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EXPERIMENTAL STUDY OF THE Cu-Al-Sn PHASE EQUILIBRIA, CLOSE TO THE COPPER ZONE

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Abstract

The ternary Cu-Al-Sn phase diagram is the base for several important types of alloys, with relevant industrial interest and applications. The knowledge of the melting/solidification alloys characteristics are determinant for their preparation and properties control. However, there is a lack of experimental information on the ternary phase diagram, at high temperature. In this work, several alloys, with high copper content and additions of Al, up to 10%, and Sn, up to 14% (in wt%), were studied by thermal analysis and by isothermal phase equilibria determination. The alloys liquidus and solidus lines and the binary α + β phase field, at 800 °C, are presented for the studied range of compositions.

Keywords**:** *Phase diagram; Cu-Al-Sn; Thermal analysis; Phase equilibria.*

1. Introduction

Aluminum bronzes are copper-based alloys used in a great number of engineering structures in applications such as shipbuilding and aerospace. They have been commonly accepted because they possess superior properties such as oxidation and corrosion resistance, excellent tribological and mechanical properties such as high strength, fatigue and corrosion resistance comparing to other bronzes [1-7]. The aluminum bronzes, according to their function, can be produced in a wide range of different compositions depending on the desired properties. In addition to aluminum, which ranges normally from 5% to 14%, this type of alloys has usually other alloying elements such as tin and nickel [8, 9]. Addition of Sn to aluminum bronze alloys allows the improvement of, for example, the corrosion and abrasion resistance. Due to these properties, Cu-Al-Sn alloys are used in marine and aircraft industry, such as the engines, ships propellers and landing gears e.g.

There are several research works concerning ternary Cu-Al-Sn alloys. Chakrabarty *et al*. [7] studied the phase equilibria in the system Cu-Al-Sn, near the copper side, in detail up to the maximum temperature of 580 ºC. The copper rich zone was studied by Watanabe *et al.* [8] by several experimental techniques, like thermal analysis and microstructural sample characterization, up to 700 °C. The low temperature phase equilibria near the copper side was also studied by Leach et al. [10]. Kotadia *et al.* studied the effect of the ultrasonic irradiation on the solidification of a vertical zone (10Cu-90Al to 10Cu-90Sn, in wt.%) with increasing Sn contents. An extensive work was done by Mirković *et al*. with the presentation of a calculated *liquidus* surface of the Al-Sn-Cu phase diagram [11]. Details of phase transformations are presented but not in the copper side of the diagram. Cherian *et al*. studied the effect of Sn content on the microstructure, hardness and wear properties of surface refined Cu-Sn bronze alloys [12]. However, for the high temperature phase transformations, near the copper side, including the melting/solidification behavior, there is a lack of experimental information in the literature [7, 11].

In this work, alloys of Cu-Al-Sn, near the copper side region (up to 10%Al and 14%Sn in wt%), were studied for their phase equilibria at 800 ºC and for the melting characteristics.

2. Experimental procedure

The Cu-Al-Sn alloys were prepared by melting, employing high purity base elements (³ 99.9% purity) in an induction furnace (3000 Hz) under an inert atmosphere (He). The samples were remelted

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twice in order to promote a good homogenization. After melting, the samples were heat treated at 800 ºC during 24 hours, for the equilibrium phase's formation and chemical composition homogenization. Then the samples were slowly cooled to room temperature. After the heat treatment, the chemical compositions of the different alloys were determined by XRF spectrometry.

All the melt and homogenized samples were characterized by DTA-TGA thermal analysis in a SDT 2960 TA Instruments. The following thermal cycle was used: first heating up to 1100 ºC (at 10 ºC/min), cooling until 500 ºC (at 20 ºC/min), a second heating step up to 1100 ºC (at 10 ºC/min) and finally a cooling stage down to room temperature at 1 ºC/min.

The equilibrium at 800 ºC was studied for different alloys. For that purpose, each sample, after the melting and homogenization stage, was submitted to a thermal treatment for phase equilibria homogenization at 800 ºC, under a reductive atmosphere, obtained by introducing samples in a closed iron box with carbon powder inside. This procedure avoided oxidation of samples during the high temperature stay. A type K thermocouple was used to measure temperature, with an accuracy of ±1.5 ºC. After a stage of 144 hours at 800 ºC, to assure the microstructural homogenization, samples were rapidly quenched in a solution of salted water, with 50 g/L NaCl, and ice at ±0 ºC. The heat-treated samples were then prepared to optical and scanning electron microscopy (SEM) observation. The equilibrium phases, at 800 ºC, were characterized in a SEM microscope and the phase chemical compositions determined by EDS analysis. The accuracy of the determination of the chemical composition is estimated as 0.5 wt. % for all the measured elements.

3. Results and discussion

The total weight change during the alloys production was always bellow 0.1 wt%, confirming that no significant changes occurred, by oxidation or other processes. Final alloys chemical composition is presented below, in tables 1 and 2. The melting and solidification behavior were studied by DTA thermal analysis.

3.1 Effect of Sn addition to a Cu-Al base alloy

A set of samples with constant Al content were selected for the melting/solidification study. The effect of Sn addition on the ternary alloys transitions, close to the melting temperature range, was studied in alloys with 0 to 6 wt% Sn, (for a constant Al content). The *Liquidus* and *Solidus* transitions temperature are presented in table 1.

The presented results were obtained in the second melting on the imposed thermal cycle of the DTA/TGA tests. No significant weight changes effect was detected during the tests. The curves for the melting of the alloys are composed by two overlapping peaks. Since there is a sequence of reactions on the–melting, the presented temperature corresponds to the peak value for each alloy (on the second a heating cycle, with an heating rate of 10 °C/min.), as is illustrated in figure 1, where DTA curves and determined transition temperatures are presented. The *Liquidus* temperature was identified by the peak value, as presented in figure 1a).

Table 2. *Alloys chemical composition (in wt%), obtained by XRF Spectrometry, and the liquidus temperature determined for each sample by DTA thermal analysis.*

Sample Nº	Composition (wt %)			*Liquidus* temperature (°C)	
	Cu	Al	Sn	Heating (10 °C/min)	Cooling (1 °C/min)
1	84.1	1	14.9	953.1	952.2
2	84.2	2	13.8	962	960.04
3	85.1	3	11.9	972.8	970.52
4	86.1	4	9.9	985.2	981.13
5	87	5	8	993.6	989.26
6	89	6	5	1011.3	1005.71
7	88	6	6	1001.3	996.01
8	89.1	7	3.9	1010.4	1003.08
9	88	8	4	1013.8	995.07
10	87	8	5	1010.3	1002.9
11	86	8	6	1004	1004.34
12	89.1	8.9	2	1032.7	1015.52
13	88	9	3	1021	1036.97
14	89	10	1	1030	1040.18

Table 1. *Alloys chemical composition (in wt%), obtained by XRF Spectrometry, and transformations temperatures.*

Sample	Composition (%)			Heating cycle		Cooling cycle	
	Cu	Al	Sn	*Liquidus*	*Solidus*	*Liquidus*	underccoling
Eutectic [1]	92.0	8.0	0.0	~1032		-	
10	88	8	4	1013.8	998.6	1001.6	10.4
11	87	8	5	1010.3	990.5	1002.2	6.2
9	86	8	6	1004	982.9	992	8.1

It is possible to verify from figure 1c) that the melting start temperatures (maintaining the Al content) decrease with the increasing of Sn in the alloys. The presented *solidus* line, corresponds to the peak value in the DTA curves, and is associated with the binary eutectic transformation occurring in this type of alloys [2]. The experimental eutectic reaction temperature evolution, with increasing Sn content, is well aligned with the binary Cu-Al transformation (1031 °C). Concerning the solidification temperature

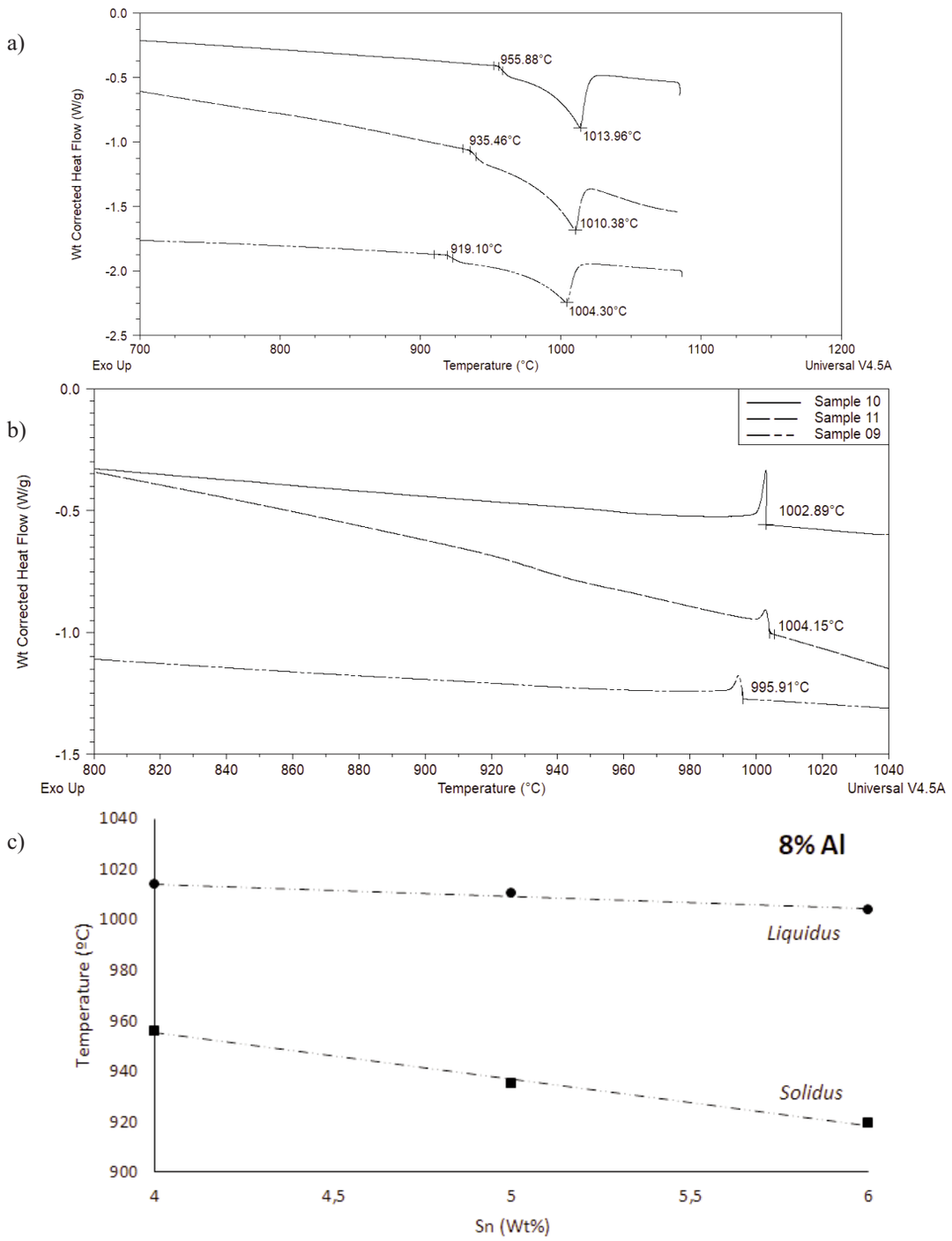


Figure 1. *Thermal analysis curves (DTA), on the second heating cycle at 10 °C/min in argon atmosphere, for samples with increasing Sn content, a) and alloy transition temperatures evolution with increasing Sn content (wt%), for a constant Al alloy content b).*

there is a decrease in the *Liquidus* temperature with the Sn content, specially between 5 and 6 wt% Sn, as presented in figure 1b). The cooling rate was of 1 °C/min. Another effect to be pointed is the relative stability of the undercooling with the amount of tin in the alloy.

3.2 Characterization of the binary α + β phase field, near the copper side

A set of 14 samples were used to describe the binary α + β phase field, at 800 °C. The obtained alloys *Liquidus* temperature and their chemical composition are presented in Table 2.

A multivariate regression analysis indicates that both Al and Sn decreases sharply the *liquidus* temperature, based on the heating cycle obtained results. The regression expression, including the melting point of pure copper (1084.9 ºC [2]), may be described as:

$$T_{Liquidus} = 1082 - 4.28\ \%\ Sn - 8.23\ \%\ Al \qquad (1)$$

(T in °C and elements in wt%)

with an $r^2 = 0.982$ and a standard error of 4.7 ºC for the estimate of the *liquidus* temperature.

Some of the studied alloys, quenched from the equilibration temperature of 800 ºC, are constituted by two-phases, a and b. The chemical compositions of the phases inside the binary (α + β) phase field, at 800 ºC, are shown in table 3. Proposed conjugated lines for that two phase field equilibrium are presented in table

Table 3. *Alloy phase compositions with the increasing of Al and decreasing of Sn.*

Sample	Element	α phase (wt. %)	β phase (wt. %)	Sample	Element	α phase (wt. %)	β phase (wt. %)
1	Al	4.28	2.79	8	Al	7.49	8.16
	Sn	6.46	17.52		Sn	2.33	5.73
2	Al	1.95	0.93	9	Al	6.6	6.58
	Sn	10.02	21.36		Sn	3.38	8.68
3	Al	3.3	1.93	10	Al	6.59	6.52
	Sn	7.96	19.56		Sn	3.15	8.72
4	Al	0.64	0.12	11	Al	6.58	6.58
	Sn	10.15	22.05		Sn	3.09	8.6
5	Al	5.19	3.83	12	Al	7.7	9.08
	Sn	5.33	15.86		Sn	1.46	3.16
6	Al	6.26	5.57	13	Al	8.29	9.53
	Sn	3.26	11.73		Sn	1.77	3.72
7	Al	5.92	3.87	14	Al	8.98	10.81
	Sn	4.27	15.49		Sn	0.49	1.1

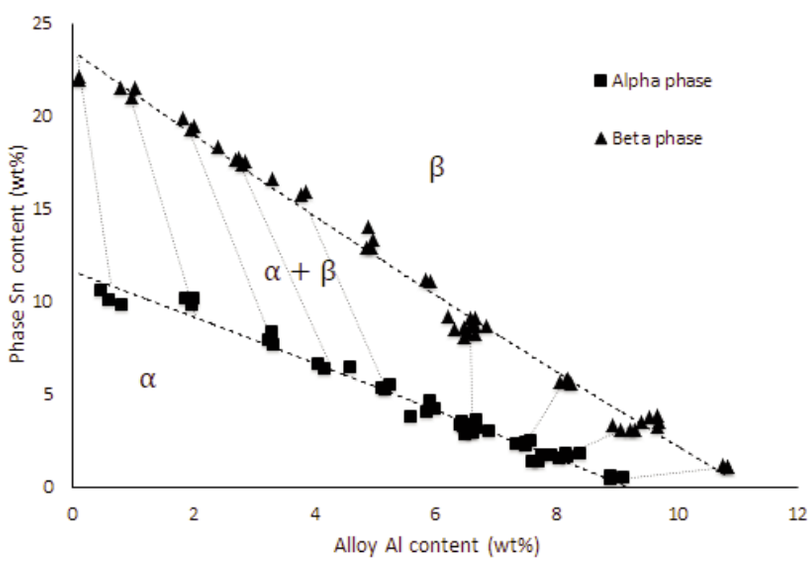


Figure 2. *Proposed conjugated lines, inside the (α + b) phase field, at 800 ºC.*

3 and Figure 2, for several alloys chemical compositions.

From the graph above it is possible to calculate the solubility limit equations:

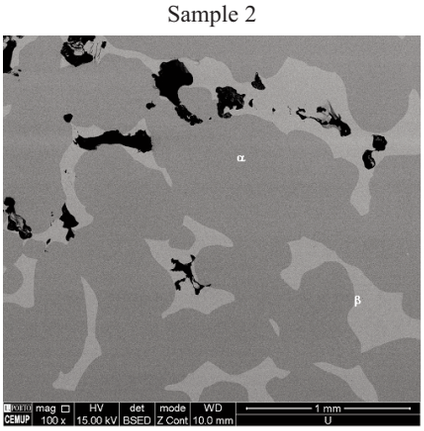
α to α+β:

$$Sn = -0.0055Al^2 - 1.216Al + 11.625 \left(r^2 = 0.977\right) \quad (2)$$

α+β to β:

$$Sn = -0.0153Sn^2 - 2.2832Sn + 23.508 \ (r^2 = 0.990) \quad (3)$$

Sample 2



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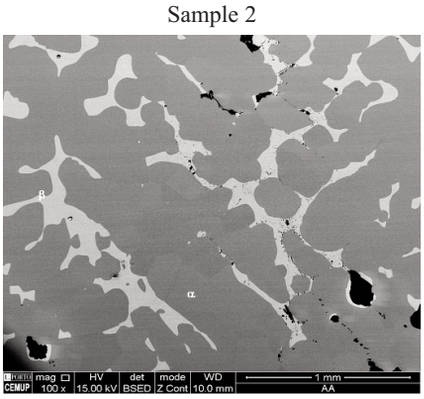

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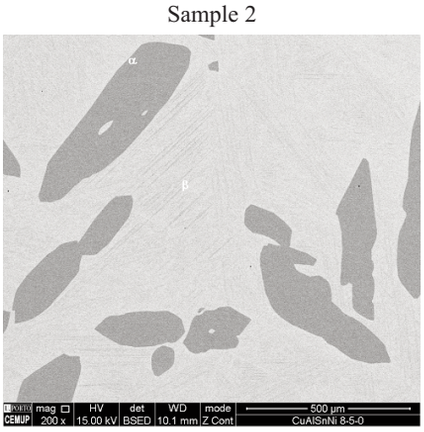

Figure 3. *Microstructure, obtained by SEM, of samples with different volume fractions of α + β phases.*

Figure 3 presents the alloy microstructures, for three samples with increasing Sn content, after homogenization at 800 ºC, and rapid quenching. All samples are in the binary phase field. The microstructure changes to a dendritic type morphology with the increase of the β phase volume fraction.

4. Conclusions

The Cu-Al alloys solidification and the effect of Sn additions were studied close to the copper side.

The melting/solidification temperatures and solid-state transformations, for several alloys, have been determined by DTA-TGA thermal analysis. A multivariate regression analysis allowed to determine the effect of the Sn addition on the *liquidus* and *solidus* lines, with a good extrapolation to the binary eutectic temperature was obtained.

Phase equilibria and chemical compositions of the phases inside the two phases (α + β) region, of the Cu-Al-Sn system, at 800 ºC, have been determined. The expressions for the chemical composition limits for both phases were determined, with a quite good accuracy.

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