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The effects of change the energy conditions and synthesis media activity on nickel aluminides type and proportion

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Abstract. The work summarizes aspects related to the effects of change the energy conditions of the synthesis of nickel aluminides by mechanical alloying in balls mills, namely of the activity of powdery media used for alitation of nickel matrixes. The experimental research revealed that the type and proportion of nickel aluminides can be changed in a controllable manner by rigorous selection of the type of mill used and of its operating conditions. The alitation has been made in powdery media including pure aluminium powder or mixtures of aluminium and iron powder (in equal weight percentages) as aluminium suppliers, instead of ferro-aluminium powders which are currently used. The alitation resulted in layers with complex phase's compositions which are directly dependent on processing temperature, matrix composition and alitation media composition. It was demonstrated that the Al-Fe mixture of powders represents a viable alternative for the ferro-aluminium powder for the alitation process.

***Keywords*:** nickel aluminides, mechanical alloying in balls mills, alitation in powdery solid media, nickel based super-alloys.

1. Introduction

The nickel aluminides show a particular interest for development, by means of different techniques, of protective layers against high temperature oxidation of nickel/nickel alloys components which support high mechanical - thermal loads in rich oxygen potential environments.
Among the five aluminides of the Al-Ni system (Al_3Ni_2, Al_3Ni_5, Al_3Ni, $AlNi_3$, AlNi) [1], the latest two are characterized by a particular thermodynamic stability

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at temperatures over 1000°C along with ductility, hardness, mechanical resistance and resistance against oxidation, carburizing and nitriding [2].
The development of protective layers is recommended when the change of chemical composition of metallic matrixes by elements contributing to the increase of their oxidation resistance results implicitly in the alteration of the mechanical characteristics of them [3].
The methods for synthesis of nickel aluminides are various [3, 4], a first classification exhibiting a first group which includes the processing methods from melting of elements, namely a second group which refers to the processing methods from powders of the elemental components [3]; in this last group the mechanical alloying [3, 5] and the alitation [6, 7, 8, 9] own a significant place.
The choose of the method for development the protective layers, in situ or by depositing of nickel aluminides is based on the necessity to ensure their perfect adherence to the support. Another important issue considered is the limiting of the occurrence of porosity: the notable differences between the diffusion coefficients of aluminium in nickel namely nickel in aluminium, corroborated with the differences between the mass fluxes transferred by diffusion from/to the alitation medium, represent the main factors generating porosity [10, 11].
Therefore, it is necessary to select and control carefully the specific parameters for synthesis and processing in order to achieve the phases composition required in the protective layer in accordance with the exploiting demands of the component targeted.

2. Materials and Equipment used in the research

The aluminium (purity 99,2%) and nickel powders (purity 99,9%) obtained by air pulverization, namely by Sherrit hydro-metallurgical process have been used in research in order to identify the effects of change the energy conditions of the nickel aluminides synthesis by **mechanical alloying in balls mills**.
The particle mean diameters of the two powders were 12,5µm, for aluminium and 90µm for nickel; in the mixtures processed in the balls mills, these components have been used in equal weight percentages.
Two types of ball mills have been used, one ceramic mill of 1,5 l which uses ceramic milling bodies with a total weight of 0,3 kg and one refractory steel mill of 2,5 l which uses milling bodies from hard alloys of sintered Widia carbides with a total weight of 4,5 kg.
The similarities in the operation of the two ball mills are related to their turning speed - 102rot/min (about. 85% of its critical turning speed), but the differences are linked to the value of rapport between the weight of the milling bodies (M_{cm}) and the weight of the powder mixture (M_{ap}) which is to be processed: M_{cm}/M_{ap}~110 for the refractory steel mill namely $M_{cm}/M_{ap}<10$ for the ceramic mill.
The processing has been performed at $T_{ambient}$ (initial temperature) in air, for different periods of time in the range 5 ... 50h.

The alitation of the nickel matrixes (electrolytic nickel with purity of 99,2%, namely nickel based superalloys -INCONEL 718 with composition in the limits of W 2.4668 grade) was achieved in powdery mixtures including Al-Al_2O_3-NH_4Cl, namely powders mixtures (Al+Fe) in equal weight percentages in the presence of NH_4Cl in amount of 2%.

These powders have been used instead of ferro-aluminium which is currently found in the industrial practice; it was introduced subsequently in the alitation receipts in order to limit the tendency of adhesion of the mixture components to the surface of metallic products processed.

The thermochemical processing has been realized at temperatures below and above the aluminium melting temperature (640°...1000°C), in electric furnaces with automatic control of the thermal regime.

The samples have been packed in solid powdery mixtures (as suppliers of active aluminium) inside sealed metallic boxes and hold for the processing time.

The capacity of powdery mixture which included aluminium powder with 26% rich aluminium nickel aluminides (AlNi, Al_4Ni_3, Al_3Ni_2) to provide itself, or in the presence of Al_2O_3 and NH_4Cl (1%), a proper alitation process of the nickel matrixes has been investigated.

The X-Ray diffraction by means of X'pert PRO MPD PANalytical and DRON 3 type diffractometers and the electronic microscopy by means of Quanta Inspect F50 microscope have been used for investigation of the results.

3. Results of the Experimental Researches. Interpretations

The calculation of the total energy (Et) released by the milling balls (in the two mills) during processing the Al-Ni powder mixtures by mechanical alloying in balls mills has considered the geometrical and operational characteristics of the mills, the milling bodies weight, the material (powder mixture) weight the mills loading and other [12, 13, 14, 15, 16, 17, 18].

The results of the calculation of the kinetic and potential energy of the ceramic milling bodies in ceramic mill revealed that for the given experimental conditions, the maximum energy released by the milling bodies was <1J/rot (0,6J/rot). By contrast, the energy released by the hard alloys milling bodies in the refractory steel mill was about one order higher, namely ~7J/rot.

In these energy conditions, the degree of transformation of Al-Ni powder mixture in nickel aluminides is obvious different: max 5% is reached for the low energy ceramic mills but 25% is attained in the high energy mills; consequently, the type of synthesized aluminides (Fig.1) changes also significantly due to the change of the mechanisms for their generation.

In the low energy mills will develop nickel rich aluminides of type Al_3Ni_5, the synthesis being initiated by the germination of the solid solution of aluminium in nickel; during processing time, according to the principle of sequence of transformations, the saturation of the solid solution with aluminium continues and consequently the Al_3Ni_5 will develop once with reaching the minimum concentrations for their germination.

Rich aluminium aluminides (Fig.1) will develop preponderantly in the case of high energy ball mills, the explanation being related to the extremely high value of the nickel diffusion coefficient of nickel in aluminium, which is different with orders of magnitude against that of aluminium in nickel [19, 20, 21].

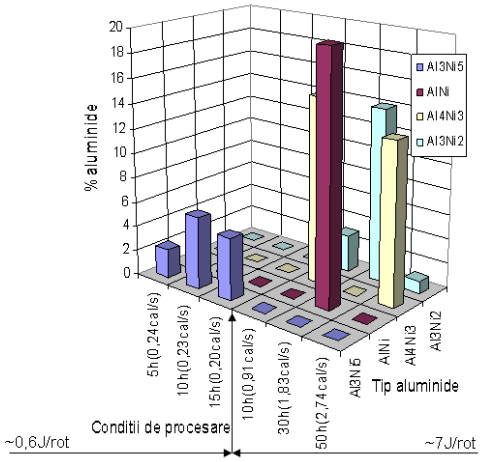


Fig. 1. Histogram showing the dependency between proportion and type of nickel aluminides and the energy of balls mills used for mechanical alloying.

In these conditions will probably occur the initiation of a process of auto-synthesis of which premises have been created by the significant increase of the local temperature (at the level of the contacts between particles); this temperature increase is due to the transformation of some mechanical energy in thermal energy together with the implications related to this phenomenon.

In the case of mechanical alloying, the increase of the defects concentrations will result in the increase of the nickel solubility in aluminium from 0% (in normal conditions) up to ~10% [3].

By change the mechanical alloying conditions such as the energy released by the milling balls to be controlled rigorously, also the proportion of the nickel aluminides in the mixtures of powders aluminium-nickel can be controlled; the nature of aluminides is also monitored depending on requirements such as to develop either rich nickel aluminides or rich aluminium aluminides.

The researches in the field of aluminides synthesis by alitation in powdery mixtures of the nickel matrixes have revealed the fact that the activity of the media composed of mixtures of powders of iron and aluminium in equal weight percentages is considerable lower than that of the media which contain aluminium powder.

The use of the mixtures of powders of iron and aluminium instead of ferro-aluminium powder is based on the hypothesis that by thermodynamic point of view, the development of Al-Fe intermetallic compounds (AlFe, Al_5Fe_2, Al_3Fe identified by Xray diffraction-Fig.3) can occur very probable also during heating of the powdery mixtures which contain these elements in pure state [22] - (Fig.2).
This conclusion was confirmed by Xray diffraction of a sample from the iron and aluminium mixture powders (in equal weight percentages) which was thermally processed for 3 hours at 950°C (Fig.3).

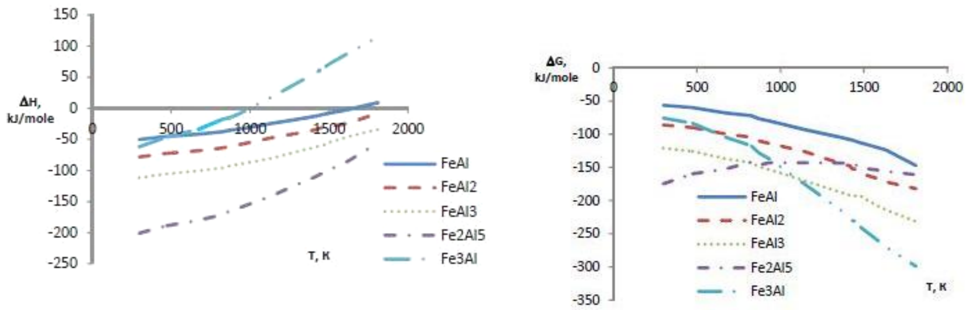


Fig. 2. Change of the enthalpy and free Gibbs energy with temperature during synthesis of the intermetallic compounds in the Al-Fe system [acc. 22].

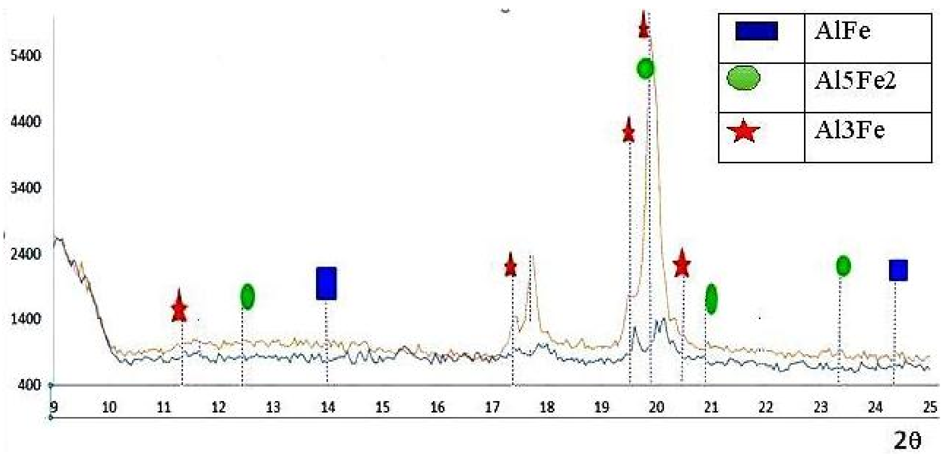


Fig. 3. The diffractograms of the ferro-aluminium powders (superior) and of the mixture of aluminium and iron powders, in equal mass proportions, thermally processed at 950°C/3h.

In these conditions it was estimated that there are no major differences between the alitation capacity of the powdery mixtures which contain ferro-aluminium powder and that of the mixtures of iron and aluminium powders.

This is due to the fact that the general kinetics of the process are mainly determined by the kinetics of reactions of development and decomposition of the aluminium chlorides at the level of the catalytic metallic surfaces or by the transfer through diffusion of the aluminium from the combinations where this is available in the alitation medium.

Note: In the industrial practice, the powder of ferro-aluminium is used on large scale for the realization of the mixtures used for alitation both by practical and economic considerations. By practical, the homogenization of the mixtures of aluminium and iron powders is difficult due to the differences between the densities of the two metals, and economical, the iron and aluminium powders have higher prices than the ferro-aluminium powder.

The results of the experimental researches confirmed the initial assumptions (Fig.4÷8), indicating major differences both in the growth kinetics of alitation layers (Fig.8) and also in their chemical and phases compositions depending on processing conditions (mainly, the alitation medium composition).

The different activities of the media used for alitation in powdery media, governed by the presence of aluminium or Al-Fe compounds, influenced the chemical and phases composition of the alitation layers obtained on the Inconel 718 matrixes (Fig.4÷7 with related tables).

The differences between the activities of the media including aluminium powder by comparison with those of the media including Al-Fe refractory products are connected to the very high thermodynamic stability of the latest (except of the Fe_3Al compound which decomposes at 555ºC, the other Fe-Al intermetallic compounds are stable up to temperatures over 1150°C [23]); the transfer of aluminium in the surface of matrix subject to alitation being realized preponderantly by diffusion through these compounds.

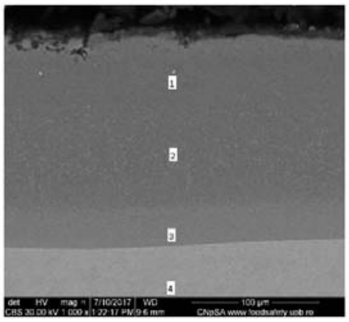
The analysis of distribution of the aluminium in the alitation layers in different conditions (composition of the powdery medium/temperature/time of isothermal holding) confirms that sometimes, independently on temperature, the media which contain Al-Fe intermetallic compounds are characterized by a much lower activity compared to that of those media containing aluminium.

Therefore, the flux of nickel atoms transferred by diffusion from the metallic matrix occurs mainly, such as in the superficial layer zones will be generated aluminides with a moderate content of aluminium and with relatively rich nickel content (Fig.6÷7).

When the medium is characterized by a high activity, the flux of aluminium atoms from the medium is leading such as in the zones adjacent to the surface will be generated aluminides with some rich aluminium concentrations (Fig.4÷5).

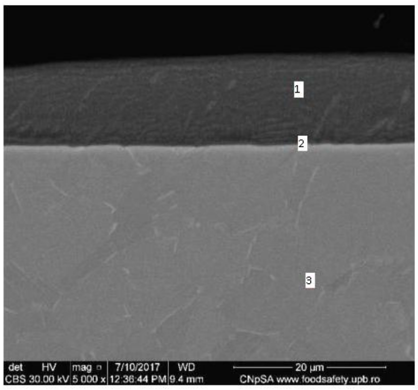
Independently of situation, the alitation layer is characterized by the specific phases sequence which states its exploitation behaviour: the layer with a rich aluminium content has a high brittleness and needs an additional annealing to the alitation in order to redistribute the aluminium by diffusion and to decrease its concentrations compared to the layers with a moderate content of aluminium and nickel which have a proper exploitation behaviour.

The EDS analysis of chemical composition related to the different zones of the alitation layer revealed that this it is composed of a sequence of nickel aluminides, either simple or alloyed, rich in aluminium or nickel, depending on the rapport between the medium activity and that of the nickel from matrix, sigma phases and very probable carbides of type $M_{23}C_6$ and/or MC in the case of superalloy INCONEL 718.



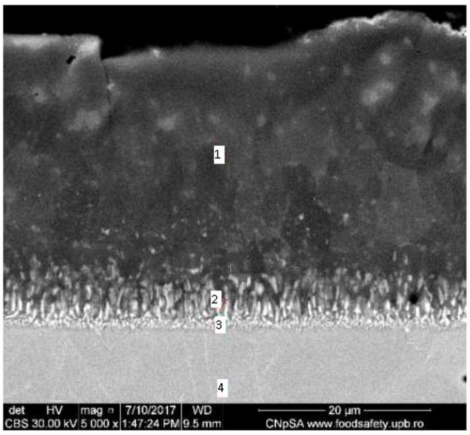
Zone	**%Al**	**%Ti**	**%Cr**	**%Fe**	**%Ni**	**%Nb**
1	63,22	0,03	8,11	8	18,21	2,43
2	63,37	0,02	8,08	-	25,42	3,1
3	34,72	0,75	10,84	12,07	32,06	9,56
4	0,38	1,14	18,67	20,15	50,5	9,17

Fig. 4* The microstructure of the aluminides layer developed by alitation of the Inconel718 matrix in a powdery mixture ($50\%Al+49\%Al_2O_3+1\%NH_4Cl$) at 900°C/5h); the above table shows the chemical composition (in wt%) of the marked zones.



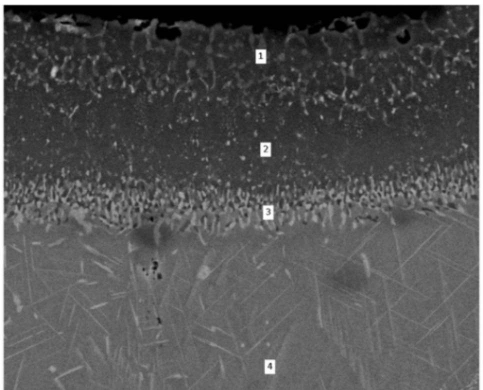
Zone	**%Al**	**%Ti**		**%Fe**	**%Ni**	**%Nb**
1	55,88	0,08	8,06	8,5	24,55	2,93
2	1,02	1,18	18,82	19,3	49,03	10,65
3	-	1,14	18,24	18,73	49,09	12,79

Fig.5 The microstructure of the aluminides layer developed by alitation of the Inconel718 matrix in a in a powdery mixture (50%Al+49%Al_2O_3+1%NH_4Cl) at 640^{o}C/2h); the above table shows the chemical composition (in wt%) of the marked zones.



Zona	%Al	%Ti	%Cr	%Fe	%Ni	%Nb
1	36,61	0,03	6,58	13,76	36,2	6,82
2	18,68	1,2	19,75	12,28	32,96	15,13
3	4,52	1,95	27,78	23,9	23,46	18,38
4	0,26	1,36	18,08	19	48,75	12,54

Fig. 6 The microstructure of the aluminides layer developed by alitation of the Inconel718 matrix in a powdery mixture (49%Al+49%Fe+2%NH_4Cl) at 900^{o}C/5h); the above table shows the chemical composition (in wt%) of the marked zones.



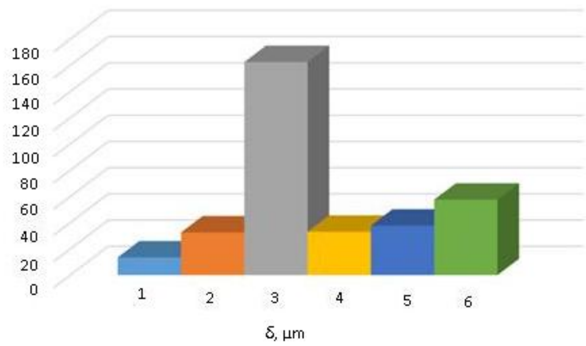
Zona	%Al	%Ti	%Cr	%Fe	%Ni	%Nb	%Mo
1	25,27		11,9	23,61	38,83		
2	23,62		5,6	8,26	62,02		
3	3,94	1,06	29,63	22,14	22,81	14,64	5,61
4		1,07	17,57	18,18	44,3	9,62	9,18

Fig.7 The microstructure of the aluminides layer developed by alitation of the Inconel718 matrix in a powdery mixture (49%Al+49%Fe+2%NH_4Cl) at 300ºC/1h + 650ºC/3h +950ºC/20h), the above table shows the chemical composition (in wt%) of the marked zones.

The different activities of the two types of solid powdery media used for alitation led to different saturation kinetics and distinct chemical and phases compositions. With regard to the media including aluminium powder, the superficial zones of the layer reach high aluminium concentrations (56%...63% weight) depending on the rapport between aluminium alitation temperature and melting temperature and the layer depths vary in the limits 13µm (640ºC/20h) and 162µm (900ºC/5h) - Fig.8.

The dimensions of the alitation layers achieved in the case of use of the powder of iron and aluminium are significantly lower than those obtained through alitation in similar conditions (processing time/temperature) in media including aluminium powder; they vary little for consistent isothermal holding times 32,5µm/900ºC/5h→ 33µm/300ºC/1h +650ºC/3h +950ºC/20h - (Fig.8).

The particular thermodynamic stability of the nickel aluminides demonstrated that the use of the mixtures of aluminium powder and nickel aluminides as active components of the alitation powdery media do not represent a very interesting solution (regimes 5 and 6 from Fig.8); the activity of these media is slightly higher than that of the media including refractory compounds of iron and aluminium mainly due to the aluminium which is free in the composition of these mixtures.



Alitation regimes:

1-640°C/20h in powders mixtures 50%Al+49%Al_2O_3+1%NH_4Cl - **INCONEL 718**
2-900°C/5h in powders mixtures 49%Al+49%Fe+2%NH_4Cl - **INCONEL 718**
3-900°C/5h in powders mixtures 50%Al-49%Al_2O_3-1%NH_4Cl - **INCONEL 718**
4-300°C/1h+650°C/3h+950°C/20h in mixtures 49%Al+49%Fe+2%NH_4Cl - **INCONEL 718**
5-1000°C/30h in powders mixtures 50%(Al+26%AlNi aluminides)+49%Al_2O_3+1%NH_4Cl - **Ni**
6-1000°C/30h in powders mictures100% (Al+26%AlNi aluminides) - **Ni**

Fig. 8. Nomograph showing the different growth kinetics of the alitation layers developed on INCONEL 718, namely pure nickel, in different processing conditions.

4. Conclusions

1. With regard to the ***mechanical allying in balls mills***:

- the low values of the rapport between the weight of the milling bodies and the weight of the material subject to the mechanical alloying, which is an expression of the low kinetic energy of the milling bodies and also the low free height for drop of the milling bodies, which is an expression of the low potential energy of the milling bodies, certifies that nickel aluminides with rich nickel content (Al_3Ni_5) will be preponderantly obtained; the energies released by the milling bodies in these circumstances are below 1J/rot;
- the high values of the M_{cm}/M_{ap} rapport together with high free heights for dropping of the milling bodies, certify that rich aluminium aluminides (AlNi, Al_4Ni_3, Al_3Ni_2) will mainly develop; the energies released by the milling bodies in these conditions are over 7J/rot; the holding time chosen for the mechanical alloying influences slightly the rate of conversion of the powders mixtures in intermetallic compounds which is max. 5% for mechanical alloying in low energy balls mills (processing time~ max. 15 h), namely max 26% for high energy mills (processing times up to 50 h).

2. With regard to the ***alitation in powdery media***, the experimental researches, revealed that:

- an increase of the conversion rate can be ensured by an increase of the geometrical characteristics of the balls mills;
- the mixtures of Al-Fe powders represent a viable alternative to the media which have as active component the ferro-aluminium;
- the mixtures of Al-Fe powders have a similar behaviour to that of the ferro-aluminium powder during heating and holding for alitation; the synthesis of the Al-Fe compounds (pre-available in the ferro-aluminium powder) takes place during heating and continues also during isothermal holding, such as the saturation in aluminium of the surfaces can be realized according to same mechanism;
- the media including aluminium powder are more active by comparison with those including mixtures of iron and aluminium in equal weight percentages; the lower content of aluminium in the layer alited in powdery mixtures of iron and aluminium, makes their brittleness to be much lower by comparison with that of the layers alited and developed in mixture of powders which have as active component the aluminium powder; consequently it is not necessary to apply an annealing subsequent to alitation with a view to control the content of aluminium in layer;
- both the chemical composition and also the phase composition of the alitation layer are extremely sensitive to the variation of the component nature which supplies aluminium from the powdery media used for alitation.

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