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Microstructure and mechanical properties of Nb₄AlC₃ MAX phase synthesized by reactive Hot Pressing

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Abstract

The present study aims at synthesizing the Nb₄AlC₃ MAX phase by reactive hot pressing using Nb:Al:NbC as starting materials. In order to identify the reaction path, interrupted tests at intermediate temperatures were performed as well as differential thermal analyses (DTA) of powders. Coupling between DTA and XRD data and SEM/EDS analyses of the samples allows a better understanding of the reaction mechanisms. Pure and fully dense Nb₄AlC₃ samples were obtained and characterized for the first time by EBSD and SEM to assess, using an original method, grain size and microstructure. For instance, in the present study, an average grain length of 5-7 μm was obtained.

Standard mechanical characterizations showed interesting properties: $K_{IC} \approx 6 \text{ MPa.m}^{-1/2}$, $E \approx 350 \text{ GPa}$ and $\alpha \approx 7.10^{-6} \text{ }^{\circ}\text{C}^{-1}$. Oxidation performance of Nb₄AlC₃ was evaluated at 1100°C under cyclic conditions. A breakaway regime was instantaneously established for this condition, thus demonstrating the impossibility of using such an unprotected material for structural applications at high temperature in air environment.

Keywords: MAX phases, Hot pressing (A), Grain size (B), Mechanical properties (C), Engine components (E)

1 Introduction

MAX phases are ternary compounds with general formula $M_{n+1}AX_n$ ($n=1$ to 3) where M is a transition metal, A a group IIIA and/or group IVA element and X either C or N. They possess good thermal and electrical conductivities, high resistance to thermal shocks, good stiffness and damage tolerance as well as relatively low coefficients of thermal expansion. Some of these compounds have also a very good oxidation resistance due to the formation of a dense and adherent alumina layer.

Among all the possible configurations leading to MAX phase compounds, only a few of them have been extensively studied, notably in the Ti-Al-C, Ti-Si-C, Cr-Al-C systems. To the authors' knowledge, only a few studies are related to the development and characterization of more refractory MAX phases, such as those corresponding to the Nb-Al-C system. Salama et al. took advantage of the complete solid solubility between Ti and Nb on the M site to produce Nb_2AlC and $(Ti,Nb)_2AlC$ compounds to optimize microstructures and mechanical properties. Hu et al. managed to produce textured nanolayered Nb_4AlC_3 ceramics having a shell-like microstructure configuration and to measure mechanical properties. Finally, Hu et al. proposed different synthesis procedures for hot pressing (HP) and spark plasma sintering (SPS) processes. Phase compositions were investigated as a function of temperature, dwell time and the pressure applied during sintering; the resulting thermophysical properties were also reported. Using hot pressing, the same authors have studied the reaction synthesis above 1500°C and have obtained a fully dense Nb_4AlC_3 MAX phase with a low amount of secondary phases. They have reported its high temperature mechanical stability: the flexural strength and the Young's modulus of Nb_4AlC_3 are maintained up to 1400°C and 1580°C , respectively, which confirms the promising application opportunities of this MAX phase at high temperature.

However, these results were obtained starting with Nb:Al:C mixtures and it was also demonstrated that the molar ratios of the starting powders could have a strong impact on the

purity of the final material and notably on the amount of retained Nb_2AlC and Al_3Nb impurities.

In this paper, a new initial powder mixture is studied to obtain a dense Nb_4AlC_3 material with a very low content of impurities. The precise reaction pathway is analyzed using a systematic coupling between differential thermal analyses (DTA), X-ray diffraction (XRD) analyses and microstructural results collected during interrupted sintering tests. New insights into microstructure of bulk Nb_4AlC_3 are brought by fine electron backscattered diffraction (EBSD) and scanning electron microscope (SEM) analyses after sintering, adding new data to the relation between microstructure and final mechanical properties / oxidation resistance.

2 Experimental details

Commercial powders of niobium (Alfa Aesar, 99.8%, -325 mesh), aluminum (Alfa Aesar, 99.5%, d_{50} : 9 μm) and niobium carbide (Alfa Aesar, 99%, < 10 μm) were used as starting materials. The selected molar ratio of Nb:Al:NbC was set to 1.2 : 1.1: 2.8 for this investigation. Al was introduced in excess to prevent potential evaporation during sintering. The mixture is deficient in C as it is often the case for Al-containing MAX phases. The powders were mixed in alcohol using WC media for 2 hours. Alcohol was then evaporated and the mixture was finally dried for 10h at 90°C. Nb_4AlC_3 was obtained by *in situ* reaction in a hot pressing device using BN-coated graphite dies. The sintering cycle comprised heating up to 1735°C (5°C/min) with a 2 hours dwell time before cooling down to room temperature. All the experiments were performed under a flowing argon atmosphere and a uniaxial pressure of 30 MPa. Following this procedure, 35x35x3mm³ plates were successfully manufactured.

To evaluate the reaction pathway, several sintering cycles were interrupted at different temperatures to analyze the nature and the abundance of phases. Interruption levels were identified through DTA performed on a Nb:Al:NbC mixture in flowing Ar (20 ml/min) up to

1550°C using a Setsys evolution 1750 apparatus (SETARAM, France). Closed alumina crucibles were used to limit Al evaporation. Phase identification was accomplished on polished surfaces using an Empyrean Panalytical diffractometer in the Bragg Brentano configuration. The diffraction range was from 8° to 94° with a 0.01° scanning step. Rietveld refinement was achieved through the MAUD® software to identify the phases and their volume fractions. Two criteria, σ (≈ 2) and R_{wp} (< 15), were used to assess the quality of the refinement. The XRD analysis being performed on the surface of monolithic samples, an arbitrary texture was taken into account in the Rietveld refinement.

Cross sections of the samples were embedded in resin before polishing down to 1 μm (mirror finish). As-polished samples were characterized using an SEM (DSM 962, Carl Zeiss) equipped with energy-dispersive spectroscopy (EDS). EBSD (Merlin, Zeiss) was performed on the same samples after a more cautious polishing with a colloidal silica suspension using a VibroMet polisher.

Fully dense pellets were prepared after *in situ* reaction at 1735°C for 1 or 2 hours and machined using electro discharge machining (EDM) to prepare mechanical and oxidation testing samples. Rectangular samples 35 x 5 x 1.5 mm³ were polished on one side (1 μm) before dynamic Young's modulus measurement at room temperature (GrindoSonic Mk5i). Flexural strength was evaluated on, at least, three samples using four-point bending tests conducted in the Z010 Zwick machine (1 kN) running at a cross-head speed of 0.3 mm/s. To avoid the presence of any surface defect which could act as crack initiation sites, the polished surfaces were oriented towards the side under tension. Finally, Vickers hardness was measured on the uncracked part of the samples. A 200 g load was used to indent the polished surface and measurements were repeated, at least, 5 times to determine an averaged value.

Toughness was evaluated using three-point bending tests performed in the Z010 Zwick machine through single edge notched beam tests (SENB). Samples were similarly rectangular in

shape ($35 \times 3 \times 1.5 \text{ mm}^3$) with an EDMed notch ($a/w=0.5$). Crack propagation was observed using a digital video camera; thus, the observed surface was polished to $1 \mu\text{m}$ as well.

Thermal expansion measurements were carried out on rectangular samples 16 mm in length and $5 \times 2 \text{ mm}$ in cross section. The Setaram Setsys Evolution 1750 device was operated under flowing argon (20 ml/min) with alumina rigs. The thermal cycle consisted in heating up to 1450°C (5°C/min) and cooling down to room temperature (5°C/min). Results were corrected using a sapphire blank test.

Finally, cyclic oxidation tests were performed using Safran facilities (vertical tubular furnace) on cylindrical samples ($\varnothing 25 \text{ mm}$, $t = 2 \text{ mm}$) machined from the plates. Samples were positioned on ceramic holders directly on an automated elevator, exposing samples, alternately, to the high temperature of the furnace and then to the room air temperature. The thermal cycles, thus obtained, were carried out in air with holding at 1100°C . The duration of each thermal cycle was approximately one hour; it included heating up to 1100°C ($\approx 5\text{-}10\text{min}$), a 45 min dwell time and, finally, cooling down to room temperature.

3 Results and discussion

3.1 Phase identification and reaction mechanisms

The linear shrinkage of the Nb:Al:NbC mixture during the reactive hot pressing is shown in figure 1. The corresponding differential thermal analysis is superimposed to allow direct comparisons.

Concerning densification of samples, two stages are visible in figure 1. A first increase in densification rate is observed around 670°C (① in figure 1) before it reduces drastically,

leading to a shrinkage plateau. Then, a second densification peak is identified at 1385°C (② in figure 1) leading to complete densification.

In order to explain such a sequence, it was chosen to interrupt tests after the first and the second densification peaks, i.e. at 740°C and 1420°C, respectively. An interruption at 1000°C allows analyzing the evolution occurring during the shrinkage plateau while stops at 1630 and 1735°C enable the analysis of the microstructure at the final stages of densification. SEM examinations of the related microstructures are presented in figure 2. XRD analyses of the corresponding specimens are presented in figure 3.

In addition, for each interrupted test, the open porosity was measured and reported in Table 1.

Table 1: Thermal treatment conditions, open porosity and densification levels of NAC materials.

Reference	TT	d_{th}	d_{app}	Open porosity (%)	d_{app}/d_{th} (%)
NAC-740	740°C-30 MPa		4.77	30	
NAC-1000	1000°C-30 MPa		4.81	30	
NAC-1420	1420°C-30 MPa		5.48	21	
NAC-1630	1630°C-30 MPa		6.64	2	
NAC-1735-1	1735°C-1h- 30 MPa	7.04	6.93	<1	98.5
NAC-1735-2	1735°C-2h- 30 MPa	7.04	6.93	<1	98.5

The data reported in Table 1 clearly demonstrate that densification is only effective after the second densification peak, i.e. 1385°C.

Regarding all the different characterizations, the reaction sequence can be interpreted as follows.

Melting of aluminum/ Formation of Nb-Al intermetallics

The first endothermic peak at 653°C can be attributed to the melting of aluminum present in the initial mixture. It matches with the beginning of the first shrinkage step observed between 650°C and 700°C. The sample stopped at 740°C reveals that the material is still very porous ($\approx 30\%$ in volume) and the microstructure looks like the initial powder mixture (figure 2a). SEM/EDS examinations reveal the presence of NbC and Nb particles as well as Al particles with a melted aspect surrounded by NbAl₃ phase. The formation of the NbAl₃ phase in conjunction with intermetallic compounds such as Nb₂Al and Nb₃Al is confirmed by XRD (figure 3). The Nb₂Al phase was also detected by several authors but at a higher temperature, around 1000°C. Nevertheless, the very low amounts of Nb₂Al and Nb₃Al intermetallic phases compared to that of the NbAl₃ phase indicate that the exothermic peak at 670°C can be attributed to the formation of NbAl₃.

Formation of Nb₂AlC

Between 740°C and 1000°C, two exothermic peaks are detected through DTA. A first peak at 824°C and a second one, poorly defined, around 920°C. The sample stopped at 1000°C is still very porous ($\approx 30\%$ in volume) but the microstructure has evolved (figure 2 b). Indeed, free Al is no more detected through SEM examinations and Nb particles are surrounded by NbAl₃ phases. Moreover, very thin particles are detected with a Nb/Al ratio between 2 and 3 according to EDS analyses. XRD analyses confirm that Al is almost no more present in the material and that the volume fraction of NbAl₃ has increased. Thus, for the following interpretation, the authors consider that Al disappears at this temperature. The proportion of NbC remains unchanged, which seems to indicate that, at this temperature, Al reacts preferentially with Nb particles to form NbAl₃. Two other phases, identified as Nb₂AlC and

Nb₂Al, were also detected. Thus, it can be assumed that the exothermic peak at 824°C corresponds to the formation of Nb₂Al which immediately reacts with Al or NbC to form NbAl₃ and Nb₂AlC phases (reactions 4 and 5).

Formation of Nb₄AlC₃

Around the second peak of densification rate ($\approx 1385^\circ\text{C}$), the interpretation of DTA results is difficult. The third interrupted test at 1420°C exhibits a decreasing open porosity (21% in volume) and the reaction (figure 2c) of NbC particles to form Nb₂AlC, Nb₄AlC₃ and intermediate phases in the Nb-Al-C system such as Nb₃Al₂C, in a small proportion. NbC and NbAl₃ are still present whereas free Nb has disappeared at this temperature. Moreover, small amounts of Nb₃Al and Nb₂Al are still detected in the diffractograms.

Final transformation

Above 1500°C, linear shrinkage of samples becomes very large and open porosity decreases rapidly. The sample stopped at 1620°C contains a few pores (2% in volume) but its microstructure is still not single-phased. Reaction is not complete since starting materials (NbC) and intermediate phases (NbAl₃, Nb₃Al₂C or Nb₂AlC) are still present (figure 2d). Nevertheless, volume fractions of Nb₂AlC and Nb₄AlC₃ MAX phases increase while NbC, NbAl₃ and Nb₂AlC proportions decrease according to XRD results (figure 3).

Finally, complete densification was reached at temperatures up to 1735°C for 1 and 2 hours. In both cases, open porosity is lower than 1 % in volume. SEM characterization (figure 2e) reveals a homogeneous microstructure without any starting material or intermediate phase. Grains are elongated in particular directions and decorated with some isolated Al₂O₃ particles randomly distributed. Their proportion seems to increase with the dwell time but is, however, too low to be detected through XRD analyses. It confirms that the major constituent is the Nb₄AlC₃ MAX phase with remaining NbC particles. From Rietveld refinements (figure 3), the

calculated cell parameters are $a=3.1314(6)$ Å and $c = 24.1494(3)$ Å for NAC-1735-1 (considering the hexagonal $P6_3/mmc$ crystal structure) which are close to the results published in the literature .

To summarize and conclude on this analysis of results, the following reaction path can be proposed in the present study:

653°C	Al melting	$Al_{(s)} \rightarrow Al_{(l)}$	(1)
667°C	NbAl ₃ formation	$Nb_{(s)} + 3 Al_{(l)} \rightarrow NbAl_{3(s)}$	(2)
824°C	Nb ₂ Al formation	$NbAl_{3(s)} + 5 Nb_{(s)} \rightarrow 3 Nb_2Al_{(s)}$	(3)
670-1000°C	NbAl ₃ increases	$Nb_{(s)} + 3 Al_{(l)} \rightarrow NbAl_{3(s)}$	(2)
	Nb ₂ AlC increases	$Nb_2Al_{(s)} + 5 Al_{(l)} \rightarrow 2 NbAl_{3(s)}$	(4)
1000-1420°C	Al disappears	$2 Nb_2Al_{(s)} + 2 NbC_{(s)} \rightarrow 2 Nb_2AlC_{(s)} + 2 Nb_{(s)}$	(5)
	Nb disappears	$NbAl_{3(s)} + 3 NbC_{(s)} + 2 Nb_{(s)} \rightarrow 3 Nb_2AlC_{(s)}$	(6)
1420-1630°C	NbC decreases	$Nb_2AlC_{(s)} + 2 NbC_{(s)} \rightarrow Nb_4AlC_{3(s)}$	(7)
	Nb ₄ AlC ₃ appears		
1420-1630°C	NbAl ₃ decreases		
	NbC decreases	$Nb_2AlC_{(s)} + 2 NbC_{(s)} \rightarrow Nb_4AlC_{3(s)}$	(7)
1630-1735°C	Nb ₂ AlC ~	$NbAl_{3(s)} + 3 NbC_{(s)} \rightarrow Nb_4AlC_{3(s)} + 2 Al_{(l)}$	(8)
	Nb ₄ AlC ₃ increases		
1630-1735°C	Total transformation in Nb ₄ AlC ₃	$NbAl_{3(s)} + 3 NbC_{(s)} \rightarrow Nb_4AlC_{3(s)} + 2 Al_{(l)}$	(8)
		$Nb_2AlC_{(s)} + 2 NbC_{(s)} \rightarrow Nb_4AlC_{3(s)}$	(7)

Using Nb:Al:C and Nb:Al:NbC as starting materials, Hu et al. and Zhang et al., respectively, have also studied the formation of Nb₄AlC₃ and Nb₂AlC.

Zhang et al. have shown that Al reacts with Nb to form NbAl₃ and was completely consumed at 700°C. Then, they propose that Nb₂Al is formed, due to a partial reaction between Nb₃Al and Nb. Finally, Nb₂AlC appears around 1100°C and its volume fraction increases up to 1650°C, thanks to the reaction between NbAl₃, Nb₂Al and NbC.

Hu et al. have used different starting materials, but they have also observed the formation of Nb_2Al around 1000°C . Moreover, they suggest that Nb_2C forms at this same temperature and report that Al was still detected at 1200°C . They propose that Nb and Al first react to form NbAl_3 , which can then be transformed into Nb_2Al (reaction with Nb). This latter phase can form Nb_2AlC thanks to its reaction with free C. Then, Nb_2Al and NbC or Nb_2C and C react to form the desired Nb_4AlC_3 phase.

Not surprisingly, the reaction path is strongly dependent on the starting materials but also on the grain size distribution of the starting materials and on the processing parameters such as the heating rate. This could explain why, in the study of Hu et al. [10] where sintering was performed with a heating rate of $15^\circ\text{C}/\text{min}$, Al ($30\text{ }\mu\text{m}$) was detected up to 1200°C , whereas, in our study, it was completely reacted at 1000°C with a $5^\circ\text{C}/\text{min}$ heating rate and finer Al particles ($9\text{ }\mu\text{m}$).

Apart from the initial choice of the starting materials, the formation of NbAl_3 and Nb_2Al phases in the reaction sequence seems obvious. Nevertheless, the formation temperature and the proportion of the Nb_2Al phase can be discussed. In our study, this phase is detected in an extremely low quantity and it was not observed in SEM pictures. Thus, it is assumed that it only consists in an intermediate phase which reacts rapidly to form Nb_2AlC or Nb-Al-C phases, which are detected through SEM examinations.

The transient condition in temperature imposes also an evolution in the phase composition, making several reactions possible for the Nb_2AlC formation (e.g. equations (5) and (6)). Once formed, Hu et al. suggested that at very high temperatures the Nb_2AlC phase can decompose and produce NbAl_3 . In this study, only Nb_4AlC_3 was detected at 1735°C . Thus, NbC observed in NAC-1735-1 is assumed to be a starting material.

Furthermore, SEM examinations reveal the formation of Al_2O_3 and Al_4C_3 inclusions in the sample core and at the edges, respectively. This contamination could be attributed to the

reaction at high temperature between Al and either the intrinsic/atmospheric oxygen or the carbon of the graphite dies, to form both phases. However, as the sample is mainly constituted of Nb_4AlC_3 , reaction (7) is assumed to be predominant, compared to reaction (8).

3.2 Microstructural characterization

3.2.1 EBSD coupled with EDS analyses

Fine characterization of such materials, constituted by elongated (large aspect ratio) grains exhibiting a strong anisotropy, is difficult and barely documented, to the authors' knowledge, in the literature. Such measurements are however essential when considering mechanical properties or oxidation resistance. The high spatial resolution of EBSD can help analyzing the tangled microstructure observed with SEM and to better understand the relations between grains.

EBSD maps of Nb_4AlC_3 microstructures, sizes of the analyzed domains and number of analyzed grains as a function of the dwell time at 1735°C (i.e. 1h or 2h) are presented in figure 4. It is clearly evidenced that grains are larger after a 2h material sintering, compared to those of the material subjected to only 1h sintering.

However, to further process these results, the OIM AnalysisTM software was used to run grain size distribution characterization and several filters were applied on data to take into account the shape of the particles. First, grains located at the edge of the picture are excluded, then, only grains having the c-axis parallel to the surface (15° tolerance angle) and with an aspect ratio lower than 0.6 are considered.

For both materials, more than 5000 grains are still considered after data processing for the microstructural analyses. Thus, each grain was modeled by an ellipse, useful approximation for

the determination of shape factors, grain sizes, areal fractions, ... The particle size distribution is presented in figure 5.

For both materials, a lot of grains are very small and the median length (in grain number) is around 3.6 μm and 4 μm for NAC-1735-1 and NAC-1735-2, respectively (figure 5, table 2). However, they represent less than 7% of the total area for NAC-1735-1 and less than 4.5% for NAC-1735-2. From table 2 and figure 5, it can be noted that the grain size distribution is large. Comparing NAC-1735-1 to NAC-1735-2, the mean and the median lengths of the grains are similar. However, the areal fraction of the larger grains ($d > d_{90}$) is higher in the case of the NAC-413-2 sample. Indeed, only 10% of the grains represent around 65% of the total area in NAC-1735-1 and 74% in NAC-1735-2. It indicates that above d_{90} the fraction of the longest grains is higher in the NAC413-2 sample than in the NAC413-1 sample.

Table 2 : Areal fraction as a function of the grain size (d_x in grain number)

	NAC- 1735-1		NAC-1735-2	
	Length (μm)	Areal fraction (%)	Length (μm)	Areal fraction (%)
d_{10}	< 2	<1	< 2	< 1
d_{50}	3.6	7	4	4.5
d_{90}	12	35.7	14	26
Shape factor		0.4		0.4

Mean, min and max length (μm)	5.7; 0.9; 130.5	6.7; 0.9; 113.4
Mean, min and max width (μm)	2.0; 0.62; 24.1	2.3; 0.62; 35.4
Median width (μm)	1.5	1.6

Compared to literature data, the grain size analyzed here is very small. As reported in Table 3, the particles described by Hu et al. are at least 3 times longer and 4 times wider although a similar process was used. Two explanations can be proposed. First, it can be noted that even using three filters to eliminate EBSD artifacts, a lot of small particles are still considered in the treatment of the data. Secondly, the grain size achieved in this work can be limited by the small size of the starting materials and the Nb-Al intermetallics nucleated during the reaction process.

3.3 Mechanical and oxidation properties

3.3.1 Coefficient of thermal expansion

Figure 6 presents the thermal expansion obtained under heating and cooling stages on the Nb_4AlC_3 sample up to 1450°C . Both curves are superimposed, which indicates a good thermal stability of the MAX phase. The average coefficient of thermal expansion (CTE) evaluated between 100 and 1450°C is equal to $7.7 \times 10^{-6} \text{C}^{-1}$, which is consistent with the coefficient measured between 200 and 1100°C ($7.2 \times 10^{-6} \text{C}^{-1}$) by Hu et al. . At low temperature, between 128°C and 282°C , some authors calculated a CTE of $6.2 \times 10^{-6} \text{C}^{-1}$ which is smaller but still coherent with this measurement.

According to these results, the coefficient of thermal expansion is dependent on temperature and the temperature derivative gives the following linear equation:

$$\alpha(T) = 1.3678 \times 10^{-9} T + 6.586 \times 10^{-6} \text{ Equation 1}$$

Some authors have also shown an increase in the CTE as a function of the temperature for the Nb_4AlC_3 material.

3.3.2 Mechanical properties

The Young's modulus evaluated using dynamic measurement is equal to 350 GPa. This result is in good agreement with the literature which reports values in the 306-365 GPa range .

Regarding hardness, measured values are around 4-5 GPa at 2 N for both materials sintered at 1735°C. This is lower than the values reported by Hu et al. for sintered and highly textured Nb_4AlC_3 : 6.2 GPa at 3 N and 7.5-8 GPa at 2 N, respectively.

Four-point bending tests at room temperature were performed on four NAC-1735-1 samples and two NAC-1735-2 samples. In both cases, mechanical behavior is brittle by nature and the discrepancy between tests is restricted (Figure 7). The mean flexural strength is around 380 MPa for both materials even if grain sizes are not exactly identical. This result is slightly higher than the values obtained on hot pressed Nb_4AlC_3 but lower than that measured on SPSeD samples . However, the authors have shown that the mechanical properties strongly decrease at 1000°C on SPSeD samples as compared to those measured on HPed samples, which remain approximately constant up to 1400°C. These values are coherent with the grain size of the Nb_4AlC_3 samples tested in this study.

Finally, toughness was evaluated using three-point bending tests on notched specimens at room temperature and the results appear to be nearly similar for both materials. The analysis of a fractured sample is presented in figure 8. The crack, propagating from the notch to the bulk material, is deflected by grain boundaries (pull-out), but can propagate through cleavage of conveniently oriented grains of the laminated structure.

Table 3 : Properties at room temperature of NAC-1735-1 and NAC-1735-2 materials and comparison with literature data.

Reference	NAC-1735-1	NAC-1735-2	Nb ₄ AlC ₃ (HP)	Nb ₄ AlC ₃ (HP)	Nb ₄ AlC ₃ (SPS)	Nb ₄ AlC ₃ (textured)
Density (g/cm ³)	6.90 ± 0.03	6.93 ± 0.01	6.97	6.89 ± 0.06	6.71	-
ρ/ρ_{th} (%)	98.0 ± 0.4	98.5 ± 0.2	99	97.6	95	-
Mean grain size (μm)	6(L) 2(W)	7(L) 2(W)	50(L) 17(W)	14(L) 4(W)	21(L) 9(W)	-
Aspect ratio (W/L)	0.33	0.3	0.34	0.3	0.43	-
E (GPa)	350 ± 2	350 ± 2	306	340 ± 4	-	353 c-axis 365⊥c-axis
σ_f 4pts (MPa)	372 ± 8	379 ± 6	346 ± 38	573 ± 39	455 ± 2 (3pts)	881 c-axis 789⊥c-axis
K_{IC} (MPa.m ^{1/2})	6.8 ± 0.5	6.3 ± 0.3	7.1 ± 0.3	6.6 ± 0.1	-	14.1 c-axis 9.3⊥c-axis
H _{v0.2} (GPa)	4.0 ± 0.4	5.0 ± 0.9	2.6 ± 0.2 (3 N)	-	3.7 ± 0.5 (10 N)	7.5-8 (2 N)
α (x10 ⁻⁶ . °C ⁻¹)	7.7 (100- 1450°C)	-	7.2 (200- 1100°C)	-	6.7 (282°C)	-

All the mechanical properties at room temperature for NAC-1735-1 and NAC-1735-2 materials are summarized in Table 3 and compared to the available literature data, taking the grain size into consideration.

It is clear from Table 3 that texture has a strong impact on mechanical properties, especially on toughness and flexural strength. It can be noted that fracture toughness in the direction parallel to the basal planes is largely lower than that in the direction parallel to the c-axis direction. As observed in Si₃N₄ ceramics, toughness is correlated to the presence of rod-shaped grains and more particularly to their aspect ratio (W/L). The lower the aspect ratio, the higher is the fracture toughness. As the aspect ratio for MAX phase particles is quite low, it could

explain the high toughness values measured on textured samples. Moreover, comparing the toughness values of the hot pressed samples of this study to the literature data, it should be noted that similar values are obtained for similar aspect ratios. Regarding the flexural strength of textured samples, the authors suggested that grain pull-out and bridging are the main damage mechanisms. Thus, at a small scale, the mechanism for crack propagation depends on the orientation of each grain and pull-out can be favored when the crack propagates parallel to the c-axis whereas cleavage is the main mechanism when it propagates perpendicularly to the c-axis.

Comparing flexural strength of NAC-1735-1 and NAC-1735-2 samples with the literature data, materials with 2 or 3 times larger grain sizes exhibit higher flexural strength whereas materials with approximately 7 times larger grain size have a lower flexural strength. This indicates that an optimal microstructure can be found without influencing notably the toughness.

3.3.3 Oxidation results

Cyclic oxidation performance of Nb_4AlC_3 at 1100°C has proved to be disastrous, despite the large amount of aluminum available in the structure to form an oxide layer. From the first cycle, the samples entered directly into an oxidation breakaway regime, with the generation of a non-protective layered structure (figure 9).

This very brittle oxide structure is generated from all the surfaces exposed to the air. The experiment was stopped after 18 cycles and a pile-up of several oxide layers is observed. Counting the number of layers on each side of the samples gives an average value of 15, which is close to the number of cycles the samples were subjected to. Thus, one potential explanation of this behavior is the formation at 1100°C of a fast growing and dense oxide layer, which is delaminated from the substrate during cooling steps. The oxygen pathway created by delamination gives rise to further oxidation and the growth of a new layer when samples are

re-heated. The thickness of the oxide layer is around $70\text{ }\mu\text{m}\pm 10\text{ }\mu\text{m}$ and the safe material is around $1.131\text{mm}\pm 0.02\text{mm}$. In other words, after 18 cycles at 1100°C only, half of the thickness of the material was converted into oxides.

The nature of the oxide scale was determined through XRD and EDS measurements (figures 9, 10 and 11). XRD analysis on crushed oxide layers reveals that it is composed mainly of Nb_2O_5 , with some NbAlO_4 . SEM examinations, performed on oxidized material after elimination of the layered structure, confirm that an almost monolithic layer is formed, which could be attributed to Nb_2O_5 . The presence of alumina nodules in the oxide layer confirms an inward oxidation of the substrate from the surface, the stable nodules being directly incorporated from the bulk into the oxide scale, due to the oxidation front propagation. Some areas with different aluminum and niobium contents are detected from figures 9 and 11.

It appears that the aluminum activity in the Nb_4AlC_3 MAX phase is not high enough to promote alumina formation at 1100°C . In the literature, it has been demonstrated that alumina scales can be formed on NbAl_3 intermetallics, provided that the aluminum content is greater than 50 at% in the bulk. It has to be compared to the 13 at% aluminum content of the Nb_4AlC_3 MAX phase. Results regarding oxide nature and proportions obtained in this study are consistent with analyses of oxide scales previously published by Zheng et al., in which Nb_2O_5 and NbAlO_4 oxides were detected in the $[500-900^{\circ}\text{C}]$ temperature range. Compared to NbAl_3 oxidation, which is accompanied by the formation of a Nb_2Al interlayer, neither transformation nor interdiffusion has been observed at the Nb_4AlC_3 /oxide interface. This can be explained by the fast diffusion of oxygen through the non-protective oxide scale, leading to the fast oxidation of Nb and Al.

The strong spallation of oxide scales could be explained by the large volume of Nb_2O_5 oxide, $1363\text{ }\text{\AA}^3$ compared to approximately $200\text{ }\text{\AA}^3$ for Nb_4AlC_3 . Furthermore, the CTE mismatch

between the oxide layer and the substrate, i.e. $5\text{--}6 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for Nb_2O_5 versus $7\text{--}8 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for Nb_4AlC_3 , does not act in favor of an extended lifetime of oxide scales on the Nb_4AlC_3 MAX phase.

4 Conclusions

In the present study, fully dense Nb_4AlC_3 MAX phase material was synthesized using *in situ* hot pressing reaction. The synthesis sequence was analyzed by interrupted tests and the maximal purity of the phase was obtained for temperatures as high as 1735°C . The materials thus obtained were subsequently characterized by EBSD and SEM, leading to an average grain length of $7\text{--}10 \text{ }\mu\text{m}$.

Standard mechanical characterizations were performed and are in good agreement with already published results, i.e. $K_{\text{Ic}} \approx 6 \text{ MPa}\cdot\text{m}^{-1/2}$, $E \approx 350 \text{ GPa}$ and $\alpha \approx 7 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. Oxidation performance of Nb_4AlC_3 was evaluated at 1100°C under cyclic conditions. A breakaway regime was instantaneously established for this condition, thus demonstrating the impossibility of using this material for structural applications at high temperature in air environment.

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Figure 1 : Heat flow and shrinkage during reactive hot pressing of Nb:Al:NbC mixture.

Temperatures indicate exo or endothermic peaks. ① and ② indicate the first and second densification peaks at 670°C and 1385°C, respectively. The temperatures achieved for each stop are indicated below the graph.

Figure 2: Microstructure of Nb-Al-C system during heat treatment up to 1735°C : (a) 740°C, (b) 1000°C, (c) 1420°C, (d) 1630°C and (e) 1735°C-1h.

Figure 3: Volume fractions of identified phases based on XRD analyses for the different interrupted tests and Rietveld refinement analysis of NAC-1735-1; experimental data in black, refined model (solid red line); their difference is reported underneath. Quality criteria are $s = 2.5$ and $Rwp = 10.4$.

Figure 4: EBSD cartographies of Nb_4AlC_3 microstructures as a function of the thermal treatment (inverse pole figure): 1735°C-1h (left) and 1735°C-2h (right).

Figure 5: Particles size distribution for (a) NAC-1735-1 and (b) NAC-1735-2

Figure 6: Thermal expansion and coefficient of thermal expansion of Nb_4AlC_3 up to 1450°C.

Figure 7: Strain-stress curves of Nb_4AlC_3 materials manufactured at $1735^{\circ}C$ -1h (a) and $1735^{\circ}C$ -2h (b).

Figure 8: SEM examination of fracture propagation of in the NAC-1735-2 sample after an SENB test.

Figure 9: (a) Photograph showing the multi-layered structure of the oxide scale formed at the top of Nb_4AlC_3 material after oxidation tests at 1100°C -18 cycles, (b) a micrograph of the adhesive oxidized layer, (c) zoom of the z area and (d) zoom of the oxide layer (y area).

Figure 10: XRD diffractogram of crushed oxide layer.

Figure 11: EDS maps of elements at the oxide/substrate interface.