Mathematical Processing and Structural Explanation of Surface Tension Polythermal Diagram Reached Out to Achieve Critical Temperature of Thermo-time Treatment for a Ni Based Superalloy

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Thermo-Time Treatment of multicomponent melting can be foreshadowed by the polythermal diagrams analysis of main physical and chemical properties, which are considered for this purpose as structural-sensitive properties: viscosity, surface tension, density or electrical conductivity [1]. Critical temperature ($T_{cr}$), i.e. temperature at which or around which, must run Thermo-Time Treatment has been experimentally marked by a sudden and seemingly contradictory deviation on polythermal diagrams of surface tension, $\sigma(T)$, reached out at cooling process for Ni base studied superalloy (MSRR 7045). A possible mathematical processing of it, is given by interpolation curves of the surface tension dependence on temperature.

Keywords: Thermo-Time Treatment (TTT), critical temperature, metallurgical heredity, surface tension, polithermal diagram

The ideas underlying genetics, metallurgical heredity respectively, appeared in more than 50 years ago in different references [1-19]. In the broad metallurgical sense heredity is the description of those properties of metals that are not only based on status, but depend on their past [3]. One of the variants of the change in a positive sense of the metallic materials heredity is the application of the so-called Thermo-Time Treatment (TTT). Prediction of treatment in liquid phase represents the analysis of polythermal diagrams of main physical and chemical properties: viscosity, density, surface tension and electrical conductivity. The dynamic premise of the link between heredity of the metallic melting and their sensitive-structural properties (physicochemical properties) indicated the so-called critical temperatures as optimal factor in determining the proper Thermo-Time Treatment [1, 2].

According to data from literature [1, 2], the critical temperature means the temperature at which or around which must take place the above treatment in order to reach the desired effect, namely, “relaxation” of metallic melting - the proximity to the structural balance and the possibility of micro-homogenization. Critical temperature has been experimentally marked by a sudden and seemingly contradictory deviation on polythermal diagrams properties on any of the sensitive-structural properties. Structural-sensitive property considered in this article was the surface tension. Taking into account the qualitative aspect of these determinations par excellence, whose purpose was to estimate the critical temperature and not a rigorous quantitative determination of the structural sensitive pair properties: surface tension-density, only the surface tension was determined at the surface of the bath for alloy in question, consequently. Overall, polythermal diagram for the surface tension can be approximated by a mathematical interpolation curve, whose physical meaning has to harmonize both experimental - quantitative side and structural - qualitative side. Overall, polythermal diagram for the surface tension can be approximated by a mathematical interpolation curve, whose physical meaning must harmonize both experimental as qualitative side and structural as quantitative side. Material chosen for the experiments is classified as super alloy-based nickel - MSRR 7045 (Materials Super alloys Rolls-Royce 7045), used in the aviation industry in hot and high corrosive areas of aircraft engines.

Table 1
CHEMICAL COMPOSITION- MSRR 7045

| Chemical Composition |
|----------------------|
| C Si Mn Cr Mo W Al Co Ti Fe B Others Ni |
| ≤0.1 ≤0.6 ≤0.6 20-23 9-10.5 ≤0.6 0.7-0.9 ≤1 2.4-2.8 ≤0.5 Ag + Bi + Pb = 0.0016 base |

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Nickel-based alloys have a cyclic polarization curve with positive hysteresis which does not lead to a repassion (the potential for corrosion is greater than that of repassion). In aqueous solution and after the anodic polarization process it is possible for the following types of nickel oxides:

\[
\begin{align*}
\text{Ni} + \text{H}_2\text{O} & \rightarrow \text{NiO} + 2\text{H}^+ + 2\text{e}^- \\
3\text{NiO} + \text{H}_2\text{O} & \rightarrow \text{Ni}_3\text{O}_4 + 2\text{H}^+ + 2\text{e}^- \\
2\text{NiO} + \text{H}_2\text{O} & \rightarrow \text{Ni}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \\
\text{Ni}_2\text{O}_3 + \text{H}_2\text{O} & \rightarrow 2\text{NiO}_2 + 2\text{H}^+ + 2\text{e}^- 
\end{align*}
\]  

Cyclic polarization curves for Ni and NiCr alloys have a similar character, with a decrease in corrosion currents compared to pure electrochemical nickel. This is due to the influence of chromium in the composition of NiCr alloys. It is known that this element together with oxygen forms very stable chromium oxides with corrosion properties, resulting in the following chemical relationships:

\[
\begin{align*}
\text{Cr} + \text{H}_2\text{O} & \rightarrow \text{Cr}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \\
\text{Cr}_2\text{O}_3 + 5\text{H}_2\text{O} & \rightarrow 2\text{CrO}_4^{2-} + 10\text{H}^+ + 6\text{e}^- 
\end{align*}
\]

**Experimental part**

**Method for determining surface tension**

Method of measuring surface tension used in determining the critical temperature is known as: **maximum pressure in the gas bubble**. This method determines the surface tension of the interface between a liquid phase and a gas bubble formed in the liquid, inside a capillary tube, as shown in figure 1.

**Experimental unit for determining surface tension**

Principle scheme of the pilot unit for measuring the surface tension by the maximum pressure in gas bubble method for metallic melting, super alloy 7045 MSRR, particularly, is shown in figure 2, [1,4].

This pattern determining surface tension is used for metallic melting maintained at high temperatures. For this purpose it uses an electric made tight resistance furnace with graphite (4), double-walled and copper electrodes chilled by water.

An overview of the furnace[1] is shown in figure 3. The sample used was consisted of pieces of super alloy MSRR 7045, with a volume of about 1-1.5cm³/piece.

**Melting process**

Stage 1: Moulding of metallic melting:

- 1.1: proper melting of super alloy small pieces;
- 1.2: determination of solid-liquid biphasic domain, between T_S (softening temperature) and T_L (liquidus temperature);
- 1.3: warming liquid sample up to 1700 °C.

Table 2 is summarizing the stage mentioned above.
Table 2

| Working process | Time, min | Temperature, °C |
|-----------------|-----------|-----------------|
| 1.1- Melting    | 15        | 500             |
|                 | 10        | 750             |
|                 | 10        | 900             |
|                 | 10        | 1100            |
| 1.2- Biphasic domain | 10    | 1300           |
|                 | 5         | 1360            |
| 1.3- Warming up | 10        | 1350            |
|                 | 15        | 1700            |

where:
- biphasic domain limits: $T_S = 1300°C$ - $T_L = 1360°C$;
- total working time until surface tension measurements is of about 75 min.

Stage 2. Measurement of the alloy MSRR 7045 surface tension at cooling process
The measured values are shown in table 3.
- Experimentally calculation of surface tension:

$$\sigma_{\text{MSRR}} = 0.5 \rho g \Delta H r$$

where:
$$\rho = \frac{2 \sigma}{r}$$

ratio between the maximum pressure in the gas bubble and surface tension
$\rho = 1000 \text{ kg/m}^3$, density of manometer liquid (H$_2$O),
$\Delta H =$ height of water column taken into account
$g = 9.81 \text{ m/s}^2$, gravitation,
$r = 3 \text{ mm}$, capillary radius drawn down into the melting.
- Theoretically calculation of surface tension:
Verification of the measured values has been made using the additional formula Folkman given to statistical approach Fowler for surface tension:

$$\sigma = \sum \sigma_j X_j$$

Due to the fact that Ni and Cr constitute an average of 88% of the super alloy MSRR 7045 composition, Folkman’s rule can be written by neglecting the remaining 12% of its composition (especially since about 10% is the Mo element with physic-chemical properties in general similar to Ni).
Accordingly, is given a theoretical value, denoted $\sigma_t$.
For example at about 1560°C, $\sigma_{\text{MSRR}} = 1.8900$, according to table 3.
New value, $\sigma_t$, which differs only in hundredths, gives confidence in experimental procedure.

Data analysis
Determination of surface tension diagram
Data collected in table 3 can be primary processed by raising polythermal diagram of surface tension, namely the graphical representation of the surface tension variation on temperature, $\sigma = \sigma (T)$ (fig. 4).

Setting-up the critical temperature, $T_{cr}$
Critical temperature has been determined by the analysis of figure 4, respectively by remarking the abnormal evolution of the measured surface tension at cooling process starting from the highest thermal threshold of 1675°C. This anomaly is a local maximum point, highlighted in the diagram chart. Taking into account the accuracy class of that method, the critical temperature of super alloy MSRR 7045 lies around temperature of 1630°C.

Equation basics for the polythermal diagram
Overall, polythermal diagram surface tension is approximated by the following mathematical curve (Figure 5).

Table 3

| Temperature, °C | Manometer Pressure, mm col. H$_2$O | Surface Tension, mJ/m$^2$ |
|-----------------|-----------------------------------|--------------------------|
| 1675            | 123                               | 1445                     |
| 1650            | 123                               | 1675                     |
| 1630            | 128                               | 1920                     |
| 1600            | 124                               | 1960                     |
| 1560            | 128                               | 1890                     |
| 1520            | 127                               | 1905                     |
| 1470            | 130                               | 1950                     |

Fig. 4. Polythermal diagram of surface tension for MSRR 7045

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Equation basics for the polythermal diagram
Overall, polythermal diagram surface tension is approximated by the following mathematical curve (Figure 5).
The equation obtained represents a polynomial (complex) function of degree 3:

\[ y = a + bx + cx^2 + dx^3 \]  

where: \( y = T \) and \( x = \sigma \) with coefficient of correlation:

\[ r = 0.89301 \]

It is obvious the difficulty to corroborate polynomial equation between itself and the explanation of its significance from the point of view of the melting structure. As a result, in order to harmonise mathematically point to the physical-structural one the initial curve has been split into two intervals, which in turn have been interpolated by equations with correlation coefficients of most favourable. That re-interpolation arose from the maximum or minimum point discrepancy from polythermal diagram with those of the polynomial equation, satisfactory with regards to the allure. These portions were chosen, taking into account the physical reality and the evolution of polythermal diagram, as follows:

- The period up to the first extreme points of the interpolation curve, i.e. between 1450 and 1640 \(^{0}\)C, re interval called low temperature. In this case it has been found the following equation interpolation (fig. 6).

The equation of the curve is logarithmic

\[ y = \ln(a + bx + cx^2) \]  

where logarithmic equation coefficients and correlation coefficients are, as following:

\[ a \approx 25.69; \quad b \approx -0.024; \quad c \approx 7.71 \times 10^{-6}; \quad r \approx 0.961 \] (exact values are shown on the graph imported). There is a very good correlation, which tends to 1.

The equation can be rewrite by applying the inverse function:

\[ y = e^{a + bx + cx^2} \]  

Analysing the coefficients of \( x \) of polynomial exponentit may be concluded that the equation above foreshadows structural anomaly: although interpolation coefficient \( c \) is positive, it gains weight only for high values of temperature, so tending to 1600 \(^{0}\)C, when surface tension increasing seemed to become abnormally direct proportional to temperature. For temperature values \((x)\) that tend towards 1450 - 1500 \(^{0}\)C balance of \( c \) becomes less significant for exponential equation, which has only nowan evolution of Arrhenius type:

\[ \sigma = \exp(-E/RT) \]  

where: \( E \) could be represented like the energy of motion of liquid phase metal atoms from the volume to the melting surface.

1. The period between 1640 and 1700 \(^{0}\)C, re interval called high temperature.

In this case it has been found the following equation interpolation (fig. 7):

The equation of the curve is logarithmic

\[ y = \ln(a + bx^2) \]  

where logarithmic equation coefficients and correlation coefficients are, as following:

\[ a \approx 8.23; \quad b \approx -2.54 \times 10^{-7}; \quad r \approx 0.993 \] (exact values are shown on the graph above).

There is a very good correlation, which tends to 1, too.

The equation can be rewrite again by applying the inverse function:

\[ y = e^{a + bx^2} \]  

In this case, by analysing again the equation above, i.e. interpolation coefficients, and taking into account a very good correlation, particularly, it can be said that once the critical temperature has been reached a substantial return
to inverse proportionialdepenedence of surface tension on temperature took normally place. In other words an almost strictlyfollowing of Arrhenius equation has been gained.

Conclusions
A possible structural interpretation of polythermal diagram shape for surface tension of Ni base super alloysshould be in accordance with the equations of curves studied previously in order to achieve an appropriate thermo-time treatment (TTT) on critical temperature bases.

The period up to the first extreme points of the interpolation curve, i.e. between 1450 and 1640°C, re interval called low temperature
From a structural point of view, increasing temperature has two opposite effects:
a: Decrease of $\delta$ in the first growth temperature interval: 1450-1540°C: as a result of volume growth generated by specific amplification of thermal motion of elementary particles, and confirmed by the theoretical literature [9-11] for the most compact configuration of the Gibbs surface as follows:

$$A = 1.09 N_A^{1/3} \times V_m^{2/3}$$

($N_A$ = Avogadro's number (6.023 x 10$^{23}$ molecules/mol) and $V_m$ = molar volume);
It touches a minimum point, i.e. the first local extreme point of the diagram:
b: Abnormal increase of $\alpha$, the range of temperatures, more exactly on the border between the two segments, i.e. approximately 1600°C, and over 1600°C, signifies the beginning of the process of structural balancing as a result of decompositions of large structural complexes followed by volume decline.

It is touched therefore a point of maximum, i.e. the second local extreme point of diagram.

The period between 1640 and 1700°C, re range of high temperatures
Actually, this range can be considered as the proper range of structural anomaly, taking as a basis the interpretation of polythermal diagram for surface tension.It is assumed that, in this period of high temperatures, decomposition of some atomic complexes made at low temperature (in the previous range) continues and completes. The result of this very complex phenomenon is that, it finally restores evolution inversely for surface tension on increasing temperature.

These findings lead to the following assumptions:
- the transition to a structure composed by harmonising the initial close order forms, which, although it retains high values for entropy (the number of elementary particles being virtually constant) could lead to a decrease for the other functions and thermodynamic potentials, so a structural quasi-equilibrium characterized by minimizing the energy component from Arrhenius type equation, consequently.
- Logically, homogenization of the newly formed structure would entail and increasing the specific volume of the melting and decreasing of surface tension, respectively.

In conclusion, the level at which treatment should be carried out in the liquid state has been established by proving the possible existence of critical temperature for the studied super alloy, so the possibility of confirmation of specific structures at high temperatures.

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