



THE Ni₃Al AND NiAl ALLOYS: A CLASS OF INTERMETALLICS WHICH CAN REPLACE THE Ni- BASE SUPERALLOYS FOR THE AEROSPACE HIGH TEMPERATURE STRUCTURAL APPLICATIONS

Mariana Lucaci, Cristian Dragos Vidu, Eugeniu Vasile

METAV S.A.- Aviation Metallurgy, Bucharest, Romania

Summary:

The paper presents the results obtained in synthesizing Ni-base refractory intermetallics from elemental powder mixes. In view of this, four mixes were made for the Ni₃Al intermetallics and five mixes for the NiAl ones. The compound synthesis was made at $T = 660^{\circ}\text{C}$ under vacuum by the SHS method, in the thermo-explosion mode. The variable parameters were the compacting pressure and the aluminium amount in the mixes. The obtained materials were then characterized by the microstructure and by the physical properties. The product synthesis degree was followed as well as their influence on the types of microstructures obtained. The reaction products were evidenced by X-ray diffraction and by quantitative chemical microanalysis. The obtained results revealed the formation of the Ni₃Al compound having a primitive cubic crystal lattice with $a_0 = 3,564 \text{ \AA}$ and the formation of the NiAl compound, of a bcc lattice having $a_0 = 2,86 \text{ \AA}$. Those obtained prove the ample influences of the powder homogeneity degree and of the powder purity on the possibility to produce an adequate synthesis, as well as the influence of the amount liquid appeared in the system on the synthesis degree, on the reaction rate and on the porosity of materials obtained.

Keywords:

Refractory nickel aluminides (Ni₃Al and NiAl), SHS, physical properties, microstructure, X-ray diffraction, EDX

1. Introduction:

The refractory intermetallics of the Ni-Al system possess an ordered structure providing them with attractive mechanical properties, especially for high-temperature structural applications. Many of the intermetallics present a very high yield strength which, in most cases, is kept as high temperatures as well. In some compounds such as Ni₃Al, the yield strength increases with the temperature, up to about 600°C (1). The intermetallics based on light elements have low densities, which represents an advantage when using them in the aircraft industry (and not only), many of the intermetallic – based commercial alloys – being produced from relatively cheap materials (2). The intermetallics containing elements such as aluminum and silicon possess a good oxidation resistance, forming adherent and impenetrable surface oxide films (3).

The major disadvantages inhibiting the commercial use of these materials are: (i) the tendency to form coarse grains during the metallurgical processing; (ii) the poor ductility and the low fracture toughness at room temperature (4).

There are several processing methods such as: exothermic melting method, controlled solidification methods and a series of powder metallurgy specific methods, such as: atomizing methods, the centrifugal pulverizing, the rotating electrode process, rapid solidification methods mechanical alloying, the self-propagation high temperature synthesis.

2. Experimental procedure:

The experiments were conducted so as to obtain four types of Ni₃Al intermetallic materials and five for the NiAl one (Tab.1) from elemental powders.

The grain size of the starting powders used were: < 100 μm for the aluminium powder and < 15 μm for the nickel powder. The wet homogenization was adopted, using 1 ml 2% polyvinilic alcohol solution for 100 g of mix. Using the homogenized mixes, cylindrical samples were obtained by uni-axial pressing. The pressures used were of 50,75, 100, 150 and 200 Mpa. The heat treatment was applied under vacuum in the following conditions: T = 660°C; t = 60 min.

Table1. The chemical compositions of the Ni₃Al and NiAl mixes

Mix type (code)	Chemical composition (%)			
	%at		%wt	
	Ni	Al	Ni	Al
I.1	75	25	86.72	13.28
I.2	76	24	87.33	12.67
I.3	74	26	86.1	13.9
I.4	77	23	87.93	12.07
II.1	50	50	68.51	31.49
II.2	55	45	72.67	27.33
II.3	60	40	76.55	23.45
II.4	65	35	80.16	19.84
II.5	35	65	53.95	46.05

3. Investigation methods:

The physical properties investigated were : green and final material density, green and final material porosity, the dimensional changes produced following the synthesis and the hardness of the obtained materials.

The microscopical investigation and the identification of the phases presents in the obtained materials were made on samples that were metallographically prepared and electrochemically etched (50% methanol – 50% HCl solution).

4. Results:

From the macroscopic point of view, for all the materials, an inhomogeneity of the starting mix was observed, evidenced by the exudation of the liquid phase and appearance of the cracks. Also, the amount of the liquid phase influences the shape of the samples as well as the material behaviour to synthesis and densification. The NiAl materials having a much higher liquid phase amount have been synthesized with a marked shape deformation.

Apparently, all the Ni₃Al – type materials present a volume shrinkage, a decrease of the porosity as compared with the compacts porosity and an increase of the density of the materials (tab.2).

Compared with the Ni₃Al intermetallics density ($\rho = 7,5 \text{ g/cm}^3$) the density of the synthesized Ni₃Al materials is much lower, proving the very porous structure of the synthesized materials.

In what the hardness values regard, noticeable they don't yet over 60 BHN, just because of the porous structure these materials have.

Table 2 The physical properties of the Ni₃Al materials

Ni ₃ Al	V _c (cm ³)	ρ_c (g/cm ³)	P _c (%)	V _s (cm ³)	P _s (%)	ρ_s (g/cm ³)	ρ_s/ρ_t x100 (%)	ΔV (%)	ΔP (%)	$\Delta\rho$ (%)	HB
I.1 50	2.256	3.39	55	1.77	40	4.30	57	-21.4	-27.4	26.9	42.5
I.1 75	1.835	3.60	52	1.43	39	4.60	61	-21.9	-25.6	27.7	44.1
I.1 100	1.626	3.75	50	1.36	36	4.45	59	-15.8	-27.8	18.4	49.4
I.1 150	1.340	4.72	37	1.33	35	4.74	63	-0.6	-6.4	0.4	54.6
I.1 200	1.026	4.44	41	1.88	33	5.15	69	83.4	-29.5	15.8	55.4
I.2 50	3.094	3.35	55	2.65	50	3.88	52	-14.1	-10.4	15.9	29.8
I.2 75	2.824	3.17	58	2.23	45	4.00	53	-20.8	-22.0	25.8	29.5
I.2 100	1.937	3.80	49	1.69	44	4.34	58	-12.7	-11.4	14.2	42.6
I.2 150	3.041	3.72	50	2.37	35	4.75	63	-21.7	-30.1	27.3	44
I.2 200	1.248	3.41	54	1.13	37	4.83	64	-8.9	-31.7	41.5	51.7
I.3 50	1.449	4.31	42	1.37	36	4.51	60	-4.9	-14.2	4.7	44.3
I.3.75	1.936	4.23	43	1.70	35	4.80	64	-12.1	-29.9	13.2	52.1
I.3.100	1.984	3.79	49	1.53	34	4.88	65	-22.5	-30.4	28.5	55.8
I.3.150	1.793	4.17	44	1.49	31	4.99	67	-16.7	-29.4	19.7	48.9
I.3.200	1.016	4.36	42	0.85	33	5.17	69	-16.0	-20.0	18.4	57.3
I.4.50	1.528	4.12	45	1.69	52	3.71	49	10.7	14.3	-9.9	32.8
I.4 75	2.293	3.63	51	2.1	47	3.89	52	-6.8	-9.1	6.9	35.4
I.4 100	1.829	3.82	49	1.67	46	4.15	55	-8.2	-6.4	8.7	36.4
I.4 150	1.688	4.23	44	1.60	43	4.45	59	-5.1	-0.6	5.1	42.5
I.4 200	1.239	4.41	41	1.55	29	3.50	47	25.4	-30.4	-20.6	26.3

The NiAl – type materials (tab.3) show a volume shrinkage, a decrease of the porosity as compared with that of the compacts and a increase of the materials density. In comparison with the reported density of the NiAl intermetallic ($\rho_{\text{NiAl}} = 5.86 \text{ g/cm}^3$), the obtained materials densities is much closer to the reported value then the Ni₃Al materials which indicate the production of a very good conversion degree of the reactants in the reaction product. The obtained NiAl material hardness was strongly influenced by the materials porosity and by their very high brittleness.

Literally, for some samples, the hardness number could not be determined due to their breakage at the time of the indentation.

Table.3. The physical properties of the NiAl materials

Proba NiAl	V_c cm ³	ρ_c g/cm ³	ρ_c/ρ_t x 100,%	P_c %	V_s cm ³	ρ_s g/cm ³	P_s %	ΔV x 100,%	ΔP x 100,%	$\Delta \rho$ x 100,%	HB
II 1 50	3.19	2.8	48	51	1.67	5.38	4.4	-47	-91	89	134
II 1 75	2.44	3.0	52	47	1.58	4.74	4.8	-35.4	-89	53	104
II 1 100	1.78	3.2	55	45	1.13	5.15	2.8	-36.6	-93	60	145
II 1 150	1.66	3.5	61	38	1.11	5.25	4.6	-33.4	-88	47	95
II 1 200	1.55	3.6	62	38	1.09	5.19	6.4	-29.6	-83	43	
II 2 50	2.74	2.9	51	49	1.33	6.14	2.7	-51.5	-94	106	281
II 2 75	1.86	3.1	54	45	0.99	5.97	3.9	-46.9	-91	88	268
II 2 100	2.12	3.3	57	43	1.29	5.64	7.8	-39.4	-81	69	139
II 2 150	1.77	3.6	62	38	1.33	4.72	17.4	-24.9	-54	30	152
II 2 200	0.80	3.9	67	32	0.58	5.62	8.6	-28.4	-73	41	
II 3 50	2.09	3.1	53	46	1.13	5.83	6.3	-46.2	-86	86	255
II 3 75	2.36	3.3	57	42	1.28	6.25	5.0	-45.9	-87	84	232
II 3 100	2.31	3.4	59	41	1.35	5.87	9.5	-41.4	-76	70	192
II 3 150	2.09	3.7	64	35	1.38	5.70	12.3	-33.9	-65	51	143
II 3 200	1.30	3.9	67	32	0.92	5.41	14.4	-28.9	-55	36	
II 4 50	2.68	3.2	54	45	1.56	5.34	21.8	-41.9	-51	67	79.1
II 4 75	2.11	3.4	59	41	1.31	5.74	17.2	-38.3	-57	66	162
II 4 100	2.63	3.5	60	39	1.72	5.41	21	-34.7	-46	52	132
II 4 150	1.77	3.9	67	32	1.42	4.94	29	-20.1	-9.6	25	101
II 4 200	0.96	4.1	71	28	0.80	5.01	30	-17.5	6	20	
II 5 50	2.81	2.5	42	57	2.02	3.49	15	-28.3	-72	39	410
II 5 75	2.28	2.7	47	52	1.79	3.53	14	-21.8	-72	26	89.5
II 5 100	2.04	2.9	49	50	1.67	3.56	17	-18.4	-69	22	
II 5 150	1.95	3.2	54	45	1.90	3.31	13	-3.0	-70	3	
II 5 200	1.16	3.3	57	42	1.14	3.37	20	-2.5	-50	0	

For the point of view of the phases present into the materials, the X-ray diffraction evidenced different behavior as a function of the intermetallic type of the compositional range. So, in the case of the Ni₃Al materials the analysis evidenced the co-existence of a number of phases in the materials (Tab.4).

Table 4. X-ray diffraction analysis - Summary of the results

Composition type	The phase present			
	Ni ₃ Al	NiAl	Al	Ni
I.1 – 75*	Majority	Minority	Minority	-
I.2 – 100*	Majority	-	-	Minority
I.3 – 150*	Majority	-	Minority	-
I.4 – 50*	Majority	-	Minority	Minority
II.1 – 50*	-	Single phase	-	-
II.2 – 100*	-	Single phase	-	-
II.3 – 200*	-	Single phase	-	-
II.4 – 75*	Minority	Majority	-	-

*- the right-side number represents the compacting pressure

As can be noticed from the Tab.4 qualitative data, in the Ni₃Al materials case, a majority of Ni₃Al is evidenced, having a cubic crystallization with lattice parameter of $a_0 = 3.564$ Å. As a function of the chemical composition and the compacting pressure, in addition to the majority phase other phases exists, such as NiAl, residual Ni, residual Al.

In the case of the NiAl materials. All the investigated compositions evidenced NiAl as a single phase, with a bcc structure, having a lattice parameter of $a_0 = 2.87$ Å, except the II.4 composition which also presented Ni₃Al phase.

The microstructural analysis evidences the above mentioned features. Figure 1(a,b,c), present details of the I.1 material microstructure as processed at 50, 100 and 200 MPa.



a) I.1-50 (x 1150)



b) I.1 – 100 (x 1420)



c) I.1 – 200 (x 1200)

Fig.1 Details of the I.1 material microstructure

When processed at 50 MPa, the material is a single phase one. A preferential grain etch is observed, as a function of the crystallographic orientation. The grains are polyhedral and are of 10-30 μm sizes and the grain boundaries are clean. At 100 MPa, the material structure contains at least two phases. The microstructural aspect evidences the same polyhedral grains but greater (40 - 50 μm) with the boundaries delimited by a lattice array of another phase. At 200 MPa, the material structure is again a single phase, with various grain sizes and clean boundaries. Inter and intra granular porosity is noticeable in this case.

At different compacting pressures, in the case of the I.1 material, different evolutions of the microstructural aspect are observed. The compacting pressure assures the initial contact between the powder particles. If the mix is well homogenized, this initial contact will allow for a correct initiation of the synthesis reaction and for combustion wave propagation in the materials volume, assuring an adequate synthesis. For the presented experiments, we cannot establish clearly the improvement role of the compacting pressure plays, exactly because of the initial powder mix non-homogeneity.

The compacting pressure and also the mix homogeneity are responsible for the appearance of the fissures and cracks, as well as for the liquid phase exudation from the samples. In the case of a material aggregation, the contact between the two types of powders is not uniform anymore in the bulk of the material. If the aggregation is made up of aluminum particles, at the processing temperature, liquid phase amount will appear locally, which all the material pores will not be able to take up on one side, and on the other side which will not be able to contribute to the synthesis reaction.

So as this liquid has the tendency to either to remove the particles from each other (fissures, cracks) or to get out to the sample surface.

The I.2 material pressed at 200 MPa (fig.2), present more or less reacted areas and the I.3 material pressed at 75 MPa (fig.3.a) presents a structure containing at least two species of grains. The fig.3.b) detail presents also a grain boundary phase as a network.



Fig.2 I.2 – 200 material (x 600)

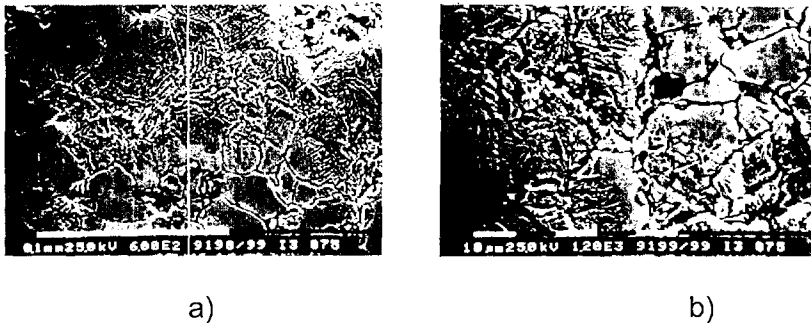
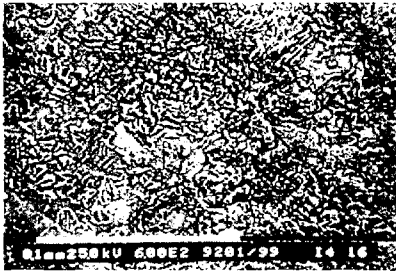


Fig.3 I.3 material (a) ensemble image (x 600); b) detail (x 1200)

The I.4 material processed at 150 MPa (Fig.4 a) is a very well reacted material with few pores and a very fine microstructure. The details from fig. 4.b present polyhedral grains of 10 μm in size.



a)



b)

Fig.4 I.4. material processed at 150 MPa; a) ensemble image (x 600); b) detail (x 1200)

In the case of NiAl materials, their structure should be of a single-phase type, except the II.4 and II.5 materials, as the diffractographic investigations show. Fig.5 presents a birds eye view of the II.1 material as processed at 200 MPa. Equiaxial grains are noticed, having inter and intra granular spherical closed pores. In some zones, as a function of the grains crystallographic orientation, a pitting preferential etch was produced (the lighter area).

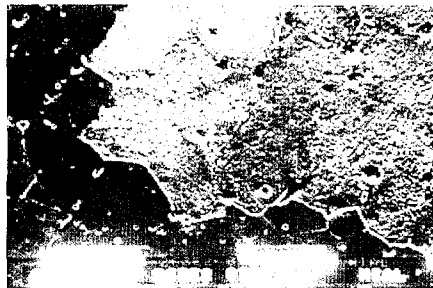


Fig.5 II.1-200 material (x 263)

5. CONCLUSIONS

Following the presented results, the main conclusions, which can be drawn, are:

- The material microstructure is very sensitive to the initial composition of the powder mix, but also to its homogeneity;
- The initial powder mix homogeneity is responsible for the correct evolution of the synthesis reaction as well as for the final material microstructural homogeneity;
- The compacting pressure improves the reaction front propagation and leads to an adequate synthesis;

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