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Application of DSC Method in Studies on Phase Transitions of Ni Superalloys

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Abstract

The paper presents results of calorimetric studies of foundry nickel superalloys: IN100, IN713C, Mar-M247 and ŻS6U. Particular attention was paid to determination of phase transitions temperatures during heating and cooling. The samples were heated to a temperature of 1500°C with a rate of 10°C·min^{-1} and then held at this temperature for 5 min. After a complete melting, the samples were cooled with the same rate. Argon with a purity of 99.99% constituted the protective atmosphere. The sample was placed in an alundum crucible with a capacity of 0.45 cm^3. Temperature and heat calibration was carried out based on the melting point of high-purity Ni. The tests were carried out by the differential scanning calorimetry (DSC) using a Multi HTC high-temperature calorimeter from Setaram. Based on the DSC curves, the following temperatures were determined: solidus and liquidus, dissolution and precipitation of the γ' phase, MC carbides and melting of the γ'/γ eutectic. In the temperature range of 100-1100°C, specific heat capacity of the investigated superalloys was determined. It was found that the IN713C and IN100 alloys exhibit a higher specific heat while compared to the Mar-M247 and ŻS6U alloys.

Keywords: Innovative materials and casting technologies, Nickel superalloys, Differential scanning calorimetry, Specific heat

1. Introduction

Superalloys are classical materials developed for high-temperature applications, requiring a high resistance to creep, fatigue and degradation under the influence of an aggressive atmosphere. The development of superalloys is connected with appearance of the jet engine, for which they have been created for the first time [1, 2]. Currently, these alloys are developed in other high-temperature applications, particularly as turbine elements for power industry [3-5]. Significant fuel consumption and limitation of pollutant emissions from aircraft engines constitute the stimuli for further evolution of the superalloys technology. According to the laws of thermodynamics, it requires application of a higher operating temperature. A characteristic feature of many nickel superalloys consists their ability to work both at a high temperature (temporarily even up to 1400°C), and at a cryogenic temperature, while maintaining excellent mechanical properties [2]. Another advantage of nickel superalloys consists in their resistance to high-temperature corrosion in an aggressive environment of sulfur, nitrogen and carbon [6, 7]. Low heat conduction (10-30% of nickel thermal conductivity) [1] may be an unfavourable feature of superalloys, leading to an increase in the temperature gradient, occurrence of internal stresses, and as a result, component failures. Alloying additions cause an increase in the mechanical properties by precipitation hardening (most often, it is an ordered γ' phase). Additions of Al, Ti, Ta are of particular importance for the γ' phase formation. Meanwhile, addition of rare earth elements – Hf, La, Y – affects the resistance to oxidation positively by fixing sulfur [8].

2. Aim of the paper

The goal of the work consisted in determination of the temperature of phase transitions in nickel superalloys during heating and cooling. Also, specific heat capacity of the investigated superalloys was calculated.

3. Material and methodology

The tests were carried out using foundry nickel superalloys: Inconel IN 100 and IN 713C, as well as ŻS6U and Mar-M247 alloys. Chemical composition of the alloys is shown in Table 1.

Table 1.
Chemical composition of nickel superalloys

No.	Chemical composition, wt.%											
	Cr	Co	Mo	W	Ta	Nb	Al	Ti	C	B	Zr	Other
1	10.0	15.0	4.2	–	–	–	5.5	4.7	0.18	0.014	0.06	1.0V
2	12.5	–	4.2	–	–	2.0	6.1	0.78	0.15	0.012	0.01	–
3	8.3	10.0	0.7	9.9	3.0	–	5.5	1.0	0.14	0.015	0.05	1.5Hf
4	8.9	9.6	1.6	9.9	–	0.9	5.3	2.6	0.2	0.03	0.03	0.12Fe 0.4Mn

where: alloy # 1 – IN100; alloy # 2 – IN713C; alloy # 3 – Mar – M247; alloy # 4 – ŻS6U.

The measurements were carried out using a Multi HTC high-temperature calorimeter from Setaram and the SetSoft program. The samples having a shape of a rectangular prism with a mass of 230 mg were heated to a temperature of 1500°C with a rate of 10°C·min^{-1} and then held at this temperature for 5 min. After a complete melting, the samples were cooled with the same rate. Argon with a purity of 99.999% constituted the protective atmosphere. The sample was placed in an alundum crucible with a capacity of 0.45 cm^3. Temperature and heat calibration was carried out based on the melting point of high-purity Ni.

For the determination of specific heat capacity, three measurements under identical conditions were carried out. The first measurement was carried out using two empty crucibles, the second on – with the testes sample, and the third one – with a standard substance (Al_2O_3 crystal). The obtained heat flux curves constituted a basis for the determination of specific heat capacity C_p, which was calculated using the following equation:

$$C_{P_s}(T) = \frac{HF_{sample} - HF_{blank}}{HF_{ref.} - HF_{blank}} \cdot \frac{m_{ref.}}{m_{sample}} \cdot Cp_{ref}(T) \quad (1)$$

where:
$C_{P\,s}$ – specific heat of the samples, J·g^{-1}·K^{-1},
HF – heat flux of the samples, the crucibles, the standards, respectively, μV,
m_{ref}, m_{sample} – mass of the standard and of the samples, g,
$C_{P\,ref.}$ – heat capacity of the standard (sapphire), J·g^{-1}·K^{-1}.

4. Results and their analysis

The phase transitions during heating and cooling of foundry nickel superalloys are complicated, which is caused by the dissolution or precipitation of the γ' phase, the γ + γ' eutectic, and carbides. The first endothermic peak during heating with a rate of 10°C·min^{-1} for the Mar-M247 and ŻS6U alloys occurs at a temperature of 1172°C and 1187°C respectively. The effect is connected with the dissolution of the γ' phase. For the Mar-M247 alloy, the heat of reaction equals to 18 J·g^{-1}, and its value is approximately four times higher than that of the ŻS6U (Fig. 1).

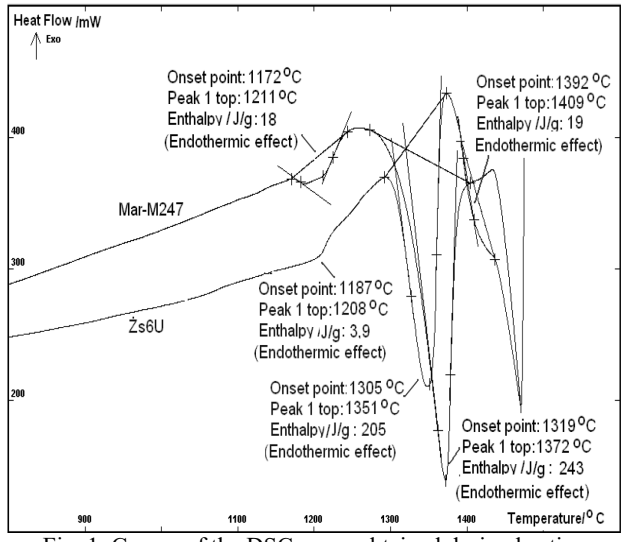

Fig. 1. Course of the DSC curve obtained during heating of the Mar-M247 and ŻS6U alloys

The second endothermic peak in the DSC curves exhibits an extremum at a temperature of 1351°C (ŻS6U alloy) and 1372°C (Mar-M247). This is the effect of melting of the γ+γ' eutectic. Above the eutectic temperature a third endothermic peak appears in the ŻS6U alloy at a temperature of 1392°C, with a relatively high heat of fusion (19 J·g^{-1}). Probably, it is an effect of dissolution of the γ phase dendrites. The solidus temperature equals to 1293°C (ŻS6U alloy) and 1270°C (Mar-M247 alloy), and the liquidus temperature – 1409°C (for ŻS6U alloy) and 1372°C (for Mar-M247 alloy).

During cooling of the ŻS6U alloy with the same rate, also three thermal effects occur in the DSC curve (Fig. 2).

The first exothermic effect in the temperature range of 1402°C-1384°C corresponds to the formation of the γ phase. This effects connects smoothly with the second exothermic peak, connected with the start of the carbides precipitation at a temperature of 1368°C. According to [9, 10], these are complex carbides of MC, M_6C and $M_{23}C_6$ types. The total heat of reaction equals to –197 J·g^{-1}. A weak effect at a temperature of 1188°C corresponds to the precipitation of the γ' phase in the result of the decomposition of the γ solid solution.

The course of the cooling curve of the Mar-M247 alloy differs from the DSC curve for the ŻS6U alloy. Formation of the γ phase occurs in a lower temperature range: from 1368°C to 1341°C, and

the heat of reaction is higher and equals to –223 J·g^{-1}. The precipitation temperature of the γ' phase equals to 1200°C, the heat of the exothermic reaction is – 8 J·g^{-1}.

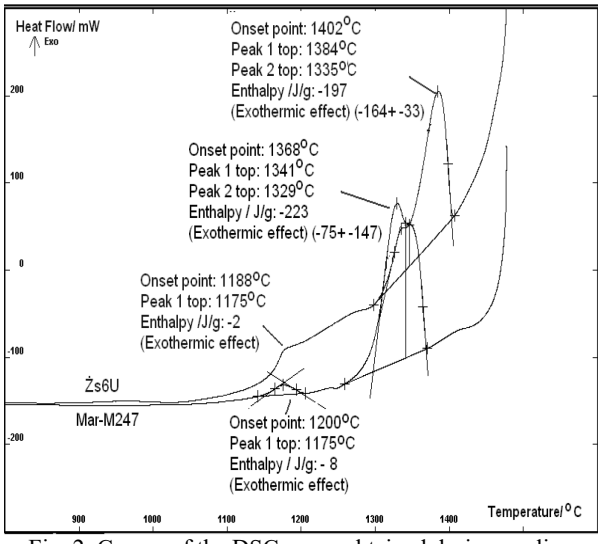

Fig. 2. Course of the DSC curve obtained during cooling for the Mar-M247 and ŻS6U alloys

The heating and cooling curves for the Inconel (IN 100) and (IN 713C) alloys are shown in Figures 3 and 4.

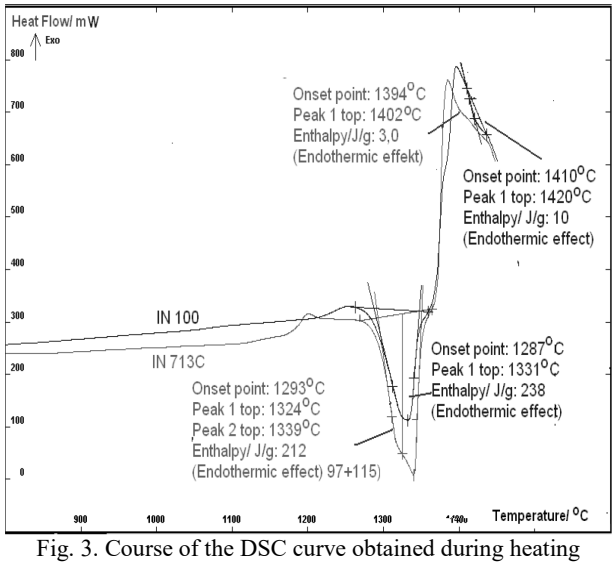

Fig. 3. Course of the DSC curve obtained during heating of the IN 100 and IN 713C alloys

The solidus and liquidus temperature of the IN 100 alloy during heating with a rate of 10°C/min equal to 1262°C and 1420°C, respectively, and for the IN 713C alloy – 1269°C and 1402°C (Fig. 3). Two exothermic peaks occur in the DSC curve obtained during cooling of the IN 713C alloy, preceding the formation of the γ phase (Fig. 4). The temperature of the reaction start equals to 1416°C and 1402°C, respectively, and the heat of reaction amounts to –5 J·g^{-1} and –4 J·g^{-1}, respectively. According to [10, 11], this reaction is connected with the precipitation of MC carbides from the liquid, which may be expressed as:

liquid + MC carbides (2)

and

liquid + MC carbides + γ phase (3)

The temperature dependence of the specific heat capacity of the studied alloys is shown in Figure 5.

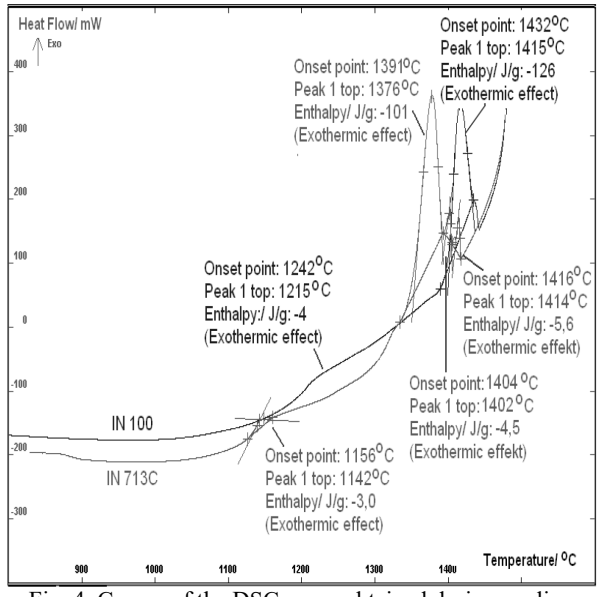

Fig. 4. Course of the DSC curve obtained during cooling of the IN 100 and IN 713C alloys

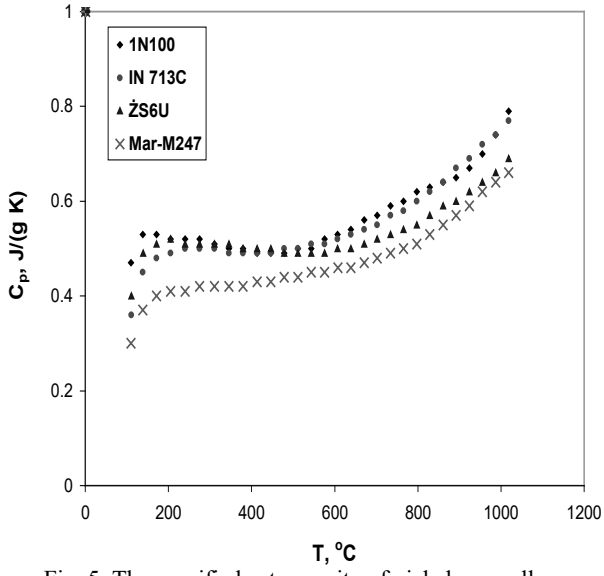

Fig. 5. The specific heat capacity of nickel superalloys *vs.* temperature

The C_p curves may be divided into two temperature ranges. In the first range, from 150°C to 600°C, a moderate increase in heat capacity is observed. In the second range, above 600°C, a relatively fast increase in the C_p value occurs, till the final temperature, *i.e.* 1100°C, is reached.
The highest C_p value is exhibited by the IN 713C and IN 100 alloys, and the lowest one – by the Mar-M247 and ŻS6U alloys.
A higher C_p value for the IN 713C and IN 100 alloys may indicate w weaker bond in the crystal lattice, because of more intense thermal vibration of atoms.

Characteristics temperature values of phase transitions and enthalpy during heating and cooling are shown in Tables 2 and 3.

Table 2.
Characteristics temperature values of phase transitions of nickel based superalloys during heating

No Alloy	Temperature, °C				
	γ' phase	Solidus	γ-γ' eutectic	MC Carbide	Liquidus
1	?	1262	1331	?	1420
2	?	1269	1339	1324	1402
3	1172	1270	1372	?	1372
4	1187	1293	1351	?	1409

Table 3.
Characteristics temperature values of phase transitions of nickel based superalloys during cooling

No Alloy	Temperature, °C				
	MC Carbide	Liquidus	γ-γ' eutectic	γ' phase	Solidus
1	1432	1415	1415	1242	1370
2	1416	1391	1376	1156	1307
3	?	1368	1341	1200	1240
4	?	1402	1384	1188	1270

where:
1 – IN100 alloy;
2 – IN713C alloy;
3 – Mar – M247 alloy;
4 – ŻS6U alloy.

5. Summary

The differential scanning calorimetry (DSC) method is used frequently for determination of equilibrium temperatures of phase transitions such as: liquidus, solidus and eutectic crystallisation. Precise measurements requires a proper calibration of the measuring apparatus using standards. It should be noted that sometimes, it is hard to define the starting temperatures and the peak extrema unequivocally in the heating and cooling curves. It is particularly the case if dissolution or precipitation occurs gradually, as for the dissolution or precipitation of the γ' phase or complex carbides of the MC type. In such a case, it may be beneficial to combine the DSC methods with other methods of thermal analysis, *e.g.* the ATD method, taking the scale effect into account.

References

[1] Sims, S.T., Stoloff, N.S., Hagel, W.C. (1987). *Superalloys II.* New York: Ed. John Wiley & Sons.
[2] Mikułowski, B. (1997). *High temperature cast alloys and Nikel-based superalloys.* Cracow: Publication AGH.
[3] Zrnik, J., Strunz, P., Vrchovinsky, V., Muransky, O., Novy, Z. & Widenmann, A. (2004). Degradation of creep properties in a long-term thermally exposed nickel base superalloy. *Materials Science and Engineering. A* 387-389, 728-733.
[4] Lee, S.H., Kim, S.W. & Kang, K.H. (2006). Effect of heat treatment on the specific heat capacity of nickel-based alloys. *Journal of Thermophysic.* 27(1), 282-292.
[5] Liu, L.R., Jin, T., Zhao, N.R., Zhang, Z.H., Shun, X.F., Guan, H.R. & Hu, Z. Q. (2003). Microstructural evolution of a single crystal nickel-base superalloy during thermal exposure. *Material Letters.* 57, 4540-4546.
[6] Balikci, E. & Raman, A., (2004). Characteristics of the γ' precipitates at high temperatures in Ni-base polycrystalline superalloy IN738 LC. *Journal of Materials Chemistry. and Physics.* 84, 284-290.
[7] Suwardiea, J.H., Artiagab, R. & Mierb, J.L. (2002). Thermal characterization of a Ni-based superalloy. *Thermochemica Acta.* 392-393, 295-298.
[8] D'Souzaa, N. & Dongb, H.B. (2007). Solidification path in third-generation Ni-based superalloys, with an emphasis on last stage solidification. *Scripta Materialia.* 56, 41-44.
[9] Bhambri, A.K., Kattamis, T.Z. & Morral, J.E. (1975). Cast microstructure Inconel 713C and its dependence on solidification variables. *Metallurgical Tranactions.* B 6B, 523-537.
[10] Zupanic, F., Boncina, T., Krizman, A. & Tichelaar, F.D. (2001). Structure of continuously cast Ni-based superalloy Inconel 713C. *Journal of Alloys and Compounds.* 329, 290-297.
[11] Przeliorz, R. & Piątkowski, J. (2015) Thermophysical Properties of Nickel-Based Cast Superalloys. *Metalurgija.* 54(3), 543-546.