The Relationship Between the Solidification Parameters and Chemical Composition of Nickel Superalloy IN-713C

F. Binczyk a, *, P. Gradoń a, J. Cwajna b, J. Szymszal a

a Institute of Metals Technology, b Institute of Materials Science
Silesian University of Technology, Krasinskiego 8, 40-019 Katowice, Poland
*Corresponding author. E-mail address: franciszek.binczyk@polsl.pl

Received 30.05.2014; accepted in revised form 15.07.2014

Abstract

The paper presents the results of studies on the development of correlation of solidification parameters and chemical composition of nickel superalloy IN-713C, which is used i.a. on aircraft engine turbine blades. Previous test results indicate significant differences in solidification parameters of the alloy, especially the temperatures $T_{\text{liq}}$ and $T_{\text{sol}}$ for each batch of ingots supplied by the manufacturer. Knowledge of such a relationship has important practical significance, because of the ability to assess and correct the temperatures of casting and heat treatment of casts on the basis of chemical composition. Using the statistical analysis it was found that the temperature of the solidification beginning $T_{\text{liq}}$ is mostly influenced by the addition of carbon (similar to iron alloys). The additions of Al and Nb have smaller but still significant impact. Other alloying components do not have significant effect on $T_{\text{liq}}$. The temperature $T_{\text{eut}}$ is mostly affected by Ni, Ti and Nb. The temperature $T_{\text{sol}}$ is not in any direct correlation with the chemical composition, which is consistent with previous research. The temperature $T_{\text{sol}}$ depends primarily on the presence of non-metallic inclusions present in feed materials and introduced during the melting and casting processes.

Keywords: Innovative casting materials and technologies, Nickel alloy IN-713C, ATD thermal analysis, Solidification parameters

1. Introduction

The temperature $T_{\text{liq}}$, at which the first solid state crystal are forming, and the temperature of the end of solidification $T_{\text{sol}}$ are the most important solidification parameters for a given casting alloy. On the basis of $T_{\text{liq}}$ the optimal pouring temperature can be determined, bearing in mind the required fluidity of molten metal, lowest possible volumetric shrinkage and minimal gas and inclusions solubility. In turn, the temperature $T_{\text{sol}}$ provides information about the operational capabilities of casts at elevated temperature and the selection of the heat treatment temperature. Various types of eutectic may form in the alloys solidification range. In case of IN-713C alloy we have the eutectic $\gamma +$ carbides + intermetallic phases. The results of previously conducted studies indicate significant differences in the solidification parameters of IN-713C alloy, mainly $T_{\text{liq}}$, between different batches of feed ingots (“master heat”) supplied by the manufacturer. What causes these differences? It seems appropriate, therefore, to establish an empirical relationship between the solidification parameters and the chemical composition of nickel alloys, based on the supplied certificate and additional analysis of the chemical composition of test casts. Solidification parameters can be easily determined by the ATD thermal analysis. The solidification process is associated with the emission of energy in exothermic effects. These effects can be
easily identified by analysing the ATD chart (T=f(t) and dT/dt) as collapses, bends and temperature stops. The short data collection time is a particular advantage of ATD method.

2. Materials and methods of investigation

The tests were conducted using an IN-713C alloy. The samples of feed ingots from different batches were analysed using the ATD method.

Melting was carried out in the vacuum induction furnace Balzers VSG-02 using Al₂O₃ crucibles characterised by high stability of technological parameters which allow to obtain high purity materials. The mass of the charge was about 1,2 kg. During melting the vacuum of 10⁻³ was maintained. Before pouring the furnace chamber was filled with argon. The pouring was carried out in the argon atmosphere at a pressure of 900 hPa.

The test casts were designed as a cylinders with dimensions 30×120 mm with a 40×45×17 mm sprue. The temperature measurement point was placed at 1/3 height of the cast (from the bottom). The type S Pt-PtRh10 thermocouple was encased in quartz glass tube. Finished ceramic moulds, made using lost wax process in WSK Rzeszów, are shown on Fig. 1. Fig. 2 shows the mould inside the VIM furnace chamber.

3. The results of investigations and discussion of results

Selected results of ATD analysis of IN-713C alloy samples made from master heat 3V6577/T5 and master heat 7V2124 are shown on Fig. 3 and Fig. 4.

Nickel superalloys significantly differ in respect of main alloying components. In IN-713C, beside the Ni base, there are additions of C, Cr, Al., Mo and Ti. Therefore it can be assumed that the solidification process is largely dependent on these components. This applies mainly to the temperature of the beginning of the crystallisation Tₗiq.
The solidification parameters of all cast samples were determined using the ATD graphs. Each cast was also subjected to the chemical composition test using optical emission spectrometer Oxford Instruments FOUNDRY-MASTER. The results of ATD and OES tests are shown in Table 1.

Table 1.
Chemical composition and solidification parameters of IN-713C samples

| No | Master Heat | T_{liq}, °C | T_{Eut}, °C | T_{sol}, °C | C | Cr | Co | Al | Ti | Nb | Mo | Ni |
|----|-------------|-------------|-------------|-------------|---|----|----|----|----|----|----|----|----|
| 1  | 6V5580      | 1348        | 1312        | 1250        | 0.0439 | 13.14 | 13.45 | 0.0673 | 6.03 | 0.725 | 2.18 | 4.43 | 74.1 |
| 2  | M3064 B     | 1340        | 1314        | 1237        | 0.0596 | 13.45 | 13.45 | 0.0673 | 6.03 | 0.725 | 2.18 | 4.43 | 74.1 |
| 3  | M3064 A     | 1333        | 1307        | 1237        | 0.0863 | 13.70 | 13.70 | 0.0655 | 6.03 | 0.947 | 2.47 | 4.59 | 71.8 |
| 4  | 7V2124      | 1340        | 1307        | 1245        | 0.0718 | 13.30 | 13.80 | 0.1860 | 6.11 | 0.954 | 2.23 | 4.18 | 72.8 |
| 5  | 3V4861 B    | 1343        | 1305        | 1262        | 0.0628 | 13.20 | 13.20 | 0.0487 | 5.98 | 0.930 | 2.23 | 4.40 | 72.9 |
| 6  | 3V4861 A    | 1342        | 1305        | 1272        | 0.0711 | 13.20 | 13.20 | 0.0464 | 6.07 | 0.935 | 2.25 | 4.31 | 72.9 |
| 7  | 3V4552      | 1345        | 1306        | 1233        | 0.0612 | 12.90 | 12.90 | 0.1030 | 6.16 | 0.920 | 2.21 | 4.25 | 72.8 |
| 8  | 3V4553      | 1345        | 1307        | 1246        | 0.0584 | 13.10 | 13.10 | 0.0720 | 5.98 | 0.890 | 2.25 | 4.30 | 73.1 |
| 9  | M3023       | 1334        | 1311        | 1233        | 0.0911 | 13.97 | 13.97 | 0.0500 | 5.84 | 0.942 | 2.23 | 4.32 | 72.8 |
| 10 | 3V5677/T3   | 1329        | 1286        | 1231        | 0.0895 | 13.65 | 13.65 | 0.0500 | 5.82 | 0.930 | 2.38 | 4.30 | 73.6 |
| 11 | 3V5677/T4   | 1328        | 1285        | 1204        | 0.0923 | 14.02 | 14.02 | 0.0500 | 5.84 | 0.920 | 2.33 | 4.31 | 73.7 |
| 12 | 3V5677/T5   | 1322        | 1281        | 1228        | 0.1210 | 14.35 | 14.35 | 0.0500 | 5.82 | 0.920 | 2.34 | 4.31 | 73.6 |
| 13 | V1542       | 1324        | 1283        | 1239        | 0.1100 | 14.25 | 14.25 | 0.0200 | 5.70 | 0.990 | 2.14 | 4.12 | 73.7 |
| 14 | 4V4106      | 1340        | 1302        | 1242        | 0.0724 | 13.20 | 13.20 | 0.0883 | 6.13 | 0.915 | 2.25 | 4.32 | 72.7 |

3. The results of investigations and discussion of results

The evaluation of relationship between the liquidus temperature and selected solidification parameters was conducted by multiple regression statistical analysis. Statistical significance of p(α) < 0.05 was selected for the analysis. Calculated value of the probability p lower than 0.05 means that the given element have a significant influence on the considered characteristic.

The probability value p determines the intensity of influence for given element and the coefficient B sign (negative or positive) determines the direction of influence (reduction or increase). The calculations were performed using licensed Statistica 7.1 software package.

Conclusion:
1. Carbon significantly reduces T_{liq}.
2. Influence of molybdenum was excluded!
3. The high value of the coefficient of determination (up to 98.53% of the results can be explained using the model).
Conclusion:
1. Carbon and niobium have significant influence on the reduction of $T_{liq}$ (carbon two times stronger).
2. Influence of cobalt was excluded!
3. The high value of the coefficient of determination (up to 98.36% of the results can be explained using the model).

| STEP 4 | Dependent variable $T_{liq}$ |
|--------|-------------------------------|
| R^2   | 0.9912                        |
| F(3.9) | 90.100, p<0.0000 Standard error of estimation: 1.4004 |
| Variable | BETA | St. error | B | St. err. | t(8) | level p |
| Ni     | -0.1876 | 0.1064 | -2.293 | 1.500 | -1.6763 | 0.1159 |
| C      | -0.1290 | 0.1057 | -2.050 | 1.263 | -1.6372 | 0.1275 |
| Al     | 0.1477 | 0.0838 | 1.766 | 0.631 | 2.3723 | 0.1275 |
| Nb     | 0.1260 | 0.0959 | 2.795 | 0.534 | 5.7607 | 0.0008 |

Conclusion:
1. Carbon and niobium have significant influence on the reduction of $T_{liq}$ (carbon two and a half times stronger).
2. Influence of titanium was excluded!
3. The high value of the coefficient of determination (up to 98.25% of the results can be explained using the model).

| STEP 5 | Dependent variable $T_{liq}$ |
|--------|-------------------------------|
| R^2   | 0.9693                        |
| F(3.9) | 104.91, p<0.0000 Standard error of estimation: 1.4555 |
| Variable | BETA | St. error | B | St. err. | t(9) | level p |
| Ni     | -0.0894 | 0.0786 | 1.047 | 0.880 | 1.1453 | 0.2974 |
| C      | 0.0011 | 0.0702 | 0.135 | 0.023 | 1.4580 | 0.0000 |
| Al     | 0.1630 | 0.0882 | 1.828 | 1.014 | 1.8004 | 0.0913 |
| Nb     | 0.7117 | 0.0632 | 11.270 | 0.523 | 21.3673 | 0.0083 |

Conclusion:
1. Carbon and niobium have significant influence on the reduction of $T_{liq}$ (carbon three times stronger).
2. Influence of nickel was excluded!
3. The high value of the coefficient of determination (up to 97.85% of the results can be explained using the model).

| STEP 6 | Dependent variable $T_{liq}$ |
|--------|-------------------------------|
| R^2   | 0.9678                        |
| F(3.10) | 134.13, p<0.0000 Standard error of estimation: 1.4766 |
| Variable | BETA | St. error | B | St. err. | t(10) | level p |
| Ni     | 1.1233 | 0.2038 | 5.553 | 2.002 | 2.7543 | 0.0086 |
| C      | 0.4298 | 0.1598 | 2.714 | 0.925 | 2.9304 | 0.0052 |
| Al     | -0.2996 | 0.1605 | -1.864 | 0.449 | -1.2485 | 0.2017 |
| Ti     | 0.8090 | 0.1642 | 5.031 | 1.528 | 3.2927 | 0.0115 |
| Nb     | 0.1106 | 0.1652 | 0.682 | 0.345 | 1.4450 | 0.1188 |

Conclusion:
1. Carbon and niobium have significant influence on the reduction of $T_{liq}$ (carbon over three times stronger).
2. Aluminium increases $T_{liq}$.
3. The high value of the coefficient of determination (up to 97.88% of the results can be explained using the model).
4. High value of Fisher statistic indicates very good accuracy of the mathematical model.

| STEP 1 | Dependent variable $T_{liq}$ |
|--------|-------------------------------|
| R^2   | 0.9763                        |
| F(8.5) | 12.732, p<0.00618 Standard error of estimation: 4.0588 |
| Variable | BETA | St. error | B | St. err. | t(9) | level p |
| Ni     | 3.1117 | 0.4279 | 7.247 | 1.500 | 2.1672 | 0.0277 |
| C      | 0.6083 | 0.1810 | 3.380 | 1.204 | 1.4488 | 0.2070 |
| Al     | -0.4489 | 0.3068 | -1.464 | 0.542 | -0.8375 | 0.3901 |
| Cr     | 0.2103 | 0.5831 | 0.370 | 1.145 | 0.2906 | 0.7331 |
| Co     | 0.1187 | 0.1065 | 1.113 | 0.508 | 0.2292 | 0.6577 |
| Ti     | -0.7286 | 0.3912 | -1.837 | 0.687 | -1.0959 | 0.1169 |
| Nb     | -0.3390 | 0.2610 | -1.265 | 0.526 | -1.2967 | 0.2568 |
| Mo     | -0.3981 | 0.4687 | -1.656 | 0.395 | -0.4034 | 0.7033 |

The final model is:

$$T_{liq} = 1311.97 - 306.43\times C(\%) - 13.67\times Nb(\%) + 13.36\times Al(\%)$$

Identical analysis was performed to evaluate the connection between the chemical composition and eutectic temperature $T_{Eut}$ and between the chemical composition and the solidus temperature $T_{Sol}$. The results for the first, fourth and last step are presented below.

For the eutectic temperature $T_{Eut}$:

| STEP 4 | Dependent variable $T_{Eut}$ |
|--------|-------------------------------|
| R^2   | 0.9764                        |
| F(8.10) | 23.406, p<0.00004 Standard error of estimation: 3.7521 |
| Variable | BETA | St. error | B | St. err. | t(10) | level p |
| Ni     | -1.1233 | 0.2038 | -5.553 | 2.002 | -2.7543 | 0.0086 |
| C      | 0.4298 | 0.1598 | 2.714 | 0.925 | 2.9304 | 0.0052 |
| Al     | -0.2996 | 0.1605 | -1.864 | 0.449 | -1.2485 | 0.2017 |
| Ti     | 0.8090 | 0.1642 | 5.031 | 1.528 | 3.2927 | 0.0115 |
| Nb     | 0.1106 | 0.1652 | 0.682 | 0.345 | 1.4450 | 0.1188 |

Conclusion:
1. Nickel reduces $T_{Eut}$.
2. Influence of chromium was excluded!
3. The high value of the coefficient of determination (up to 95.32% of the results can be explained using the model).

| STEP 6 | Dependent variable $T_{Eut}$ |
|--------|-------------------------------|
| R^2   | 0.9726                        |
| F(8.10) | 24.969, p<0.00007 Standard error of estimation: 4.6252 |
| Variable | BETA | St. error | B | St. err. | t(10) | level p |
| Ni     | -1.1733 | 0.1447 | -7.058 | 2.473 | -4.8095 | 0.0009 |
| Ti     | 0.7104 | 0.1254 | 5.714 | 1.564 | 3.6661 | 0.0062 |
| Nb     | 0.4565 | 0.1319 | 6.187 | 1.451 | 2.9621 | 0.0107 |

Conclusion:
1. Nickel, carbon, titanium and niobium reduces $T_{Eut}$ (nickel has the strongest influence).
2. Influence of aluminium was excluded!
3. The high value of the coefficient of determination (up to 93.60% of the results can be explained using the model).
Conclusion:
1. Nickel, carbon, titanium and niobium reduces $T_{\text{Eut}}$ (nickel has the strongest influence).
2. The high value of the coefficient of determination (up to 87.84% of the results can be explained using the model).
3. High value of Fisher statistic indicates very good accuracy of the mathematical model.
4. A very small value of the estimation error, only 4.63

The final model is:

$$T_{\text{Eut}} = 3008.38 - 20.06 \times \text{Ni} - 135.46 \times \text{Ti} - 51.81 \times \text{Nb}$$

For the solidus temperature $T_{\text{sol}}$:

Conclusion:
1. None of the components has any significant impact on the temperature $T_{\text{sol}}$.
2. Influence of nickel was excluded.
3. The low value of the coefficient of determination means that only 63.75% of the results can be explained using the model.

The final model is:

$$T_{\text{sol}} = 1440.27 - 14.88 \times \text{Cr}$$

Very low values of the coefficient of determination and Fisher statistic indicate poor accuracy of the model. Because of this the model cannot be accepted as correct representation of reality. This results are confirmed by previous studies on the assessment of metallurgical quality of feed ingots [4-6]. Many impurities can be introduced to the alloy during melting. This impurities can originate from:

- contaminated feed materials,
- ceramic material of the crucible,
- contaminated furnace atmosphere (ex. with oxygen),
- products of reaction between the melt and the mould material, especially when pouring temperature is high.

Refining processes are impossible because of the vacuum requirement (closed furnace chamber) for melting the nickel superalloys. Thus any of the aforementioned factors can lead to contamination of the melt by intermetallics or gases. These phenomena can consequently lead to shrinkage porosity and non-metallic inclusions, in particular at the grain boundaries.

Most non-metallic impurities are characterized by low pour point, which causes their accumulation on the front of solidification as they crystallize last. Thus the temperature of the end of solidification is significantly reduced, in the case of contamination of the melt, irrespective of the influence of the main alloying elements.

4. Conclusions

Based on the research and the statistical evaluation of the obtained results it can be concluded that:

1. The temperature $T_{\text{liq}}$ of the IN-713C alloy is influenced by the additions of carbon and niobium (reduction) and aluminium (increase). The final relationship is:

$$T_{\text{liq}} = 1311.97 - 306.43 \times \text{C} - 13.67 \times \text{Nb} + 13.36 \times \text{Al}$$

2. The eutectic temperature $T_{\text{Eut}}$ of the IN-713C alloy is influenced by the additions of nickel, titanium and niobium, which reduce $T_{\text{Eut}}$ (nickel the strongest). The final relationship is:
\[ T_{\text{eut}} = 3008.38 - 20.06 \times \text{Ni}(\%) - 135.46 \times \text{Ti}(\%) - 51.81 \times \text{Nb}(\%) \]

3. Only chromium has any impact on the temperature \( T_{\text{sol}} \) (reduction). Because of very low values of the coefficient of determination and Fisher statistic only 28.53% of results can be explained using the model:

\[ T_{\text{sol}} = 1440.27 - 14.88 \times \text{Cr}(\%) \]

The model cannot be accepted as correct representation of reality. This results are confirmed by previous studies on the assessment of metallurgical quality of feed ingots.

4. It is possible to create the empirical relationship between the \( T_{\text{liq}}, T_{\text{eut}} \) and the alloying elements of studied alloys.

5. The studied alloys are presently poured in temperature 1500 to 1520°C. On the basis of ATD analysis it can be concluded that this is too high. Pouring temperature should be between 1460 to 1480°C. However the liquid metal fluidity in case of thin walled castings of aircraft turbine blades should be taken into consideration.

6. In case of high content of impurities the temperature \( T_{\text{sol}} \) for IN-713C alloy was about 1235°C. This can lead to melting of the low melting point eutectic during heat treatment which can cause additional porosity.

Acknowledgments

Financial support of Structural Funds in the Operational Programme - Innovative Economy (IE OP) financed from the European Regional Development Fund - Project No POIG.0101.02-00-015/08 is gratefully acknowledged.

Project INNOTECH the program paths In-Tech (NCBiR): “Manufacturing technology for range of precise, polycrystalline, cored castings of thin-walled, large rotor blades for the low-pressure turbine of the next generation aircraft engine GP7200”

References

[1] Jura, S. (1992). Calorimetric curve for thermal analysis and derivational process of crystallization of metals and alloys. Krzepnięcie Metali i Stopów. 14. PAN-Katowice, Komisja Odlewnictwa. ISSN 1897-3310.

[2] Jura, S. & Jura, Z. (1992). Calorimetric curve and a source of heat in thermal analysis and derivational iron solidification process. Krzepnięcie metali i Stopów. 16. PAN-Katowice, Komisja Odlewnictwa. ISSN 1897-3310.

[3] Jura, S., Sakwa, J. & Borek, K. (1988). The use of differential thermal analysis to determine the parameters of the chemical composition Krzepnięcie Metali i Stopów. 2. PAN-Katowice ISSN 1897-3310.

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

[5] Binczyk, F., Cwajna, J., Roskosz, S. & Gradoń, P. (2012). Evaluation of metallurgical quality of master heat IN-713C nickel alloy ingots. Archives of Foundry Engineering. 12(4), 5-10. ISSN 1897-3310.

[6] Binczyk, F., Cwajna, J., Sozańska, M. & Gradoń, P. (2013). The influence of impurities of ingots on the quality of castings made from nickel superalloy IN-713C. Archives of Foundry Engineering. 13(4), 5-9. ISSN 1897-3310.