Dimensional changes following the SHS process of the refractory intermetallics NiAl and Ni₃Al

Mariana LUCACI¹⁾, Mihai COJOCARU²⁾ Cristian Dragos VIDU³⁾

1) METAV S.A. – Aviation Metallurgy, Research Department, PO 18, 71529 Bucharest - 1, Romania

2) University "POLITEHNICA", Faculty of Materials Science and Processing, 77206 Bucharest - 6, Romania

3) METAV S.A. – Aviation Metallurgy, Nondestructive Testing Laboratory, PO 18, 71529 Bucharest - 1, Romania

The paper presents a study on the obtaining of NiAl and Ni₃Al refractory intermetallics in their stoichiometric and homogeneity range, obtained by self-propagation high temperature synthesis, the thermo-explosion variant. The processing variables were the compacting pressure and the material chemical composition. The influence of unreacted materials green porosity on the sintered materials contraction/ expansion was determined. The interdependence of the liquid amount appeared during synthesis of the reaction products and the green as well as final material porosity were established.

KEY WORDS: Nickel aluminides, Self- Propagation High Temperature Synthesis, Dimensional changes, Porosity

1. Introduction

The refractory intermetallics represent an intermediate class of materials between the metallic alloys and ceramics [1]. The long-range order of these materials provides mechanical properties that make them commercially advantageous, particularly for the high-temperature structural applications. Many of the intermetallics present a very high yield strength which, in most cases, is kept at high temperatures as well. In some compounds such as, Ni₃Al, the yield strength increases with the temperature, up to about 600°C. The strong interatomic liaison also determines a high elasticity module, which usually is kept at high temperatures too. The strong bond and the complex atomic arrangement of the intermetallics, determine much lower self- diffusion coefficient than that of the disordered alloys, inducing a high diffusion creep strength. The intermetallics containing elements such as aluminum and silicon posses a good oxidation resistance, forming adherent and impenetrable surface oxide films.

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. The above outlined properties give an enviable combination making the materials based on the Ni₃Al and Ti₃Al intermetallics usable for the gas turbine structural applications, while NiAl has already been used as coating material for the turbine blades. The major disadvantages inhibiting the commercial use of these materials are: (1) the tendency to

form coarse grains during the metallurgical processing that affects some mechanical properties, in which the most important is the ductility; (2) the poor ductility and the low fracture toughness at room temperature due to the strong interaction between the two atomic species.

The reason of their fragility varies depending on material. Initially, it was considered that the high temperature properties could be maintained only if an ordered structure is maintained so sacrificing the low temperature ductility.

Because of this, at the beginning of the 1970, the research works on the ordered alloys and on the intermetallics slowed down because of the lack of progress made in improving the ductility and their creep strength. The interest for the use of these intermetallics as structural materials was renewed when discovering that the addition of some alloying elements (B, Hf, etc) could lead to an increase of the low temperature ductility [2].

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 processes, mechanical alloying and mixed methods (Osprey pre-forming process, the self-propagating high temperature synthesis). By the latter process are obtained those intermetallics having high heat of formation. This gives the possibility for a high heat amount to be evolved by forming these materials from pure elementary substance mixes. This simple principle constitutes the base of the reaction synthesis and this was much used to process inorganic materials made of

elementary powders. The self propagation high temperature synthesis, also called combustion synthesis, benefited of much attention the last years while being an easy method to produce advanced materials such as: refractory and hard compounds, intermetallics, intermetallics matrix composites, ceramics and ceramic matrix composites [3].

The method can be applied in more than one technological variants, all based on the exothermic reaction ability to self sustain and to generate a high amount of heat which is delivered to the system, on one side to form the synthesis product and on the other side to obtain compacts with controlled structure and properties. Although various ranges of materials are obtained by this method, the basic phenomena are still insufficiently known. As main variants of the self propagation high temperature synthesis, two reaction initiation ways are known: (1) the one with self propagation, or wave propagation, where the homogenized and compacted powders are burnt in a point with an acetylene torch, an electric arc, an induction coil, or a laser spot. After the reaction is initiated, the heat, which is to be propagated by the combustion wave, is obtained from the formation heat of the synthesized product. The unreacted portion in front of the combustion wave, heated by the heat evolved during the reaction initiation, has the synthesis reaction and then, by the reaction and the combustion wave propagation, the total consumption of the elemental powders of the system is realized; (2) the thermo-explosion way consists of the sample heating into the furnace. The furnace can be brought to the reaction initiation temperature, after which the sample is introduced and heated with the furnace, at a predetermined rate. In this way the synthesis reaction can take place – more or less simultaneously – in many points of the sample. Although the combustion products obtained by both methods are similar, differences can exist between the residual porosity and the final dimensions of the so-synthesized products.

2. Experimental Procedure

Four compositions were made for the Ni_3Al intermetallic and five compositions for the NiAl intermetallic (Table 1).

Table 1. The chemical compositions of the Ni_3Al 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
I.1-B*	74.9	24.86	86.72	13.23
I.1-(B)**			86.44+0.28	13.23
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
II.1- B*	49.94	49.86	68.51	31.44
II.1- B)**			68.23+0.28	31.44

*other elements : B (0.2 %at; 0.05 %wt)

** other elements B as NiB (0.33 % wt NiB, which represents 0.05 % wt B and 0.28 % wt Ni)

For the stoichiometric compositions, boron was also added, using metallic boron or NiB (15 % B), in an amount of 500 ppm. The grain size of the starting powders used were: < 100µm for the aluminum powder; < 15µm for the nickel powder; 10 µm for the metallic boron powder and < 100 µm for the NiB powder (obtained by grinding).

The wet homogenization method 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 (20 mm diameter and 16 mm diameter, respectively). 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.

3. Results

The samples treated to obtain intermetallics were then characterized macroscopically and by the dimensional changes produced following the synthesis, as well as by the green and final material porosity. 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 cracks. Also, the amount of the liquid phase given by the quantity of aluminum powder presented in the composition influences the shape of the samples as well as the material behavior to synthesis and densification. The NiAl compositions having a much higher liquid phase amount have been synthesized with a marked shape deformation. The dimensional changes are more pronounced for the samples pressed at 200 MPa. The above mentioned aspects are more or less significant as a function of the composition type, compacting pressure and homogenization degree of the mix. In the case of the NiAl materials, the most deformed samples are those made up of the stoichiometric composition mix. The greatest modifications were observed for all the samples pressed at 200 MPa. The surface of the samples obtained from material II.4 has a fingerprint aspect, indicating the reaction front appearance and propagation direction. The samples made of the II.5 composition, which contain the highest aluminum content, present lower shape changes than the II.1 composition samples. For the reacted materials the physical characteristics values were determined by weighting on a hydrostatic balance. The fact was evidenced that all materials present important volume contractions.

The NiAl materials present more pronounced contractions for the lower pressures. In the case of the Ni_3Al materials, by a compacting pressure increase, lower volume contractions are obtained. Regarding the porosity of the material, there is a decrease as compared with the initial porosity of the green compact, for all the materials obtained. The NiAl materials show marked decreases of porosity, especially when using low compaction pressures.

The obtained experimental data were statistically processed to establish how the process variables influence the studied physical characteristics. For both materials the programming method chosen was the orthogonal compositional central programming of the second order, for $k = 2$ (k – number of the studied variables) [4]. Table 2 presents the programming matrix including the results obtained in the experimental scheme and Table 3 presents

the basic levels and the variation intervals of the variables used.

Table 2. The second order orthogonal compositional central programming matrix for $k=2$

No exp	x_0	x_1	x_2	x_1x_2	$x_1^2 = x_1^2 - 2/3$	$x_2^2 = x_2^2 - 2/3$	$y_{\Delta VNi3Al}$	$y_{\Delta PNi3Al}$	$y_{\Delta VNiAl}$	$y_{\Delta PNiAl}$
1	+1	-1	-1	+1	+1/3	+1/3	-12.71	-11.45	-34.7	-46.4
2	+1	-1	+1	-1	+1/3	+1/3	-8.91	-31.75	-17.5	-15.8
3	+1	+1	-1	+1	+1/3	+1/3	-16	-20.08	-2.5	-50.9
4	+1	+1	+1	-1	+1/3	+1/3	-22.56	-30.43	-18.4	-69.4
5	+1	+1	0	0	+1/3	-2/3	-16.79	-29.48	-3	-70
6	+1	-1	0	0	+1/3	-2/3	-21.77	-30.19	-20.1	-43.5
7	+1	0	+1	0	-2/3	+1/3	-6.59	-19.52	-29.6	-83.1
8	+1	0	-1	0	-2/3	+1/3	-13.77	-27.83	-36.6	-93.7
9	+1	0	0	0	-2/3	-2/3	-6.96	-23.7	-33.4	-88.1

Table 3. The basic levels and the variation intervals of the variables used

Variable	Z_1 (%Al)		Z_2 (p)	
	Ni ₃ Al	NiAl	Ni ₃ Al	NiAl
Code	X_1	X_1	X_2	X_2
Basic level, z_0	25	50	150	150
Variation interval, Δz_i	1	15	50	50
Superior level (+1)	26	65	200	200
Inferior level (-1)	24	35	100	100

4. Discussion

4.1. The statistical processing of the experimental data obtained for the Ni₃Al materials

By statistical processing the following non-linear patterns were obtained for the volume variation of this type of material, as a function of the green compact volume (1) and of porosity variation as a function of the green porosity (2), respectively:

$$Y_{\Delta V} = -9.1 - 7.35 x_1^2 + 2.92 x_2; \quad (1)$$

$$Y_{\Delta P} = -24.94 + 7.66 x_1 x_2; \quad (2)$$

The material volume variation analysis as a function of the green compact volume at different compacting pressure (Fig.1), leads to the conclusion that the volume contractions decrease with the increase of the compacting pressure, for all the adopted aluminum contents. At 100 MPa pressure, a modification of the line slopes appears which can be interpreted by the fact that at pressures higher than 100 MPa, expansion phenomena appear in the material, due to the closer positions of the initial powder particles, which makes the liquid appeared in the system increases the distance between the particles, tending to occupy the empty spaces between the particles. For the stoichiometric Ni₃Al composition the lowest volume contraction were obtained. When the aluminum content increases (Fig.2) the materials present a decrease of the volume contraction for all the compacting pressures used, up to 25 %at Al, after that a new contraction phenomenon occurs. Up to 25 %at Al, the liquid amount that appears in the system being low is easier distributed in the system pores, facilitating the liquid-solid contacts, the synthesis reaction among the two components, and its exhaustion in a shorter time. At higher aluminum

contents, the volume contractions can be explained by the fact that the excess liquid phase participates to the synthesis reaction and it distributes into the material pores. With the increase of the compacting pressure, the curves move toward low dimensional variations.

Fig.1. The material volume variation as a function of the green compact volume, at different compacting pressures

Fig.2. The material volume variation as a function of the green compact volume, at different aluminum contents

The analysis of the obtained materials porosity as a function of the green porosity, for different compacting pressures (Fig.3) leads to the conclusion that the material of stoichiometric composition does not modify its porosity, regardless the compacting pressure used, being maintained at a constant level of 24%. At less than 25 %at Al, the lines have negative slopes, which means that the porosity decreases with the increase of the compacting pressure, while at higher than 25 %at Al contents the porosity increases with the increase of the compacting pressure. In this case too, one can note a change of the line slope at 100 MPa and an intersection of the lines at 150 MPa, which indicates that at this pressure the material porosity is the same, regardless the aluminum content. The material porosity variation as a function of the green porosity, at different aluminum contents (Fig.4), presents a similar behavior. The existence of the lines intersection point at 25 %at Al indicates that the porosity of material is constant regardless the compacting pressure. When the aluminum content increases, the porosity decreases up to 100 MPa compaction pressure, while at high pressures the porosity increases with the increase of the aluminum content.

Fig.3. The material porosity variation as a function of the green porosity, at different compacting pressure

Fig.5. The material volume variation as a function of the green compact volume, at different compacting pressures

Fig.4. The material porosity variation as a function of the green porosity, at different aluminum contents

Fig.6 The material volume variation as a function of the green volume compacts, at different aluminum contents

4.2. The statistical processing of the experimental data obtained for the NiAl materials

This processing leads to the following non-linear models (3); (4):

$$Y_{AV} = -33.2 + 17.17 x_1^2 + 8.07 x_1 + 6.68 x_2; \quad (3)$$

$$Y_{AP} = -88.3 + 38.97 x_1^2 - 14.1 x_1 + 9.95 x_2; \quad (4)$$

The volume changes of the NiAl materials as a function of the green compacts volume at different compacting pressures (Fig.5) show as straight lines in groups of two, and modify their slopes at 100 MPa. When the compacting pressure increases, the volume contraction decreases. The lowest volume contractions are recorded for the material with 65 %at Al.

At different aluminum contents, the materials volume change (Fig.6) is like a parabola, having a minimum at 47 %at Al. Up to 47 %at Al, an increase of the materials contraction is remarked for all the compacting pressures used, which means that up to 47 %at Al the liquid amount is efficiently distributed into the material pores, leading so an adequate synthesis, after which, at higher aluminum contents, the expansion phenomena are activate in the material, due to the liquid phase access. With the increase of the compaction pressure, the volume contraction decreases. The lower volume contraction was noticed for the material with 65% at Al.

The porosity decreases when the compacting pressure increases (fig.7), the lowest values being obtained for the stoichiometric composition materials and in its neighborhood. At 100 MPa a change of the line slopes is noticed, which prove that at pressures higher then 100 MPa this phenomena leading to the porosity increase are more active.

At different aluminum contents, the porosity variation shows as curved shape with a minimum at 53 %at Al (Fig.8). In this case too, a decrease of the porosity is observed when the compacting pressure increases, the curve being moved toward the higher porosity. At aluminum contents higher then 53 %at Al, the expansion phenomena becomes again active for all the compacting pressure used, due to the appearance of the excess liquid phase.

Fig.7. The material porosity variation as a function of the green porosity, at different compacting pressures

Fig.8. The material porosity variation as a function of the green porosity, at different aluminum contents.

The composition having the 500 ppm B addition shows a similar behavior to that of the stoichiometric compositions, in view of the studied characteristics. The boron addition influences the microstructure of the material. When adding the boron as NiB, a very fine microstructure was observed, with less than 3 μm grains size (Fig.9), compared with the much coarser microstructure of the boron-free intermetallics (fig.10).

Fig.9. Microstructure of the material I.1. (B) pressed at 200 MPa electrolytic etch (x 5000);

Fig.10. Microstructure of the material I.1. pressed at 200 MPa electrolytic etch (x 1200)

5. Conclusions

The evolution of dimensional change and porosity of the obtained material are influenced by the amount of liquid appeared in the system, as well as by the green material porosity, which is given by the compacting pressure used. It has been noticed that the compacting pressure influences the volume contractions and the porosity of the Ni_3Al materials following a first-degree function, while for the aluminum content an influence of second degree showing a maximum was observed. For these materials a critical compaction pressure of 100 MPa was remarked, at which the lines slope is modified indicating the activation of the expansion phenomena. The Ni_3Al material porosity varies following a first-degree function for both analyzed variables. The existence of an intersection point was remarked, corresponding to 150 MPa and 25 %at Al, respectively.

In the NiAl materials case, the same linear dependence of the characteristics studied on the compaction pressure used was obtained, while for the aluminum content of the system the variation follows a second degree function presenting a minimum. For the variation of the characteristics studied as a function of the compacting pressure, it has been noticed that they vary as value pairs grouped as follows: 60-35 %at Al; 55-40 %at Al; 45-50 %at Al, for the dimensional changes and 40-65 %at Al; 45-60 %at Al; 50 - 55 %at Al, for the porosity modifications.

REFERENCES

- 1) P.R. Munroe; I. Baker – Structural Intermetallic compounds, Metals and Materials, (1988), 435.
- 2) Kampe et al. – US Patent, no. 4,915,905, (1990).
- 3) R.L.Orban – SHS Processing of Advanced Materials. An overview, Proceedings – International Conference on Powder Metallurgy, (1996).
- 4) D.Taloi, E.Florian, C.Bratu, E.Berceanu – Optimizarea proceselor metalurgice, Ed. didactica si pedagogica Bucuresti, (1983), 96.