TWARDYCH Ag-Cu-Zn-Sn O NISKIEJ ZAWARTOŚCI SREBRA

The paper present selected results of the research conducted for elimination of toxic cadmium from silver based brazing alloys of Ag-Cu-Zn-Cd type. The investigations were conducted with nine new alloys of constant, low silver content (25%) and diversified copper (38.8-46%), zinc (19-32%) and tin (3-10%) contents. Tin was selected as potentially the best cadmium substitute basing on literature review and analysis of equilibrium systems.

For examinations and tests a series of ingots in laboratory scale was manufactured, as well as some ingots in pilot scale for the selected, most promising alloys. Complex metallographic examinations of the brazing alloys samples produced in various conditions were made as well as analyses of their phase composition. Also mechanical properties of the samples both in ambient and in elevated temperatures were examined, and physical and technological properties and usability of the alloys were determined. The last stage of the study covered laboratory trials of brazing using the selected alloys.

Basing on the results it can be said that there is a possibility to substitute selected cadmium containing silver-based alloys with environmentally friendly alloys of Ag-Cu-Zn-Sn type of relatively low silver content. Low range of melting point was reached, as preliminary assumed. Mechanical properties of the studied alloys strongly depend on temperature, and present limited plasticity in room temperature, while at high temperature (over 500°C) present superplasticity. The examined alloys show good spreadability and the brazing tests confirmed their good reactions both with copper and brass base in a wide temperature range.

Keywords: cadmium, silver, environmentally friendly alloys, brazing alloys, mechanical properties, microstructure, phase composition

W niniejszym artykule przedstawiono wybrane wyniki prac, których celem jest wyeliminowanie toksycznego kadmu ze srebrowych spoiw twardych typu Ag-Cu-Zn-Cd. Badaniami objęto 9 nowych gatunków stopów o stałej, niskiej zawartości srebra (25%) oraz zróżnicowanej zawartości miedzi (38,8-46%), cynku (19-32%) oraz cyny (3-10%). Cyna została wytypowana, na podstawie analizy literaturowej oraz układów równowagowych, jako potencjalnie najlepszy zamiennik kadmu.

Wytworzono szereg wlewków w skali laboratoryjnej oraz dla wybranych, najbardziej obiecujących gatunków spoiw, wlewki w skali półtechnicznej przeznaczone do badań i prób. Przeprowadzono kompleksowe badania metalograficzne próbek spoiw wytworzonych w różnych warunkach oraz dokonano analizy składu fazowego. Wykonano także badania właściwości mechanicznych próbek zarówno w temperaturze otoczenia jak i podwyższonej oraz badania właściwości fizycznych, technologicznych i użytkowych. W ostatnim etapie pracy przeprowadzono laboratoryjne próby lutowanie przy zastosowaniu wybranych spoiw.

Uzyskane wyniki badań pozwalają stwierdzić, że możliwe jest zastąpienie wybranych gatunków spoiw srebrowych kadmowych stopami ekologicznymi z grupy Ag-Cu-Zn-Sn o stosunkowo niskiej zawartości srebra. Uzyskano, zakładany we wstępnym etapie prac, niski zakres temperatury topnienia. Właściwości mechaniczne badanych stopów silnie zależą od temperatury, charakteryzują się one ograniczoną plastycznością w temperaturze pokojowej, by w wysokiej temperaturze (ponad 500°C) wykazywać cechy nadplastyczne. Badane spoiwa charakteryzują się dobrą rozpływnością, a próby lutowania wykazały, że dobrze reagują zarówno z podłożem miedzianym jak i mosiężnych w szerokim zakresie temperatury.

1. Introduction

Many grades of very good and popular silver-based brazing alloys of high cadmium content are produced all over the world for many years already and they are mainly applied in brazing of stainless steel, copper, nickel and their alloys, as well as precious metals alloys. Application of cadmium in those materials as the main alloy addition results from its favourable properties, such as low melting point, resistance to atmospheric corrosion as well as good plasticity and plastic workability [1-5].

---

* INSTITUTE OF NON-FERROUS METALS, 44-100 GLIWICE, 5 SOWIŃSKIEGO STR., POLAND

Cadmium, however, despite its merits, is also a strongly toxic element. Both its fumes and compounds are poisonous, since the metal cumulates in living organisms, mainly in a liver, kidneys and lungs, and can result in cancerogenic and teratogenic effect. Therefore, for a long time already various countries and organisations have been trying to introduce limitations in application of cadmium and other harmful elements. Also European Union takes such measures. The introduced in 1976 already Directive no 76/769/EEC (with amendments of 1991) refers to the limitations in launching and using some of hazardous substances and preparations. In 1996 the Directive 96/61/EC was published on integrated pollution prevention and control, and in 2003 the Directive 2002/95/EC restricting the use of hazardous substances in electrical and electric equipment, however putting this Directive into operation is still delayed [6-10].

It is the reason why search for substitutes is conducted in many branches of industry (especially in metallurgy) for many years already, to eliminate cadmium and its compounds from industrial practice and from circulation in natural environment. One of the directions pursued is focused on new brazing alloys which can substitute silver-based brazing alloys with cadmium content.

To analyse possibilities for production of substitutes of silver-based brazing alloys with cadmium content it was necessary to characterise at first currently operating and successfully used materials.

Currently there are several standardized alloys of Ag-Cu-Zn-Cd group on the market of diversified contents of alloy components. They are gathered in two main documents in European EN 1044 and American ANSI/AWS A5.8/A5.8M:2004 standards (Table 1). Silver content in those alloys usually is between 20 and 50%, copper from 15 to 40%, zinc from 15.5 to 28% and cadmium from 13 to 27%. Those materials are used in brazing of almost all nickel, iron and copper alloys, as well as many precious metals. They are highly valued in many branches of industry (heating, cooling, air-conditioning and mining industry) for their brazing properties, such as capabilities to fill up the gaps, good wettability of surface and adhesion, but most of all for relatively low melting and brazing temperature, the lowest among silver-based alloys. Their solidus temperatures are within the range 600 to 640°C, while liquidus in the range from 620 to 760°C, and their density from 9 to 9.5 g/cm^3. Zinc, cadmium and tin reduce melting point in those alloys. Zinc additionally reduces cost, while tin increases wettability. Cadmium increases plasticity and flowing power. Usually those alloys are made in a form of strips, powder, paste or as a compound of layered products [1-5, 11-14].

TABLE 1

Silver-based brazing alloys with cadmium addition Ag-Cu-Zn-Cd

Symbol		**Composition [%]**				**Temp. solidus/ liquidus [°C]**	**Brazing temp. [^{o}C]***
		Ag	**Cu**	**Zn**	**Cd**		
short code	EN ISO 3677:1995	**according to PN-EN 1044**					
AG301	B-Ag50CdZnCu-620/640	49-51	14-16	14-18	17-21	620/640	635-745
AG302	B-Ag45CdZnCu-605/620	44-46	14-16	14-18	22-26	605/620	620-730
AG303	-Ag42CdCuZn-610/620	41-43	16-18	14-18	23-27	610/620	–
AG304	B-Ag40ZnCdCu-595/630	39-41	18-20	19-23	18-22	595/630	ok. 610
AG305	B-Ag35CuZnCd-610/700	34-36	25-27	19-23	16-20	610/700	702-843
AG306	B-Ag30CuCdZn-600/690	29-31	27-29	19-23	19-23	600/690	ok. 680
AG307	B-Cu30ZnAgCd-605/720	24-26	29-31	25,5-29,5	15,5-19,5	605/720	680-760
AG309	B-Cu40ZnAgCd-605/765	19-21	39-41	23-27	13-17	605/765	ok. 750
UNS	AWS classification	**according to ANSI/AWS A5.8:2004**					
P07450	BAg-1	44-46	14-16	14-18	23-25	607/618	618-760
P07500	BAg-1a	49-51	14,5-16,5	14,5-18,5	17-19	627/635	635-760
P07350	BAg-2	34-36	25-27	19-23	17-19	607/702	702-843
P07300	BAg2a	29-31	26-28	21-25	19-21	607/710	710-843
P07251	BAg-27	24-26	34-36	24,5-28,5	12,5-14,5	605/745	745-860
P07252	BAg-33	24-26	29-31	26,5-28,5	16,5-18,5	607/682	681-760

*Data from Lucas Milhaupt, Inc. (WHX Corporation), BrazeTec (Umicore AG & Co. KG)

The literature review showed that substitution of silver-based and cadmium containing brazing alloys with other alloys, taking into account their very good properties and wide applications, can be difficult. In theoretical discussions it was considered to substitute those alloys with materials of Ag-Cu group with addition of such elements as zinc, antimony, tin, indium, as well as silver-less alloys, e.g. of the Cu-Zn group with phosphorus addition. It seems, however, that the best solution is to replace cadmium in Ag-Cu-Zn-Cd alloys with other, more environmentally friendly, element. Therefore, the studies for development of substitutes of those alloys were conducted with new configurations of alloys of Ag-Cu-Zn group with addition of tin, which seems to be the most suitable to replace cadmium because of its properties [13-19].

The alloys of Ag-Cu-Zn-Sn group are manufactured for many years already and in some of the applications are used as a substitute for silver-based cadmium alloys. Broadening of that group with new grades seems to be the simplest way to reach the research objective. Currently there are several silver-based alloys of that group which are used for brazing iron alloys (including stainless steel), copper, brass, bronze and others, wherever cadmium application is forbidden (e.g. direct contact with food). The standardised grades of those alloys usually contain, beside silver (from 25 to 60%) also from 21 to 40% of copper, from 14 to 33% of zinc and 2 to 5% of tin (Table 2). Their solidus temperatures are within the range 620 to 680°C, while liquidus in the range from 655 to 760 °C. Brazing temperature range is usually between 650 and 900 °C. Their density is at the level 8.0 to 8.6 g/cm^3. They create strong and plastic joints. Tin addition decreases melting point of the alloys and improves flowing power and corrosion resistance [1-2, 11-14].

The main objective of the study is to produce new alloys of properties and applications similar to the silver-based alloys with cadmium addition, at the same time at lower cost of production and product itself, which would substantially broaden the group of environmentally friendly substitutes. Considering the fact, however, that those materials show limited plastic workability, and time consuming process of their production and high metal prices, i.e. high product price, the task is not easy. Currently the alloys and brazing alloys are more often designed to meet customers, often very specific, requirements.

The research is mostly focused on examination of properties and structure of newly-produced materials, their behaviour during deformation in room and elevated temperatures, influence of temperature on properties and structure. Additional important aspect of the investigations is to study brazing properties, including laboratory tests of brazing.

TABLE 2

Cadmium-free silver-based brazing alloys Ag-Cu-Zn-Sn

Symbol		**Composition [%]**				**Temp. solidus/ liquidus [°C]**	**Brazing temp. [°C]***
		Ag	**Cu**	**Zn**	**Sn**		
short code	EN ISO 3677:1995	**according to PN-EN 1044**					
AG101	B-Ag60CuZnSn-620/685	59-61	22-24	12-16	2-4	620/685	–
AG102	B-Ag56CuZnSn-620/655	55-57	21-23	15-19	4-6	620/655	652-760
AG103	B-Ag55CuZnSn-630/660	54-56	20-22	20-24	1,5-2,5	630/660	ok. 660
AG104	B-Ag45CuZnSn-640/680	44-46	26-28	23,5-27,5	2-3	640/680	677-813
AG105	B-Ag40CuZnSn-650/710	39-41	29-31	26-30	1,5-2,5	650/710	710-843
AG106	B-Cu36AgZnSn-630/730	33-35	35-37	25,5-29,5	2-3	630/730	ok. 710
AG107	B-Cu36ZnAgSn-665/755	29-31	35-37	25,5-29,5	1,5-2,5	665/755	ok. 740
AG108	B-Cu40ZnAgSn-680/760	20-22	34-36	30-34	1,5-2,5	680/760	ok. 750
UNS	AWS classification	**according to ANSI/AWS A5.8:2004**					
P07563	BAg-7	55-57	21-23	15-19	4,5-5,5	618/652	652-760
P07401	BAg-28	39-41	29-31	26-30	1,5-2,5	649/710	710-843
P07380	BAg-34	37-39	31-33	26-30	1,5-2,5	649/721	721-843
P07454	BAg-36	44-46	26-28	23-27	2,5-3,5	646/677	677-813
P07253	BAg-37	24-26	39-41	31-35	1,5-2,5	688/779	779-885

*Data from Lucas Milhaupt, Inc. (WHX Corporation), BrazeTec (Umicore AG & Co. KG)

2. Material for the investigation and experimental

The study covered 9 new alloys of the Ag-Cu-Zn-Sn group of relatively low, constant silver content (25 %) and changing content of other alloy additions. Planned and obtained chemical compositions of the materials are presented in Table 3.

TABLE 3

Examined material

Grade of alloy	Chemical analysis result [%]			
	Ag	Cu	Zn	Sn
Ag25Cu43Zn29Sn3	24,3	42,3	30,4	3,0
Ag25Cu41,2Zn27,8Sn6	24,4	40,5	29,7	5,4
Ag25Cu38,8Zn26,2Sn10	24,1	39,6	27,1	9,3
Ag25Cu46Zn26Sn3	24,1	45,8	26,9	3,2
Ag25Cu46Zn23Sn6	24,5	45,4	24,1	5,9
Ag25Cu46Zn19Sn10	25,6	44,5	20,2	9,7
Ag25Cu40Zn32Sn3	23,1	41,1	32,4	3,4
Ag25Cu40Zn29Sn6	24,2	40,6	29,6	5,5
Ag25Cu40Zn25Sn10	24,0	40,7	26,2	9,1

The examined alloys were made in a laboratory using resistance furnace with graphite crucible of capacity 1700 g Ag. Pure metals (copper and electrolytic zinc, tin in a form of ingots) were used as a charge material as well as initial alloy of the following composition Ag56Cu22Zn17Sn5. Protective cover was used in every melt, in a form of dried charcoal. The alloys were cast in a form of rods of 7 mm diameter into cast iron mould.

Microstructure of the alloys was examined with an optical microscope (Olympus GX71) and scanning electron microscope with energy dispersive attachment (LEO Gemini 1525 with Roentec V-ray microanalyser). Plasticity was assessed during the test of compression of samples in a form of cylinders of dimensions ø6×7 mm in ambient and elevated to 500°C temperatures and with the deformation rate of about 2×10^{-3} s^{-1} (testing machine Intron 4505/5500R). The samples after compression test were examined for microstructure and phase composition. Thermal effects during heating up and cooling down at the rate of V=10 K/min were also studied with differential thermal analysis (Bähr DTA 702 system). The samples were placed in alundum crucible, and as a comparative material an Ag sample was used. Specific density was determined (AccuPyc 1330 V2.01 Micromeritics), electric conductivity (SigmaTest 2069 Foerster), hardness HV5/30 (Dia Testor 2RC Wolpert). Also studies into spreadability of the alloys were performed. Three different bases were used (copper, brass and nickel sheet), 4 different temperatures (760, 780, 810, 850°C) and universal Flux 16. The experiments were conducted in the air atmosphere in resistance furnace of capacity 15 l. Duration of the test was 6 minutes. Also test of furnace brazing of the copper and brass sheets in a form of strength testing samples was conducted using a lap joint. Brazing temperature was 900°C, and universal Flux 16 was used.

3. Results

Metallographic examinations of the alloys in the cast state showed their diversified microstructure which depends mainly on chemical composition of individual grades of alloys, rate of cooling during casting and place of observation (Fig. 1-5). The common feature of all the examined materials, however, was their typical casting dendrite structure. In most of the cases smaller dendrites were produced because of the high cooling rates applied, but with better formed main and secondary axes (Fig. 1-3). In some pictures precipitates on grain boundaries were observed. Occasionally also casting defects were observed.

The conducted analysis of chemical composition in microregions (Fig. 6-8) and studies of the phases by X-ray diffraction method (Fig. 8-9) have shown that the main structural components of the alloys are:

- terminal solid solution of copper, zinc and tin in silver – phase (Ag)
- terminal solid solution of silver, zinc and tin in copper – phase (Cu)
- phase present in the Cu-Zn system as well as in the Ag-Zn system, which contains relatively high mass of tin (about 14 %) - phase (β),

The contents of the elements in individual phases varied depending on the applied conditions of casting.

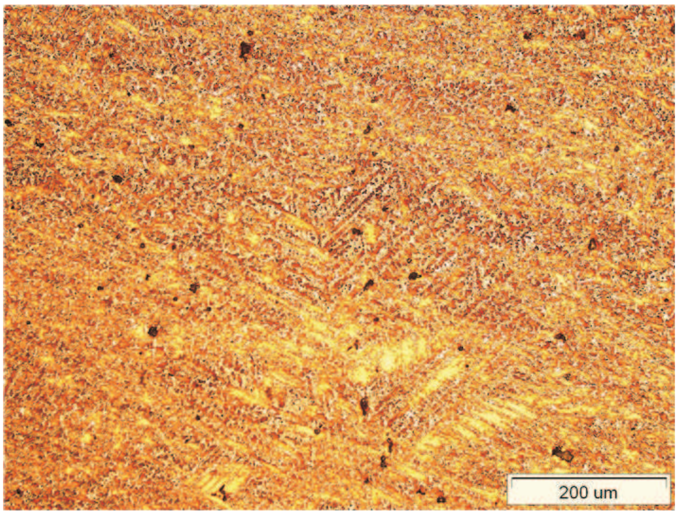

Fig. 1. Microstructure of Ag25Cu46Zn26Sn3 alloy in a cast state

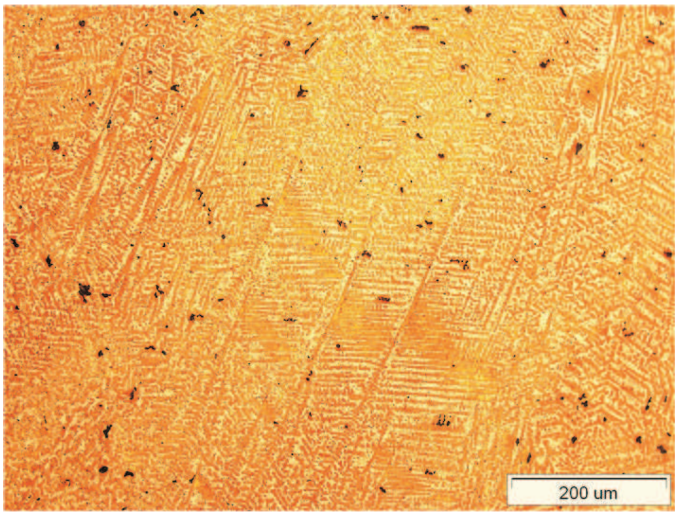

Fig. 2. Microstructure of Ag25Cu46Zn23Sn6 alloy in a cast state

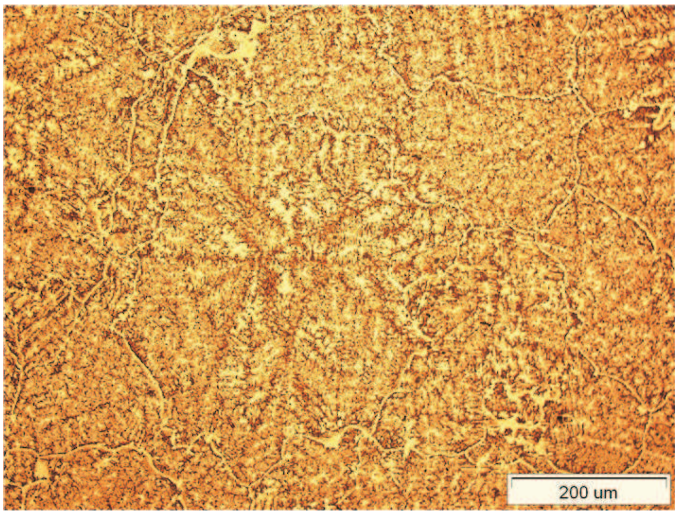

Fig. 3. Microstructure of Ag25Cu40Zn25Sn10 alloy in a cast state

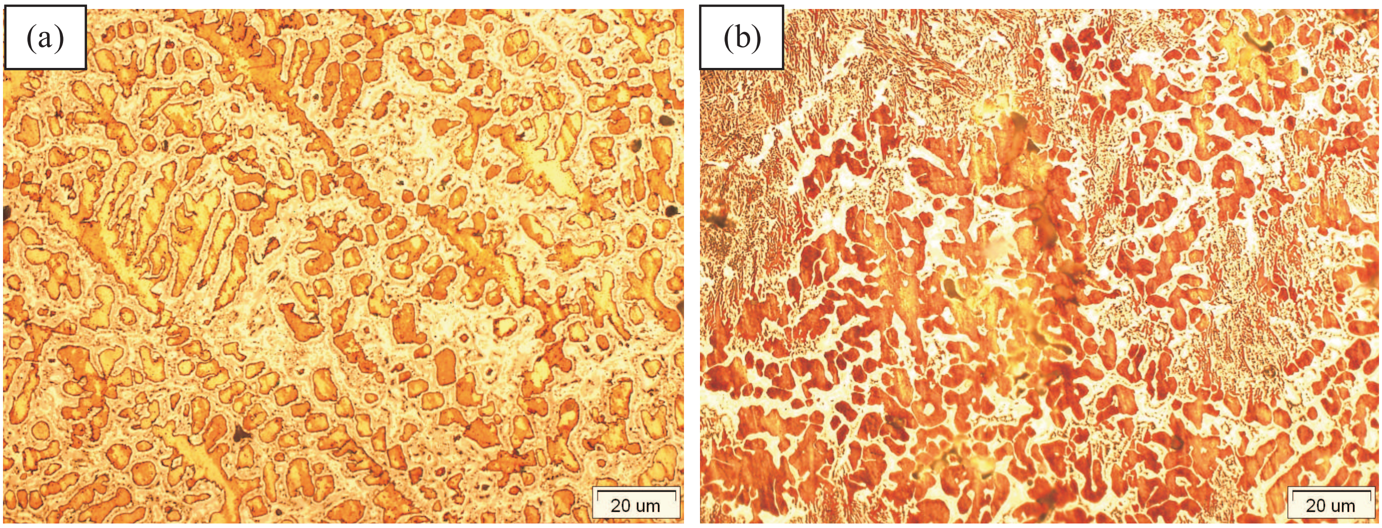

Fig. 4. Microstructure of Ag25Cu46Zn23Sn6 alloy in a cast state in the top (a) and bottom (b) part of the ingot

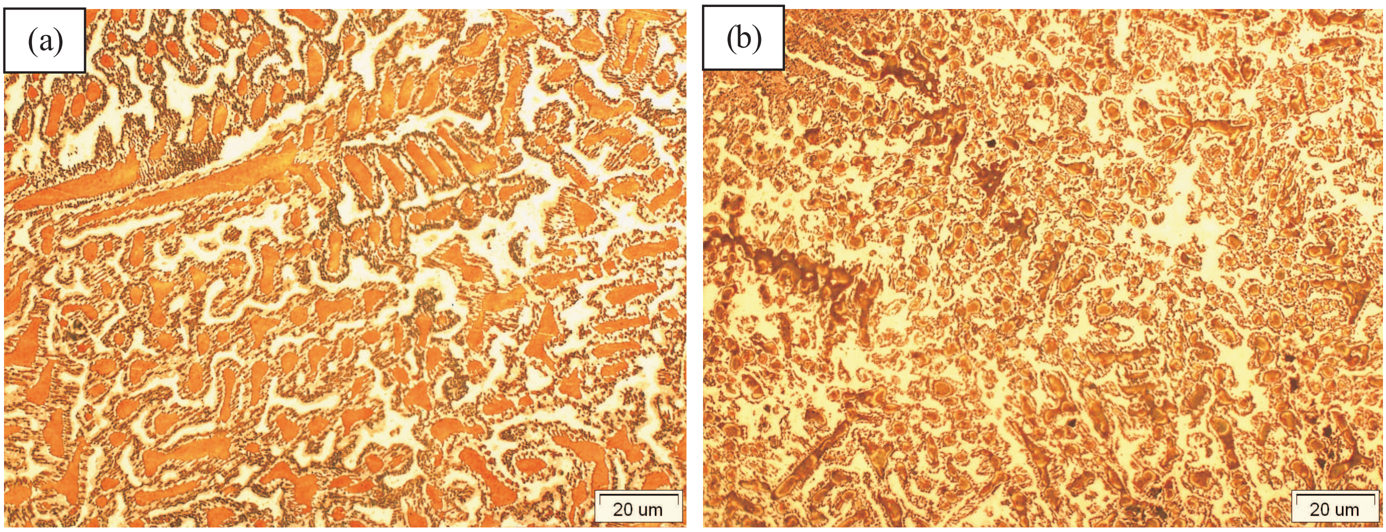

Fig. 5. Microstructure of Ag25Cu46Zn19Sn10 alloy in a cast state in the top (a) and bottom (b) part of the ingot

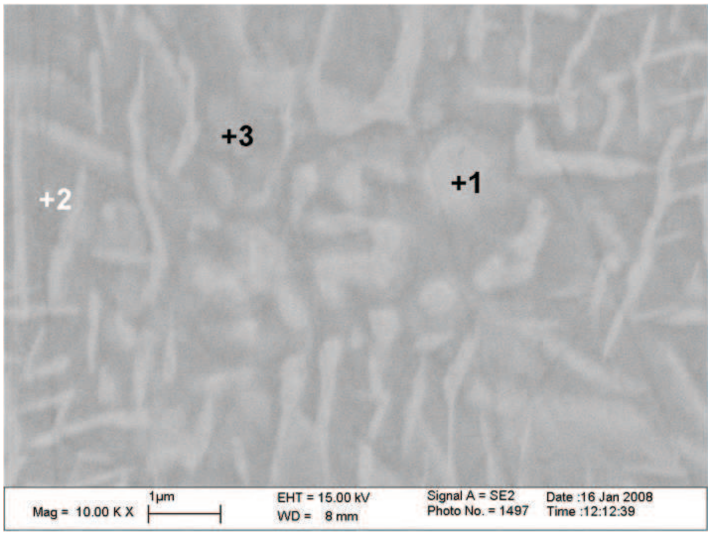

Fig. 6. Electron image and analysis of chemical composition of Ag25Cu41,2Zn27,8Sn6 alloy precipitates: point 1 – Ag78,6Cu7,1Zn14,3; point 2 – Ag9,7Cu51,6Zn32,9Sn5,8; point 3 – Ag10,2Cu50,1Zn28,7Sn11

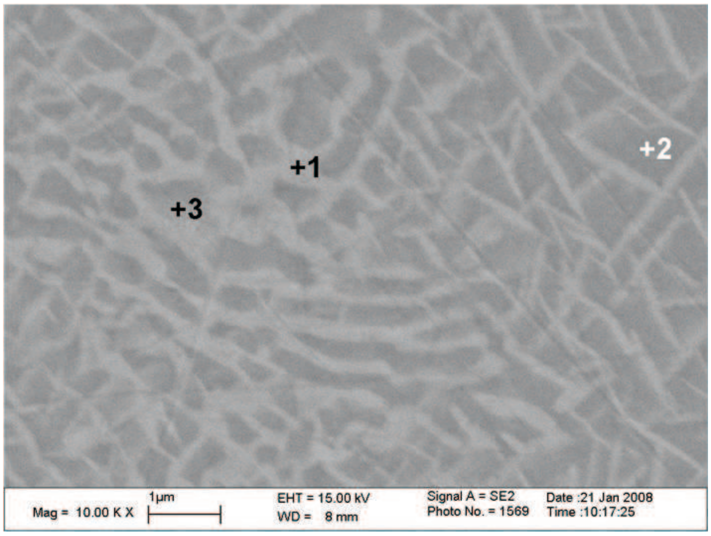

Fig. 7. lectron image and analysis of chemical composition of Ag25Cu40Zn32Sn3 alloy precipitates: point 1 – Ag60,8Cu16,2Zn23; point 2 – Ag7,7Cu51,2Zn38,2Sn2,8; point 3 – Ag22Cu39,9Zn31,7Sn6,4

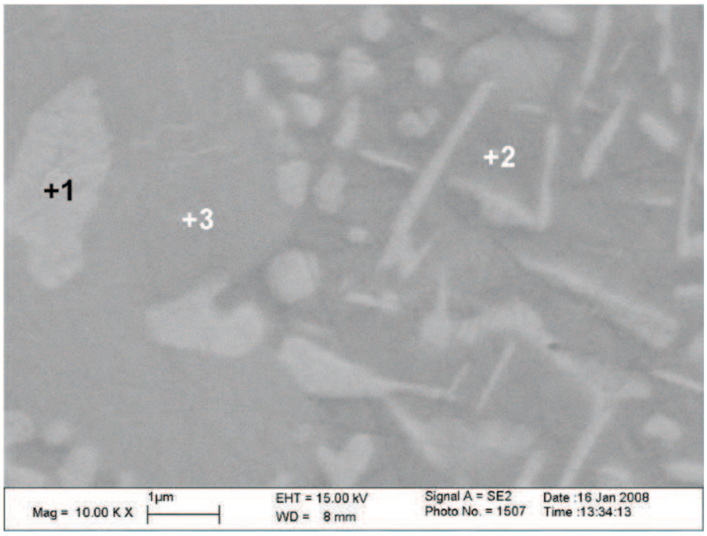

Fig. 8. Electron image and analysis of chemical composition of Ag25Cu38,8Zn26,2Sn10 alloy precipitates: point 1 – Ag80,3Cu5,7Zn14; point 2 – Ag10,2Cu51Zn34,9Sn3,9; point 3 – Ag14,6Cu45Zn25,3Sn15,1

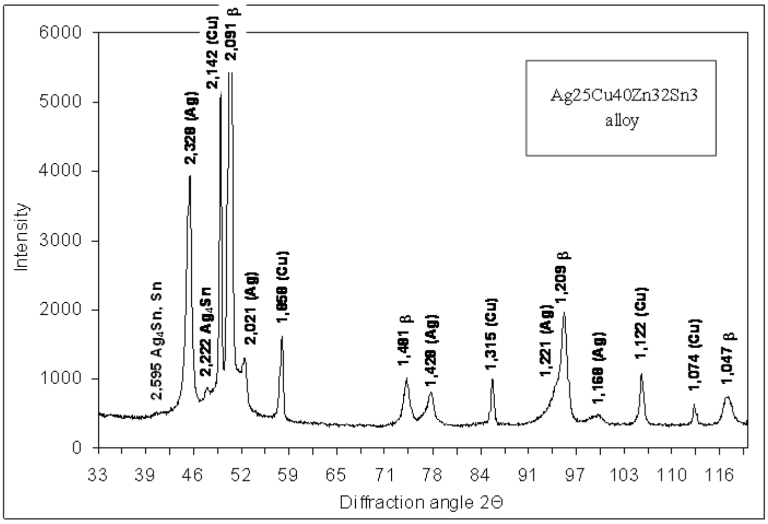

Fig. 9. Diffraction pattern of Ag25Cu40Zn32Sn3 alloy

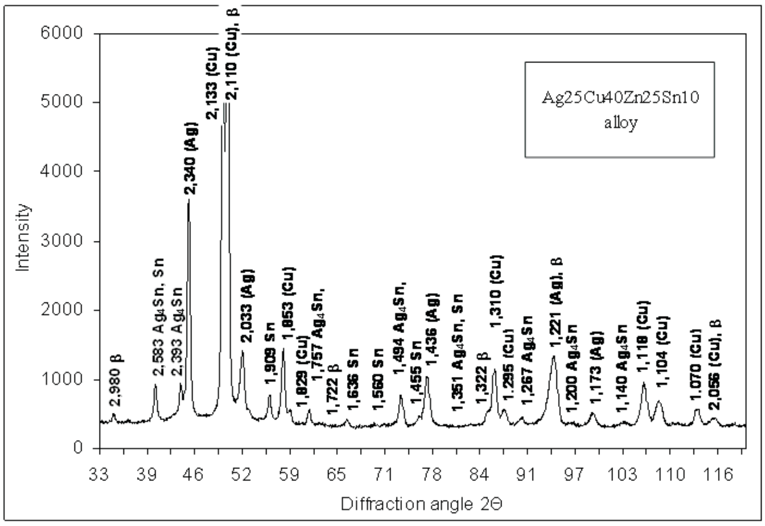

Fig. 10. Diffraction pattern of Ag25Cu40Zn25Sn10 alloy

TABLE 4

Properties of new brazing alloys Ag-Cu-Zn-Sn

Grade of alloy	**temperature [°C]**		**Density [g/cm^3]**	**Electrical conductivity [MS/m]**	**Hardness HV5**	**shortening of the sample [%]***
	solidus	**liquidus**				
Ag25Cu43Zn29Sn3	650	790	9,04	9,79	148	11,9
Ag25Cu41,2Zn27,8Sn6	610	760	9,13	8,27	192	6,1
Ag25Cu38,8Zn26,2Sn10	560	715	9,12	5,42	285	1,4
Ag25Cu46Zn26Sn3	620	795	9,10	8,93	112	16,0
Ag25Cu46Zn23Sn6	575	780	9,10	7,02	154	7,2
Ag25Cu46Zn19Sn10	550	745	9,18	5,34	239	3,1
Ag25Cu40Zn32Sn3	650	760	9,03	11,02	177	4,7
Ag25Cu40Zn29Sn6	610	740	9,11	8,30	222	1,9
Ag25Cu40Zn25Sn10	560	710	9,08	5,35	293	1,6

**unit shortening of the sample in the compression test of slowly cooled material*

Properties of the alloys, such as solidus/liquidus temperature, specific density, electric conductivity, Vickers HV5 hardness and deformability (shortening of the sample in compression test) were also examined. The results are presented in Table 4. In all the examined alloys relatively low range of solidus/liquidus temperature was observed, between 550-800°C. The lowest values were reached for the alloys with 10% tin addition. The solidus temperatures was about 550°C, while liquidus in the range from 710 to 745°C. With the decrease of tin content in the alloys to 6% and 3% the increase of both solidus and liquidus temperature was observed (by about 50°C and 100°C, respectively). The broadest range of solidus/liquidus temperature was reached for the Ag25Cu46Zn23Sn6 and Ag25Cu46Zn19Sn10 alloys (in both cases about 200°C). Specific density in all the alloys was similar – in the range 9.0-9.2 g/cm^3. Electric conductivity was highly diversified. The values were in the range from 5.3 to 11 MS/m. The best conductivity was observed in Ag25Cu40Zn32Sn3 alloy. Also HV5 hardness results showed high diversity. With the increase of tin addition significant increase in material hardness is observed (each 3% addition of Sn increases the hardness on average by 50%). The lowest value was reached for Ag25Cu46Zn26Sn3 alloy (112 HV5), and the highest for Ag25Cu40Zn25Sn10 (293 HV5). Studies into deformability in the compression test showed that the alloys of lower tin content have the best deformability (12-16% shortening), in other cases shortening of the sample was below 6%. The best result was reached for Ag25Cu46Zn26Sn3 alloy.

The scope of the conducted investigations covered also analysis of influence of deformation temperature (in compression test) on the value of yield stress. Figures 11 and 12 show the results, as exemplified by two alloys in which most advantageous set of properties was reached and which are characteristic for the whole tested batch. Compression test showed that in the room temperature the investigated alloys present various plastic properties. In the case of Ag25Cu40Zn32Sn3 alloy in temperature of 20°C reduction of 30% was reached at the stress of 700 MPa. The increase of compression temperature brings significant decrease of the value of yield stress, which above 400°C reaches relatively low value (below 50 MPa) at very high reduction of about 70%. In the temperature of 500°C plastic flow of the material is observed as indicated by the flat curve. In the case of Ag25Cu40Zn25Sn10 alloy in room temperature very low plasticity is observed. The maximum value of stress is 900 MPa at 12% reduction. With the increase of compression temperature the behaviour of the alloy is similar to the previous one. In the temperature of 500°C almost totally flat curve of stress/deformation can be observed at very large reduction which exceeds 70%. In every of 9 examined alloys the obtained results indicate possibilities for their easy shaping by classical plastic working methods in the temperature of 400°C already.

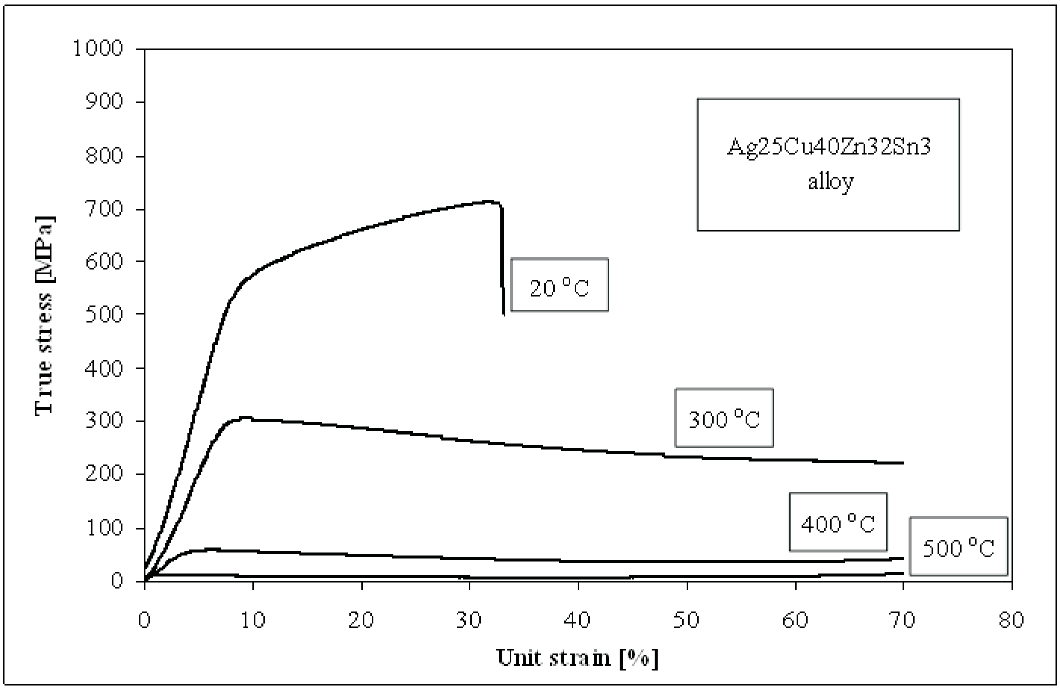

Fig. 11. Stress-deformation relation in compression of samples made of Ag25Cu40Zn32Sn3 alloy in various temperatures

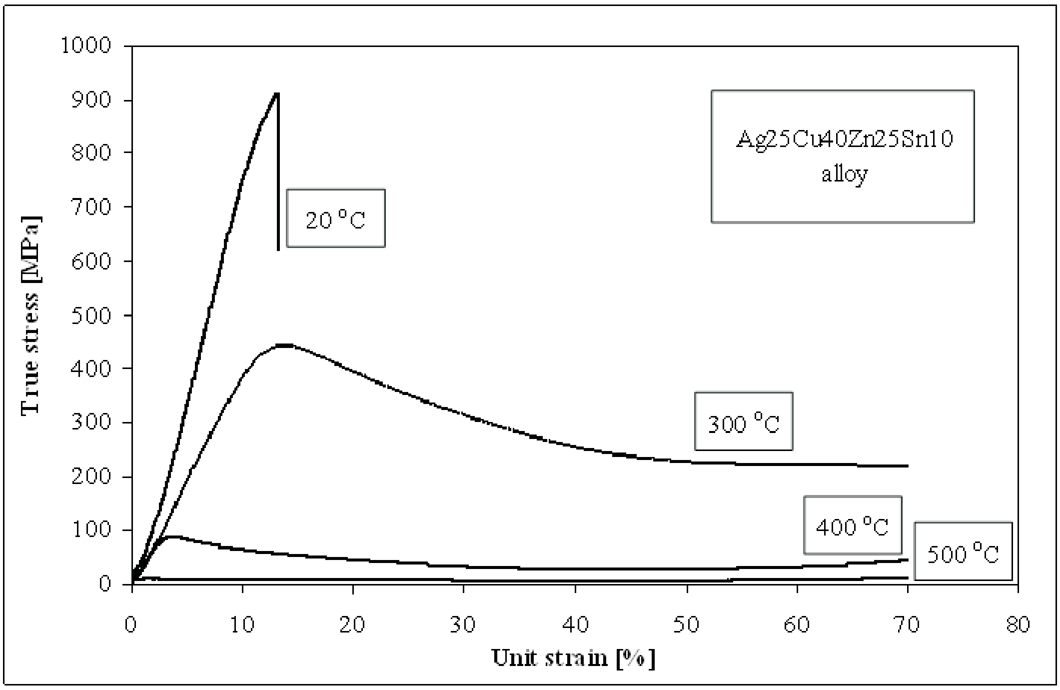

Fig. 12. Stress-deformation relation in compression of samples made of Ag25Cu40Zn25Sn10 alloy in various temperatures

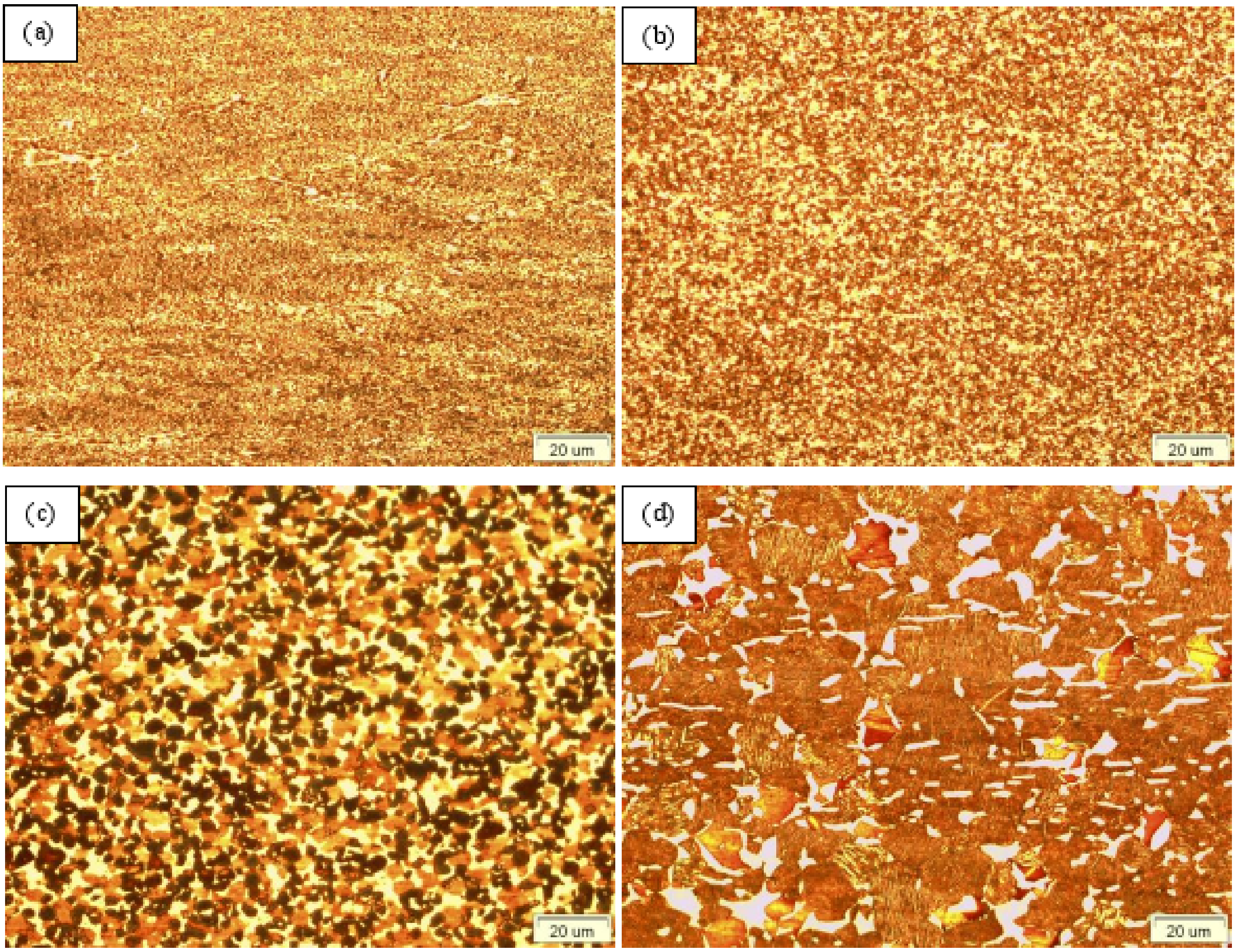

Fig. 13. Microstructure of Ag25Cu41,2Zn27,8Sn6 alloy after deformation in compression test at temperature of: (a) 300°C, (b) 400°C, (c) 450°C, (d) 500°*C*

The examined materials after hot deformation presented strongly diversified microstructure (Fig. 13). The sample compressed in the temperature of 300°C showed traces of original structure with high degree of deformation (Fig. 13a). In the temperature of 400°C, however, strong fragmentation of the structure is observed resulting from processes of recrystallization (Fig. 13b), while over 450°C processes of structure reconstruction are observed as well as coagulation of recrystallized grains, and effects of grain growth are noticeable (Fig. 13c-d).

The alloys were also subjected to the investigation of spreadability in various conditions (Table 5). Figure 14 shows examples of the images of the samples. The best spreadability was reached for the alloys melted on nickel base (about 1200 mm^2), the lower was observed on copper base (600 mm^2 on average), while on the brass base the spreadability was 10 times lower than for nickel sheet.

The final stage of investigations covered tests for brazing copper and brass with selected alloys. The examples of microstructure can be seen in Figure 15.

TABLE 5

Results of spreadability test in selected temperatures of the alloys of Ag-Cu-Zn-Sn group

Symbol	Test temp. [°C]	Spreadability [mm^2]		
		Cu	Brass	Ni
Ag25Cu43Zn29Sn3	850	657	176	1256
Ag25Cu41,2Zn27,8Sn6	810	415	114	1258
Ag25Cu38,8Zn26,2Sn10	780	982	115	1518
Ag25Cu46Zn26Sn3	850	455	143	1075
Ag25Cu46Zn23Sn6	850	809	265	1270
Ag25Cu46Zn19Sn10	810	431	276	1102
Ag25Cu40Zn32Sn3	810	284	103	888
Ag25Cu40Zn29Sn6	810	498	91	1257
Ag25Cu40Zn25Sn10	760	857	82	1295

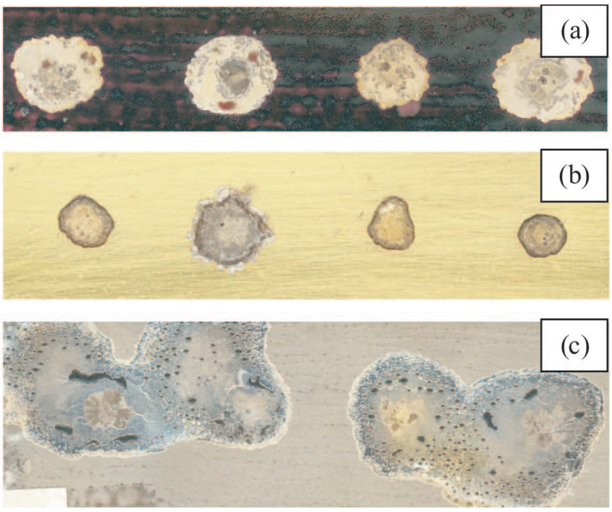

Fig. 14. Sample after spreadability test in temperature of 810°C on the base of: (a) copper, (b) brass (c) nickel. Examined alloys (from left): Ag25Cu41,2Zn27,8Sn6; Ag25Cu46Zn19Sn10; Ag25Cu40Zn32Sn3; Ag25Cu40Zn29Sn6

The tests were conducted with 2 grades of the alloys: Ag25Cu40Zn32Sn3 and Ag25Cu40Zn25Sn10. In both cases joints of good quality were produced, as confirmed in a tensile test. Breaking of the sample occurred outside the joint area. Tensile strength for copper and brass was 220 i 320 MPa, respectively. No defects in joints in a form of cracks, bubbles or intrusions were observed.

4. Conclusions

The conducted investigations into 9 new grades of alloys of Ag-Cu-Zn-Sn group indicate that they may represent potential, environmentally friendly substitutes of cadmium containing brazing alloys. Basing on the results it is possible to select two alloys of most favourable set of properties, i.e. Ag25Cu40Zn32Sn3 and Ag25Cu40Zn25Sn10 alloys, and to formulate the following conclusions:

- the studies confirmed possibility for replacing selected cadmium containing alloys with environmentally friendly alloys of Ag-Cu-Zn-Sn group of limited silver content (25%),

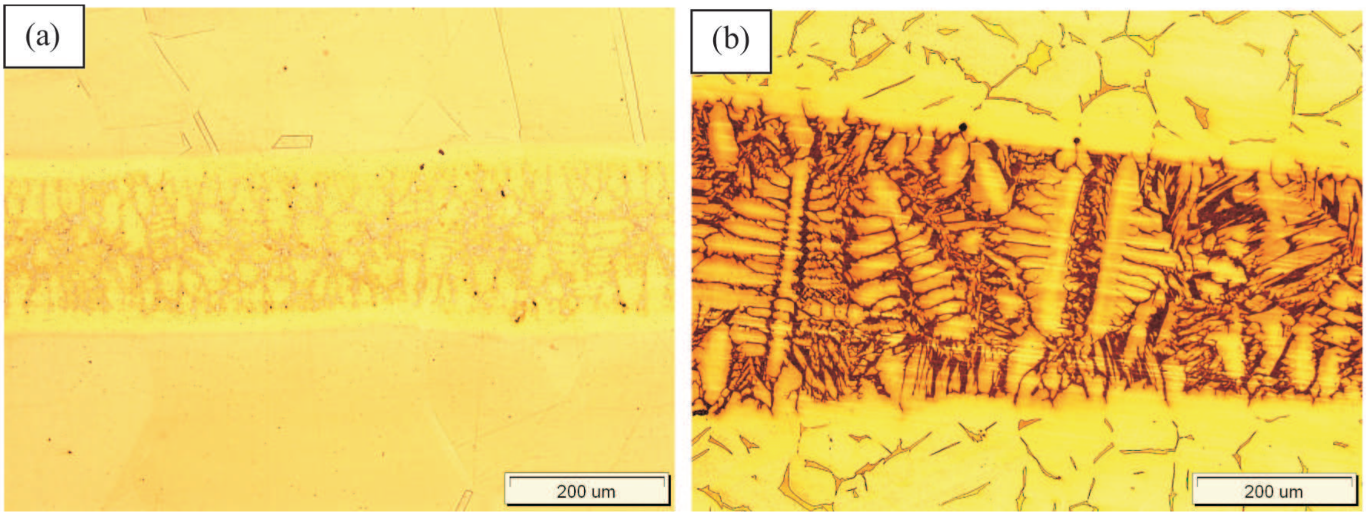

Fig. 15. Microstructure of samples after brazing test with Ag25Cu40Zn32Sn3alloy on the base of: (a) copper, (b) brass

- low level of melting point for all the examined alloys was reached (the lowest liquidus value at the level of 700°C), which directly results in advantageous brazing temperature,
- the studied alloys react well with copper, brass and nickel base in a wide temperature range, presenting good spreadability which confirms their usability as materials for brazing applications,
- the conducted brazing tests brought positive results, and joints of good quality were produced, showing high strength and no typical defects,
- classic plastic working of the examined alloys by rolling or extrusion and drawing is possible in elevated temperature only, where material becomes more prone to deformation; a significant increase in plasticity observed above 350°C already is related to the process of recrystallization,
- mechanical properties of the investigated alloys are strongly dependant on temperature, the alloys are characterised by limited plasticity in room temperature, while in the temperature above 500°C they show superplasticity; in the test of cold compression the best results were reached with materials of lowest tin content (3%),
- the main structural components of the alloys are: terminal solid solution of copper, zinc and tin in silver (Ag), terminal solid solution of silver, zinc and tin in copper (Cu) and phase (β) present in the Cu-Zn system as well as in the Ag-Zn system, which contains relatively high mass of tin (about 14%), the content of elements in the phases changed with casting conditions,
- microstructure of the cast samples depended on chemical composition and cooling rate, and in all cases presented dendritic character,

The study conducted within the scope of the project PBR no R07 002 01 financed from national scientific fund in the years 2006–2009

REFERENCES

[1] M.M. Schwarz, Brazing, ASM International, Metals Park, (2003).

[2] T. Radomski, A. Ciszewski, Lutowanie, WNT, Warszawa, (1985).

[3] D. Brandon, W. D. Kaplan, Joining processes. An introduction, John Wiley and Sons, Chichester, (1997).

[4] J. Nowacki, M. Chudziński, P. Zmitrowicz, Lutowanie w budowie maszyn, WNT, Warszawa, (2007).

[5] J. Pilarczyk, Poradnik inżyniera. Spawalnictwo, tom 2, WNT, Warszawa, 565-646, (2005).

[6] E. Gawęda, Kadm i jego związki w środowisku pracy – zagrożenia, ocena ryzyka zawodowego, Bezpieczeństwo pracy 10 (387), 17-19 (2003).

[7] S. Kumorkiewicz, J. Pruś, I. Surma, Kadm (Cd), Wydział Farmaceutyczny Collegium Medicum, http://farmacja.cm-uj.krakow.pl/.

[8] Dyrektywa Rady WE 76/769/EWG z dnia 27 lipca 1976 r. w sprawie zbliżenia przepisów ustawowych, wykonawczych i administracyjnych Państw Członkowskich odnoszących się do ograniczeń we wprowadzaniu do obrotu i stosowaniu niektórych substancji i preparatów niebezpiecznych (Dz.U. W.E. L262/201 z 27.09.1976, s. 317).

[9] Dyrektywa Rady UE nr 96/61/WE z dnia 24 września 1996 r. dotycząca zintegrowanego zapobiegania zanieczyszczeniom i ich kontroli (Dz.U. L 257 z 10.10.1996, str. 26).

[10] Dyrektywa 2002/95/WE Parlamentu Europejskiego i Rady z 27.01.2003 w sprawie ograniczenia stosowania

niektórych niebezpiecznych substancji w sprzęcie elektrycznym i elektronicznym (Dz.U. L 37 z 13.2.2003, s. 19).

[11] PN-EN 1044, Lutowanie twarde. Spoiwa, (2002).

[12] ANSI/AWS A5.8/A5.8M:2004, Specification for filler metals for brazing and braze welding, (2004).

[13] Lucas Milhaupt, Inc. - WHX Corporation, materiały informacyjne.

[14] BrazeTec – Umicore AG & Co. KG, materiały informacyjne.

[15] B. Cwolek, R. Życiński i inni, Opracowanie bezkadmowego stopu o niskiej zawartości srebra (do 40% Ag) i obniżonej temperaturze likwidusu (poniżej 650°C), spr. IMN nr 5856/I-II/2001-2002, niepublikowane.

[16] J. Stobrawa, Ł. Wierzbicki, L. Ciura, W. Malec, B. Cwolek, B. Juszczyk, Podatność do przeróbki plastycznej stopów Ag-Cu-Zn-Sn, Hutnik **76** (8), 442-445 (2008).

[17] J. Stobrawa, Ł. Wierzbicki, L. Ciura, W. Malec, B. Cwolek, Microstructure and properties examination of cast Cu-Zn-Ag-Sn brazing alloys, Congress and Exhibition on Advanced Materials and Processes MSE, Nürnberg (2008).

[18] M.F. Arenas, V.L. Acoff, R.G. Reddy, Physical properties of selected brazing filler metals, Science and Technology of Welding and Joining **9**, 5, 423 (2004).

[19] S.C. Dev, C.S. Sivaramakrishnan, An indigenous technology for a silver brazing alloy, Materials and design **17**, 2, 75-78 (1996).

Received: 20 August 2010.