ATD and DSC Analysis of IN-713C and ZhS6U-VI Superalloys

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Abstract

Paper presents the results of ATD and DSC analysis of two superalloys used in casting of aircraft engine parts. The main aim of the research was to obtain the solidification parameters, especially T_{sol} and T_{liq}, knowledge of which is important for proper selection of casting and heat treatment parameters. Assessment of the metallurgical quality (presence of impurities) of the feed ingots is also a very important step in production of castings. It was found that some of the feed ingots delivered by the superalloy producers are contaminated by oxides located in shrinkage defects. The ATD analysis allows for quite precise interpretation of first stages of solidification at which solid phases with low values of latent heat of solidification are formed from the liquid. Using DSC analysis it is possible to measure precisely the heat values accompanying the phase changes during cooling and heating which, with knowledge of phase composition, permits to calculate the enthalpy of formation of specific phases like γ or γ'.

Keywords: Innovative casting materials and technologies, Nickel superalloys, ATD, DSC, Solidification parameters

1. Introduction

Structure and phase composition of turbine blade castings have immense effect on their usability and properties [1]. Because of that good understanding of processes taking place during solidification and cooling of castings is important. In this, the various thermal analysis techniques, like thermal-derivative analysis (ATD), differential thermal analysis (DTA) or differential scanning calorimetry (DSC) are useful tools.

Phase transitions are an exothermic and endothermic processes and thus can be observed by precise temperature measurements [2-4]. The differential techniques are more complex however tend to be more precise than derivative analysis, for example the DSC allows for more precise observation of solid state phase transitions [5-7].

The most commonly used solidification parameters characteristic for any casting alloy are solidus (T_{sol}) and liquidus (T_{liq}) temperatures. T_{liq} is the temperature in which the very first solid crystals are formed in the molten metal and is useful in optimisation of the pouring temperature to ensure the good balance between liquid metal fluidity, casting shrinkage and solubility of impurities. T_{sol} temperature is useful in design as a limiter of operation temperature and for optimisation of heat treatment processes [8-11].

Depending of alloy composition, varied eutectics can form during solidification. The low-melting point eutectics precipitating in the last stages of solidification may have adverse influence on high-temperature properties of the alloy especially when high-temperature heat treatment is used because during such procedures these eutectics melt and their constituents are dissolved into the alloy matrix leading to dangerous increase in micro-porosity [12].

The formation of low melting point eutectics often imply impurity of the alloy. Presence of these phases can be detected using thermal analysis. In ATD analysis the presence of low-
melting point eutectics significantly lengthens the last stage of solidification and lower the value of \( \frac{dT}{dt} \) derivative. It also changes the inclination of the tangent to the derivative line on the ATD graph [13]. Sample situation is presented in Fig. 1.

![ATD graph for the ending of solidification for high quality alloy (left) and low quality alloy (right)](image)

Fig. 1. ATD graph for the ending of solidification for high quality alloy (left) and low quality alloy (right)

2. Materials and methods of investigation

Research was carried out using ZhS6U-VI and IN-713C (from different delivery batches) that were provided by Pratt & Whitney Rzeszow foundry.

Correct interpretation of ATD data is possible only when the conditions of the test are kept the same in all cases. This was ensured by using as follows:
- ceramic test moulds of same dimensions and material,
- precise, good quality type S thermocouples,
- closely matched quantities of tested alloy (≈ 800 g),
- closely matched pouring temperatures (≈ 1500 °C).

The test casting for ATD analysis was designed as a \( \varnothing 30 \times 120 \) mm rod with \( 40 \times 45 \times 17 \) mm riser. The temperature was measured by type S thermocouple shielded with quartz glass and placed at 1/3 of the casting height (from the base).

Melting was carried out using the Balzers VSG-02 VIM furnace in a Al₂O₃ crucible. The charge was about 1200 g. Protective atmosphere of Ar gas at a pressure of \( 9 \times 10^4 \) Pa was used during melting process. The temperature of molten metal was measured by a type S thermocouple immersed in the crucible. The ceramic mould placed in a VIM furnace chamber is shown in Fig. 2.

![Ceramic mould in a furnace chamber](image)

Fig. 2. Ceramic mould in a furnace chamber

Calorimetric analysis was carried out using Multi HTC S60 differential scanning calorimeter. The weight of samples varied from 140 to 250 mg. Tests were carried out under protective argon atmosphere with heating and cooling rate of \( 10 \) °C/min. Preheating temperature was set to 1450 °C.

Knowledge about the metallurgical quality of feed ingots before production allows to greatly reduce the share of faulty castings. Feed ingots may be contaminated by oxides present in shrinkage cavities formed during preparation of the ingot and, because the superalloy ingots are cast in shape of long rods, the concentration of impurities is not homogeneous. Schematic representation of the phenomena and the photography of actual cross section of the ingot are shown in Fig. 3.

![Shrinkage cavities in feed ingots: a) schematic, b) actual defects on the cross section of the ingot](image)

Fig. 3. Shrinkage cavities in feed ingots: a) schematic, b) actual defects on the cross section of the ingot

During previous ATD analysis of IN-713C [8,10,13] it was found that good metallurgical quality is indicated by:
- \( T_{\text{high}} \) higher than 1335 °C,
- \( T_{\text{low}} \) higher than 1250 °C,
- low (\( T_{\text{E lut}} - T_{\text{sol}} \)) difference, ordinarily lower than 60 °C,
- low (\( t_{\text{sol}} - t_{\text{liq}} \)) time range, ordinarily lower than 50 s,
- absence of abnormal thermal effects,
- high derivative \( V' \) (°C·s⁻¹), ordinarily above 1.5 °C·s⁻¹.

Thermal properties of ZhS6U-VI alloy are similar [14,15] therefore the aforementioned indicators are valid for both alloys.

3. The results of investigations and discussion of results

ATD graphs and characteristic temperature values register in the course of the experiments are shown in Figs. 4, 5 and 6.

![The ATD analysis of ZhS6U-VI alloy](image)

Fig. 4. The ATD analysis of ZhS6U-VI alloy

| Parameter | Time [s] | Temperature [°C] |
|-----------|----------|------------------|
| \( T_{\text{max}} \) | 4 | 1405 |
| \( T_{\text{liq}} \) | 29 | 1343 |
| \( T_{\text{E lut}} \) | 56 | 1332 |
| \( T_{\text{E ult max}} \) | 67 | 1324 |
| \( T_{\text{sol}} \) | 126 | 1270 |
Data obtained during ATD analysis was used to assess the metallurgical quality of selected alloys:

**Alloy ZhS6U-V1**
1. Low value of $T_{\text{liq}} = 1343 \, ^\circ\text{C}$
2. High value of $T_{\text{sol}} = 1270 \, ^\circ\text{C}$
3. Significant difference ($T_{\text{sol}} - T_{\text{liq}}$) = 57 s.
4. Significant difference ($T_{\text{Eut}} - T_{\text{liq}}$) = 54 °C.
5. $V' = 1.28 \, ^\circ\text{C}/\text{s}^{-1}$.
Graph is acceptable, especially in the last stage of solidification (no additionally heat effects), which signifies **good** metallurgical quality of the alloy.

**Alloy IN-713C (batch 4V5910)**
1. High value of $T_{\text{liq}} = 1342 \, ^\circ\text{C}$
2. Lower value of $T_{\text{sol}} = 1255 \, ^\circ\text{C}$ (compared to Zh6U-V1 alloy).
3. Small difference ($T_{\text{sol}} - T_{\text{liq}}$) = 39 s.
4. Small difference ($T_{\text{Eut}} - T_{\text{liq}}$) = 48 °C.
5. $V' = 1.88 \, ^\circ\text{C}/\text{s}^{-1}$.
Graph is acceptable, especially in the last stage of solidification (no additionally heat effects), which signifies **very good** metallurgical quality of the alloy.

**Alloy IN-713C (batch 6V8173)**
1. High value of $T_{\text{liq}} = 1341 \, ^\circ\text{C}$,
2. Low value of $T_{\text{sol}} = 1255 \, ^\circ\text{C}$ (compared to Zh6U-V1 alloy),
3. Large difference ($T_{\text{sol}} - T_{\text{liq}}$) = 61 s,
4. Large difference ($T_{\text{Eut}} - T_{\text{liq}}$) = 63 °C,
5. $V' = 1.36 \, ^\circ\text{C}/\text{s}^{-1}$.
6. Additional heat effect from oxide eutectic.
Graph, especially in the last stage of solidification (additional heat effects), signifies **low** metallurgical quality of the alloy.

Sample DSC analysis data for ZhS6U-V1 alloy obtained during heating and cooling are presented in Figs. 7 and 8.

**Fig. 5.** The ATD analysis of IN-713C alloy (batch 4V5910)

**Fig. 6.** The ATD analysis of IN-713C alloy (batch 6V8173)

The DSC data for IN-713C alloy samples were similar to presented results for ZhS6U-V1 alloy. Values of characteristic temperatures are higher during melting than during solidification which is caused by overheating and overcooling.

Energy balance of $\gamma$ to $\gamma'$ (cooling) and $\gamma'$ to $\gamma$ (heating) transitions indicates smaller initial share of $\gamma$ phase in the
samples. The total heat value change during solidification is less than this value during melting (which is normal because of the energy losses).

A more detailed analysis of the DSC results requires knowledge of the structural composition of the samples before and after the tests.

The ATD results show that this method is exceptionally useful for detecting a low-heat primary phase transitions at the beginning of solidification where, especially in comparison to DSC analysis in which small weight of the samples makes these phenomena hard to notice.

On the other hand, the precision of DSC analysis allows to better interpret the solid-state phase transitions which are common for nickel superalloys (most of all the order – disorder, \( \gamma \) to \( \gamma' \) transition)

The determined values of characteristic solidification parameters (\( T_{NI} \) and \( T_{sol} \)) are comparable between both the ATD and DSC analysis. However during the calorimetric analysis, it is also possible to calculate the enthalpy of phase transitions.

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References

[1] Reed, R.C. (2006). The Superalloys – Fundamentals and Applications. New York: Cambridge University Press.

[2] Jura, S., Sakwa, J. & Borek K. (1980). The use of thermal and derivative analysis to determine chemical composition parameters. Solidification of Metals and Alloys. 2, 101-113. (in Polish). ISSN 0208-9386.

[3] Pietrowski, S. & Władysiak, R. (1996). Control of piston sileums by ATD method. Solidification of Metals and Alloys. 28, 160-172. (in Polish). ISSN 0208-9386.

[4] Sponseller, D.L. (1996). Differential thermal analysis of nickel-base superalloys. In Eighth International Symposium on Superalloys, 22-26 September 1996 (pp. 259-270). Champion, Pennsylvania, USA: TMS Society.

[5] Chapman, L.A. (2004). Application of high temperature DSC technique to nickel based superalloys. Journal of Materials Science. 39(24), 7229-7236. DOI: 10.1023/B:JMSC.0000048736.86794.12.

[6] Przeliorz, R. & Piątkowski, J. (2015). Thermophysical properties of nickel-based cast superalloys. Metallurgija. 54(3), 543-546. ISSN 0543-5846.

[7] Przeliorz, R. (2015). Characterisation of thermophysical properties of nickel superalloys Mar M 200, Mar M 247 and Re 80. Hutnik-WH. 82(7), 441-445. (in Polish). DOI: 10.15199/2015.7.4

[8] Binczyk, F., Sleziona, J., Cwajna, J. & Roskosz, S. (2008). ATD and DSC analysis of nickel superalloys. Archives of Foundry Engineering. 8(3), 5-9. ISSN 1897-3310.

[9] Zietlinska, M., Stieniawska, J. & Wierzbowska, M. (2008). Effect of modification on microstructure and mechanical properties of cobalt casting superalloy. Archives of Metallurgy and Materials. 53(3), 887-893. ISSN 1733-3490.

[10] Binczyk, F. & Gradon, P. (2013). Analysis of solidification parameters and macrostructure of IN-713C castings after complex modification. Archives of Foundry Engineering. 13(3), 5-8. ISSN 1897-3310.

[11] Matysiak, H., Zagorska, M., Balkowiec, A., Adamczyk-Cieslak, B., Dobkowski, K., Koralnik, M., Cygan, R., Nawrocki, J., Cwajna, J. & Kurzydłowski, K.J. (2016). The Influence of the Melt-Pouring Temperature and Inoculant Content on the Macro and Microstructure of the IN713C Ni-Based Superalloy. JOM. 68(1). 185-197. DOI: 10.1007/s11837-015-1672-5

[12] El-Bagoury, N., Waly, M. & Nofal, A. (2008). Effect of various heat treatment conditions on microstructure of cast polycrystalline IN738LC alloy. Materials Science and Engineering A. 487(1), 152-161. DOI: 10.1016/j.msea.2007.10.004

[13] Binczyk, F., Cwajna, J., Gradon, P., Sozańska, M. & Cieślą, M. (2014). Metallurgical quality of feed ingots and castings made from nickel and cobalt superalloys. Solid State Phenomena. 212, 215-219. DOI: 10.4028/ www.scientific.net/SSP.212.215.

[14] Polianskii, V.M., Gavrilyuk, V.V., Zagorskii, V.Z., Logunov, A.V., Polianskii, A.M. & Silis, M.I. (2004). Structure, properties, and fracture mechanism of cast refractory nickel alloy. Metal Science and Heat Treatment. 46 (9-10), 392-397. DOI: 10.1023/B:MSAT.0000049813.06232.81.

[15] Protasova, N.A. (2012). Some features of monocristalline turbine blade regeneration after high-temperature treatment. Russian Aeronautics. 55(1), 83-90. DOI: 10.3103 S1068799811020138