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The Application of ATD and DSC Methods to Study of the EN AC-48000 Alloy Phase Transformations

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Abstract

Tests concerning EN AC 48000 (AlSi12CuNiMg) alloy phase transition covered (ATD) thermal analysis and (DSC) differential scanning calorimetry specifying characteristic temperatures and enthalpy of transformations. ATD thermal analysis shows that during cooling there exist: pre-eutectic crystallization effect of Al₉Fe₂Si phase, double eutectic and crystallization $\alpha(\text{Al})+\beta(\text{Si})$ and multi-component eutectic crystallization. During heating, DSC curve showed endothermic effect connected with melting of the eutectic $\alpha(\text{Al})+\beta(\text{Si})$ and phases: Al₂Cu, Al₃Ni, Mg₂Si and Al₉Fe₂Si being its components. The enthalpy of this transformation constitutes approx. +392 J g⁻¹. During freezing of the alloy, DSC curve showed two exothermal reactions. One is most likely connected with crystallization of Al₉Fe₂Si phase and the second one comes from freezing of the eutectic $\alpha(\text{Al})+\beta(\text{Si})$. The enthalpy of this transformation constitutes approx. -340 J g⁻¹. Calorimetric test was accompanied by structural test (SEM) conducted with the use of optical microscope Reichert and scanning microscope Hitachi S-4200. There occurred solution's dendrites $\alpha(\text{Al})$, eutectic silicon crystal (β) and two types of eutectic solution: double eutectic $\alpha(\text{Al})+\beta(\text{Si})$ and multi-component eutectic $\alpha+\text{AlSiCuNiMg}+\beta$.

Keywords: Al-Si cast alloy, Thermal analysis, Differential scanning calorimetry, Phase transformations and Enthalpy

1. Introduction

Phase transformations are known as thermodynamic processes consisting in transition of one thermodynamic phase into another which occur towards the decrease of the system's free energy. These processes, connected with the change of physical state, influence primary structure and performance of metal alloy. The visual effect of these transitions are heat reactions which can be measured using, among others: thermal analysis (ATD) [1-5] and differential scanning calorimetry (DSC) [6-9]. These methods consist in measuring of thermal power during heating and cooling and in consequence thermal effects of chemical and phase transformation reactions are set. The analysis of accompanying

phenomena may be determined by the performance and the area of application. It is essential to assess thermal stability which through the determination of the system's enthalpy is helpful to calculate Gibbs' thermodynamic potential. The consequence of this is, among others, the assessment of the existence of spontaneous reactions constituting the selection of production technology of machines working in high temperatures [10, 11].

2. Aim and scope of tests

The goal of the work is to assess the phase transformations using thermal analysis (ATD) and differential scanning

calorimetry (DSC) of EN AC-AlSi12CuNiMg alloy. Scope of the research, among others: thermal analysis (ATD), calorimetric test (DSC), structural test (SEM), identification of phases, summary and conclusions.

3. Material and methodology

Test covered EN AC 48000 (AC-AlSi12CuNiMg) alloy used, among others, for cast valve piston, cylinder blocks and bodies in automotive industry. Selected alloy was melted from cast piston scarp in SiC crucible of 600 cm³ in induction furnace VSG 02/631. Thermal analysis (ATD) was conducted in the place equipped with multichannel temperature register Crystaldigraph NT3-8K with the use of Mlab program. The alloy was poured to ATD probe Heraeus Elektro Nite of 130g with the speed of approx. 2°C·min⁻¹. Samples for differential scanning calorimetry and structural tests were cut from the place of temperature measurement using thermocouple NiCr-NiAl.

Phase transformation test using differential scanning calorimetry was conducted using high temperature calorimeter Multi HTC Setaram in an argon atmosphere (99.9999 dew points) within temperatures ranging from 20°C to 800°C. Temperature was measured using thermocouple Pt-Rh10 Pt. Reference mixture constituted powder Al₂O₃. Calibration was conducted using highly volatile Al within the temperature ranging from 500°C to 800°C. Heating and cooling rate was used within the range of 10°C·min⁻¹. Calorimetric sample of 10mg is cylindrical in shape of 3mm. Upon degreasing in ethyl alcohol the sample was placed in crucible with Al₂O₃ of 0.45 cm³. The place for conducting thermal analysis (ATD) and calorimetric test (DSC) is presented on the Figure 1.

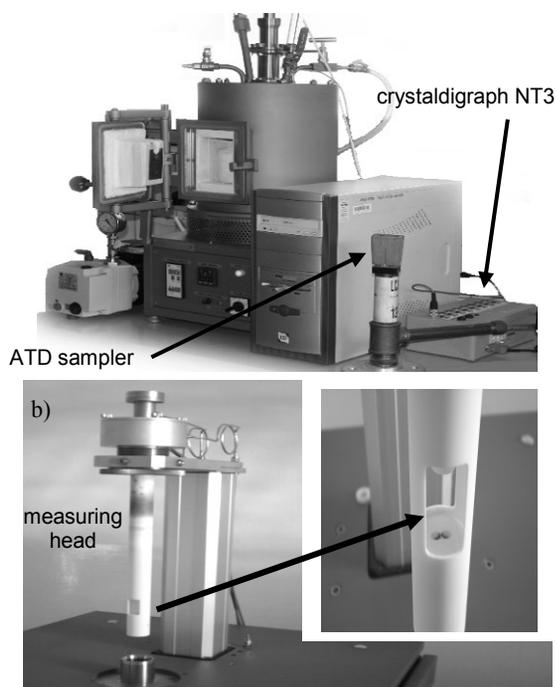


Fig. 1. Place for conducting thermal tests: a) ATD; b) DSC

Metallographic microsections were conducted on the basis of standard method. Metallographic tests were conducted using light microscope MeF-2 Reichert. Phase qualitative analysis was conducted using scanning microscope Hitachi S-4200 along with x-ray spectrometer EDS Voyager manufactured by Noran.

Identification of phases was conducted using ICDD record. Calorimeter calibration was conducted using the template Al (>99.998, T_{melt} = 660.3°C, ΔH = 401 J·g⁻¹). Calibration conditions were the same as the one during the experiment. Temperature of reversible transformations was set on the basis of DSC curve which occurred during heating and cooling rate.

Liquidus temperature was determined by the temperature of local endothermic minimum of thermal effect during heating. "onset" temperature was determined during cooling. This method is used during the use of DSC and ATD methods. Eutectic temperature was determined as T_{onset} temperature.

4. Research results and analysis

Chemical composition of EN AC 48000 alloy in presented in Table 1. ATD curve during cooling is presented on the Figure 2 and reduce scope of crystallization is presented on the Figure 3.

Table 1.

Chemical composition of EN AC 48000 cast alloy

Alloy	Si	Cu	Mg	Ni	Fe	Mn	Zn	other
AlSi9	11.86	0.98	1.06	0.92	0.52	0.30	0.26	0.2

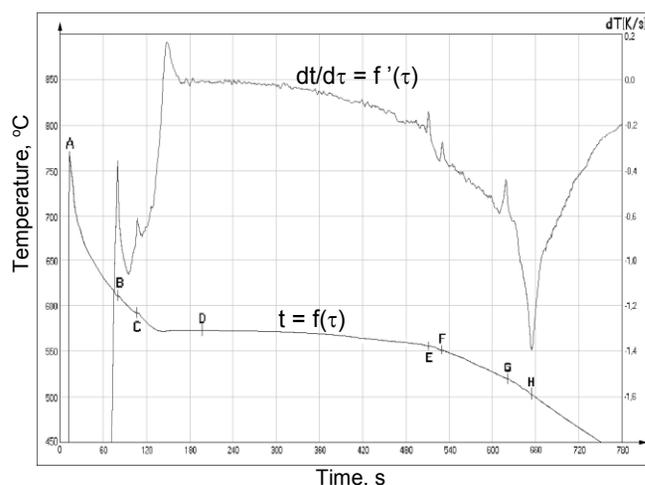


Fig. 2. Thermal analysis graph of EN AC 48000 alloy

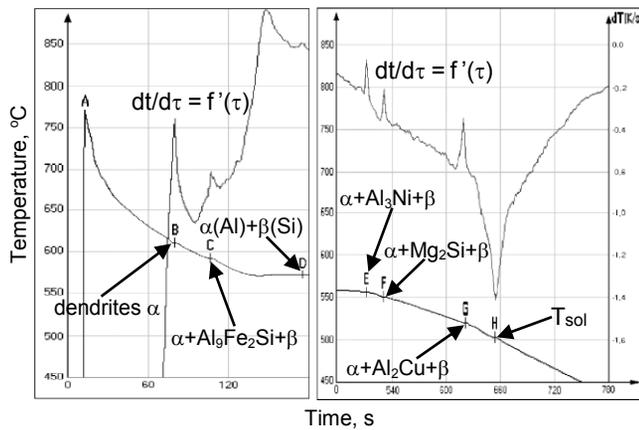


Fig. 3. Reduce scope of crystallization of EN AC 48000 alloy

Summary of characteristic temperatures showed by ATD graph is presented in Table 2.

Table 2.
Characteristic temperatures of ATD graph (Figures 2 and 3)

Point	A	B	C	D	E	F	G	H
Temp. °C	T_{start}	$T_{liq.}$	$T_{(Fe)}$	T_E	$T_{E(Ni)}$	$T_{E(Mg)}$	$T_{E(Cu)}$	$T_{sol.}$
°C	770	610	582	574	560	553	525	514

where:

T_{start} – temperature of solidification start record,
 $T_{liq.}$ – temperature of dendrites crystallization $\alpha(Al)$,
 $T_{(Fe)}$ – temperature of eutectic crystallization containing Fe,
 T_E – temperature of eutectic crystallization $\alpha(Al)+\beta(Si)$,
 $T_{E(Ni)}$ – temperature of eutectic crystallization containing Al_3Ni ,
 $T_{E(Mg)}$ – temperature of eutectic crystallization containing Mg_2Si ,
 $T_{E(Cu)}$ – temperature of eutectic crystallization containing Al_2Cu ,
 $T_{sol.}$ – temperature of alloy crystallization end,

DSC curve of tested alloy during heating and cooling is presented on the Figures 4 and 5. Characteristic temperatures of DSC graph (Figures 4 and 5) are presented in Table 3.

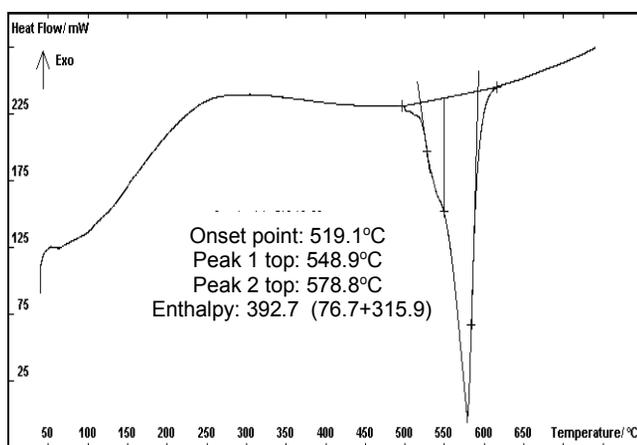


Fig. 4. DSC curve during heating rate of EN AC 48000 alloy

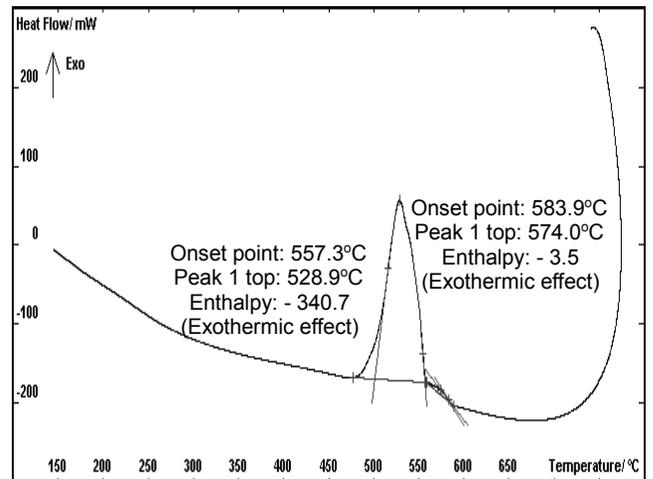


Fig. 5. DSC curve during cooling rate of EN AC 48000 alloy

Table 3.
Characteristic temperatures of DSC graph (Figures 4 and 5)

Temp. °C	$T_{liq.}$	T_E	$T_{sol.}$
during heating	579	549	519
during cooling	584	557	529

During heating of alloy at the speed of $10^{\circ}C \cdot min^{-1}$ DSC curve shows strong endothermic effect connected with melting of eutectic (Figure 4). Temperature range for melting of the eutectic constitutes $519-578^{\circ}C$. The shape of the thermal effect shows the presence of inter-metallic phases which may constitute the components of the eutectic. Probably, these are the following phases: β' (complex compound composed of: $\alpha+Al_2Cu+\beta$ or $\alpha+Al_3Cu_2Si_6+\beta$), Al_3Ni , Mg_2Si and Al_9Fe_2Si . The enthalpy of melting is approx. $+392 J g^{-1}$.

During solidification of the alloy, at the same speed, DSC curve shows two exothermic effects (Figure 5). At the temperature of $583^{\circ}C$ (liquidus temperature) the embryos of the phase $\alpha(Al)$ are created and phase Al_9Fe_2Si may undergo crystallization. Solidification heat connected with the crystallization of the above-mentioned phases constitutes approx. $-3 J g^{-1}$. Second thermal effect is connected with the crystallization of the eutectic $\alpha+\beta$ and $\alpha+AlSiCuNiMg+\beta$. The beginning of crystallization of this solution is conducted at the temperature of $557^{\circ}C$ and the crystallization heat constitutes approx. $-340 J g^{-1}$.

Differences between temperatures in ATD and DSC analysis may result from various weight of samples. Sample for thermal analysis test was of 130 g, while sample for calorimetric test was of 110mg. The next difference results from different cooling rate: $10^{\circ}C \cdot min^{-1}$ – for DSC and $2^{\circ}C \cdot min^{-1}$ – for ATD analysis.

As it results from Tables 2 and 3 temperatures of transformations phase are similar and constitute:

Liquidus temperature $T_{liq.}$ 579-584°C (DSC) 610°C (ATD)

Eutectic temperature $\alpha+\beta$ 557-549°C (DSC) 574°C (ATD)

Solidus temperature $T_{sol.}$ 520-529°C (DSC) 514°C (ATD)

Structural tests served as the supplement to calorimetric test and thermal analysis. An example of the microstructure of test alloy presented on the Figure 6.

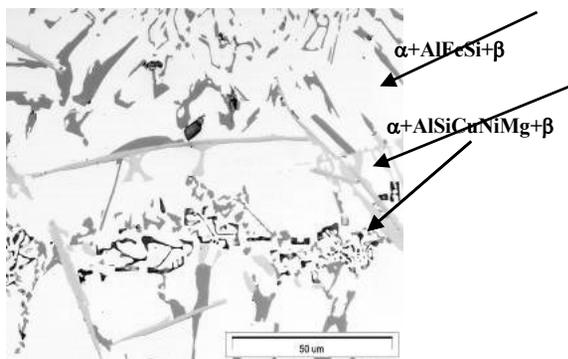


Fig. 6. Microstructure of EN AC 48000 cast alloy

Since the microstructure of tested alloy showed the presence of external phases, x-ray phase analysis was conducted. Diffractogram of tested alloy is presented on the Figure 7. Possible eutectic images containing Al_3Ni , Al_2Cu and $\text{Al}_9\text{Fe}_2\text{Si}$ phases are presented on the Figure 8.

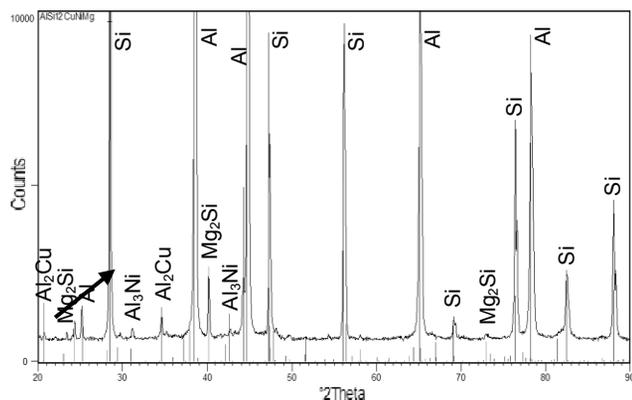
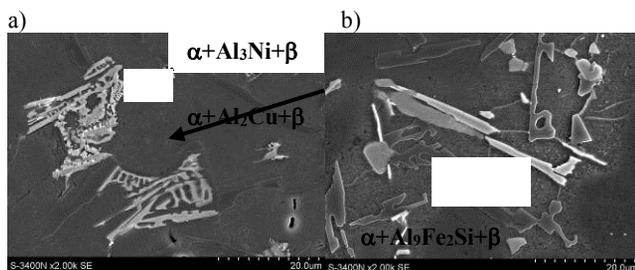


Fig. 7. Diffractogram of EN AC 48000 cast alloy

Fig. 8. Microstructure of EN AC 48000 alloy with visible eutectic mixtures containing: Al_3Ni , Al_2Cu and $\text{Al}_9\text{Fe}_2\text{Si}$ phases

5. Conclusion

Tests were conducted to identify components and phases existing in EN AC 48000 (AlSi12CuNiMg) cast alloy and the assessment of thermal stability which by the determination of the enthalpy of the system, makes it possible to calculate Gibbs thermodynamic potential. The consequence is the establishment

of production technology for machines working at high temperatures, for example engine pistons.

ATD curve shows pre-eutectic thermal effect coming from the crystallization of the eutectic containing $\text{Al}_9\text{Fe}_2\text{Si}$ phase (582°C). In a temperature range approx. 549 to 557°C (for DSC) and 574°C (for ATD) double eutectic crystallizes $\alpha(\text{Al})+\beta(\text{Si})$, and then the following eutectic crystallizes: $\alpha+\text{Al}_3\text{Ni}+\beta$ containing Mg_2Si (553°C) and eutectic $\alpha+\text{Al}_2\text{Cu}+\beta$ containing phase Al_2Cu (525°C). Within temperature solidus (514°C) eutectic and the whole alloy finish crystallization tested alloy.

DSC curve, during the heating rate of the alloy, shows endothermic effect connected with melting of the eutectic (549°C). The shape of this effect shows the presence of additional phases being the components of eutectic. Total thermal effect of melting reaction constitutes approx. $+392 \text{ J g}^{-1}$. During solidification of alloy, DSC curve showed two exothermic effects. The weak effect at the temperature of 584°C is connected with the crystallization of the above-mentioned phases. Solidification enthalpy constitutes about -3 J g^{-1} . The second exothermic effect is connected with solidification of the eutectic. Crystallization temperature constitutes 557°C and solidification heat is -340 J g^{-1} .

As it is shown by Table 2 and 3 temperatures of transformations phase are similar to each other and differences in temperatures come from various sample masses (130 g from ATD and 110 mg for DSC) and various cooling rate ($2^\circ\text{C}\cdot\text{min}^{-1}$ for ATD and $10^\circ\text{C}\cdot\text{min}^{-1}$ for DSC analysis).

XRD method is not best suited to analyse this type of phenomena because in this material there are probably present small amounts of various phases connected to additions of manganese, zinc or iron (Table 1) and not only the main Al_2Cu or the Al_3Ni phases. In such situation, a more precise TEM with electron diffraction analysis would be better suited.

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