NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY POLITEHNICA BUCHAREST

DOCTORAL SCHOOL OF MATERIAL SCIENCE AND ENGINEERING

Doctoral thesis

Research on the influence of thermal shock at high temperatures on René 41 and Inconel 718 alloys

Abstract

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Abstract

Due to their characteristics of excellent mechanical strength, resistance to thermal creep deformation, good surface stability and good corrosion/oxidation resistance up to temperatures of the order of 0.7 of the melting temperature and even above this temperature, nickel-based superalloys meet special requirements, characteristic of top fields, including nuclear energy. The requests in operation that impose heating in the domains of temperatures of solubilization of the secondary phases, or at higher temperatures, determine structural and property changes that influence the characteristics in operation.

This doctoral thesis brings contributions regarding the influence of thermal shocks at high temperatures on the microstructure and properties of René 41 and Inconel 718 nickel-based superalloys, hardenable by precipitation with the formation of nickel-titanium-aluminum or nickel-cobalt intermetallic compounds. Testing at high temperatures, up to 1000°C, was performed by cyclic thermal shocks with rapid heating in the solar oven. The samples were characterized by hardness and thermal diffusivity determinations, XRD phase qualitative analysis, MEB EDS morphology and elemental chemical composition.

The results highlighted the evolution of hardness and thermal diffusivity, in correlation with the microstructure, depending on the number of shock cycles carried out at the same temperature and the temperature of application of the thermal shock for the same number of cycles, important factors in the solubilization processes /cooling and structural transformations that occur during operation at high temperatures.

Key words: *superalloy, thermal shock, solar energy, microstructure, hardness, thermal diffusivity.*

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Synthesis of main ideas structured on chapters

Part I Presentation of the Research Theme

Chapter 1. Introduction

In order to achieve high performances, imposed by the new technologies, the research in the field is focused in two directions: the development of new materials with higher performances and the study of the behavior of the materials known under the conditions imposed by the new technologies.

Increasing the performances of the equipment through the development of new materials, especially for the peak areas such as aerospace, nuclear energy, cars, results in materials with mechanical characteristics and superior corrosion resistance associated with a specific weight.

In the category of research on the behavior of materials already known under conditions imposed by new technologies, the studies on the properties of nickel -based superalloys are also included in extreme conditions. René 41 and Inconel 718 superalloy, designed for high temperatures use, are frequently studied for uses in extreme conditions. They offer excellent properties in corrosion and wear conditions, resisting extremely high temperatures without losing their properties or mechanical resistance.

Chapter 2. The current stage of research on nickel -based superalloy by precipitation

The name of superalloy describes a wide range of high-performance materials that combine high mechanical characteristics with corrosion resistances at temperatures higher than 650 ° C, characteristic of martensitic steels.

The first supervisions appeared at the beginning of the 20th century, the English patent for the 80 ni-20CR alloy with high corrosion resistance used for steam turbines, dates from 1906.

In 1984, 60 years after their appearance, C. Sims performs a synthesis of the evolution of supervision, presenting the compositional and microstructural characteristics of these high-performance alloys, from the Nimonic Alloy to today's family of forged alloys from Lingos, metal and cast powders, showing the importance of microstructural defects on essential characteristics. This work was a basic bibliographic reference for a large number of subsequent works on nickel -based supervision. [3]

During that period, scientific research in the field of superficiality is directed to the development of new alloys and for the increase of functional parameters, the resistance of corrosion superfood at high temperatures. [4-14]

Their resistance to high temperatures can be obtained by alloying and by the thermal treatment that performs the hardness of the solid solution and the precipitation of phases that give stability at high temperatures. The grain limits, by the precipitates present here that reduce the possibilities of migration, give these alloys mechanical resistance to low temperatures and reduce the strength resistance.

The basic characteristics of the super alloys are:

- excellent mechanical resistance;
- resistance to deformation by thermal fluage;
- good surface stability;
- good corrosion/oxidation resistance.

The common structural characteristic of the materials included in the category of superalloys is the cubic crystalline structure with focused faces, specific to the austenite.

Depending on the base metal, the superalloys are: nickel, iron or cobalt base.

Nickel base superalloys have excellent mechanical properties and high fatigue resistance at high temperatures, features that are particularly required in the aerospace industry for turbine engines.

In the nickel base systems, a large number of secondary phases can be formed, including numerous intermediate compounds, some of which are very harmful. In order to avoid their appearance, the composition of commercial superalloys has been optimized. These compositions established within strict limits greatly restrict the possibilities of developing new alloys. [37-41]

The main phases present in nickel -based superalloys are:

a) the phase γ - solid network with cubic network with centered faces, FCC, which contains diluted large quantities of CO, CR, MO, RU and Re and forms a continuous matrix that includes the other phases;

b) precipitated phases, mainly nickel compounds and carbons of alloying elements

The basic alloying elements that confer the properties of Ni -base superalloys are aluminum and/or titan that can be 10% AT, concentrations in which, in the equilibrium structure, are present in two phases: γ and γ ' NB alloys (see Fig.2.11)

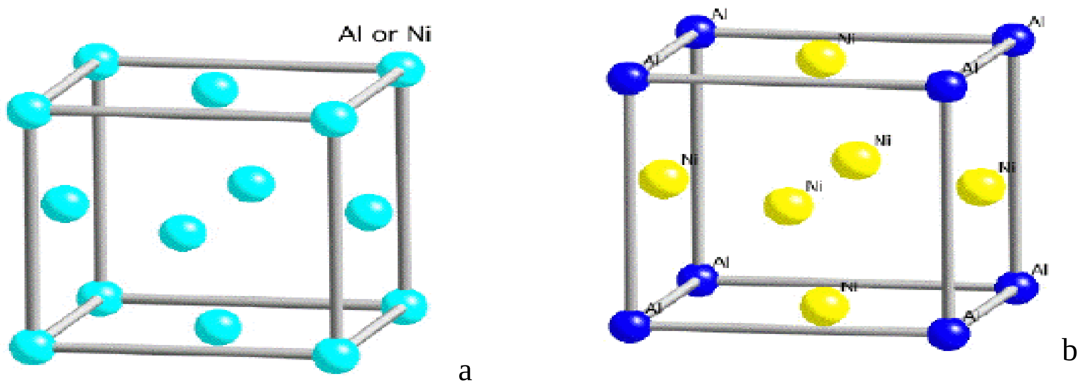


Fig.2.11 Crystalline structure: a- phase γ and b - phase γ ', after [42]
H.K.D.H.Bhadeshia,https://www.phase-trans.msm.cam.ac.uk/2003/Superalloys/ superalloys.html

Heating at high temperatures lead to solubilization of secondary phases, decreased hardness and growth. When cooling, the precipitation of the secondary phases takes place by following the limits of initial grains, a phenomenon often called "the limits of grains". The phenomenon was observed in the case of the 617 alloy at a service temperature of 700 ° C, for which within the limits of grains, the M23C6 particles with a high boron content. [57]

The microstructural and mechanical properties of the metal materials are affected by the cooling speed during the thermal treatment. The distribution of the temperature and the corresponding cooling speed are determined by the thermal transfer coefficient.

AKCA ENES and GURSEL Ali have correlations between the technology of processing the Inconel 718 supervisory under a thermal structural hardening treatment and its microstructure and its properties [89].

The phase transformations that take place during the treatment of return of the hardened superalloy by precipitating the secondary phases, occur with the release of the latent heat and with the variation of the temperature in the stages of formation and growth of the grains; the distribution of the temperature in the sample is determined by the thermal transfer properties of the alloy. [90]

Part II of experimental research

Chapter 3. The Research Program

The general objective: the doctoral research project aims to determine the influence of cyclical thermal shocks at high temperatures on the microstructure, hardness and thermal transfer properties of René 41 and Inconel 718.

Specific goals:

 Establishing a methodology of testing and characterizing the two superalloys, collaborations, at national and international level, necessary to achieve the general objective;

 Testing the alloys in cyclical thermal shocks at temperatures of 700-1000 ° C, using solar energy;

 determining the influence of thermal shocks on the hardness by the depth marked by the increase of the temperature in relation to the "hot" end of the samples;

 Determining the influence of thermal shocks on the thermal diffusivity, under constant temperature conditions with the increase in the number of shocks applied and for a constant number of shocks applied ranging the temperature of the shocks;

 study of the microstructures of the alloys treated by thermal shock;

 Comparative study of the two supervisions requested under conditions of thermal shock at high temperatures.

Experimental Research Program

 Preparation of samples and characterization of materials in the state of delivery

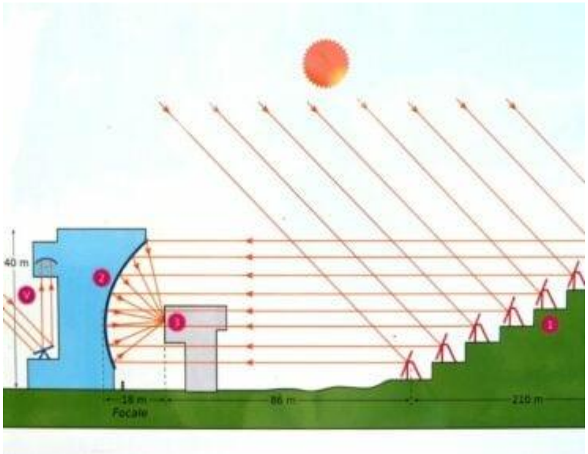
 Testing in cyclical thermal shocks at high temperatures using solar energy, in the Promes-Solar Oven Laboratory from Font-Romeu-Odeillo, France, using European funding

- Determining the influence of thermal shocks at high temperatures on the microstructure of superalloy, within the advanced materials laboratory in the Regional Center for Research and Development for Materials, Processes and Innovative Products for the Automobile Industry, CRC & D-Auto
- Determining the influence of thermal shocks at high temperatures on the thermal diffusivity of the two alloys, in collaboration with the specialists from the National Institute of Material Physics, Măgurele
- Microstructural and elemental chemical characterization within the Laboratory of Advanced Materials in the Regional Center for Research and Development for Materials, Processes and Innovative Products for the Automobile Industry, CRC & D-ATO
- Qualitative phase analysis, within the Laboratory of Advanced Materials in the Regional Center for Research and Development for Materials, Processes and Innovative Products for the Automobile Industry, CRC & D
- The comparative study of the microstructure and properties of the two superalloys subjected to thermal shocks at high temperatures

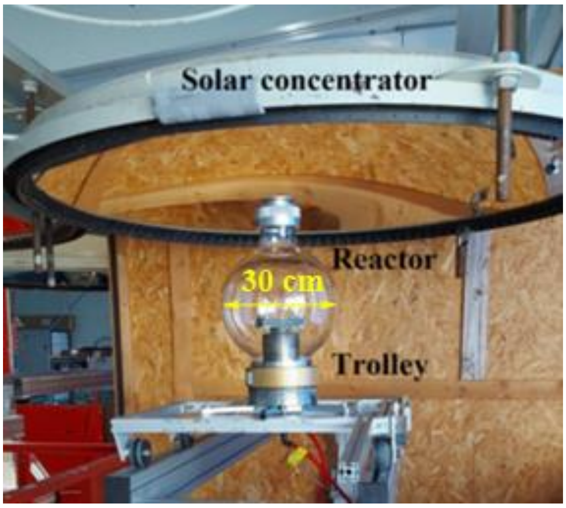
Experimental techniques

The tests for thermal shock test have a parallelepiped shape with a 7mm side square and 10mm height. The height of the sample is oriented according to the direction of deformation of the alloy.

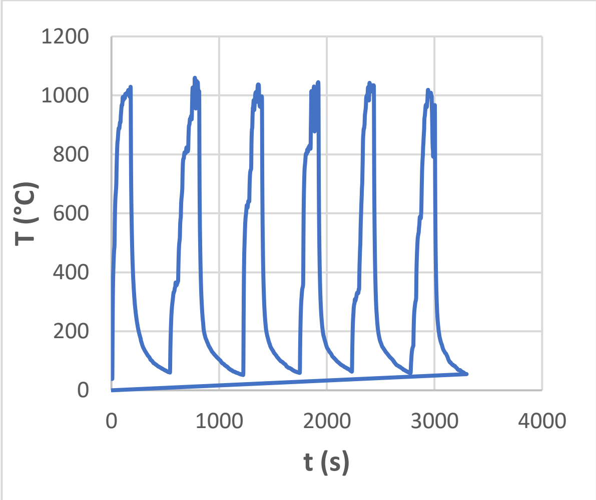
a



b



c



d

Fig.3.1 Testing the samples in cyclical thermal shocks in the solar oven: a- Image the solar oven, the Promes laboratory; b- principle scheme of the solar oven; C- Test installation d) Cyclogram for treatment at 1000C, 6 cycles**.**

The testing at thermal shocks was done in the solar oven in the Promes Laboratory, Font-Romeu-Odeillo, France, as part of the FP7 Program Program "Study of Variation of the Mechanical Properties of Superalloys Inconel 718 and René 41 Under Thermal Shook", TERMOINCORENÉ P1601300180, Sphere 2016. Cyclic thermal shocks were used in the temperature range of 700 ° -1000 ° C, with the constant temperature duration of each 30S cycle (Figure 3.1).

The thermal transport properties were investigated at the National Institute of Materials Physics, Măgurele with the help of a Flash laser analyzer (Netzsch LFA 457 microflash) from room temperature to 1050 ° C. The LFA equipment allows the direct measurement of the thermal diffusivity, α, by analyzing the temperature variation of a sample surface when a calibrated laser impulse is applied to the other surface. The specific heat of the materials, CP can be determined by a differential method using a reference sample (in this case MO, NIST SRM781 certificate). The thermal conductivity was calculated as $\lambda = \alpha \times \rho \times Cp$, where ρ is the density of the sample. The density of the samples was measured by the Archimedes method using a high resolution balance. The equipment used, LFA-457 and DIL-402C, are produced by Netzsch GmbH, Selb, Germany.

The microhardness measurements were performed with Falcon equipment, 500 Series, for Micro Vickers, Vickers, Micro Brinell.

For microstructural analysis, the samples were prepared by mechanical grinding and attacked with the Adler reagent.

The microscopic analysis used the Olympus BX51M optical microscope in the light field (BF) and dark (DF) at the increases of x100, x200 and x500. The microscope used is produced by Olympus, Tokyo, Japan.

The characterization of the SEM-EDS was done with a Hitachi Su5000 electron microscope equipped with a retro-spread electron detector and the fluorescence spectroscopy module for elemental analysis. This electron microscope has as producer Hitachi, Tokyo, Japan.

The X diffractograms for the analyzed samples were purchased using a Rigaku last IV diffractometer with vertical goniometer, under the following conditions: Bragg-Brentano assembly, Ultra Unidimensional Detector and Graphite monochrome on the diffracted beam; Acceleration voltage of 45 kV and current filament of 40 mA; Scan range 2 during 25□-100□], step 0.05□ and scan speed 2□/min. The qualitative phase analysis was performed with the help of the integrated PDXL2 software (Rigaku, version 2.8.4.0) and the PDF4+ 2023 Database (ICDD) database. This type of equipment is produced by Rigaku, Tokyo, Japan.

Chapter 4. Influence of cyclical thermal shocks on René 41 alloy

Following the experiments of cyclical thermal shocks in the solar oven, the René 41 samples were subjected to testing the influence of these shocks on their microstructure, hardness and diffusivity. The samples were characterized by optical microscopy, scanning electron microscopy HV hardness, thermal speaker and X diffraction analyzes. All observations were noted following the completion of all these analyzes.

In Chapter 4, the characterization of the René 41 alloy began in delivery state, which was achieved by determinations of physical properties, HV hardness measurements, morphological characterization by optical and electron microscopy, EDS elemental chemical composition and qualitative phase analysis, XRD.

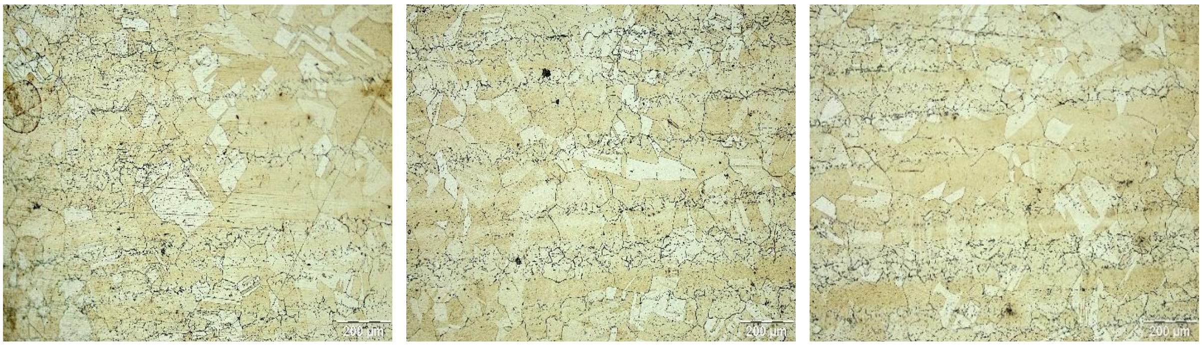
The microstructure of the René 41 alloy in the original state is a structure in bands, typical of plastic deformation, with hard phases oriented according to the direction of deformation and matrix with polyhedral structure (see Figure 4.2). The strips that contain precipitates to the grain limit have a fine structure, and the solid solution band γ have large grains, with grain limits that are not well defined (see Figure 4.2 A, B). The precipitates are of two types: large dark precipitation and fine light precipitate (see Figure 4.2 C, D, E).

The presentation of the treatment through cyclical shocks was continued by examples of macrography and graphics for the thermal shock cyclograms.

Following the HV hardness measurements, performed on the height of the samples, from the surface opposite the shock to the shock application surface were found: the hardness of the samples decreases from the opposite surface to the application surface of the thermal shocks. For the same temperature, the hardness in the vicinity of the shock application surface decreases with the increase in the number of cycles (see Figure 4.6). The exception is the test treated at 1000 ° C, 12 cycles for which the hardness stabilizes around 350 HV, with a slight increase (Figure 4.6A); And for the same number of cycles, the hardness in the vicinity of the treatment area has the same decrease trend with the increase in thermal shock temperature (see Figure 4).

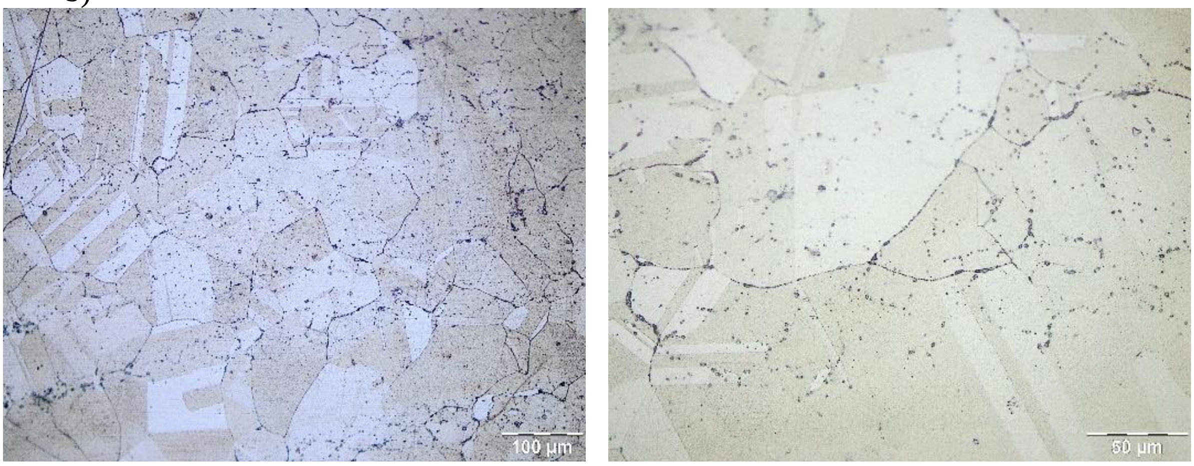
For the microstructural characterization by optical microscopy, the analysis was performed along the sample length, the images being presented from the end opposite the application of thermal shocks to the surface subject to thermal shock and on the two surfaces. It was observed, for example, for the sample subject to shock at 700 ° C, that the microstructure on the lateral surface preserves the orientation of the precipitates in rows parallel to the deformation direction, forming bands alternating with the polyhedral matrix. In the microstructure of the bases, a section perpendicular to the deformation direction, polyhedral macles and the presence of precipitates within the grain limit are well highlighted. After 3 shock cycles there are no obvious differences between the structure of the two bases (comparison for 50µm).

a)



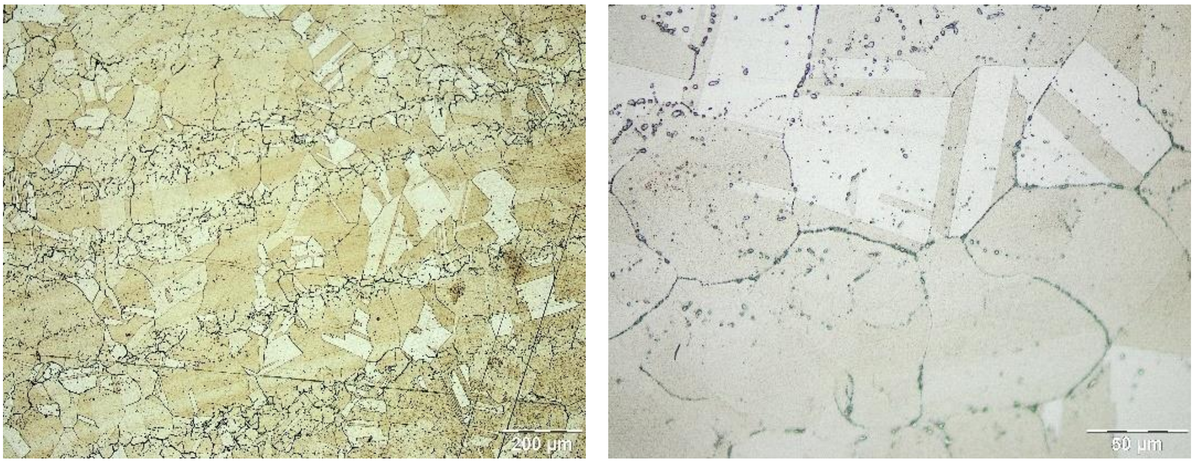
200µm

b)



100µm 50µm

c)



200µm 50µm

Fig.4.8 Microstructures for the sample treated at 700 ° C, 3cycles: a) on the lateral surface, from the surface opposite the shock to the application surface of the thermal shock; microstructures obtained on the bases of the parallelepiped sample: b) the opposite surface of the shock application and c) the shock application surface

Morphological and elemental chemical analysis by scanning electron microscopy made for René 41 samples highlighted, for example for the test treated at 700 ° C, 3C, the alloy microstructure has a metallic matrix of solid solution with polyhedral maclets in which precipitates are oriented majority in rows (fig 4.17), similar to the material in delivery state. The EDS analysis in line shows precipitate NI3TI (γ ') and molybdenum carbides (fig.4.17).

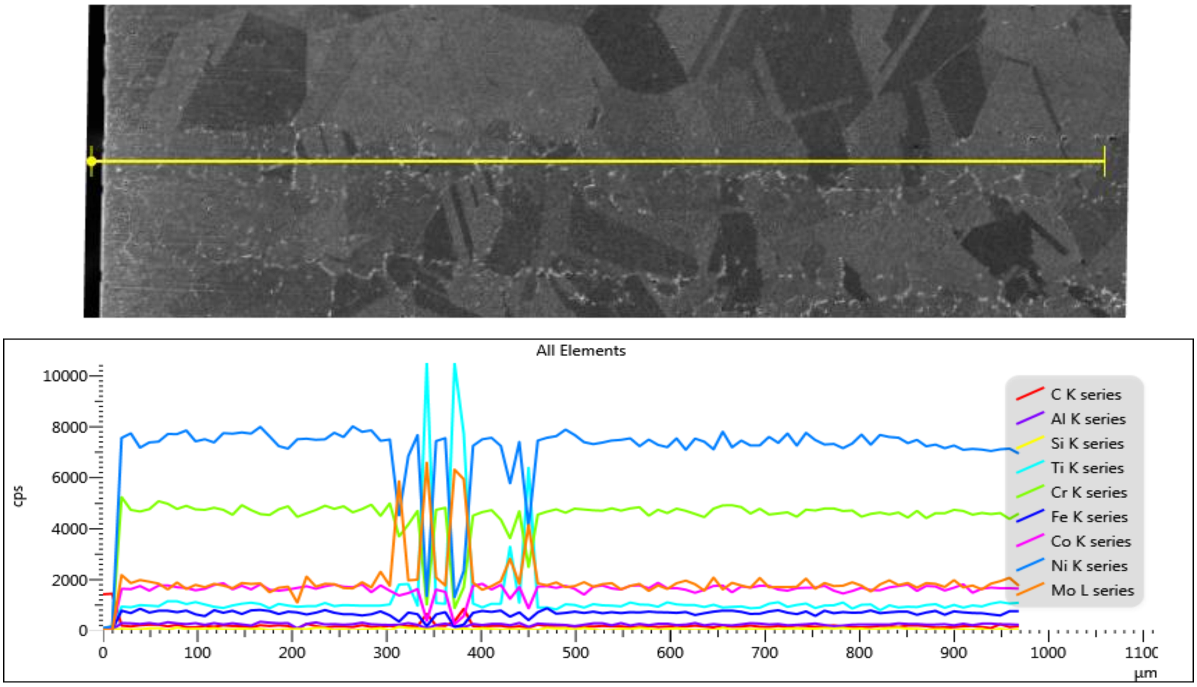


Fig.4.17 EDS On Line analysis in section for René 41 test treated at 700 ° C, 3C

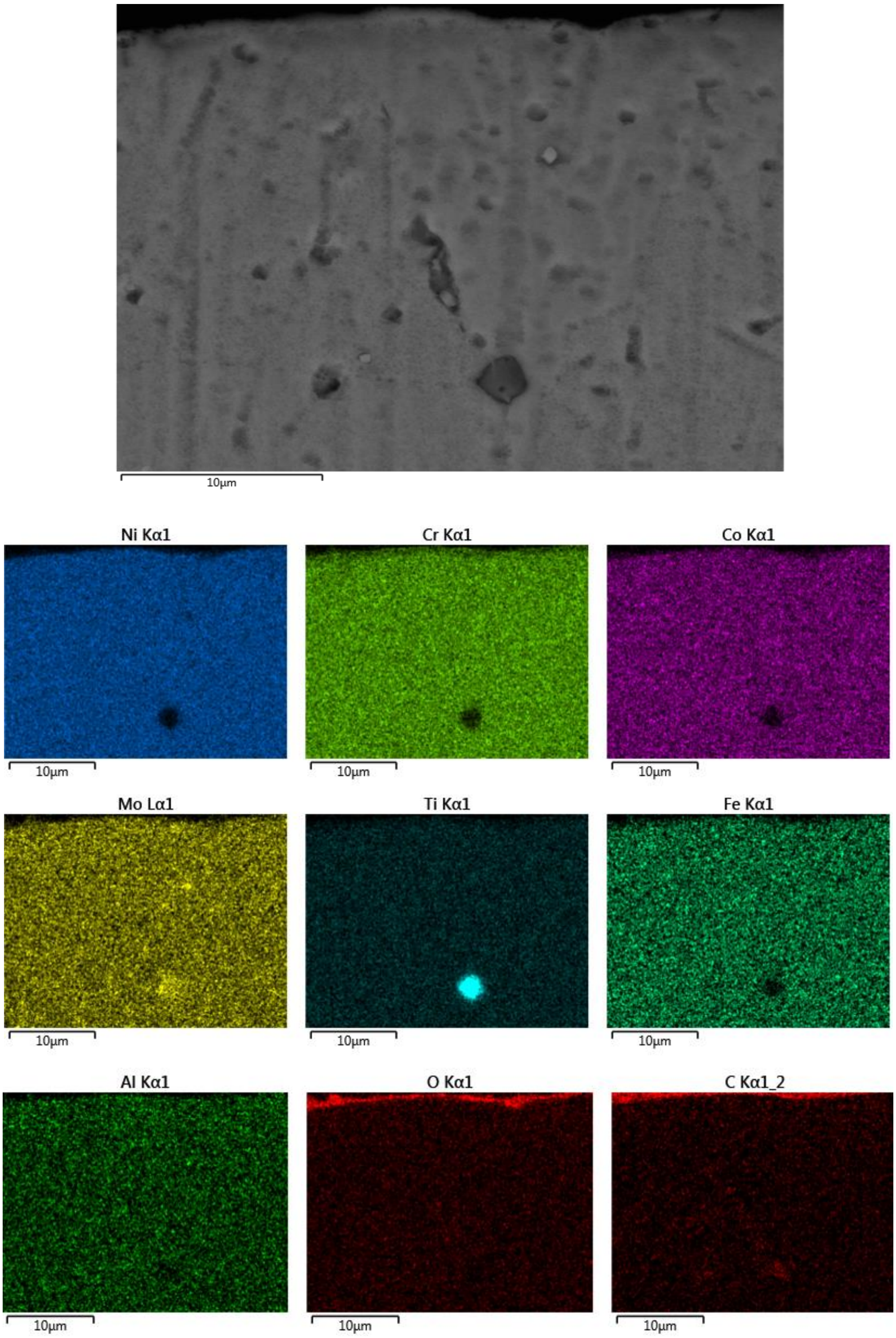
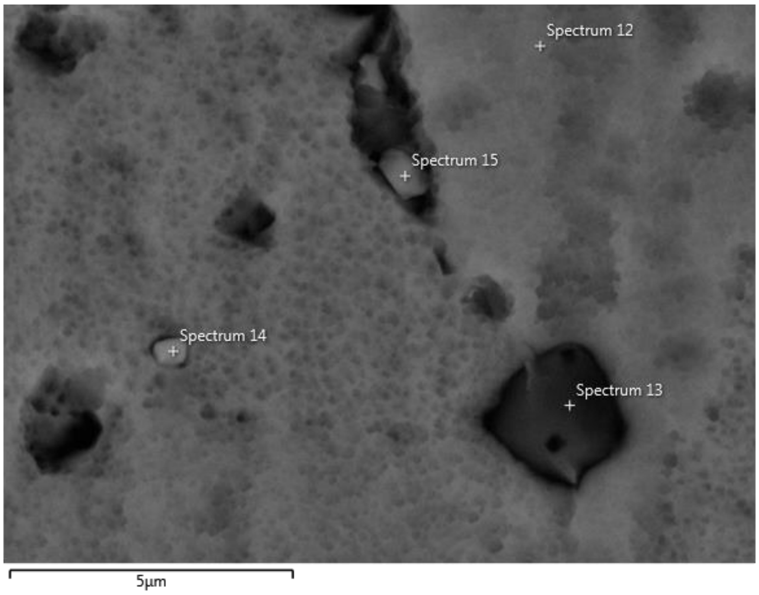


Fig.4.18 The map of elemental composition, the René 41 -treated sample at 700 ° C with 3 thermal shock cycles



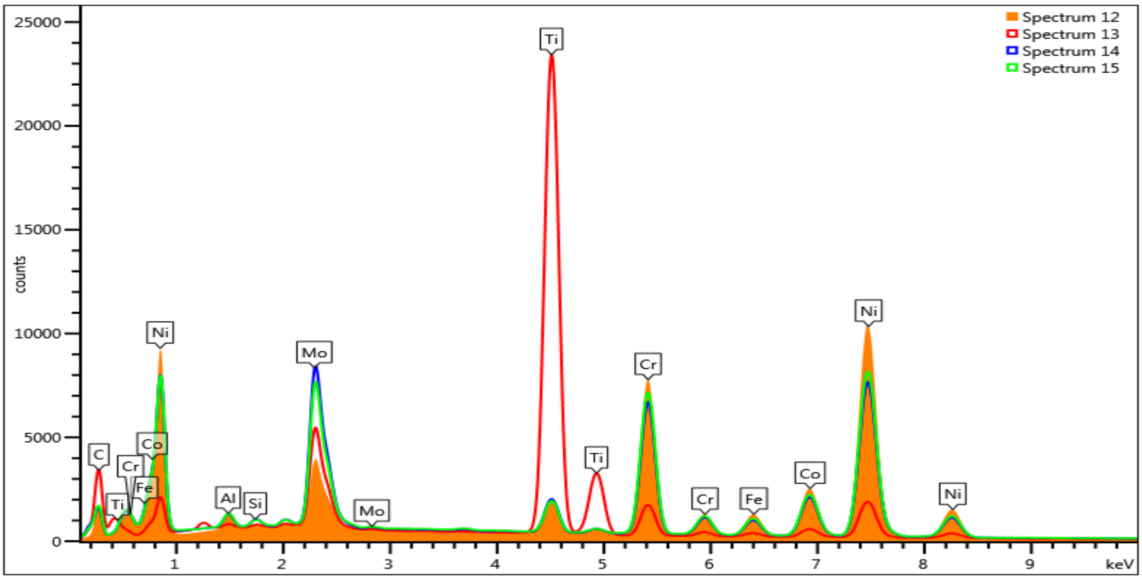


Fig. 4.19 Elemental chemical analysis of the René 41 treatment treated at 700 ° C, 3 thermal shock cycles, overlapping spectrum: Spectrum 12-Matric, Spectrum 13-Composed in Ti and spectra 14, 15-composed in MO

Tabel 4.4 Compositions [% WT] determined in points 12, 13, 14, 15 for rené 41 treated at 700 ° C with 3 thermal shock cycles

Spectrum	Spectrum 12 [%wt]	Spectrum 13 [%wt]	Spectrum 14 [%wt]	Spectrum 15 [%wt]	
Al	1.98	0.37	1.47	1.53	
Si	0.19	0.20	0.59	0.54	
Ti	3.39	62.75	3.86	3.49	
Cr	19.13	6.17	18.04	18.76	
Fe	3.53	0.87	2.89	3.05	
Co	10.18	2.35	8.89	9.18	
Ni	50.47	11.15	38.32	40.26	
Mo	11.13	16.15	25.94	23.20	
Total	100.00	100.00	100.00	100.00	

The map of the elemental chemical composition (fig.4.18) and the elemental chemical analysis by superimposed spectra (fig. 13, Fig, 4.19, Table 4.4), and the small light precipitates are rich in molybdenum, carbides (fig.4.19, table 4.4, spectra 14 and 15) [94-95]. The composition of the solid solution matrix γ is given by spectrum 12.

The X diffraction of the analyzed samples present, mostly, diffraction lines associated with the matrix, FM3M space (225), with the FCC structure [24] and the intermediate compound γ '(Ni3 (Al, Ti) [25]. The main elements that form precipitate (with Ni) in the structure of René alloys are Al and Ti [24].

In the superficial layers of the samples treated at 700 ° C, 800 ° C and even at 900 ° C with 3 cycles, you can see the appearance of oxides: Ti0.24 CR1.76 O3 (DB card 04-015-979), FE3 O4 (DB card 01-084-2782) and NIO (DB card 04-004-8992), Figure 4.34.

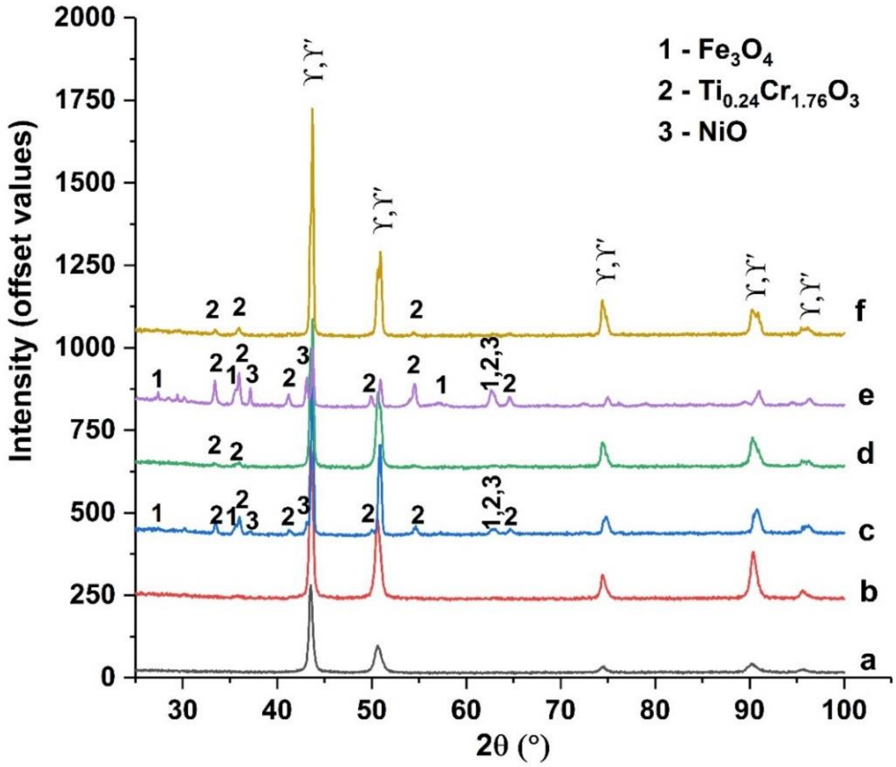


Fig.4.34 Diffractograms for René -41 standard and samples treated by thermal shocks: 700 ° C with 3 cycles -B, 700 ° C with 9 cycles -C, 800 ° C with 3 cycles -D, 800 ° C with 9 cycles -e and 900 ° C with 3 cycles -f

The variation with the temperature of the thermal diffusivity of the samples subjected to thermal shocks has a maximum in the range 600-800 ° C, similar to the standard sample, but the maximum of the samples subjected to thermal shocks is more pronounced.

Unlike the standard sample, the variation with the temperature of the diffusivity of the samples subjected to thermal shocks also has the second maximum in the range 900-1000 ° C.

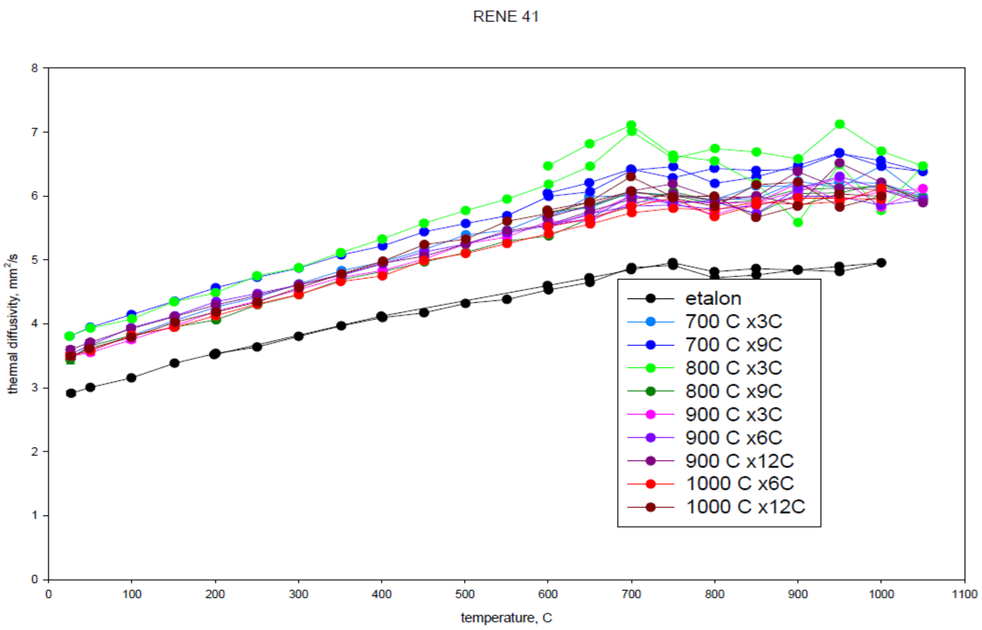


Fig.4.41 Synthesis for diffusivity values for René 41 samples treated by cyclical thermal shocks

Chapter 5. Influence of cyclical thermal shocks on Inconel 718 alloy

In Chapter 5, the characterization of the Inconel 718 alloy began in delivery state, which was achieved by determinations of physical properties, HV hardness measurements, morphological characterization by optical and electron microscopy, EDS elemental chemical composition and qualitative phase analysis, XRD.

SEM analysis (Fig.5.2) highlighted a relatively uniform distribution of intragranular precipitates at the limit of grains (fig.5.2 a, c), polyhedral structure with macled grains of solid solution ɣ (5.2.b), presence of intergranular precipitation with lamellar /acicular form within the grain limit (Fig 5.2b-F).

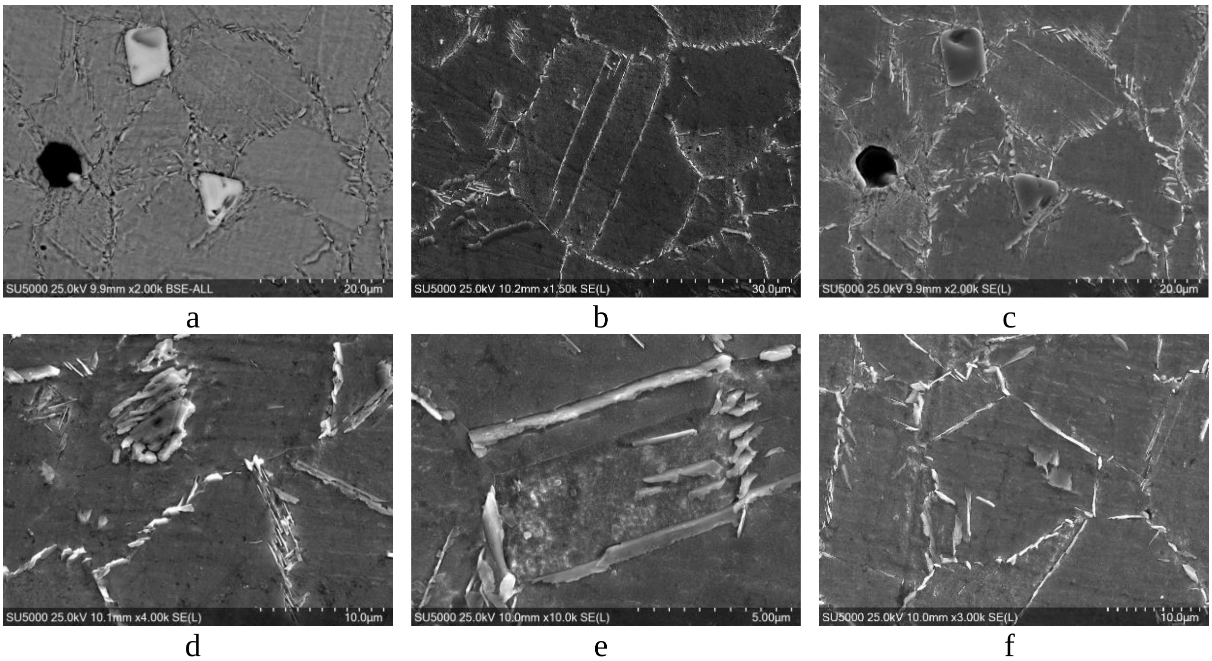


Fig.5.2 SEM microstructures for the alloy in delivery state

The SEM EDS analysis at points highlighted the elemental chemical composition of the solid solution matrix and the phase ɣ”, the NI3NB compounds.

The presentation of the treatment through cyclical shocks was continued by examples of macrography and graphics for the thermal shock cyclograms.

Following the HV hardness measurements, performed on the height of the samples, from the surface opposite to the shock surface, the following were found: for the same number of cycles, the hardness near the shock application decreases with the temperature increase (A is see Fig.5.8).

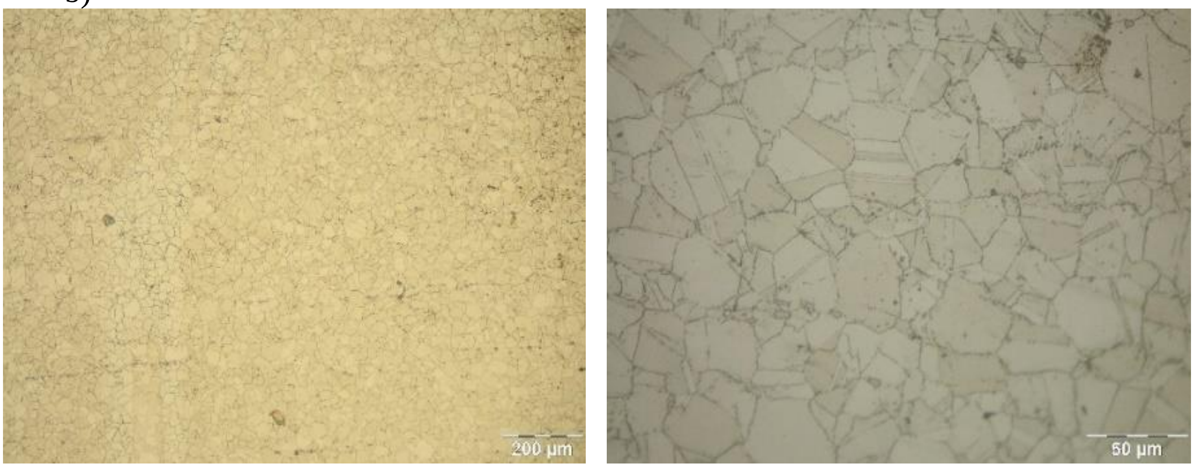
The decrease in hardness is due to the increase of the energy stored in the sample by increasing the shock temperature and the number of shocks, which causes diffusion and dissolution processes, decreasing the proportion of hard phases.

For the microstructural characterization by optical microscopy, the analysis was performed along the sample length, the images being presented from the end opposite the application of thermal shocks to the surface subject to thermal shock and on the two surfaces. It was observed, for example, for the 718 Inconel 718 sample at 1000° C, 6 cycles, the difference in grain size between the surface in the vicinity of the shock and the opposite.

a)

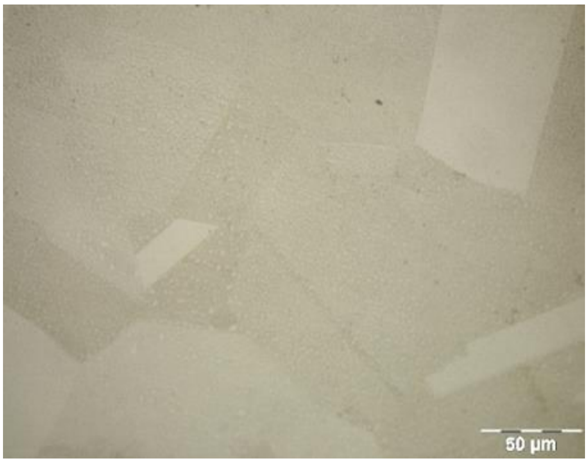
200µm

b)



200µm 50µm

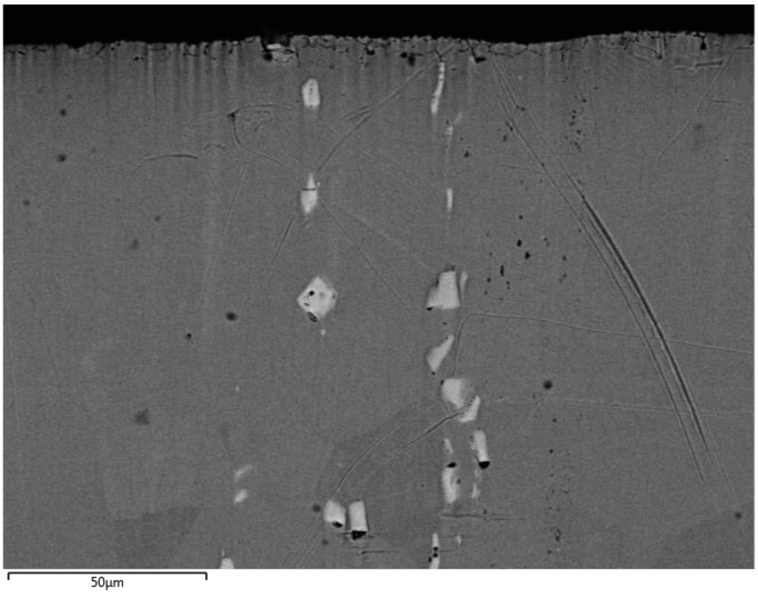
c)



200µm 50µm

Fig.5.20 Microstructures for the 718 Inconel sample treated at 1000 ° C, 6 Cycles: a) the evolution of the microstructure on the lateral surface of the sample from the end of the shock to the application surface; microstructures obtained on the bases of the parallelepiped sample: b) in the surface opposite the shock application and c) in the vicinity of the shock application surface.

An example of SEM/EDS analysis for shock sample at 700 ° C, 20 cycles, shows that by increasing number of shock cycles large precipitates appear in line, oriented perpendicular to the shock application surface, rich in NB and MO and those rich in Ti, as well as an oxidic superficial layer (fig.5.33)



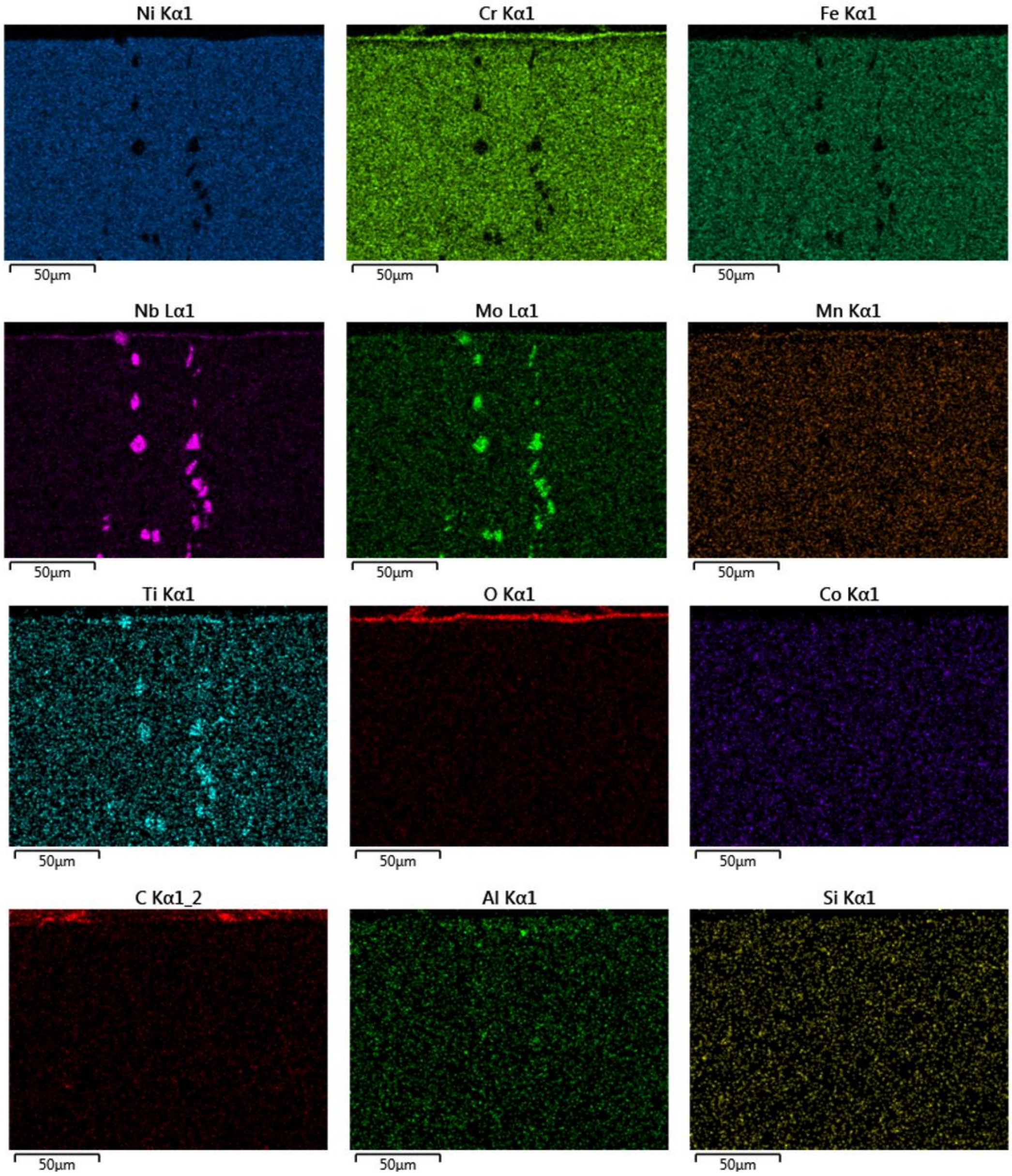
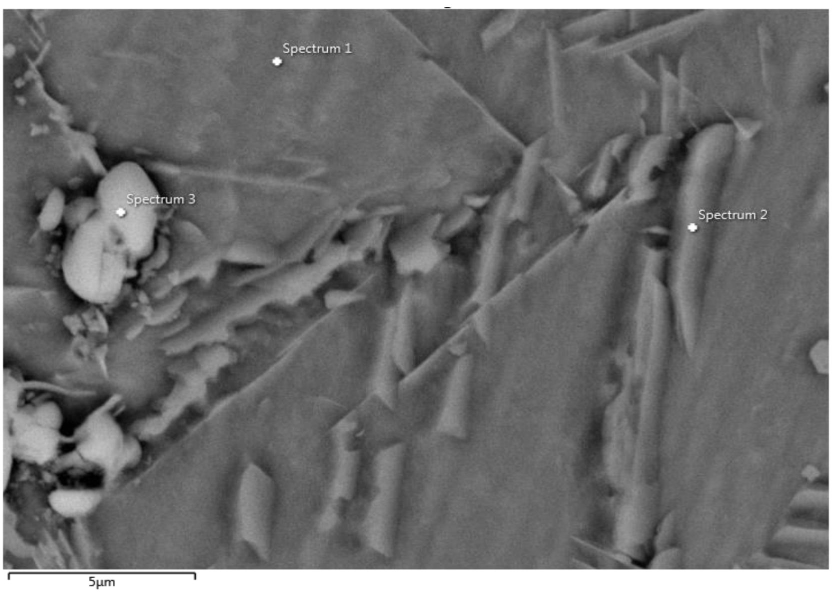


Fig.5.33 The map of the elemental composition of the 718 Inconel sample at 700 ° C, 20 cycles



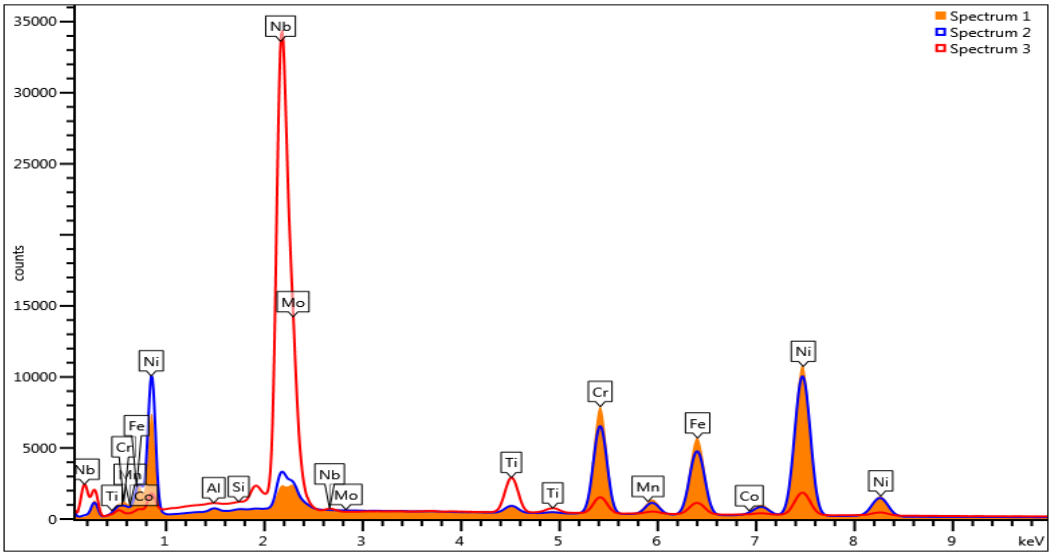


Fig.5.35 Elemental chemical analysis of the sample treated at 800 ° C, 9C; A-shaft of elemental chemical composition; B-superimposed spectrums

Tabel 5.4 Elemental Composition [%WT] in points 1-3

Spectrum	Spectrum1	Spectrum 2	Spectrum 3
Al	0.68	0.61	0.08
Si	0.14	0.14	0.09
Ti	0.97	1.10	6.38
Cr	18.24	16.43	3.35
Mn	0.21	0.18	0.00
Fe	18.44	16.58	3.04
Co	0.44	0.40	0.07
Ni	51.74	51.85	7.50
Nb	5.55	9.46	78.91
Mo	3.60	3.24	0.57
Total	100.00	100.00	100.00

At 9 cycles (800 ° C) lamellar precipitate appears at the border of grain and gross precipitate with rounded forms, very rich in niobium (fig. 5.35, table 5.4). The increase of up to 78.91%NB in light, coarse color and decrease of NB content in matrix is noted.

Qualitative phase analysis by diffraction with X-ray has indicated for all analyzed samples the presence of diffraction lines associated with the matrix γ of the alloy with a structure in the space group 225: FM-3M and the phase ɣ 'being part of the space group 221: PM-3M [140]. For the unclear alloy sample and for the 800 ° 9C INCONEL sample, the presence of the phase ɣ specific to this alloy is also observed [140].

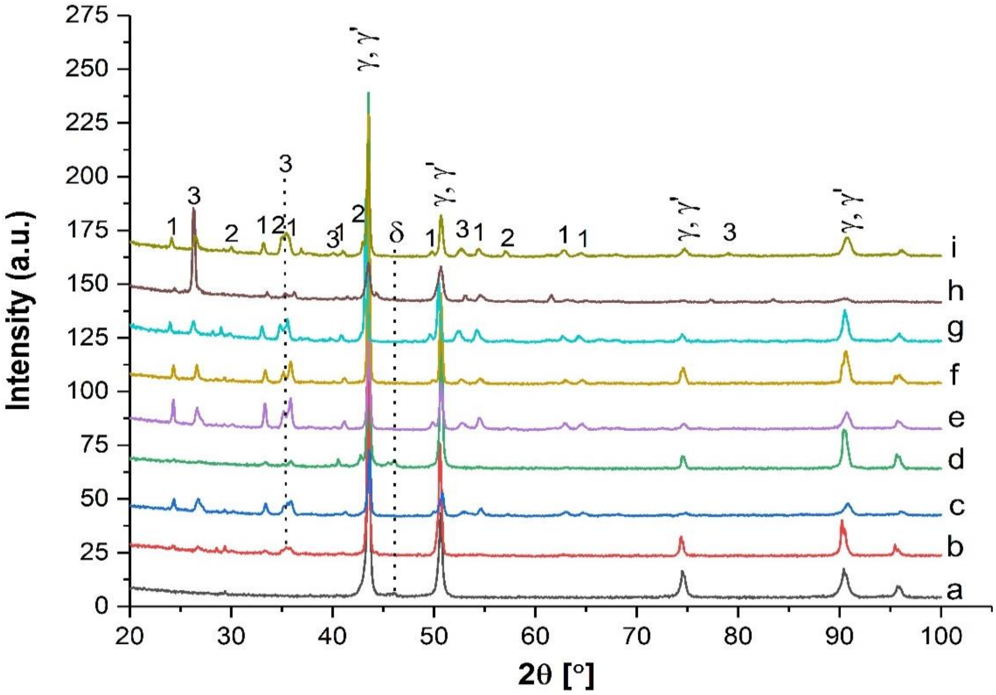
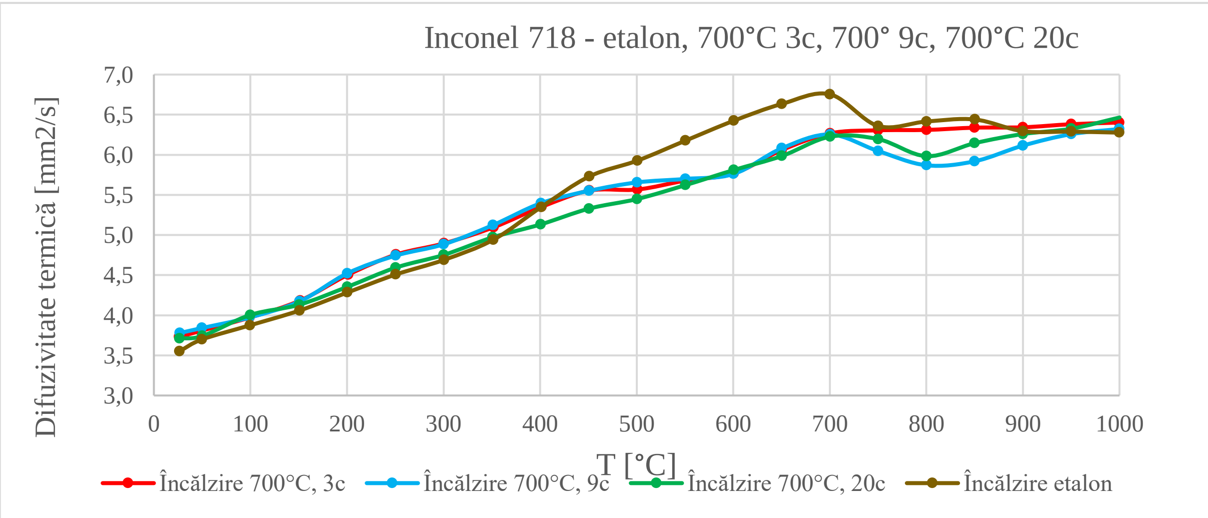


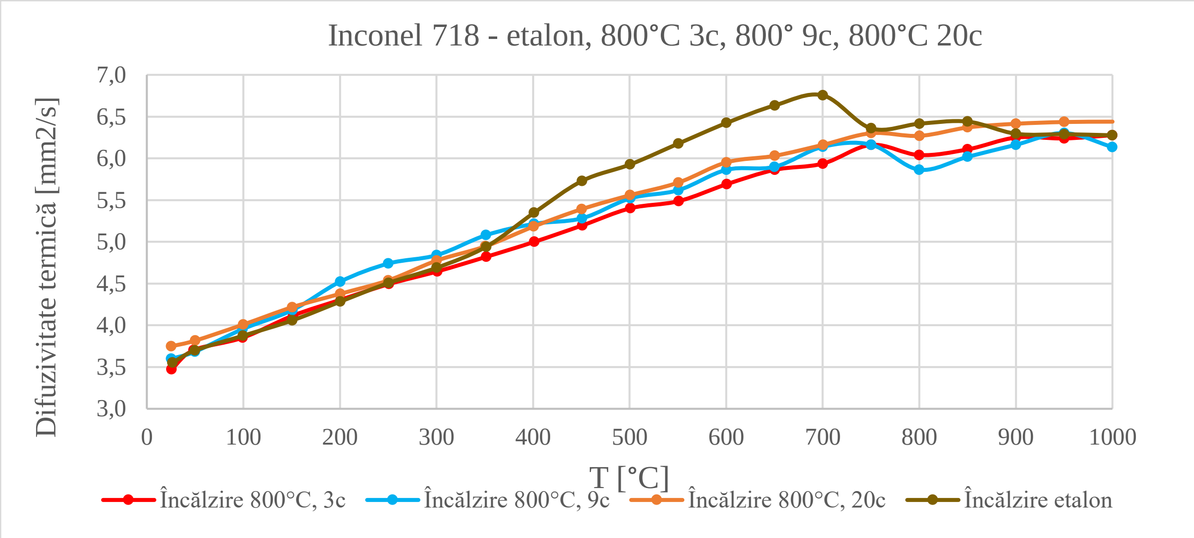
Fig.5.43 Diffractograms for Inconel 718 Standard and samples treated by thermal shocks: 700 ° C with 3 cycles, 700 ° C with 20 cycles -C, 800 ° C with 9 cycles -D, 800 ° C with 20 cycles -E, 900 ° C with 15 cycles -F, 900 ° C with 20 cycles -G, 1000 ° C with 6 cycles, 1000 ° C with 20 cycles

The curves of variation of the diffusivity of the samples treated with a different number of shocks performed at the same temperature have an ascending variation with a maximum within the range of return temperatures, the domain in the way is below those of the standard, after which the variation is small or even zero.

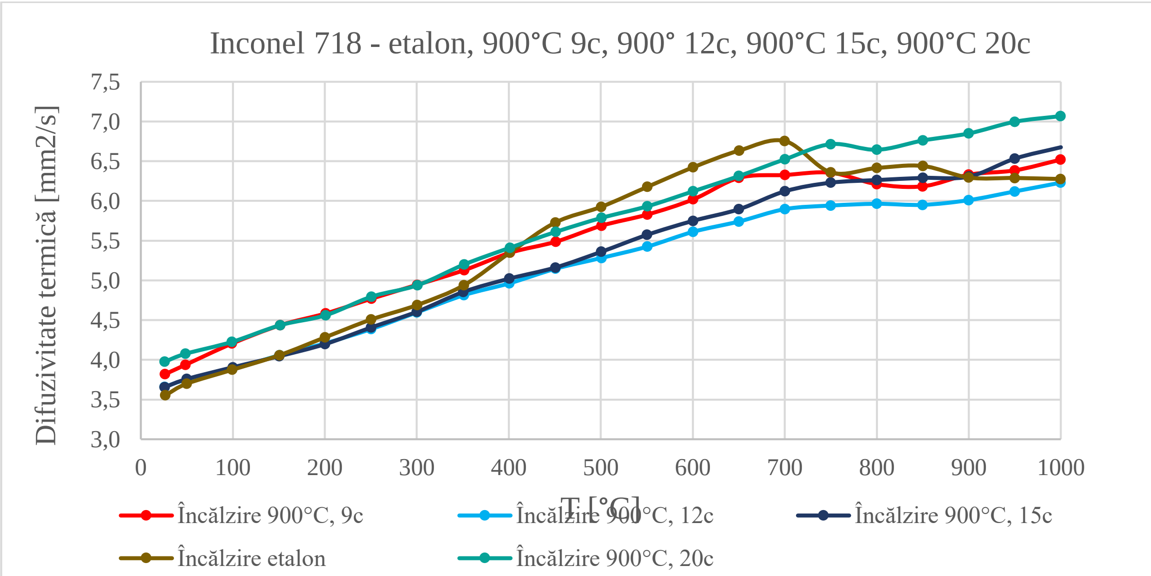
Exception is the test treated at 1000° C with 6 cycles that have constantly higher values than the standard.



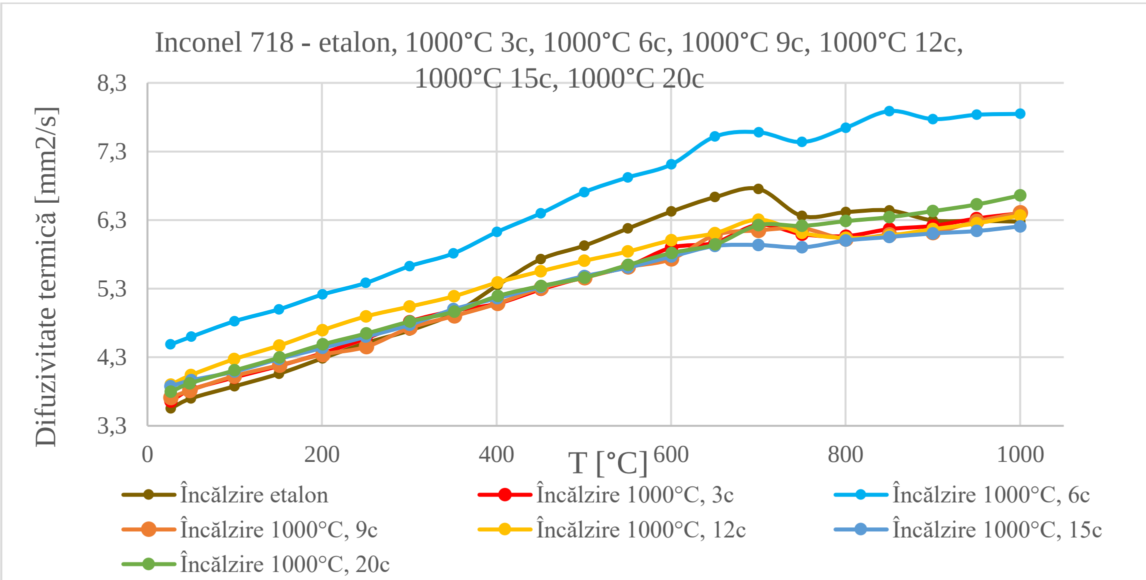
a



b



c



d

Fig.5.50 Variation of thermal diffusivity with the number of cycles applied to: A-700 ° C; B-800 ° C; C-900 ° C; D-1000 ° C.

Chapter 6. Comparative study on the influence of thermal shocks at high temperatures on the structure and properties of the two supervisions

The essential differences between the two alloys result from chemical compositions. Nickel is the basic element of the alloys and forms the solid solution matrix γ with cubic network with centered faces.

They are highly allied with Cr, the nickel-chromium association gives the two excellent supervisions to corrosion resistance to high and high temperatures. In both alloys CR participates in increasing mechanical characteristics, as a hard element that forms carbides.

The structural constituents of the two alloys are: the highly allied solid solution and hard phases, γ ′, γ ′ ′ and carbides of the alloying elements. Both alloys are harshly hard by the high degree of alloying of the solid solution and by aging.

The hard element in René 41 is mainly the titan, which forms with nickel secondary phases the phase γ ′ Ni3 (Al, Ti) or Ni3ti, stable at high temperatures, which give stability to the alloy.

The main hardness element in Inconel 718 is the Niobium that forms the hard γ ", Ni3NB (TVC) phase, stable at working temperatures up to 650 ° C. At higher temperatures, in the process of over aging, γ " is transformed into the ẟ Ni3NB (orthorhombic) phase with the acicular structure. NB is very susceptible to segregation and tends to form phases ẟ and Laves, a process that causes decreased ductility and fatigue and fluage resistance. Due to the presence of the Inconel 718, the phase γ ′ and γ "appear simultaneously, the phase γ ′ being 4 times less than the phase γ".

The thermal speaker for all samples has increasing values with the measurement temperature. The curves for the standard alloys and for the samples treated at 1000 ° C with 6 thermal shock cycles have similar evolutions (fig.6.2 and fig.6.5). For the other treatments, the curves for René 41 and Inconel 718 have very close variations, even with overlapping areas.

The determined values and the comparative study allow the estimation of the thermal transfer and, implicitly the evolution of the microstructure of the two alloys under similar temperature conditions and the number of requests by thermal shock.

Chapter 7. Conclusions, personal contributions and perspectives

Conclusions

Research that is part of the object of the thesis represents the behavior of René 41 and Inconel 718 alloys at high temperatures under thermal shock conditions, in installations in which the temperature control immediately realizes the recovery conditions. An example is nuclear energy.

The alloys in the state of delivery were characterized by determining the microhardness, the microstructure, the chemical composition and the temperature variation, in the range of 25-

1000 ° C, of the thermophysical properties (specific heat, thermal conductivity and the thermal dilation) and of the specific elongation.

The simulation of the temperature rise in the field 700-1000 ° C, for short durations, was made by thermal shocks with a duration of 30s, by heating in the solar oven, which provides high heating and cooling speeds.

The hardness of the alloy decreases considerably near the surface of thermal shock, a phenomenon associated with the dissolution of the hardness phases and the growth of the grains. The increase of the temperature and the duration of the thermal shocks determines the increase of the thermally influenced area by decreasing the hardness, in relation to the area of application of the shocks.

The structure of René 41 samples treated by cyclical thermal shocks presents the characteristic phases of this alloy: solid solution, defined compounds and carbides. With the increase of the shock temperature to 900 ° -1000 ° C, the number of precipitates decreases and the dimensions of the precipitates γ ′ Ni3 (Al, Ti) increase, remaining only large particles, evolution in accordance with the published studies regarding the evolution of the phase ′ [9]. The FCC austenitic matrix of Rene-41 contains a large amount of CR, CO and MO. At high temperatures Cr diffuses to the surface where it forms a protective layer. Part of CR and MO are tied in carbides.

XRD analysis did not determine the type of secondary carbide formed within the grain limit. According to the specialized literature, the large contents of Ni, MO and CO determine the transformation of the M23C6 carbide into M6C carbide. [29,87,92,132-135]

The curves of variation of the thermal diffusivity with temperature for the samples subjected to thermal shocks have the look similar to that of the standard (under delivery conditions) and values up to 40% higher than those of the standard sample highly allied solid solution, reducing the amount of precipitate and decreased hardness.

The microstructure of the 718 Inconel samples treated by cyclical thermal shocks presents the characteristic phases of this alloy: solid solution γ, defined compounds and carbides. The precipitates of γ 'within the limit of the grains were not highlighted by X -ray diffraction, a fact explained by fineness, but their presence is attested by the content of Ti [120, 138,142]. The rapid increase of the precipitates of constant Ni3NB with the increase of the temperature and the duration of the thermal shocks is in accordance with the data in the literature [142]. At high temperatures the precipitates contain an important proportion of MO and CO, in accordance with the research carried out by Alexander Glotka [92], according to which the content greater than 4% MO determines the increase of CO and MO percentage.

The curves of variation of the thermal diffusivity with the temperature of the shock, for the same number of shocks applied are close to that for the standard, at temperatures higher than 400 ° C have values below the standard curve.

Personal contributions

The study on the influence of cyclical thermal shocks at high temperatures on the two nickel -base supervisions, intended for applications at high and high temperatures, even under extreme temperature and corrosion conditions, is original by:

• simulation of accidental conditions with rapid increase in temperature in the range 700-1000 ° C was achieved by solar energy heating;

• The evolution of morphology and elemental chemical composition with the temperature and the number of applied cyclical shocks was studied. The distribution of the alloying elements and its evolution with the treatment by cyclical thermal shocks was determined. The influence of molybdenum was highlighted in both alloys, an aspect insufficiently researched in normal operating conditions;

• the morphology and distribution of the elements in the corrosion layers were studied;

• Determining the profile of variation of the hardness in relation to the shock application area allows the evaluation of the thermally influenced area;

• The comparative study of the variation of the hardness of the two supervisions allows appreciation regarding the evolution of mechanical properties at high temperatures;

• The variations of the diffusivity of the samples subjected to cyclical thermal shocks, depending on the temperature of the shocks and the number of shocks applied have been evaluated in comparison with the evolution with the temperature of measuring the alloy in the delivery state. The evolution of the speaker of the alloys with the measurement temperature, gives us information on the thermal transfer in the alloy in the range 20-1000 ° C, which correlated with the heating/cooling speed gives us information on the structural transformations;

• The comparative study of the thermal transfer in the two alloys allows the evaluation of the possibilities of use at different operating temperatures, but also the evaluation of the cooling /heating speed during the thermal treatment.

Given the very small volume of information existing in the literature on thermal transfer in the two nickel -base superalloys, created in order to be used at high and high temperatures, I believe that the experimental data presented in the work contributes to the enrichment of the database of René 41 and Inconel 718 alloys.

Perspectives

In perspective, we consider the comparative study of the properties of candidate alloys as structural materials for new generation nuclear reactors.

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List of published papers

Articles based on the results presented in the doctoral thesis

1) **Elisabeta Roxana Ungureanu Arva**; Denis Aurelian Negrea; Andrei Galatanu; Magdalena Galatanu; Sorin Georgian Moga; Daniel-Constantin Anghel; Mihai Branzei; Livia Stoica; Alexandra Ion Jinga; Mircea Ionut Petrescu; Corneliu Munteanu; Marioara Abrudeanu: The Influence of Cyclic Thermal Shocks at High Temperatures on the Microstructure, Hardness and Thermal Diffusivity of the Rene 41 Alloy, Materials 2024, Volume 17, Issue 10, 2262; https://doi.org/10.3390/ma17102262; IF 3,4, Q2

Articles elaborated in connection with the theme of the doctoral thesis

1) Daniel-Constantin Anghel, Andreea Elena Rosu, Gabriel Neacsu, Iustin-Alexandru Popa, Mihai Branzei, Vasile Rizea, Catalin-Marian Ducu, Maria Magdalena Dicu, Alin Daniel Rizea, **Elisabeta Ungureanu**, Marioara Abrudeanu: The Influence of Thermal Shocks on the Thermophisics Properties of the Zircaloy-4, Revista de Chimie (Rev. Chim.), Year 2019, Volume 70, Issue 2, 575-577, https://doi.org/10.37358/RC.19.2.6958

Papers presented at international conferences

1) **Ungureanu E**, Anghel DC, Negrea D, Abrudeanu et al. Influence of thermal shocks at high temperatures on microstructure and hardness of RENE 41 alloy. IOP Conf. Ser. Mater. Sci. Eng.; 2019. Doi:10.1088/1757-899X/564/1/012046

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- William Sean James et al :High-temperature failure and microstructural investigation of wire-arc additive manufactured Rene 41, January 2023, The International Journal of Advanced Manufacturing Technology 125(5-6):1-17, DOI:10.1007/s00170-023-10885-5. IF 3.87
- William Sean James, Supriyo Ganguly and Goncalo Pardal: A performance comparison of additive manufactured creep-resistant, SCIENCE AND TECHNOLOGY OF WELDING AND JOINING, https://doi.org/10.1080/13621718.2023.2187925, IF 3,5