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Titano-Aluminizing of Nickel based Super-Alloys

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***Abstract*.** The experimental researches aimed to find a way how to increase the percentage of γ'-Ni_3(Al, Ti) phase in the superficial layers of the nickel base super-alloys, particularly of the INCONEL 738 super-alloy and also to determine the thermodynamic stability conditions of this strengthening phase by ensuring an over-unity Al wt%/Ti wt% ratio in these layers. The chosen solution was to realize a simultaneous Al-Ti cementation (Titano-Aluminizing) using solid powdery media containing TiO_2 and Al powder as active suppliers of Ti and Al. Besides these components, in the cementation media there are, or not, other components which participate actively in the reduction of TiO_2 such as fluoride and magnesium powder. These components have as role the dispersing/blocking of the sintering tendency of the mixture components. In the mixture, there are also components which have as role cleaning/activation of the surfaces subject to thermochemical processing.
The experimental results led to the conclusion that the Al wt%/Ti wt% ratio can be widely modified, but with keeping of it over-unity, by means of rigorous control of solid powdery media phases composition, such as to ensure that the strengthening phase γ'-Ni_3 (Al, Ti) is existent and stable in the superficial zone of the simultaneous cemented layers.

***Keywords*:** simultaneous Al-Ti cementation (titano-aluminizing); INCONEL 738; indicator: (Al wt%/Ti wt% ratio).

1. Introduction

The improvement of exploitation performances of the nickel based super alloys can be ensured by increase the aluminium and/or titanium concentrations [1;5], in whole volume during the elaboration process, or only in the products superficial layers - by

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thermochemical treatments. The effects of this increase will be reflected in the proportion of the Ni_3Al or Ni_3Ti, namely $Ni_3(Al, Ti)$ intermetallic compounds appeared by replacement of up to 3 atoms, from each 5 Al atoms group of Ni_3Al compound, with titanium atoms. The compound $Ni_3(Al, Ti)$ realizes a higher strengthening of this category of super-alloys than Ni_3Al compound; this conclusion led to the necessity of growth simultaneously the Al and Ti concentrations in these alloys.

However, the high complexity of alloying of matrixes of these super-alloys implies that most probably will result complex alloy aluminides, which have in their composition also other elements such as cobalt and molybdenum [5]. It was established that the over-unity ratio of Al and Ti, elements which generate strengthening phases in the nickel based refractory alloys [2;3;4], is strongly influencing the long-term resistance and especially the plasticity after thousands of hours testing. The nickel based super-alloys of generation IV-VI (without titanium) were not considered in the analysis. INCONEL 738 is part of the nickel based super-alloys group where the aluminium and titanium ratio is about 1 (the mass percentage of these two elements varies in the same range, 3,2÷3,7%). The niobium available in these alloys will be in the range 0,6÷1,10% either in the carbides or in the metallic phases, and the boron if it is higher than 0,01wt% (0,007÷0,012% are the limits of grade) will probably affect the alloy deformability. To increase the exploitation performances of the products realized from these alloys by thermochemical processing, the medium activity has to be rigorously controlled such as to keep an over-unity Al wt%/Ti wt% ratio. Adversely, the $Ni_3(Al, Ti)$ phase become metastable and has the tendency to become stable through titanium separation, phenomenon which determines an increase of brittleness and a decrease of the alloy capacity to operate under long-term loading.

2. Materials and equipment used in research

Samples of INCONEL 738 nickel based super-alloy with sizes of 15x15x10mm and chemical composition shown in the below table 1, have been cemented simultaneously with aluminium and titanium in powdery solid medium. The active components of the cementation medium changed. The effect of these changes on the Al and Ti mass percentages reached in the superficial layers of the samples treated at 950oC/3-5 h holding time, have been determined.

Table 1. Chemical composition of INCONEL 738 samples used in the research (Spectrometer used: SPECTROMAXX –LMMO4-Germany).

0,108%C; 0,315%Si; 0,011%Mn; 0,0061%P; 0,0039%S; 15,23%Cr; 1,92%Mo; 0,058%Fe; 3,08%W; 0,032%V; 2,90%Al; 8,67%Co; 0,011%Cu; 0,63%Nb; 0,018%Sn; 1,71%Ta; 3,38%Ti; 0,020%B; 0,013%Mg; 0,055%Zr; <0,0002%P; 61,8%Ni

Note: It can be observed that based on its carbon content, the super-alloy is in the category of low carbon alloys, INCONEL 738LC and the initial value of the Al wt%/Ti wt% ratio is under unity (0,858).

The powdery solid media include 65% alumina (Al_2O_3), which ensures the dispersing of the active components and blocking of sintering tendency, 5% ammonia chloride (NH_4Cl), which is actively participating to the growth of the medium activity and 30% active component as follows:

a) 50%TiO_2 + 50%Al (mass percentages);

b) (20÷35) %TiO_2 + (30÷25) %Al + (20÷25) %CaF_2 + (20÷25) %Mg

Measured active components of the medium have been mixed in refractory steel mills with volume of 2,5 l, equipped with milling bodies from sintered hard alloys (Widia spheres with a total mass of 4,5 kg). The ratio between the mass of the milling bodies and the mass of solid powdery media was 9, the processing time was 30 h and the milling bodies speed was about 0,8% of critical speed (~102rot/min).

The X-ray diffraction of the mixtures of powders TiO_2-Al, namely TiO_2-Al-CaF_2-Mg (representing the active component of the cementation media), realized by means of diffractometer D8 Advance type (BRUKER-AXS), Cu-Kα radiation (1,54nm) were presented in Fig.1 and Fig.2. The X-ray diffraction does not revealed that new phases resulted following to the extended process of fragmentation in the balls mills of high energy; the only effects are those related to the continuation of fragmentation and to the high uniformity ensured by the reciprocal repartition of components. The initial dimensional characteristics of the powders used for the realization of the mixture were: whiskers of TiO_2(99,6%, with ρ=4÷4,2g/cm^3, ratio l/d~13,l=4,3÷17,4μm and d=0,6÷0,8μm):aluminium powders with average sizes below 100μm (obtained by air pulverization -ALCOA Process, with apparent density of ~0,9 g/cm^3): magnesium powders, obtained by pulverization with argon, with medium dimensions below 100 μm (apparent density ~0,8g/cm^3), fragments of fluoride with medium dimensions at mm order.

The final mixtures, well homogenized, containing the active component, the neutral component and the activation component, together with the sample (which was degreased properly) have been introduced in refractory steel recipients such as to not get in contact between them and also to not get in contact with the recipients" walls; the recipients have been sealed and heated in furnaces equipped with automatic control of temperature.

After the isothermal holding, the recipients have been cooled up to 350°C and then into air; the removal of the samples from recipients has been made at temperatures below 100°C.

The analysis of results has been achieved by means of optical microscopy (REICHERT UNIVAR microscope) and electronic (Quanta Inspect F50 microscope).

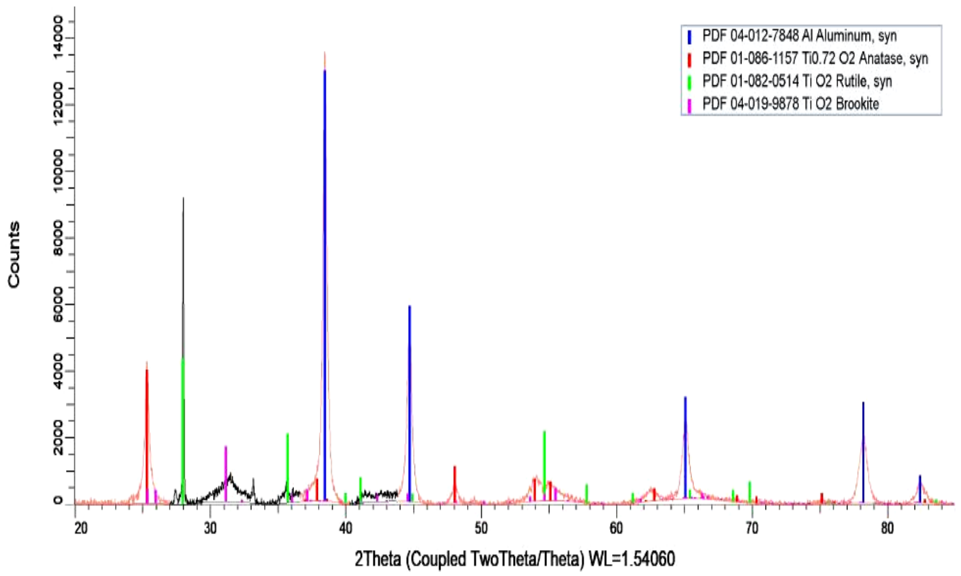


Fig. 1. X-ray diffraction of the equal-mass mixture of powders of TiO_2 and aluminium, processed for 30 hours in balls mills with energy of ~10J/rot.

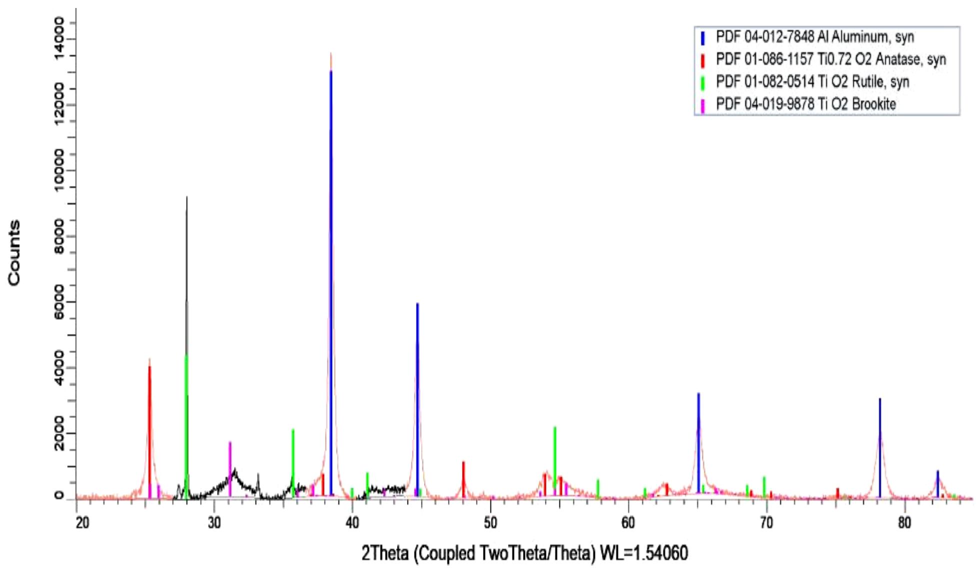


Fig. 2. X ray diffraction of powder mixture TiO_2-Al-CaF_2-Mg, processed for 30 hours in balls mills with energy of ~10J/rot.

3. Experimental results. Interpretations

The experimental researches aimed at determination the effects of variation the chemical composition of the active component (in the powdery solid medium used for simultaneous Al and Ti cementation of the INCONEL 738 super-alloy base nickel matrixes) on the Al wt%/Ti wt% ratio reached in the superficial layers of the thermochemically processed products. This ratio has been selected as indicator of the thermochemical processing.

The TiO_2-Al equal-mass mixture was selected as active component of the titano-aluminizing medium because by thermodynamic point of view, is very probable to occur, the reaction between the two components and also having a significant thermal effect:

$$3TiO_2+4Al=2Al_2O_3+3Ti \qquad (1)$$

$$\Delta G^{950°C} = -404{,}56 KJ/mol;\ \Delta H^{950°C} = -556{,}3 KJ/mol\ [13]$$

The experimental results confirm the conclusion that such a composition of the medium is active in the selected processing conditions. The saturation speed was about 2,8μm/hour, the Al wt%/Ti-wt% ratio is over-unity (~2,9) in the layers adjacent to surface, but the oxygen concentration on about 10μm depths from surface reaches approx. 36%wt, and then, at higher depths become negligible (fig.3).

The oxygen can be found in these areas most probably as Al_2O_3, oxide which is stable, and ensures high oxidation resistance at high temperatures for the product.

The calcium chloride ($CaCl_2$), calcium and magnesium act actively for the reduction of the titan dioxide [14]; it is very probable by thermodynamic point of view, that the calcium fluoride to act in similar way as the calcium chloride or even in a more intense way.

In the presence of calcium chloride (used as flux in the titanium production process by reduction of its oxide) and of calcium as direct reducer, the following reactions can take place:

$$TiO_2+2CaCl_2=TiCl_4+2CaO \qquad (2)$$

$$\Delta G^{950°C} = +420{,}4 KJ/mol;\ \Delta H^{950°C} = +403{,}3 KJ/mol$$

$$TiCl_4+Ca=Ti+CaCl_2 \qquad (3)$$

$$\Delta G^{950°C} = -619{,}1 KJ/mol;\ \Delta H^{950°C} = -760{,}1 KJ/mol.\ [14]$$

or the direct reaction (which is more thermodynamically probable):

$$TiO_2+CaCl_2+2Ca=Ti+2CaO+CaCl_2 \qquad (4)$$

$$\Delta G^{950°C} = -289 KJ/mol;\ \Delta H^{950°C} = -346{,}4 KJ/mol.$$

In the presence of calcium fluoride, used as flux (replacing the calcium chloride) and of magnesium as reducer, the following reaction occurs:

$$TiO_2+CaF_2+Mg=Ti+CaO+MgF_2 \qquad (5)$$

$$\Delta G^{950°C} = -68{,}6 KJ/mol;\ \Delta H^{950°C} = -143{,}3 KJ/mol.$$

In the presence of aluminium in the powdery solid media used for titano-aluminizing, the reaction (5) becomes more probable by thermodynamic point of view and has also a higher thermal effect.

$$2TiO_2+CaF_2+Mg+2Al=2Ti+CaO+MgF_2+Al_2O_3 \qquad (6)$$

$$\Delta G^{950°C} = -236{,}5 KJ/mol;\ \Delta H^{950°C} = -349{,}8 KJ/mol.$$

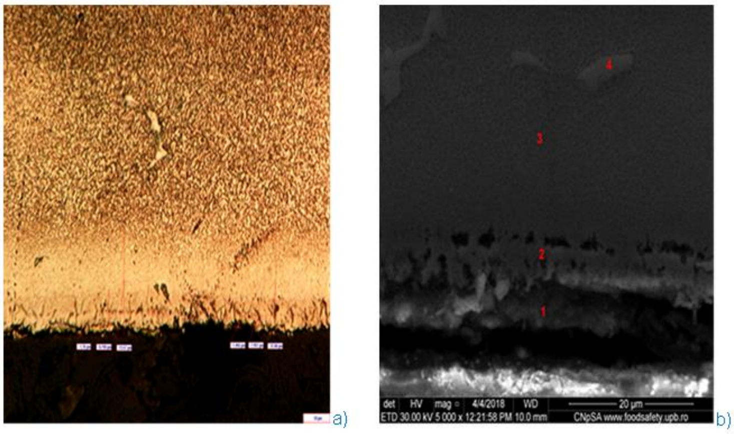
The titanium in active state, is very probable to appear also following to a possible reaction of disproportioning of its fluoride, TiF_2 (reaction 8):

$$Ti + F_2(g) = TiF_2(g) \quad (7)$$

$$\Delta G^{950°C} = -653 KJ/mol \quad \Delta H^{950°C} = -608{,}6 KJ/mol$$

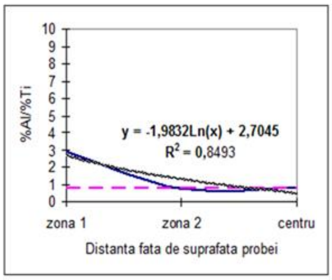
$$3TiF_2 = 2TiF_3 + Ti \quad (8)$$

$$\Delta G^{950°C} = -249{,}8 KJ/mol \quad \Delta H^{950°C} = -491{,}9 KJ/mol$$



Zone	wt%			%Al/%Ti
	O	Al	Ti	
1	35,71	25,05	8,66	2,9
2	0	1,41	1,8	0,8

Note. The oxygen is exclusively concentrated in the superficial zone, characterized by a rich aluminium content, namely dialuminium trioxide (Al_2O_3).



The distribution of Al %wt/Ti %wt in the titano-aluminized layer.

Fig. 3. Images of optical microscopy (a), electronic (b) and chemical microanalysis in the superficial zone of the INCONEL 738 samples, titano-aluminized at 950ºC/3 h in solid powdery medium with phase composition :30%(50%TiO_2+50%Al) +65%Al_2O_3+5%NH_4Cl.

The decision to use the calcium fluoride and magnesium in the composition of the solid powdery media meant to titano-aluminizing is supported also by the data from the literature related to the beneficial effect of the presence of calcium, magnesium and respectively of fluorine in the matrixes of the nickel based super-alloys [6;7;8;9;10;11;12].

According to these sources, in the presence of magnesium and calcium, the ductility of this category of alloys increases considerably, at high temperature [6; 10; 11] and fluorine provides an increase in the oxidation resistance in the range 900 ÷ 1200oC by stimulating the formation of dense Al_2O_3 films [7; 8; 9].

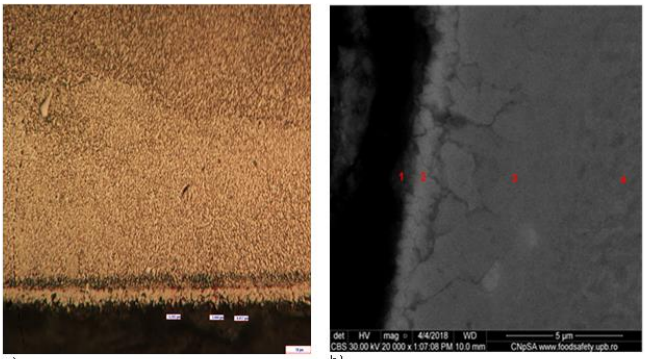
As for the to the aluminum needed to saturate the surface, this it appears as a result of performing the disproportionation reactions of its chlorides or fluorides ($AlCl_2$ or AlF_3) in the presence of halides (mainly of hydrochloric acid vapours, resulting from the decomposition of ammonium chloride, respectively hydrofluoric acid - 11 reaction) in the reaction medium:

$3AlCl_2=2AlCl_3+Al$ $\Delta G^{950°C} = -87,3 KJ/mol$ $\Delta H^{950°C} = -298,5 KJ/mol$ (9)

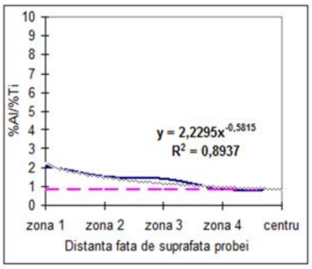
respectively:

$3AlF_2=2AlF_3+Al$ $\Delta G^{950°C} = -92,8 KJ/mol$ $\Delta H^{950°C} = -303,9 KJ/mol$ (10)

$F_2(g)+H_2(g)=2HF(g)$ $\Delta G^{950°C} = -560 KJ/mol$ $\Delta H^{950°C} = -552 KJ/mol$ (11)



Zone	% masics						%Al/%Ti
	O	F	Mg	Al	Ca	Ti	
1	19,95	0,22	0,81	6,75	0,84	3,23	2,09
2	4,2	0	1,19	4,8	0,87	3,1	1,56
3	0	0	0,26	4,16	0,15	2,93	1,42
4	0	0	0	3,09	0	3,61	0,85

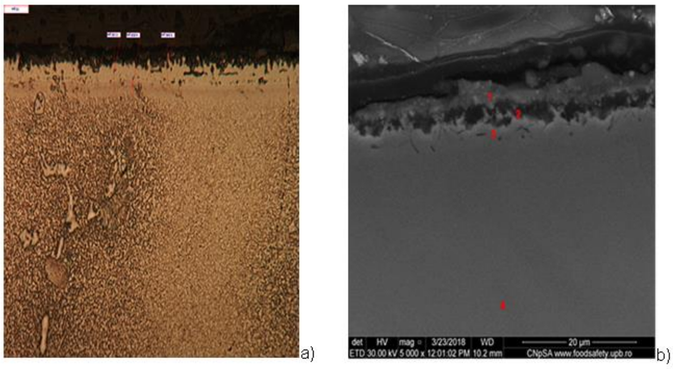


c) The distribution of the ratio between the mass proportions of aluminum and titanium in different areas of the alloyed titanium layer.

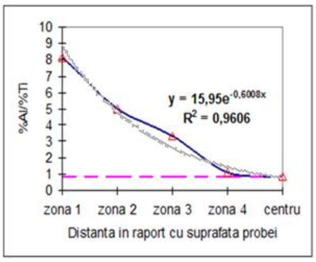
Fig.4. Optical microscopy images (a), electronic (b) quantitative chemical microanalysis in different sample areas of INCONEL 738, titano-aluminized at 950 ° C / 3 hours in solid powdery medium with phase composition: 30% (35% TiO_2 + 25% Al + 20% CaF_2 + 20% Mg) + 65% Al_2O_3 + 5% NH_4Cl.

Obs. The average global chemical composition of the powdered solids mixture used for titan aluminization, determined by quantitative chemical microanalysis, is: 26% O_2; 13% F_2; 11% Mg; 35% Al, 8% Ca, 7% Ti (% Al /% Ti = 5).

The analysis of the results obtained using the new environmental compositions (Figures 4 - 5) revealed interesting aspects related to the kinetics as well as the high sensitivity of the environment activity to the modification of the proportions ratio of the components containing aluminum and titanium from the active component of the powdered solid medium used for titano-aluminization: an increase in layer growth rate of 2.8 μm / h, in the case of compositions having an equal-mass proportions of TiO_2 and aluminum as an active component, to 4.3 μm / h for media containing 35% TiO_2 + 25% Al, fluorine and magnesium (950°C / 3h - fig. 4) and 4.8μm / h for media containing 20% TiO_2 + 30% Al, fluorine and magnesium.



Zone	%masics						%Al/%Ti
	O	F	Mg	**Al**	Ca	**Ti**	
1	2,43	45,71	22,27	18,75	0,96	2,31	8,12
2	0	0	1,76	22,22	3,13	4,47	4,97
3	0	0	0,7	2,2	0,38	0,66	3,33
4	0	0	0	3,6	0	3,3	1,09



Distribution of the ratio between the massic proportions of aluminum and titanium in different areas of the titanium-aluminized layer.

Fig. 5. Images of optical microscopy (a), electronics (b) and quantitative chemical microanalysis in different samples areas of INCONEL 738, titanium at 950oC / 5 hours in solid powdery medium with phase composition: 30% (20% TiO_2 + 30% 25% CaF_2 + 25% Mg) + 65% Al_2O_3 + 5% NH_4Cl).

The concentrations of aluminium and titanium in the titano-aluminized layer are particularly sensitive primarily to the variations in the proportions of the active components in the powdered solid medium used containing these elements.

Thus, a 5% increase in the proportion of aluminum in the powdered solids medium containing fluorine and magnesium and the 15% decrease in the proportion of titanium dioxide associated with an increase of the isothermal maintenance time to a processing temperature of 950°C by ~ 67% an increase in the proportion of aluminum in the superficial layers of the layer by ~ 177% and a decrease in the proportion of titanium in the same areas by ~ 28%.

Particularly interesting are also observations related to the change of masic proportion ratio of the elements of interest, aluminium and titanium to the titano-

aluminized layer obtained under the different processing conditions: increasing the proportion of aluminum in the thermo-chemical processing environment (by 5%), associated with an increase in the isothermal maintaining period (~ 67%) considerably amplifies the value of this ratio (~ 4 times) in the superficial areas of the layer.
The consequence of these changes in the titano-aluminized layer is the increase in the proportion of Ni_3 (Al, Ti) intermetallic compound and its stability, with all its implications which it involves.

Obs. Compared with the previous situation, in the environment composition has increased the massic aluminum composition (from 25% to 30%) while the TiO_2 mass ratio (from 35% to 20%) has decreased.

The presence of aluminum and oxygen in high concentrations in the marginal areas of the titanium layer, adjacent to the layer-medium interface, creates ideal conditions for generating dense films, resistant to oxidation at elevated temperatures, stimulated phenomena and of the presence of fluoride in these areas.
From a thermodynamic point of view, appearance of the aluminum oxide films of the Al_2O_3 type is highly probable (reaction 12), so that these areas will be found together with intermetallic compounds Ni_3 (Al, Ti) with a hardening role and the films stable oxides of the type Al_2O_3.

$$4Al+3O_2=2Al_2O_3 \qquad \Delta G^{950°C} = -2574 KJ/mol;\ \Delta H^{950°C} = -3382,67 KJ/mol \qquad (12)$$

4. Conclusions

Experimenting research on a superficial saturation domain simultaneous with aluminum and titanium in nickel-based superalloy (customized on INCONEL 738) highlighted the following:

- powdered solid media containing rutile (TiO_2), fluorine (CaF_2), magnesium and aluminium can serve as sources of aluminium and titanium to superficially saturate with those elements of these superalloys with nickel base; the activity of these media is superior to the activity of TiO_2 and Al or TiO_2-$CaCl_2$-Ca and Al mediums (as active components), a conclusion based on the results of the concentrations of the two elements of interest, Al and Ti, respectively the evolution of their ratio of mass in the titano-aluminized layer obtained under different environmental conditions and its growth rate.

Changing the proportions of TiO_2 and Al, respectively, in the complex solid powdery mixture used for titanium-aluminizing has direct implications on the proportions of aluminum and titanium in the layer, ensuring the possibility of increasing their proportions and keeping a supraunit value for the ratio of their mass proportions permanently (aspect equivalent to ensuring the conditions formation of the y-Ni_3 (Al, Ti) hardening phase and its stability);

- in the titano-aluminized layer obtained on nickel-based superalloys by processing in complexes solid powdery media containing rutile, fluorine, magnesium and aluminum, advanced mixed together with alumina, as a dispersing and blocking component of the sintering trend and NH_4Cl respectively with the activator role will be intermetallic compounds of the type γ '-Ni_3 (Al, Ti), with a hardening role and dense and stable oxide films of Al_2O_3, resistant to high temperature oxidation.

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