Chapter 6

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THE INFLUENCE OF THE HEATING AND COOLING RATES ON THE TEMPERATURE OF THE PHASE TRANSITIONS

Abstract: During the heat-treating processes (heating and cooling) of metal alloys phase transitions occur that affects their crystalline structure and properties. It is, therefore, important in metallurgy to know the exact transition temperature and the impact of these processes on the structure o the alloys. The aim of this research was to determine the influence of the heating and cooling rates on the temperature of phase transitions and to study how these processes proceed. Thermal analysis was carried out using Differential Scanning Calorimetry (DSC) in the heat flow regime. Two materials were investigated: eutectic alloy aluminum-silicon AK12 and aluminum-iron-manganese bronze BA1032. The following heating and cooling rates were used; 5, 10 and 15^{o}C/min. Obtained results demonstrate that these rates strongly influence such transition parameters as: temperature, enthalpy and the heights of the peaks of the melting and crystallization.

Key words: thermal analysis, DSC, differential scanning calorimetry, phase transformation, silumin, AK12, aluminium bronze, BA1032, CuAl10Fe3Mn2.

6.1. Introduction

During the heating and cooling of alloys at a specific temperature phase transformations occur, which are accompanied by the absorption and release of heat. Knowledge of the temperatures of phase transitions is the basis for the development of operations and procedures in thermal manufacturing processes elements of machine parts. Calorimetric methods allow detection of these changes.

Differential scaning calorymetry DSC is used as a method thermoanalytical in studies of polymers, pharmaceuticals or food. In addition, it is increasingly used in physical metallurgy where it is

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necessary, the use of such measurement methods, which enable to study the flow of energy effects, without the need for dissolution of the solid body (FRĄCZYK A., BRECZKO T. 2010).

Calorimetry is one of the most accurate and convenient methods for the study of solids by determining their specific heat as a function of temperature, phase transitions and phase diagrams. Calorimeters are used for the qualitative assessment of endothermic and exothermic processes and quantitative determination of the degree of progress of reaction (SOLOMON H., SOLOMON, N. 2012).

The DSC curve shows the amount of heat exchanged by the sample per unit time as a function of time or temperature dH/dT=f(T). At the time of onset of reaction or phase transition, the baseline is at the peak. The measured signal calorimetry available for the user, is expressed in units of power (mW lub μW) (SECKO J., RÓŻAŃSKI, P. 2011, SZUMERA M. 2012, SZUMERA, M. 2013).

DSC as a method of thermal analysis that allows for the qualitative and quantitative characterization of the heat flux changes as a function of time and temperature, performed during physical and chemical changes in the heating conditions of the sample, is characterized by several advantages, which include short analysis time, wide temperature range of the investigated transformations, the possibility of quantitative description of the reactions, a small amount of material (usually a few milligrams), high sensitivity, namely, registration phase transformations, followed by a weak thermal effect. (GANCARZ T., PSTRUŚ, J. 2015).

6.2. Methodology

The study involved a samples siluminu AK12 and aluminium bronze BA1032. The aim of the study was to determine the temperatures of phase transformations occurring during heating and cooling.

Samples was tested by dynamic thermal analysis which involves a linear increase and decrease in temperature. The applied method is a fast analytical technique. Analyses were conducted in the DSC Phoenix 204 F1 differential scanning calorimeter (Netzsch) which measures the energy required to establish a zero temperature difference between the analyzed sample and a reference sample. The measured parameter is free heat flow.

The temperature of phase transformations assigned on the basis of registered DSC curves of heated to a temperature of 705^{o}C at a speed of 5, 10, 15^{o}C/min and then cooled to ambient temperature with the same speed.

On the basis of the obtained curves of melting and crystallization were analyzed the following parameters:

- the temperature of the beginning (Onset) and end (Endset) transition,
- temperature of the maximum of the transition (Peak) - temperature at which the transition occurs most intense,
- enthalpy of melting and crystallization ΔH [J/g] - designated as the peak area,
- the height of the peak melting and crystallization – the absolute maximum value of the heat flux h [MW/mg].

Before the analysis, DSC curves were adjusted with the use of the "DSC Horizontal On" function. This operation was performed to bring the area under the curve where no reactions took place to zero.

6.3. Results

The first research was conducted on three samples from silumin AK12 weight from 17.89 to 18.12 mg. They made experiments aimed to explain the influence of heating and cooling rates on crystallization and melting. Figure 6.1 shows DSC curves of melting and crystallization silumin AK12, depending upon the heating rate.

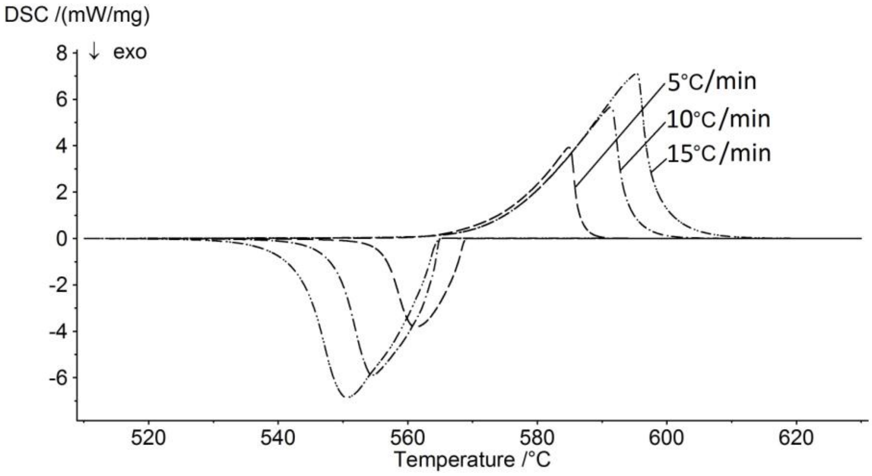

Fig. 6.1. DSC curves for silumin AK12 obtained for different heating and cooling rates: 5, 10, 15°C/min

Source: own study

The upper peaks represent the melting process (α+β→liquid), while the lower crystallization process (liquid→α+β).

On the obtained curves of melting and crystallization was observed a significant influence of heating and cooling rates on the thermodynamic parameter values. With increase in heating rate increases the enthalpy and temperature of end of transition. The maxima of the peaks shift towards higher temperatures. With increasing cooling rate, the enthalpy increases and the temperature of end of transformation is reduced. The maxima of the peaks shift toward lower temperatures. In the figures 6.2, 6.3, 6.4 presents the DSC curves with the point out of the beginning and end of phase transformations and the values of the enthalpy of the individual peaks, at the heating and cooling speeds 5, 10 i 15°C/min.

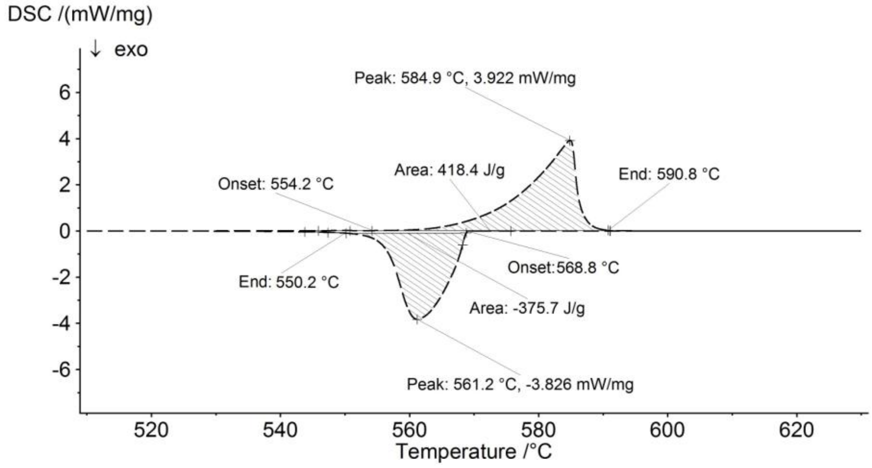

Fig. 6.2. DSC curves for AK12 presenting the main reactions taking place at a temperature from 510 to 600°C and a heating and cooling rates of 5°C/min

Source: own study

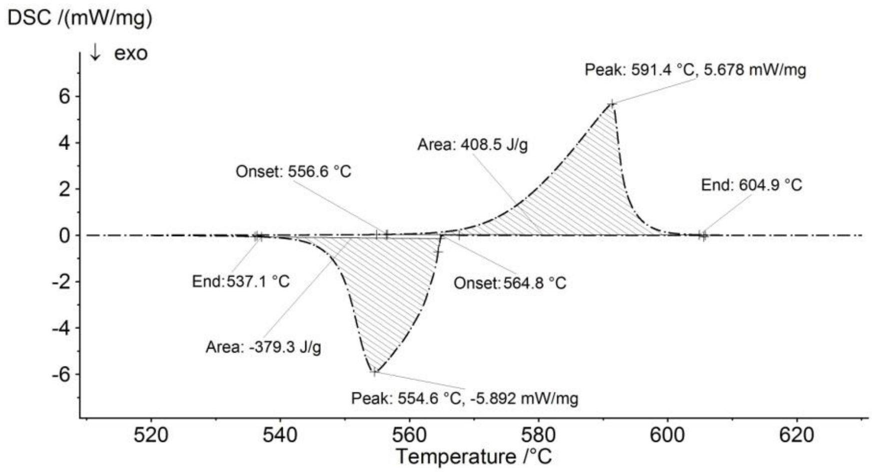

Fig. 6.3. DSC curves for AK12 presenting the main reactions taking place at a temperature from 510 to 600°C and a heating and cooling rates of 10°C/min

Source: own study

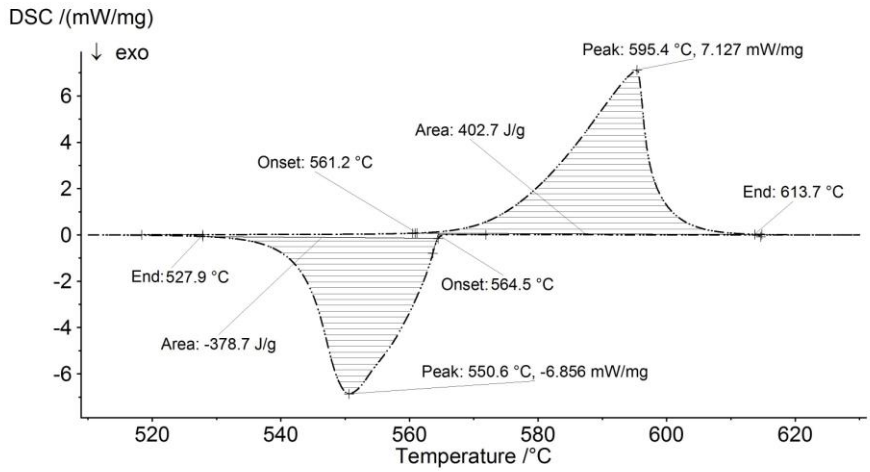

Fig. 6.4. DSC curves for AK12 presenting the main reactions taking place at a temperature from 510 to 600°C and a heating and cooling rates of 15^{o}C/min

Source: own study

From more detailed analysis it can be seen that the temperature of beginning of endothermic transition also occurs a shift towards higher temperatures by an average of nearly 3°C, but growth doesn't follow on linearly. The exothermic transition beginning at a temperature 568,8 ^{o}C during cooling at a rate of 5°C /min. During raise the temperature of the cooling, start temperature of transformation decreases, however, when cooling rates of 10 and 15°C/min is very close and the difference is only 0,3 °C, which is within the border error. Table 6.1 provides an overview of the data on crystallization and melting, depending on the heating and cooling rates.

Table 6.1. Primary crystallization and melting parameters of silumin AK12 determined by DSC

Heating and cooling rates	**5°C /min**	**10°C /min**	**15°C /min**
heating			
Onset peak [°C]	554,2	556,6	561,2
Maximum peak temperature [°C]	584,9	591,4	595,4
End peak [°C]	590,8	604,9	613,7
Enthalpy [J/g]	418,4	408,5	402,7
Height of the melting peak [mW/mg]	3,922	5,678	7,127
cooling			
Onset peak [°C]	568,8	564,8	564,5
Maximum peak temperature [°C]	561,2	554,6	550,6
End peak [°C]	550,2	537,1	527,9
Enthalpy [J/g]	-375,7	-379,3	-378,7
Height of the crystallization peak [mW/mg]	-3,826	-5,892	-6,856

Source: own study

Another test material was aluminum bronze BA1032. The mass of samples is in the range of 75.65 to 75,78 mg. The characteristic points for BA1032 on the phase equilibrium diagram of Cu-Al are the temperature of peritectoidal transition (ν+α→α+γ2), amount to 363°C and temperature of eutectoidal transition (α+γ→α+β) amount to 565°C. Figure 6.5 presents DSC curves of aluminum bronze, at various speeds of heating and cooling.

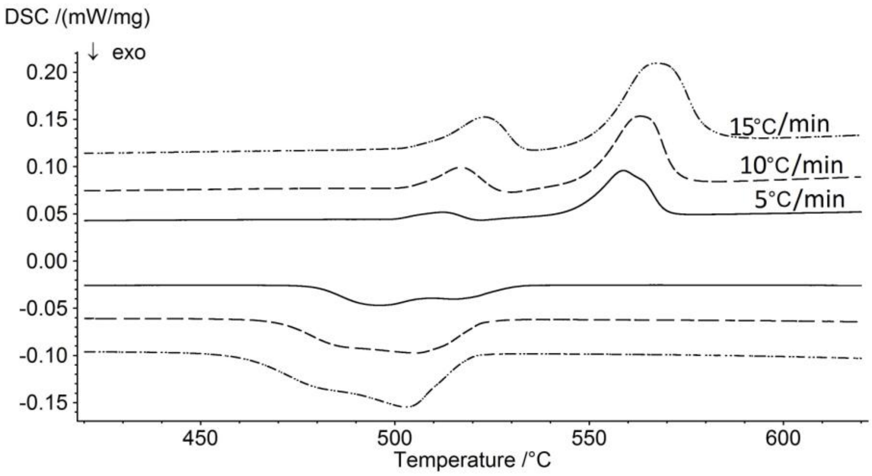

Fig. 6.5. DSC curves for aluminium bronze BA1032 obtained for different heating and cooling rates: 5, 10, 15°C/min

Source: own study

On heating curves are visible peaks, creating a double endothermic effect and it reflects the eutectoid transformation proceeding at temperature of 565oC, in accordance with phase equilibrium diagram Cu-Al. Analogical effect can be observed during the cooling, of the sample. From the above figure it shows that the heating and cooling rates have a significant effect on the shape of the curves, and the parameter values of the thermodynamic. In the figures 6.6, 6.7, 6.8 presents the DSC curves with the point out of the beginning and end of phase transformations and the values of the enthalpy of the individual peaks, at the heating and cooling speeds 5, 10 i 15°C /min.

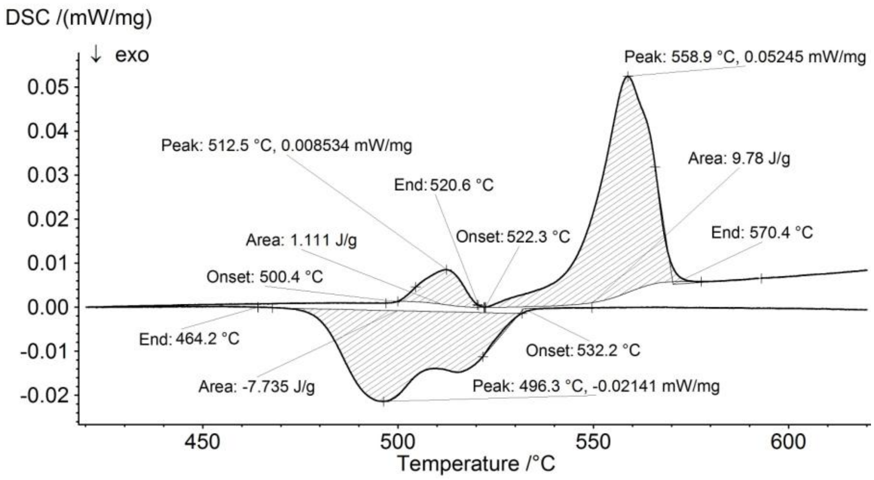

Fig. 66. DSC curves for aluminium bronze BA1032 presenting the main reactions taking place at a temperature from 420 to 620°C – 5^{o}C/min

Source: own study

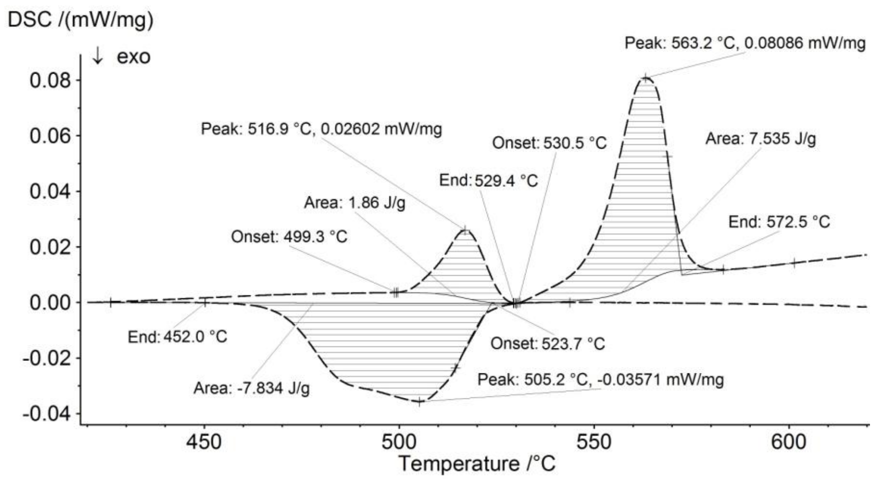

Fig. 6.7. DSC curves for aluminium bronze BA1032 presenting the main reactions taking place at a temperature from 420 to 620°C – 10^{o}C/min

Source: own study

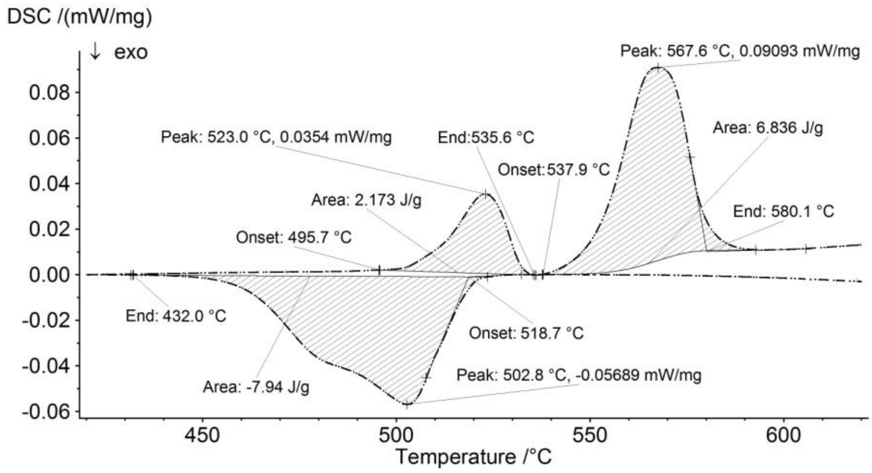

Fig. 6.8. DSC curves for aluminium bronze BA1032 presenting the main reactions taking place at a temperature from 420 to 620°C – 15°C/min

Source: own study

Increasing the heating rate one can observe that the graph shows peaks behave very similar to those in silumin AK12. However, there are some differences. When increasing the heating rate, the temperature of the onset of the first peak decreases, which means that the transformation starts early. In the second peak, with increasing heating rate, the enthalpy decreases. Increasing the cooling rate, the value of the exotermic transition increases. This causes the phase transition impose itself. Table 6.2 presents the basic data concerning changes taking place at a temperature of from 420 to 620°C, depending on the heating and cooling rates.

Table 6.2. Primary heating and cooling parameters of aluminium bronze BA1032 determined by DSC

Heating and cooling rates	**5°C/min**	**10°C/min**	**15°C/min**
heating (first peak)			
Onset peak [°C]	500,4	499,3	495,7
Maximum peak temperature [°C]	512,5	516,9	523,0
End peak [°C]	520,6	529,4	535,6
Enthalpy [J/g]	1,111	1,860	2,173
Height of peak [mW/mg]	0,009	0,026	0,035
heating (second peak)			
Onset peak [°C]	522,3	530,5	537,9
Maximum peak temperature [°C]	558,9	563,2	567,6
End peak [°C]	570,4	572,5	580,1
Enthalpy [J/g]	9,780	7,535	6,836
Height of peak [mW/mg]	0,052	0,081	0,091
cooling			
Onset peak [°C]	532,2	523,7	518,7
Maximum peak temperature [°C]	496,3	505,2	502,8
End peak [°C]	464,2	452,0	432,0
Enthalpy [J/g]	-7,735	-7,834	-7,940
Height of peak [mW/mg]	-0,021	-0,036	-0,057

Source: own study

6.4. Conclusions

Accomplish the studies of the influence heating and cooling rates on the temperature and the progress of phase transition during heating with a constant speed of 5, 10 and 15°C/min. The research conducted leads to the following conclusions:

- the heating and cooling rates affects the temperature of the beginning and end of phase transition, enthalpy and height of the melting and crystallization peaks,
- higher heating rate should not necessarily cause an increase in enthalpy,

- peak height increases with increase of the heating or cooling rates. This is essential for the sensitivity of the method. Peaks with the low enthalpy is more visible,
- the increase a heating and cooling rates leads to the imposition of the phase transitions. Thus, it is possible to enhance the effect only in the case where the interval between transitions is large,
- applying the same heating and cooling rates during the study, it is important to obtain comparable results.

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