www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

Arch. Metall. Mater. **68** (2023), 2, 689-696

DOI: https://doi.org/10.24425/amm.2023.142450

A. MADETKO[1*], K. SOŁEK[1], P. DROŻDŻ[1]

NUMERICAL MODELLING OF PHASE DIAGRAMS OF COPPER ALLOYS FOR OPTIMIZATION OF SEMI-SOLID FORMING

Processing of metal alloys in semi-solid state is a way of producing many near net-shape parts and nowadays is commercially successful. Particular behaviour of alloys in the partially liquid state, having non-dendritic microstructure, is a base for thixoforming processing. Processing materials in the semi-solid state concerns alloys with relatively wide solidification range. Thermodynamic modelling can be used as a one of a potential tools that allow to identify alloys with proper temperature range. It means that the key feature of alloys suitable for thixoforming is a widely enough melting range, allowing for precise control of material temperature. The data gathered from thermodynamics calculations can also pay off in the industrial thixoforming processes design. The goal of this paper is to identify copper alloys which can be successfully shaped in the semi-solid state. Apart to thermodynamic calculations, the observations on high temperature microscope was carried out. During experiments the solidus, liquidus and also deformation temperatures can be determined. An experimental work allows confirming results obtained within the confines of thermodynamic calculations and firstly to determine the deformation temperatures which are the optimal for shaping processes. The basic achievement of this work is an identification of copper alloy groups possible for shaping in the semi-solid state. At the first part of the paper, the basic criteria of suitable alloys were described. Next, both the solid fraction curves for copper alloys with different alloying elements using ProCAST software and the phase diagrams were determined to identify the solidification temperature ranges of these alloys. In the second part of these paper, the identification of the deformation temperatures was carried out with use of high temperature microscope observation.

Keywords: thixoforming; thermodynamic calculations; copper alloys; phase diagram

1. Introduction

This paper concerns the selection of copper alloys for semi-solid processes, using both the thermodynamic calculations and experimental work. Suitability of metals for thixoforming is usually referred to as a term, thixoformability. The basic criterion is a wide melting range of metal alloys.

Semi-solid metallic alloys processing was discovered in 1972 at MIT (Massachusetts Institute of Technology) by Spencer during the investigation of Sn-15% Pb viscosity [1]. This discovery initiated extensive research of semi-solid metal processing and led to the development of various processes. It can be categorized into two technological routes: thixocasting and thixoforging commonly called as thixoforming [1]. These processes allow to obtain complex shape of products (near net shaping) in a single technological operation. This is why, they use an advantage of the rheological behaviour of the alloys in the mushy zone (the temperature range between solidus and liquidus points) caused by thixotropic properties.

The amount of solid fraction in the mushy zone changes during progress of solidification process. And of course it influences on rheology of shaped metal alloys (which can be described using apparent viscosity or the flow stress parameters). The rheology changes also have very big impact on the forming processes in the semi-solid state. This is why a lot of investigations of rheological properties in this state could be found in the literature [1].

The thixoforming processes are carried out in non-isothermal conditions. Lower temperature of the shaping tools than the formed alloys can cause solidification of the material before the shaping process will be completed. In order to avoid that situation, both a relatively high solidification temperature window [2] and high shear rate of the material should be applied.

Then this paper is focused on selection of copper alloys having such feature. The copper alloys are the point of interests of the authors due to relatively rare literature data concerns to these alloys in the semi-solid state. At this state of the art, a lot

---

[1] AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AL. MICKIEWICZA 30, 30-059 KRAKOW, POLAND

* Corresponding author: madetko@agh.edu.pl

of research activities devoted to low melting point alloys [2], such as alumina and magnesium alloys, and high melting point alloys such as steels [3,4]. Moreover, alumina and magnesium alloys are shaped for industrial scale [5]. In the case of copper alloys in the context of semi-solid processing, it is very difficult to find in the literature detailed data and real industrial applications. A lot of copper alloys are characterized by low plasticity and such approach seems very promising. Additionally, copper alloys have relatively low melting point what make present technological solutions possible to use, even in the industry.

The thixoforming of copper alloys offers many advantages. Copper alloys, bronzes in particular, are very versatile. This paper presents an analysis of those alloys, which have a relatively wide solidification range. They are mainly aluminum and tin bronzes. The analysis does not take into account those alloys for which this range is relatively large, but in practice their use is difficult or impossible. Examples are beryllium bronzes, which are highly toxic in the liquid state, or lead bronzes, which in practice contain other elements (e.g. CuSn10Pb10, CuSn5Pb20). The thixoforming processes of copper alloys can be carried out on the basis of both forging or foundry technologies. In fact, thixoforging is used more often due to the higher pressures of forging presses. These processes can be carried out at lower temperatures, for which the solid fraction varies in the range of 0.5-0.7. Therefore, it is important that the solid phase content in this respect should be as little susceptible as possible to temperature changes. In the case of thixocasting processes, the solid fraction should be a little less, approximately 0.4.

In order to assess susceptibility of metal alloys for semi-solid shaping, a few parameters should be considered. First of them is difference between liquidus and solidus point which determines solidification temperature window $\Delta T^{solidus/liquidus}$. The second important parameter is the sensitivity of liquid fraction on changes of temperature $(\mathrm{d}fs/\mathrm{d}T)^{fs=0.6}$. And the third parameter is the temperature range for the solid fraction between 50 to 70% $\Delta T_{fs=0.5\text{-}0.7}$. In the thixoforming process, the optimal proportion of the solid fraction is from 50 to 70%. The apparent viscosity is optimal in these ranges, as well for this temperature the phase segregation is rather limited. Temperature processing window should be relatively wide for mushy zone, at least 15 K between 50% to 70% fraction solid. Changes of this fraction are controllable, especially in the case when the solid fraction sensitivity for this temperature window is low. Otherwise, the alloys are not sufficiently thixoformable [5,6]. The fraction solid sensitivity should be as low as possible to avoid large variations of this fraction with changes in the temperature. Determination of solid fraction as a function of temperature could be realized using thermodynamic calculation based on the analysis of the phase Gibbs energy and visualized using binary phase diagrams.

The solidification ranges of selected copper-tin and copper-aluminium alloys using both numerical simulations and physical experiments were analysed. To examine the solid fraction – temperature relationship, the thermodynamic calculations using the ProCAST package and FactSage software were used. In the case of ProCAST package, it is easy to determine the solid fraction curves on the basis of chemical composition of analysed alloys. Such results were next analysed in terms of the aforementioned criteria of thixoformability. Behaviour of selected chemical compositions was next confirmed and clarify using the phase diagrams calculated using FactSage software. These results also allow explaining an influence of some alloying components on the width of the solidification temperature windows. Among others, in this paper the thixoformability of the copper-tin alloy was analysed to identify the most suitable compositions by adding from 1 to 12% tin. At the end, an experimental work based the melting processes of small axisymmetrical samples was executed using Leica heating microscope. The physical experiments were carried for selected copper-tin and copper-aluminium alloys. During these experiments, the behaviour of the samples was observed on the high temperature metallurgical microscope. Thanks to this experiment the solidus and liquidus temperatures of selected copper alloys were confirmed and also the temperatures of samples deformation, caused by the melting process, were determined. These experiments proved correctness of thermodynamic models implemented in ProCAST and FactSAGE software. Generalizing, such apparatus could be used to test metal alloys intended for thixoforming processes.

2. Research methods

ProCASTpackege

With ProCAST package, it is possible to perform a comprehensive virtual casting process validation to predict his effects on microstructure, mechanical properties and thermal deformation. ProCAST supports decision concerning prototyping, increasing efficiency, industrial trials and lowering production costs. It can be used as a tool for solution of basic casting problems such as predicting of mould filling, alloys solidification and porosity. Thanks to the finite element method, complex problems such as deformation and residual stresses can also be predicted [7]. Special modules of this package allow to take into account also hot tearing processes and determination of thermodynamical properties of metal alloy (Fig. 1). Furthermore, special settings of models parameters for specific processes such as high/low pressure die, centrifugal, investment casting and also thixoforming process are supplied [8].

The software is organized around a manager that provides the following modules. First, the CAD model geometry is loaded into Visual-Mesh to generate a FEM mesh. The process numerical model is then set up in Visual-Cast module. The visualization of results is possible in postprocessor Visual-Viewer. Finally, the results can be analysed or exported, for further processing in another postprocessor. In the Visual-Cast module, the thermodynamic database is available for automatically determination of material properties. Before the ProCAST solver, a “data conditioner” called DataCAST is run [8].

Material properties, such as density, thermal conductivity, viscosity, the enthalpy curve and the fraction of solid curve versus temperature can be computed automatically from thermodynamic databases. The ProCAST software has implemented thermodynamic databases to calculate these properties. Such computation is based upon the chemical composition, for the different systems and the different alloying elements. Among others the calculation of Al, Fe, Ni, Ti, Mg and Cu alloys properties are possible. In the case of cooper alloys an influence of such elements as Al, B, C, Cr, Fe, Mn, Ni, P, Pb, Si, Sn, Ti, Zn is possible. Solidification process can be analysed in terms of various conditions. This is why the different solidification models such as “Scheil”, “Lever” and “Back Diffusion”, which correspond to different micro segregation conditions, are possible. During the thermodynamic database calculation, the results concerned the phase fractions, as well as the composition of each phase for each temperature, are determined. This information is not necessary for a ProCAST calculation, but it can be interesting for other purposes (e.g. growth kinetics calculations). Generally, the solid fraction curves are calculated on the basis of the minimum of the Gibb’s free energy function or the linear combination of these functions for different phases. The use of Gibb’s free energy functions to determine equilibrium phase diagrams also allows taking into account the thermal effects related to the latent heat of the solidification process.

The thermodynamic database implemented in the ProCAST software calculates the liquid fraction versus the temperature with high precision. The comparison of the liquid fraction curves shown in Fig. 3 with the range of the mushy zone shown in Fig. 4 proves the ProCAST software accuracy. The phase diagram presented in Fig. 4 was calculated using FactSAGE package.

In summary, it should be said that, the scope of the application of the thermodynamic database, implemented in the ProCAST software, was determination of the solid fraction in the mushy zone for different copper alloys. It means that this software was used to calculate the solid fraction curves shown in Fig. 3, 5, 6, 10.

FactSage software

One of the biggest fully integrated database computing systems in chemical thermodynamics is FactSage. It was introduced in 2001 and is the fusion of the FACT-Win/F*A*C*T and ChemSage/SOLGASMIX thermochemical packages [9].

FactSage was originally founded by process pyrometallurgists. Since then, it is expanded its applications to include electrometallurgy, hydrometallurgy, corrosion, ceramics, environmental studies, etc. This software package consists of a series of information, calculation modules, manipulation modules and database that allow user to access pure substances and solution database. This enables to perform a wide range of thermochemical calculations and generate graphs and tables of complex phase diagrams and chemical equilibria for multicomponent and multiphase systems [10].

There are two types of thermochemical databases in FactSage –- the compound database (pure substances) and the solution database. The View Data, Compound, and Solution modules provide the ability to list and manipulate database files. It is possible to interact with software and databases in a variety of ways, and to calculate and display thermochemical equilibria and phase diagrams in a variety of formats. FactSage offers a variety of modules that can process tabular and graphical final results, or preprocess reagent inputs for complex equilibrium calculations in Equilib. The result’s module is used to generate graphical output from Equilib calculations and create different charts from one set of balance tables [11]. For example, phase diagram sections of a general component can be generated with a wide range of axis variables. Solid/gas/matte/metal/slag equilibria can be accurately calculated, tabulated and plotted for industrial systems [9].

Generally, the phase diagrams are calculated on the basis of the minimum of the Gibb’s free energy function or the linear combination of these functions for different phases. For a binary phase diagram, such a situation can be shown in Fig. 1.

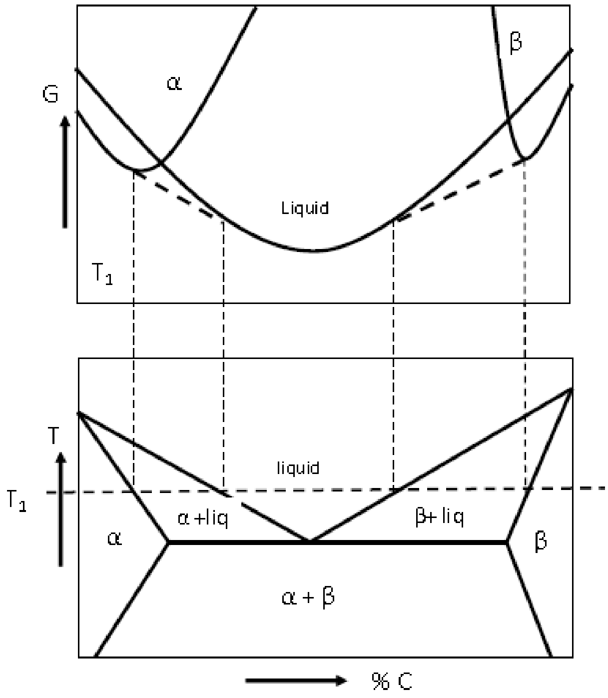

Fig. 1. Binary phase diagram with corresponding Gibb’s free energy curves for each phases

The thermodynamic database implemented in FactSAGE software gives similar binary phase diagrams with comparison to diagrams presented in the literature. But the main advantage of this software is calculation of phase diagrams for three or more components, which are not available in the literature. Such calculations give possibility of analysis of an influence of different elements content on the solidification range for multi elements systems.

In summary, it should be said that, the scope of the application the thermodynamic database, implemented in the FactSAGE software, was calculation of the phase diagrams impossible to visualize using ProCAST software. It means that this software was used to calculate the phase diagrams shown in Fig. 4, 7, 8, 9.

Leica Heating Microscope

The physical experiments were carried out using Leica heating microscope. This device use CCD camera to permanently capture test piece image. In regular time intervals, the software fetches images and analyses them. In order to do that, they are converted to true black-and-white image. The test piece is shown as black on a white background. On that basis, the contours of test piece and object carrier (baseline) are determined. Contour data is a base for founding corner angle, contact angle, cross intersection area, shape factor and also height and width of a test piece's.The image is automatically stored using given in the control software criteria. It is also possible to manually trigger the storing at any time. During the measurement, the program recognizes changing in the test piece's silhouette and stores images for the purpose of documentation. In the course of measurement, the characteristic temperatures of metal alloys can be found. Especially, it means deformation temperature, hemisphere temperature, sphere temperature and flow temperature. After the measurement, the user can determine the start of sintering of the test piece's, if appropriate. During the procedure, measured values are continuously stored and can be presented in a tabular form or as a graph.

Evaluation can be carried out at any time, but normally will follow the measurement. Evaluation mainly consists of compiling the results because the characteristic temperatures (deformation, flow, sphere and hemisphere) were determined during the measurement with exception to the start of sintering. It can be determined after the completion of the measurement. The determination of the sintering temperature is facilitated by a graph showing the sample cross-sectional area during the measurement.

It is important to present the key methods that are used in the program during calculations. The area of the test piece's is the count of all image points that are classified as belonging to the shadow of the test piece's. The measure for the difference between an ideal semicircle and the test piece's shadow is a shape factor. To determine it, first the circumference of a semicircle with the same area as the test piece's shadow is calculated. Second, the length is put into relation to the actual test piece's circumference. When the shape factor has changed by 1.5% in relation to the first image and the tracked corner angle has increased by 10% then the deformation temperature is determined. The hemisphere temperature is the first temperature at which the test piece's height is half of it is base width and shape factor is at least 0.98. The range between deformation and hemisphere temperature is the deformation range [12].

Fig. 2. Melted sample of CuSn10 tin bronze inside high temperature microscope

3. Numerical modelling of solidification temperature range of copper alloys

Semi-solid shaping is reasonable for alloys with relatively width solidification temperature range. This is why at first the copper alloys with components having significant different melting temperature were considered. One of such component is tin, which melting temperature equals approximately 232°C. Moreover, Cu-Sn alloys are classified as casting alloys having relatively low plasticity.

Another casting copper alloys are bronzes with aluminium. But for size of mushy zone, the additions of ferrous and manganese are responsible. In this case, the CuAl10Fe3Mn2 bronze was considered.

Copper-tin bronzes

Generally, bronze is an alloy defined as made of copper and another metals, most frequently tin. It can also contain aluminium, nickel, silicon, phosphorus, arsenic, zinc or manganese. It is one of the first metals known to a man. Bronze properties depend on its composition and how it is processed. It is usually golden, hard and brittle metal. It is also mellable, good conductor of electricity and heat. An important property for this paper is that some bronzes are poorly ductile [13]. At first, the calculations of solid fraction of Cu-Sn family bronzes were carried out. The results of the calculations are shown in Fig. 3. Another visualization of these results is the phase diagram of Cu-Sn alloy determined using FactSage software, presented in Fig. 4. This phase diagram shows coexistence of two phases, the liquid phase (LIQUID) and the solid phase (FCC_A1 – face-centered cubic structure), in the mushy zone for the range of 0-12 Sn content.

Phase diagrams are an important tool for presenting information about phase equilibria. For the purposes of this article, the calculations were made in the FactSage program. Temperature is on the Y-axis, and the proportion of tin in the alloy is on the X-axis. The diagram shows the phase distribution for the copper tin alloys. It confirms the previously presented dependence – an increase in the proportion of tin causes an increase in the range of the semi-solid phase, along with a decrease in the temperature necessary for the formation of this phase.

According to criteria of thixoformablity, exact solidification parameters of Cu-Sn alloys were determined. They are given in TABLE 1. They contain the solidification temperature range, fraction solid sensitivity and the temperature range for solid fraction between 50 and 70%. The fraction solid sensitivity was calculated for 0.6 solid fraction $(\mathrm{d}fs/\mathrm{d}T)_{fs=0.6}$.

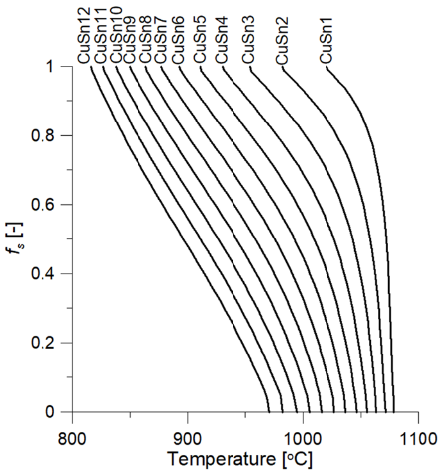

Fig. 3. Distribution of the solid fraction for the copper tin alloys

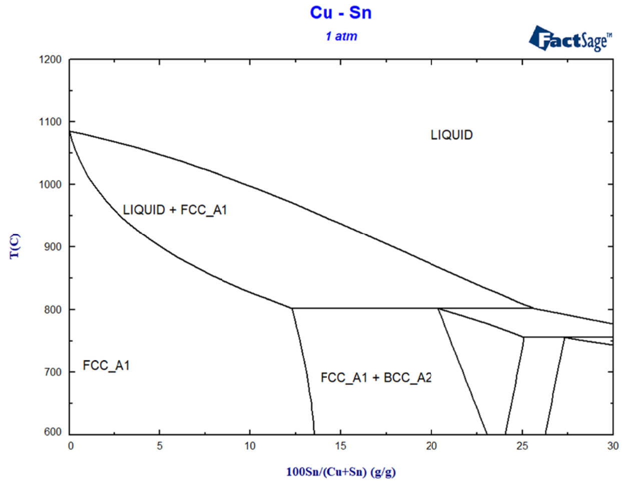

Fig. 4. Binary phase diagram of copper tin alloy

Solidification parameters of copper tin alloys are also shown on Fig. 5 in the form of appropriate curves.

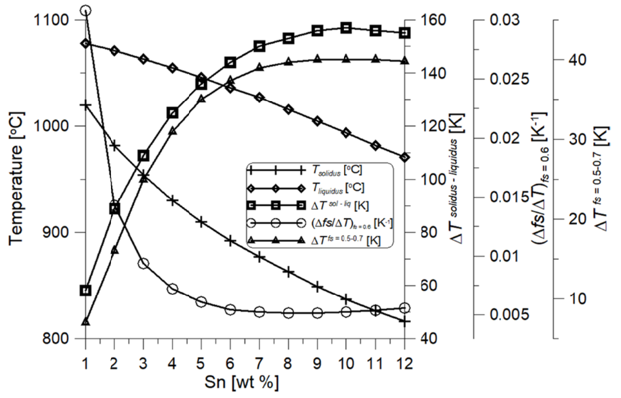

Fig. 5. Solidification parameters of copper tin bronzes

TABLE 1

Solidification parameters of Cu-Sn alloys

Sn (wt%)	$T_{solidus}$ (°C)	$T_{liquidus}$ (°C)	$\Delta T^{solidus/liquidus}$ (K)	$(\mathrm{d}fs/\mathrm{d}T)_{fs=0.6}$	$\Delta T^{0.5\text{-}0.7}$ (K)
1	1020	1078	58	0,030775	7
2	982	1071	89	0,014315	16
3	954	1063	109	0,009350	25
4	930	1055	125	0,007215	31
5	910	1046	136	0,006104	35
6	892	1036	144	0,005432	37,4
7	877	1027	150	0,005245	39
8	863	1016	153	0,005158	39,7
9	849	1005	156	0,005132	40
10	837	994	157	0,005236	40
11	826	982	156	0,005391	40
12	816	971	155	0,005576	39,8

Copper-aluminium alloys

The second part of the analysis concerned copper-aluminium alloys. This analysis was based on determining the influence of other elements. Using the ProCAST program, a simulation was carried out for the solid phase fraction versus temperature, taking into consideration the influence of manganese, iron and nickel. The CuAl10Fe3Mn2, CuAl9Fe3, CuAl10Fe4Ni4, CuAl9Mn4, CuAl5 copper alloys were taken into consideration.

At first, the calculations of solid fraction versus temperature of mentioned above bronzes were carried out. The results of the calculations are shown in Fig. 6. In the case of copper-aluminium alloys, the addition of aluminium does not give a wide solidification temperature window. It is clearly seen in Fig. 7 presented binary phase diagram of copper-aluminium alloy. Wider solidification temperature range is observed in alloys having ferrous and manganese as alloying elements. Phase diagrams, determined using FactSage software, for aluminium alloys with these additions are shown in Fig. 8 and Fig. 9.

In the TABLE 2 the solidification parameters of selected copper-aluminium alloys were presented. This table contains the solidification temperature range, fraction solid sensitivity and the temperature range for solid fraction between 50 and 70%. The fraction solid sensitivity was calculated for 0.6 solid fraction $(\mathrm{d}fs/\mathrm{d}T)^{fs=0.6}$.

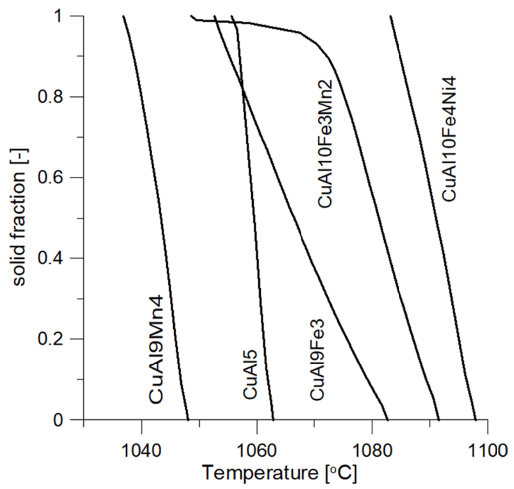

Fig. 6. Distribution of solid fraction versus temperature for copper-aluminium alloys

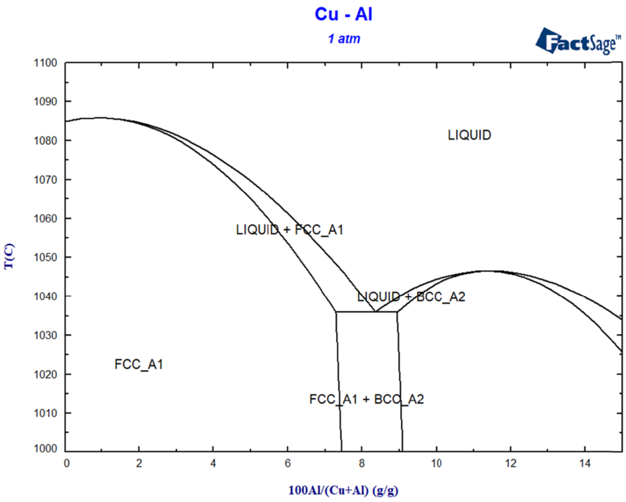

Fig. 7. Binary phase diagram of copper-aluminium alloy

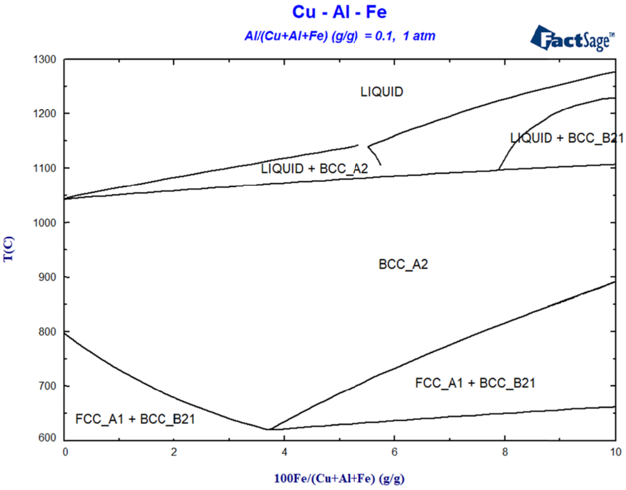

Fig. 8. Binary phase diagram of copper-ferrous alloy including 10% aluminium

Solidification parameters of copper-aluminium alloys are also shown in Fig. 10 in the form of appropriate curves.

4. Identification of copper alloys deformation temperatures

The experiments for copper-tin and copper-aluminium alloys were carried out using Leica heating microscope. The alloys were hated to a temperature above its melting point. Fig. 11 shows the example results for CuSn10 alloy. During the experiments, solidus temperature was determined at 830°C, liquidus temperature was determined at 999°C. Shape factor has changed by 1.5% in relation to the first image and the tracked corner angle has increased by 10% at the temperature 934°C – it is the deformation temperature identified in this experiment for this alloy. The tested sample at different stages of experiment is presented on Fig. 11. The changes of geometrical parameters of the sample as a function of experiment time are shown on Fig. 12. The shape of the sample at deformation temperature of 934°C is shown in Fig. 13.

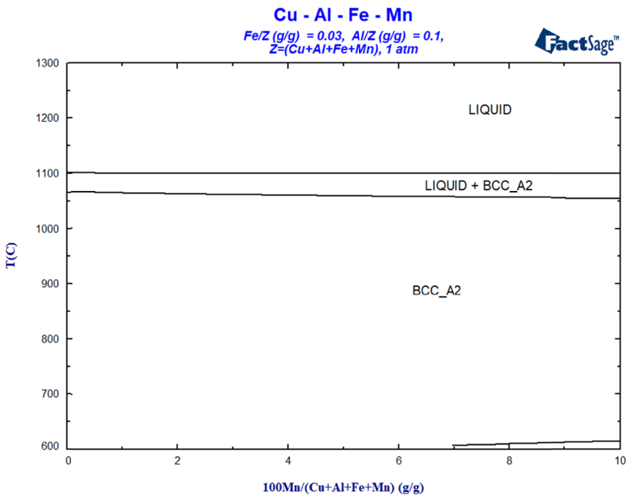

Fig. 9. Binary phase diagram of copper-manganese alloy including 10% aluminium and 3% ferrous

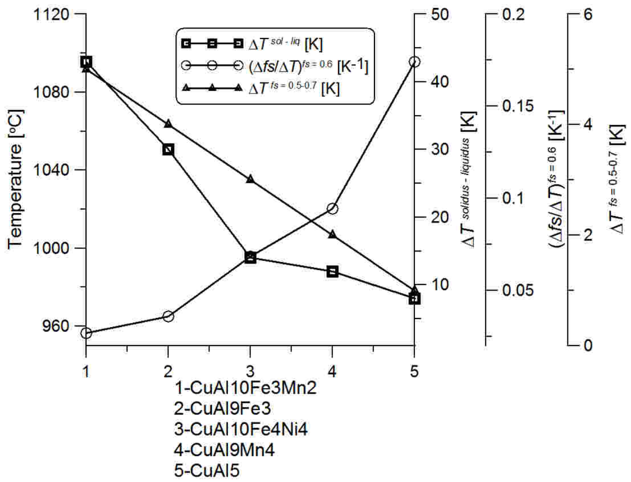

Fig. 10. Solidification parameters of selected copper-aluminium bronzes

TABLE 2

Solidification parameters of Cu-Al bronzes

Bronze	$T_{solidus}$ (°C)	$T_{liquidus}$ (°C)	$\Delta T^{solidus/liquidus}$ (K)	$(df_s/dT)_{fs=0.6}$	$\Delta T^{0.5\text{-}0.7}$ (K)
CuAl10Fe3Mn2	1048	1091	43	0.026921	5
CuAl9Fe3	1052	1082	30	0.035914	4
CuAl10Fe4Ni4	1083	1097	14	0.068591	3
CuAl9Mn4	1036	1048	12	0.094520	2
CuAl5	1055	1063	8	0.174033	1

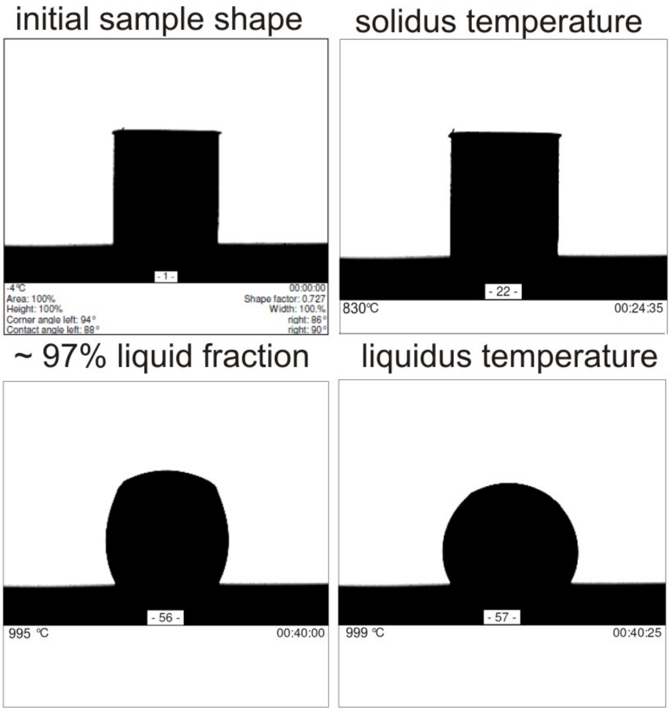

Fig. 11. Melting process of CuSn10 alloy observed on high temperature microscope (tested sample at different stages of melting process)

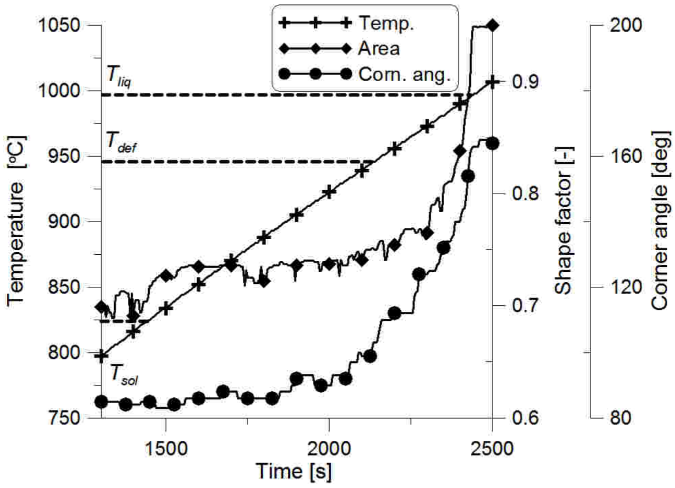

Fig. 12. Changes of geometrical parameters of the CuSn10 sample as a function of experiment time on high temperature microscope

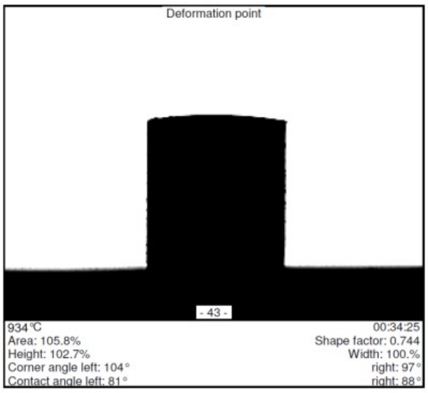

Fig. 13. Shape of the CuSn10 sample at deformation temperature of 934°C determined using high temperature microscope

5. Results discussion

The thixorormability of copper alloys can be improved by adding different alloying elements. One of them is a tin, which have the biggest impact. The effect of an increasing of its content on the distribution of the solid fraction is shown in Fig. 3. As it increases, the temperature processing window for the solid fraction range, suitable for semi-solid processing, also increases. Exact solidification parameters of Cu alloy modified with tin are given in TABLE 1. With the increase of tin content in the copper alloys, the temperature range at which melting occurs increases. By increasing the content from 1% to only 4%, this range is doubled and increases by 67 degrees from 58 to 125 degrees. Later, the growth rate slows down and reaches a maximum of 157 degrees for a 10% tin addition in the alloy. A similar, rapid increase can be observed for the working window between 0.5 and 0.7 of the solid fraction, where the temperature rises from 7 to 40 degrees. An increase in the proportion of tin to 4% in the alloy causes a fourfold increase of this parameter and reaches 31 degrees. Similarly to the previous parameter, the maximum is reached with a 10% tin content. The reduction of fraction solid sensitivity is also rapid, and the value of this parameter decreases from 0.031 to 0.005. This parameter was determined for the solid fraction at the level of 0.6. In the Fig. 5 the solidus and the liquidus temperature curves were shown. Both parameters decrease with increasing of tin content. However, changes of the solidus temperature are greater, which causes increase of the solidification range from 58 to 157 degrees. In addition, the energy consumption of the process decreases because the melting process begins at a lower temperature. Based on this diagram, it can be shown that the addition of tin in the bronze alloys causes large changes in the solidification parameters in the range of 1-6%. Later the curves flatten with exception to the liquidus and solidus temperatures.

Generally, thixoformable alloys should have low sensitivity of solid fraction on temperature changes. For Cu-Sn alloys, the reduction of solid fraction sensitivity at 0.6 solid fraction is from 0,031 to 0,005 by adding tin from 1 to 12 wt%. In this point, the slope of the curves at 0.6 fraction solid $(\mathrm{d}fs/\mathrm{d}T)^{fs=0.6}$ becomes less steep. Another important parameter is the temperature working window between 0.5 and 0.7 solid fraction $\Delta T^{fs=0.5/0.7}$.In the case of CuSn alloys, it increases from 7 to 40 K. An increase in the content of tin in the Cu alloy also cause increasing of the melting range from 58 to 157 K. Additionally, the temperature needed to start this process decreased by 200 degrees from 1020 to 816°C. Taking into consideration the literature data, which includes the critical values of these parameters, the Cu-Sn alloys are suitable for thixoforming. Among others, the temperature window between solidus and liquidus point should be relatively wide (greater than 60 K). The sensitivity of 60% fraction solid should be less than 0.025 K^{-1}. The temperature processing window for the fraction solid from 50 to 70% should be also relatively wide (greater than 15 K).

In the case of copper-aluminium alloys, the situation is different. No alloy meets the thixoforming criteria. The copper-aluminium alloy (CuAl5) has the most narrow solidification temperature range. Addition of manganese (CuAl9Mn4) has a minimal effect on its increase. On the other hand, the temperature needed to start the melting process decreases slightly. The opposite effect was achieved by the addition of iron and nickel (CuAl10Fe4Ni4), which caused an increase in energy requirements to start melting of the alloy. The solidification temperature range increases by adding ferrous (CuAl9Fe3) and both iron and manganese together (CuAl10Fe3Mn2) (see Fig. 10).

6. Summary

Application of numerical simulations can be used successfully for determination of parameters of melting process of metal alloys. It can help to design thixoforming processes within the confines of selection of metal alloys susceptible to such shaping techniques. This way, it is possible to meet requirements occurred in the real industry. Numerical simulations allow limiting very expensive industrial trials as well as some mistakes. Both the ProCAST and FactSage software are suitable for this purpose.

The Cu-Sn alloys mostly meet the thixoforming criteria described in this paper in details, except CuSn alloy. Among others, for all other alloys the temperature windows between solidus and liquidus point are relatively wide (greater than 60 K). The sensitivity of 60% fraction solid on temperature changes is less than 0.025 K^{-1}. And the temperature processing windows for the solid fraction from 50 to 70% are also wide (greater than 15 K).

In the case of analysed in this paper Cu-Al alloys, any thixoforming criteria are not met. Therefore, none alloy is recommended for industrial semi-solid processing. There are two main reasons which can cause some technical problems. First of them is precise control of temperature, what is not technically possible for such high temperature level. Narrow solidification temperature range, preventing repeatability of the processes. The second one is cooling of the shaped alloys by the moulds. In such case, full die filling before the end of solidification process could be in brief impossible. But, the authors of this paper decided within the confines of further research activity to test the alloy having one of the biggest solidification temperature window. It means, CuAl10Fe3Mn2 alloy.

The experimental work based on the analysis of melting process using high temperature microscope allowed to determine the deformation temperatures of investigated alloys. Moreover, the values of the solidus and liquidus temperatures of these alloys were confirmed. The deformation temperatures, identified on the basis of changes of samples geometrical parameters during heating process, means the point of material weaknesses. The significance of this result is in finding the best forming temperature that will give the optimum alloy viscosity for thixoforming processes. For example, for CuSn10 alloy, the deformation temperature of 934°C gives the solid fraction equals the values of 0.4. The real value of viscosity can a bit differ, due to level of solid phase agglomeration, what is of course the essence of the thixotropy phenomenon. For another tested alloys, the deformation temperatures also occur for about 0.4 solid fraction.

Acknowledgement

This research was financed by AGH University of Science and Technology, project no. 16.16.110.663.

REFERENCES

[1] N.H. Husain, A.H. Ahmad, M.M. Rashidi, An overview of thixoforming process, 4th International Conference On Mechanical Engineering Research (ICMER2017) **257** (2017).
[2] K.P. Sołek, R.M. Kuziak, M. Karbowniczek, The application of thermodynamic calculations for the semi-solid processing design, Archives of Metallurgy and Materials **52** (1), 25-32 (2007).
[3] K, Solek, M. Korolczuk-Hejnak, W. Slezak, Viscosity measurements for modelling of continuous steel casting, Archives of Metallurgy and Materials **57** (1), 333-338 (2012).
[4] J. Dutkiewicz, L. Rogal, K. Solek, Z. Mitura, P. Kapranos, Thixoforming of spray formed M2 tool steel, International Journal of Material Forming **3**, 755-758 (April 2010).
[5] A.M. Camacho, H.V. Atkinson, P. Kapranos, B.B. Argent, Thermodynamic prediction of wrought alloy compositions to semi-solid processing, Acta Materialia **51**, 2319-2330 (2003).
[6] D. Liu, H.V. Atkinson, H. Jones, MTDATA thermodynamic prediction of suitability of alloys for thixoforming, Proc. 8th Int. Conf. on Semi-Solid Processing of Alloys and Composites, Limassol, Cyprus (2004) CD-ROM.
[7] https://sourceforge.net/software/product/ProCAST/
[8] Procast2021.0 – User Guide (Visual-Cast ProCAST – Rev B)
[9] https://www.factsage.com/fs_general.php – General information
[10] C.W. Bale, E. Belisle, P. Chartrand, S. A. Decterov, G. Eriksson, A. Gheribi, K. Hack, I. H. Jung, J. Melancon, A. D. Pelton, S. Petersen, C. Robelin, Recent developments in Factsage Thermochemical Software and Databases. 2014. Extraction and Processing Division Symposium on Pyrometallurgy in Honor of David G.C. Robertson, held at the 143rd TMS Annual Meeting & Exhibition, San Diego, CA, FEB16-20, 2014.
[11] C.W. Bale, E. Belisle, P. Chartrand, S.A. Decterov, G. Eriksson, K. Hack, I.-H. Jung, Y.-B. Kang, J. Melancon A.D. Pelton, C. Robelin, S. Petersen, FactSage thermochemical software and databases – recent developments, Calphad-Computer coupling of Phase Diagrams and Thermochemistry **33** (2), 295-311 (Jun 2009).
[12] Axel Hesse, Image Analysis for Heating Microscopes, Optical Dilatometer, Manual, Hesse Instruments, 2002.
[13] Anne Marie Helmenstine, Ph.D. "Composition and Properties of Bronze." ThoughtCo, Aug. 25, 2020, thoughtco.com/bronze-composition-and-properties-603730.