

THE INFLUENCE ON NIOBIUM AND TITANIUM ON ELECTRICAL RESISTIVITY IN LIQUID STATE AND SOLIDIFICATION OF IN718 ALLOY

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Abstract

The electrical resistivity of IN 718 alloy was studied in a liquid state with contactless induction method of rotating magnetic field. Solidification process was studied by differential thermal analysis. It was founded that electrical resistivity varies in a complicated way with increasing temperature. It is shown that heating of the liquid metal above certain temperatures causes of hysteresis, i.e. discrepancy between the temperature dependences of heating and cooling. It was revealed, that the changes of niobium contents within alloy composition do not lead to a qualitative change of temperature dependence type, but accompanied by some peculiarities. Effect of titanium content on electrical resistivity changes within the alloy composition does not clearly detect. The temperature of maximal melt heating determines the degree of supercooling of liquid alloy.

Keywords: Electrical resistivity, differential thermal analysis, nickel based alloy IN 718, liquid state, temperature dependence, niobium and titanium influence

1 Introduction

The precipitation-hardening iron-nickel based alloy IN 718 is widely used in manufacture of high-temperature components in the gas turbine industry, power plant and petrochemical plants [1, 2]. It is a superalloy, having a compensation of high strength at moderate temperatures, corrosion and oxidation resistance. Because of its excellent balance of properties and reasonable cost, IN718 is accounting for more than 50% of commercial superalloy productions in the world [1]. With the development of land-based power generation and aircraft propulsion, scaling-up of components has become the necessity.

The size of IN 718 ingot produced by VIM-ESR-VAR triple melting has increased dramatically over the past 10 years in response to market demands [2-4]. However, the solute segregation problem, mainly niobium segregation, is a big obstacle for producing large size IN 718 ingots. Particularly, some macro-segregations defects such as freckles and white spots formed during the solidification process will lead to entire failure for the whole ingot.

It has been founded for a lot of steels and alloys that the melting temperature represents melt superheat, which has a great effect on liquid structure, as-cast microstructure and combination of properties of the alloy [5-12]. So, the information about structural transformation in a liquid state during heating has a great importance for the elaboration of melting processes [13]. One of the methods of study of structural transformation in the liquid metal is measuring of temperature dependences of structure-sensitive properties of melt, such as electrical resistivity, kinematic viscosity, density, surface tension and others. Previously it has been founded by the [13] that the

electrical resistivity constitutes most represented property for nickel-based superalloys. In this connection, this work is devoted to study the influence of niobium and titanium contents in the range of alloy composition on the temperature dependences of electrical resistivity of IN 718 alloy.

2 Experimental material(s) and methods

It has been investigated five different chemistries of IN 718 alloy. The chemical composition of ingots is given in **Table 1**.

The table shows that content of Nb and Ti in the samples mainly varies in alloy composition. Thus, there is the ability to distinguish two series of samples. In the first of a series, samples differ by high (1 and 3) and low (2 and 4) niobium content. In the second series, samples differ by high (1 and 2) and low (3 and 4) content of titanium.

Table 1 Chemical composition of the investigated IN 718 alloy

Number of specimens	Alloy content, mas. %							
	C	Cr	Ni	Fe	Nb	Ti	Al	Mo
1	0,026	16,44	54,20	18,55	6,13	1,13	0,45	3,00
2	0,026	19,12	54,32	17,89	3,95	1,19	0,45	3,00
3	0,026	16,74	53,77	18,87	6,26	0,78	0,45	3,00
4	0,026	19,57	52,82	18,81	4,27	0,89	0,45	3,00
5	0,026	17,62	53,43	18,49	5,86	0,96	0,45	3,00

Preliminary metallographic analysis testified that modification of titanium and niobium concentration in IN 718 alloy does not change the phase composition but however, leads to a change in the quantity of phases and redistribution of alloying elements between them.

The contactless induction method of rotating magnetic field was used in this work [15]. Its advantages are the versatility of measurements as in solid as in the liquid state, the ease of construction and a possibility of studying of small amounts of investigated materials.

The physical principle of the method is that the specimen in the crucible is inserted into rotated magnetic field. Field lines are threading the specimen put on inductive current. The magnitude of current depends on from specimen conductivity. The inductive currents, in turn, create the inside magnetic field that interacts with outside magnetic field. The rotation force moment operates on the specimen but the elastic force moment of the suspended elastic thread. As a result, the specimen turns on the angle φ relatively its starting position. The magnitude of φ angle depends on from the electrical resistivity of the specimen, its sizes, rotated magnetic field induction B , its frequency ω and elasticity coefficient of the thread. This method was proposed by Regel and well described in work [15].

The relative method of measuring is more foolproof and suitable. Usually, the high-melting metal with well-known electrical resistivity chooses for the standard. The measurements take part in a crucible of cylinder form.

If the relative method is used and the quantity of magnetic field B is defined by the quantity of current I that flow through the magnet winding the final relation for calculation of electrical resistivity take the form:

$$\rho = \rho_{st} \cdot \left(\frac{M \cdot d_{st}}{M_{st} \cdot d} \right)^{1,76} \cdot \left(\frac{\varphi_{st}}{I_{st}^2} \cdot \frac{\varphi}{I^2} \right) \quad (1.)$$

where ρ , M , d is electrical resistivity, mass and density of investigated specimen, ρ_{st} , M_{st} , d_{st} is electrical resistivity, mass and density of standard specimen, φ , I – torsion angle of pendent system and current in magnet winding during measuring of investigated specimen, φ_{st} , I_{st} – torsion angle of pendent system and current in magnet winding during measuring of standard specimen. The relative error of measurement of electrical resistivity is 3 %, during studying the temperature dependence of ρ is 1 %.

All the experiments carried out in a neutral atmosphere of Helium. Before the experiment system, that consists of a metallic chamber with electric resistance-type furnace and measuring cell with investigated specimen, was previously degassed to pressure of $1,33 \cdot 10^{-2}$ Pa and filled by pure helium to a pressure of $1,11 \cdot 10^5$ Pa. The temperature during the investigation was measured by the tungsten-rhenium thermocouple.

DTA experiments were performed on a fully automated unit [16]. Tests were performed in BeO crucibles in the tungsten cell. The termogram recording was made from 100°C up to the maximum temperature of melt heating and down to 1100°C. The tests were carried out at a constant heating and cooling rate 20°C/min, under Helium protection. Tungsten was the reference material. Reaction temperatures were determined by finding the temperature at which DTA curve deviated from local base-line.

3 Results and discussion

The main information about results of investigations of temperature dependences $\rho(t)$ is shown in **Fig. 1**.

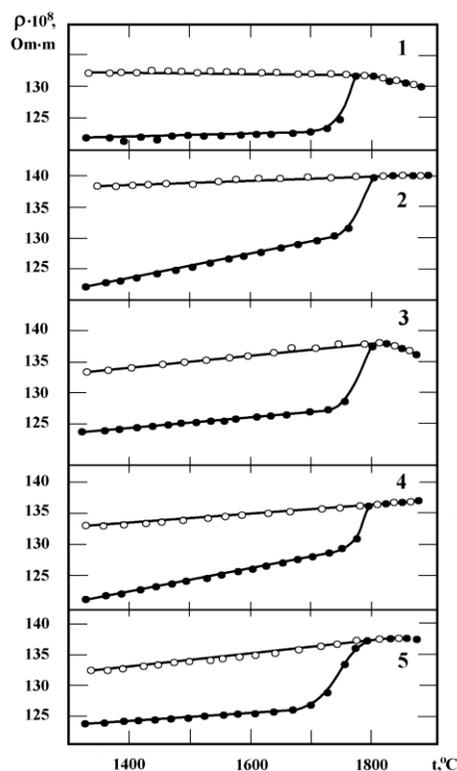


Fig. 1 Temperature dependences of electrical resistivity on IN 718 alloy in a liquid state:
● – heating; o – cooling; Numbers near curves – alloys from **Table 1**

As will be seen from the submitted plots, the electrical resistivity of the specimen after its melting is a slow rise in during heating. In the temperature range from 1700 to 1800°C ρ is elevated intensively. Following the heating to the temperature of 1770-1800°C electrical resistivity depends on from chemistries; the upgrading of ρ is stopped.

If the liquid metal was heated above 1770-1800°C during the following cooling, the electrical resistivity is slowly diminished. The cooling-curve of ρ is outstripped by its heating-curve. The phenomenon of electrical resistivity hysteresis takes place.

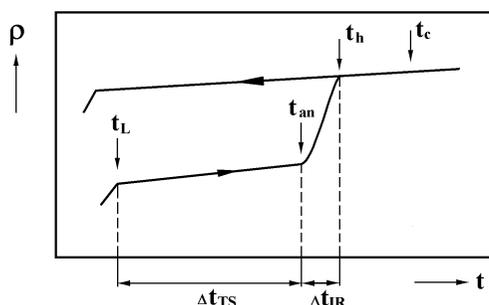


Fig. 2 Characteristic temperatures and temperature intervals on temperature dependence of electric resistivity of IN 718 alloy in liquid state

So it can be distinguished several characteristic temperatures and temperature intervals on the temperature dependence of electric resistivity of all studied samples of the IN 718 alloy (**Fig. 2**):

- anomaly temperature (t_{an}) that characterizes the beginning of an intensive transformation of the melt;
- critical temperature (t_c) - temperature heated to which leads to irreversible transformation melt;
- the interval of thermal stability of primary melt structure (Δt_{ts}) located between the Liquidus temperature (t_L) and anomaly temperature (t_{an}), i.e. $\Delta t_{ts} = t_{an} - t_L$;
- temperature range of intensive restructuring of melt (Δt_{ir}) is located between anomaly temperature and temperature of polyterm hysteresis, i.e. $\Delta t_{ir} = t_h - t_{an}$.

After melting and heating up to the temperature of anomaly (t_{an}) the slight growth of electrical resistivity can be seen due to additional scattering of conduction electrons. Possible structural changes occur in the diffusive regime, does not associate with processes of dissociation and a modification of the nature of chemical bonds.

In the temperature range from t_L to t_{an} effect of burden materials and the technological background is maintained on the structure of the melt, i.e. essentially it is the interval of thermal stability the primary structure of a liquid metal (Δt_{ts}).

The main technological operations of alloy melting are carried out at small overheating above liquidus temperature. The physically justified temperature regulation does not exist in most technological cycles of alloy production. Accordingly, in cases where the liquid metal is characterized by the considerable value of Δt_{ts} , to accelerate the process it needs to use energy influence, capable of destroying interatomic interaction in the initial charge.

The absence of such possibilities predetermine the preservation of hereditary factors and to address them; it needs to use a temperature increasing or an increase holding time at certain temperatures.

When melt heated above the t_{an} intensity of structural change increases dramatically in connection with exceeding of the average energy of thermal motion on activation energy of the atom isolation. Sustainability of nonequilibrium clusters decreases and then tends to destruction [10, 17-18].

Melt heating above t_{an} is accompanied by a dramatic increase in the electrical resistivity ρ . It jumps longer than at melting in 2-3 times. During melting, when the long order is a loss, ρ is increased by 3-4%, while at t_{an} on 6-9%. This fact indicates about major change of the short order structure. Temperature range of intensive restructuring of Δt_{ir} lies between anomalous and hysteresis temperature.

Changing the structure of the melt in the temperature range of Δt_{ir} carries out mostly in kinetic swift-flowing mode. Above t_h the changing takes part mainly in the diffusion mode and ends at critical temperature (t_c), which leads to irreversible structural changes and the emergence of hysteresis of politerm ρ .

Formation of the structure that closes to equilibrium takes part along with the destruction of nonequilibrium melt state in the interval of intensive structure transformation (Δt_{ir}) (**Fig. 2**). Formed equilibrium clusters have the higher energy of interatomic interaction. In this connection, the reduction of the number of conduction electrons contributes to the growth of electric resistivity.

The influence of niobium and titanium on the behavior of electric resistivity of samples of IN 718 alloy has been investigated. Firstly the increasing of niobium content in alloy results in the following changes in the temperatures of transformations in the melt (**Table 2**): anomaly temperature is decreased and interval of Δt_{ir} increases.

Change of niobium concentration affects on the absolute values of the electric resistivity. However, this effect is observed only when the specimen has been heated up to hysteresis temperature. During the subsequent cooling of the liquid metal, this effect retains.

The variation of niobium content influence on temperature resistivity coefficients change (**Table 3**): in the interval, Δt_{ist} temperature resistivity coefficient falls with increasing of niobium content. The most interesting effect of niobium on the behavior of $d\rho/dt$ is founded at temperatures above t_h . At low concentrations of Nb (specimens 2 and 4) increasing of heated temperature leads to the growth of resistance. At high contents of niobium in increasing alloy temperature accompanied by an anomalous decrease of ρ (specimens 1 and 3).

Table 2 The influence of niobium content on temperatures of structural transformation in liquid IN 718 alloy

Number of specimens	Anomaly temperature, t_{an} , °C	Hysteresis temperature, t_h , °C	Interval of thermal stability of primary melt structure (Δt_{ts}), °C	Temperature range of intensive transformation of melt (Δt_{ir}), °C
1	1700	1780	370	80
2	1730	1800	415	70
3	1730	1790	400	60
4	1740	1790	415	50
5	1700	1770	370	70

That peculiarity can be explained by the change of electric resistance dependence from metallic to semiconductor type.

Effect of titanium content on electrical resistivity changes within the alloy composition does not clearly detect.

Table 3 The influence of niobium content on temperature resistivity coefficients in liquid IN 718 alloy on different temperature interval

Number of specimens	$\Delta\rho_{ts}/dt \cdot 10^{-11}, \Omega \cdot m/K$	$\Delta\rho_{ir}/dt \cdot 10^{-9}, \Omega \cdot m/K$	$\Delta\rho_h/dt \cdot 10^{-10}, \Omega \cdot m/K$
1	1,6	1,1	-2,7
2	20,1	1,5	0,3
3	9,2	1,5	-3,3
4	20,3	1,5	0,7
5	7,3	1,5	0

It was found out the deviation from base line of DTA-curve that connected with as carbide as matrix melting. For the samples with high niobium content, the additional peak caused by eutectic melting was fixed. The average temperatures of phase transformations during melting of IN 718 chemistries are tabulated in **Table 4**.

The DTA-curves of all samples is similar in the liquid state. After melting in metal, the process connected with heat absorption happens. The further increasing of temperature leads to coincide of DTA-curve with the base line. The derivation from base line testifies that some exothermic effects take place in the liquid metal.

Analysis of DTA-curves made it possible to draw following results.

The maximum melt heating temperature (t_{heat}) determines the degree of supercooling of the liquid metal. But this dependence is nonlinear. If $t_{heat} < t_{an}$, the observed supercooling increasing with heating to 80-100 °C. Heating to the temperatures that are in the range of intensive structure transformation of the melt contributes to reducing the supercooling, and after heating above t_c supercooling decreases to initial values.

Table 4 The influence of niobium and titanium content on melting process

Number of specimens	Solidus temperature, °C	Temperature of carbide eutectic melting, °C	Liquidus temperature, °C
1	1157	1238	1349
2	1157	1243	1343
3	1145	1238	1353
4	1155	1240	1345
5	1152	1243	1355

The results can be explained by a quasichemical model of the micro-inhomogeneous structure of liquids proposed by Baum [18].

It's the main concept is as follows:

- The melt is composed of microregions, i.e. clusters, where the atomic arrangement is determined by a certain (short-range) order.
- Owing to the relatively strong thermal motion of the particles, the clusters do not have any clear boundaries. For the same reason, the lifetime of the clusters is limited and depends on the energy of the chemical bonds in them as well as on the temperature. The different clusters of two and more types of ordering can exist.
- Energetic inequality of interatomic interaction of different types is the cause for generating clusters of different composition and structures having dissimilar stabilities with time.

d) This model takes into account energy field peculiarities of the melt atoms.

On this model after melting liquid nickel-based superalloys represent a nonequilibrium microheterogeneous system: high alloyed nickel solution and composite clusters. These groups in a certain degree inherit the short-range order of the phase existed in solid metal.

Microgroups of atoms of superalloys is apparently dynamic clusters based on intermetallic $Ni_3(Nb,Al,Ti)$.

The irreversible changes of the structure of liquid metal do not take part in the temperature range from melting until the t_{an} . When melt heat up to the temperature range $t_{an} - t_h$ irreversible destruction of clusters starts. Higher the temperature in this area is, smaller the size of clusters takes place. And finally, temperature micro homogeneous and an equilibrium state is formed above the hysteresis.

During the subsequent cooling of the liquid metal, preheated to t_h , previously destroyed clusters do not form again. Clusters on the base of Me-Al and Me-C bonds, that form both individual and complex micro groups on the base of the (Me-C) + (Me-Al) type may occur before the crystallization in this equilibrium melt. It notes, that the size of these formations significantly lower than micro groups existed in a liquid metal after melting.

Conclusion

1. The electrical resistivity of molten IN 718 with different Nb and Ti content were measured with a contactless induction method of rotating magnetic field. Electrical resistivity is a slow rise in during heating to anomaly temperatures. In the temperature range from 1700 to 1800oC ρ elevated intensively. The phenomenon of electrical resistivity hysteresis takes place.
2. The increasing of niobium content in alloy results in decreasing of anomaly temperature and temperature resistivity coefficient. Effect of titanium content on electrical resistivity changes within the alloy composition does not clearly detect.
3. The experimental results explained by a quasichemical model of the micro inhomogeneous structure of liquids. After melting liquid IN 718 represents a nonequilibrium microheterogeneous system: high alloyed nickel solution and composite clusters. When melt heated to the temperature range $t_{an} - t_h$ irreversible destruction of clusters starts. Above the hysteresis temperature, microhomogeneous and an equilibrium state are formed. During the subsequent cooling of the liquid metal, preheated to above t_h , previously destroyed clusters do not form again. In this equilibrium, melt may occur clusters with another composition and structure.
4. Results of investigation testify that supercooling of IN 718 alloy during crystallization have the identical character and is defined by melt heating temperature and Nb and Ti concentration. Deep supercooling is reached after melt heating to the anomalous temperature.

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