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# Rapid Synthesis of Metallic Reinforced in Situ Intermetallic Composites in Ti-Al-Nb System via Resistive Sintering

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**Abstract:** Intermetallics are known as a group of materials that draws attention with their features such as ordered structure, high temperature resistance, high hardness and low density. In this paper, it is aimed to obtain intermetallic matrix composites and also to maintain some ductile Nb and Ti metallic phase by using 99.5% purity, 35-44 μm particle size titanium, niobium and aluminium powders in one step via recently developed powder metallurgy processing technique - Electric current activated/assisted sintering system (ECAS). In this way, metallic reinforced intermetallic matrix composites were produced. Dominant phases of $TiAl_3$ and $NbAl_3$ which were the first compounds formed between peritectic reaction of solid titanium, niobium and molten aluminum in Ti-Al-Nb system during 10, 30 and 90 s for 2000 A current and 1.5-2.0 voltage were detected by XRD and SEM-EDS analysis. Hardness values of the test samples were measured by Vickers indentation technique and it was detected that the hardnesses of intermetallic phases as 411 HVN whereas ductile metallic phase as 120 HVN.

**Keywords:** Ti-Al; Nb-Al; Intermetallics; Resistive Sintering.

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## 1 Introduction

Due to their regular structure and covalent bonding, intermetallics exhibit high elastic modulus, maintain high strength at high temperatures and are resistant to creep, recrystallization and corrosion [1,2,3,4,5]. Titanium and niobium aluminides show particular interest due to their high specific strength. The greatest limitation of practical use is their fragility at low temperatures [6]. For this reason, the processing of alloys has become a major challenge in the development of these alloys by increasing low temperature ductility [2,7,8,9]. Therefore, for optimization of room-temperature toughness, microstructural modifications are required [4,7,8,9]. In-situ toughening is an alternative technique to enable a combination of brittle intermetallic matrix with a ductile metallic phase in one step [8,10,11,12]. Some conventional methods such as, casting, melting, mechanical alloying techniques or self-propagating high-temperature synthesis (SHS) can be used for manufacturing intermetallic [8,13]. To produce metallic-reinforced intermetallic-based composites, the pressure-assisted electric-current- activated sintering method is an alternative method. The use of ECAS for consolidating samples not only provides a faster heating time and shorter dwell time but also gives lower sintering temperatures [8,10,11,14,15,16].

The starting materials used in our study is metallic Nb, Al and Ti powders. From this perspective it is high importance to describe phases within Ti-Al, Nb-Al phase diagram in terms of production conditions. The Nb-Al phase diagram (Figure 1.a), shows three intermediate phases: $NbAl_3$ ($D0_{22}$, $TiAl_3$-type tetragonal); σ ($D_{8b}$, also denoted $Nb_2Al$); and $Nb_3Al$ ($A_{15}$, denoted δ) [8,17]. Among these aluminides $NbAl_3$ with its high melting point (1680°C), low density (4.54 g/cm$^3$), is attractive as a potential material for high-temperature applications [8,13]. Ti-Al phase diagram (Figure 1.b) depicts a number of intermediate phases. $TiAl_2$ forms at 1215°C from $Ti_5Al_{11}$ and is stable at low temperatures and forms peritectically at 1460°C. (βTi) [body-centered cubic (bcc), also denoted β] and liquid undergo a peritectic reaction at 1490°C to yield (αTi), (close-packed hexagonal, also denoted α). $Ti_3Al$, commonly called $α_2$, has the $D0_{19}$ [17,18]. $TiAl_3$ ($D0_{22}$-type tetragonal) forms peritectically at 1387°C and decomposes eutectoidally at 735°C [4,17]. $TiAl_3$ has the lowest density among Ti-Al family, of 3.4 g/cm$^3$, the highest micro hardness of 465–670 kg/mm$^2$ and the best oxidation resistance even at 1000°C [9,19].

The aim of this work was a precise description of the production of Nb-Ti in situ reinforced intermetallic matrix composites from metallic Ti, Al and Nb powders in one step resistive sintering method in a very short process time without using any controlled atmosphere. Special attention was paid to peritectical reactions of intermediate phases occur during production of intermetallic matrix zone. Especially it is aimed to produce $NbAl_3$-$TiAl_3$ intermetallics as matrix because of its superior properties mentioned above.

## 2 Experimental Procedures

Powders of titanium (35-44μm size and of purity >99.5%), aluminum (35-44 μm size and of purity >99.8%) and niobium (35-44μm size and of purity >99.8%) were used as starting materials. The powders were initially blended to the desired composition of Ti–30Al–50Nb (wt.%). Ti, Al and Nb powders were ball milled at room temperature at a rotation speed of 200 rpm for 2 h milling times. Process parameter are shown in Table 1. After ball milling process, powder mixture was cold-pressed before sintering, to form a cylindrical compact in a metallic die under a uniaxial pressure of 200MPa. Dimensions of the compact were 15mm diameter and 5 mm thickness. The production of intermetallic compound was performed via electric current activated sintering technique in an open atmosphere at 2000 A, for 10, 30 and 90 second using the electric-current-activated sintering technique in an open-atmosphere ECAS system, as shown in Figure 2. After the sintering, the specimens were unloaded and cooled to room temperature.

The microstructure and chemical composition of the samples were analysed using scanning electron microscopy (SEM) (Model JEOL JSM-6060, FEI Co., Japan) with energy dispersive spectroscopy (EDS). X-Ray diffraction (XRD (Model D/MAX-B/2200/PC, Rigaku Co., Japan) was used to identify phases formed in the specimens with a wavelength of 1.5418 A over a 2θ range of 10–80º with Cu-Kα source radiation. The micro-hardness of the test materials was measured using by a Vickers indentation technique with a load of 0.98 N using Leica WMHT-Mod model Vickers hardness instrument.

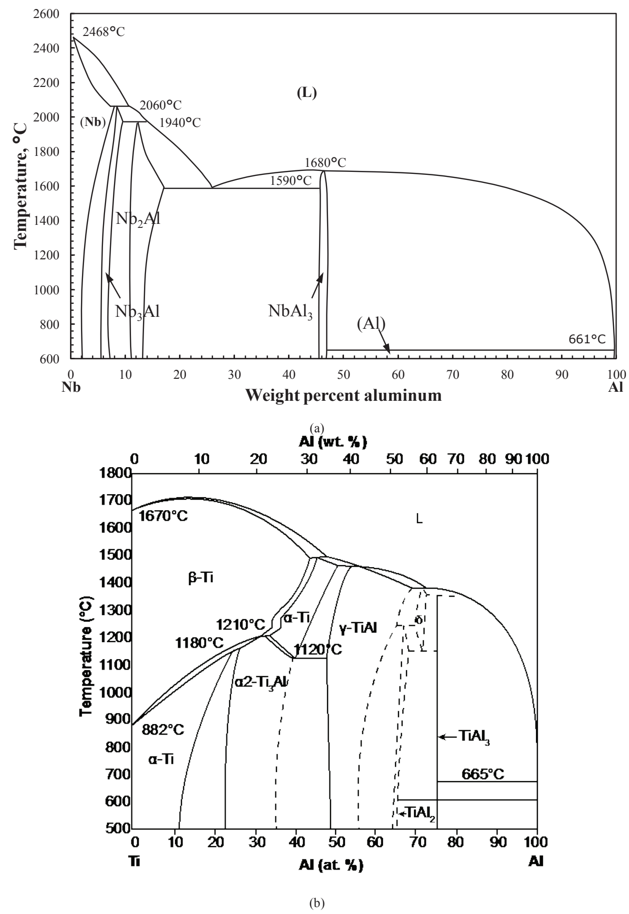



Figure 1: Phase diagram (a) Nb-Al, (b) Ti-Al [20].

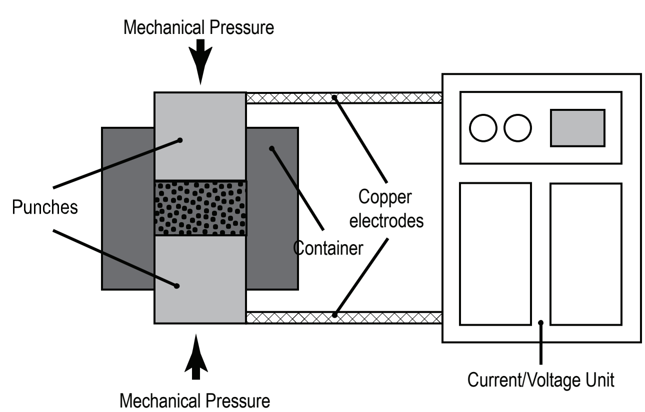
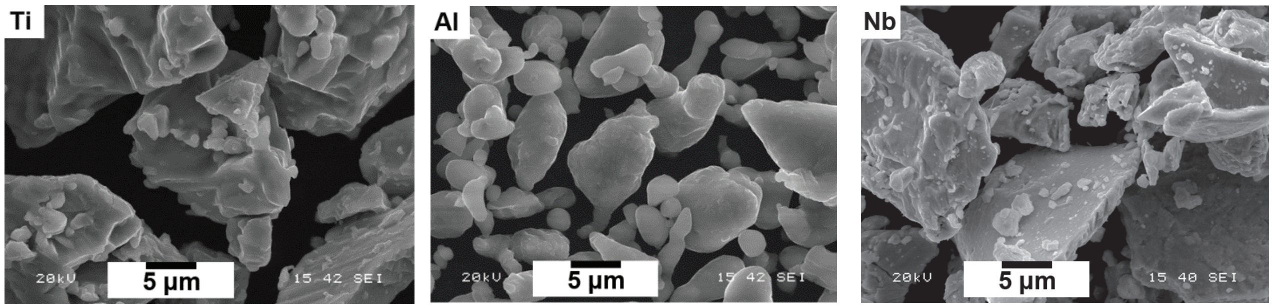



Figure 2: Schematic representation of ECAS system.

Ethical approval: The conducted research is not related to either human or animals use.




(a) (b) (c)

Figure 3: SEM Migrographs of (a) Ti, (b) Al, (c)Nb powders.

**Table 1:** Process Parameters.

| Sample code | Wt.% | Current (A) | Voltage (V) | Holding Time (s) |
|---|---|---|---|---|
| C1 | 20Ti–30Al–50Nb | 2000 | 1.5 – 2.0 | 10 |
| C2 | | | | 30 |
| C3 | | | | 90 |

# 3 Results and Discussion

## 3.1 SEM-EDS Analyses

The morphologies of Ti, Al and Nb powders are shown in Figure 3. Metallic Al powder particles are generally spherical with a diameter of 10 µm. Some of particles are agglomerated and it is clear that the grain size is thinner than 35-40 µm. Unlike aluminum powder, Ti and Nb powder have sharp irregular corners and the grain size is more than 40 µm. For Nb powder, it is seen that the grain size range is quite wide. Very fine powder particles are also present in the structure.

Typical backscattered electron (BSE) micrographs of samples are given in Figure 4. As can be seen in the micrograph of the C1-coded sample (Figure 4a), the sintering time of 10 s is not enough for the reaction of metallic powders, almost no bonding occurred between metallic Ti, Nb and Al yet. The Nb-rich phases give rise to the brightest image because Nb has the highest atomic number (41) of the elements present. Ti (22)-rich areas also lighter than Al(13). Al gives rise to the darkest image because it has the lowest atomic number then it can be said that the dark gray matrix consists of aluminum [9]. The reaction between the phases rapidly started at the C2 sample which was obtained by raising the reaction time from 10 s to 30 s (Figure 4b). In addition to the intermetallic $TiAl_3$ phase TiAl and $Nb_2Al$ phases were formed in the body. However, it is clear that the metallic niobium phase still does not react sufficiently. When it comes to 90 s (Figure 4c), new phases can be easily detected such as $NbAl_3$ around ductile niobium particulates. C3 sample composed of not only brittle $TiAl_3$ and $NbAl_3$ phases but also metallic ductile Ti and Nb phases as desired. $TiAl_3$ phases present gray image due to Ti atoms replaced by Al atoms from liquid aluminum [9].

$Nb_2Al$ and $TiAl_3$ are produced from peritectical reactions [17]. Nice micrographs of peritectial transformation of $Nb_2Al$ phase can be seen in Figure 5. Generally, the term peritectic refers to reactions in which a liquid phase reacts with at least one solid phase to form one new solid phase [21]. This reaction can be written as:

$$\alpha + L \rightarrow \beta \text{ (peritectic reaction)} \quad (1)$$

Here, in our study, L refers to liquid aluminium, and β is Nb. In this type of reaction, because the Nb phase surrounds the solid α particles (new solid phase $Nb_2Al$), as shown in Figure 5, α atoms must diffuse through the Nb crust to reach the liquid for the reaction to continue. However, diffusion through the solid phase is much slower than diffusion through a liquid. As the peritectic reaction continues, the α layer gets thicker and the reaction slows down even more. Unless the cooling rate is very slow, a cored segregated structure will result [21].

Among the Ti-Al binary system as mentioned in introduction section, it can be seen that several intermetallic compounds, such as $Ti_3Al$, TiAl, $TiAl_2$ and $TiAl_3$, form in the Ti-Al system. Many studies involving synthesis of titanium aluminides showed that $TiAl_3$ formed prior to the formation of any other titanium aluminides present in this system [9,10]. From EDS analysis of C3 sample, it can be detected that the dominant phase is as $TiAl_3$ reaction phase between Al and Ti. Initial processing

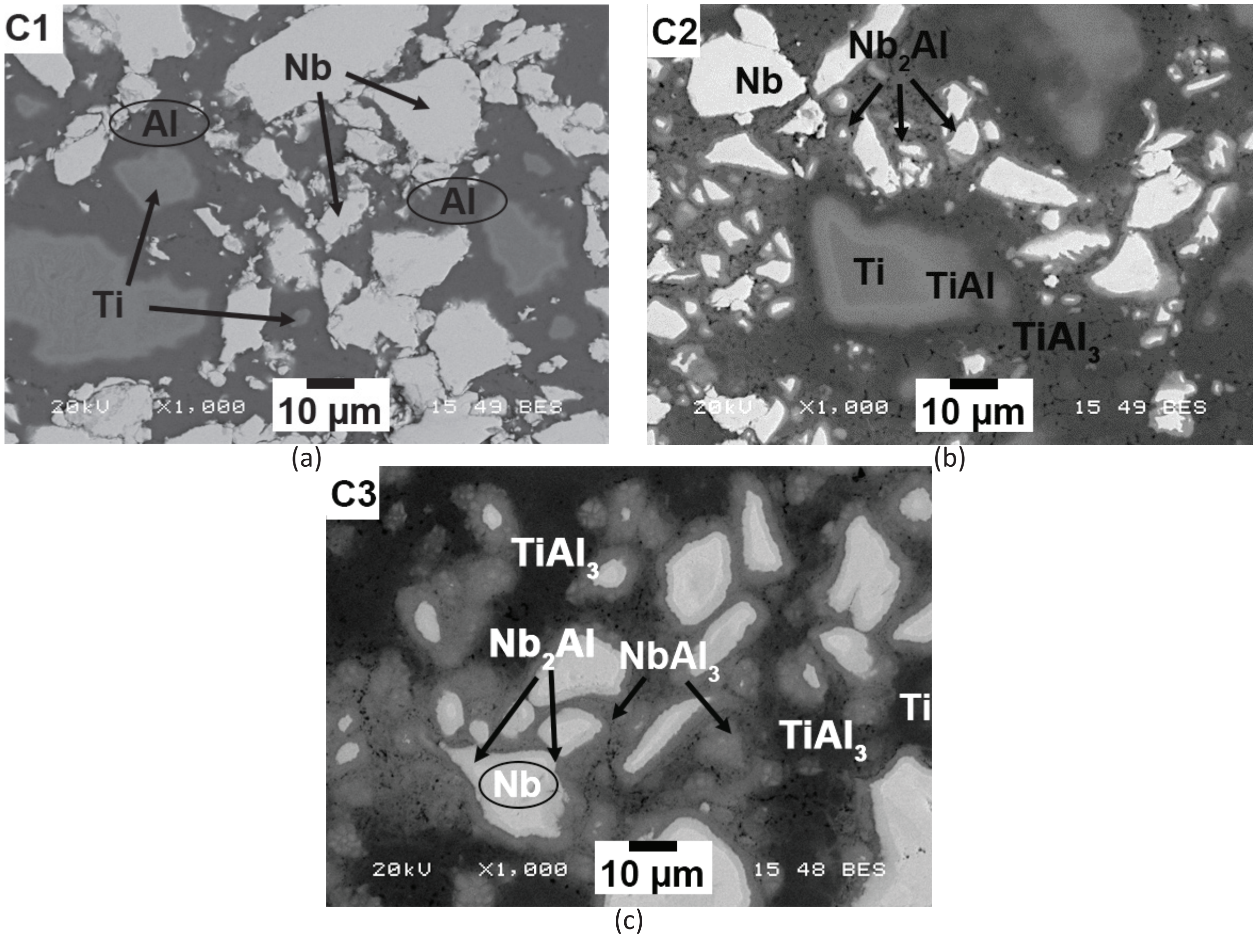



**Figure 4:** SEM Micrographs of (a) C1, (b) C2 and (c) C3 sample.

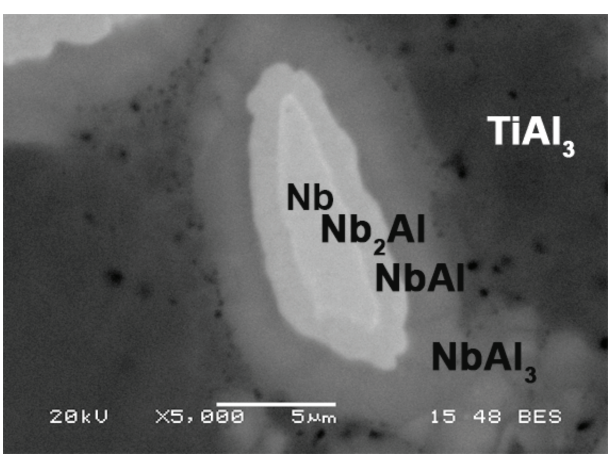
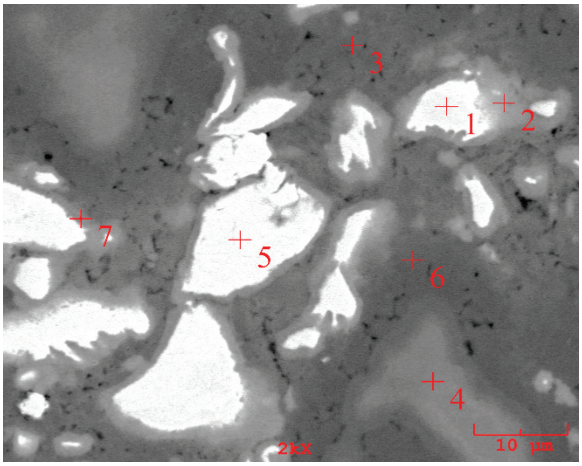



**Figure 5:** Peritectial reaction of Nb-Al phases.

stage, titanium, which is reinforced to maintain ductile phase in the composite as well as to produce intermetallic [10,15]. But it is seen from EDS analyses, almost all metallic titanium transformed to intermetallic. Titanium is only available in a small area within small islands. When it comes to niobium, besides brittle intermetallic matrix formation, Nb is also analyzed in the composite as metallic ductile form as it is desired. Unreacted Nb particles play important role in ductility of the composite [8,10]. Another dominant phase in the matrix is $NbAl_3$.

SEM-Map analyses of C3 sample is given in Figure 7. This analysis is important in terms of showing that there is almost no oxidation in the composite structure even though it is carried out in an open atmosphere. ECAS allows reactions to occur in much shorter times and at lower temperatures than conventional production methods [14,22] . Thus, short-term processing interferes with possible oxidation during formation of intermetallic. According to Map analyses it is clear that niobium aluminide and titanium aluminides is homogeneously distributed in the matrix. In addition, that unreacted ductile metallic niobium can be seen in the analyses.

The main phases in the composite are detected as Nb, Ti, $TiAl_3$ and $NbAl_3$ from XRD analyses (Figure 8). Looking at the XRD analysis of the C2 sample (at the bottom), it is seen that the Nb phase peaks is higher than




| Elt. | Marks | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| | wt(%) | | | | | | |
| Al | - | 41,10 | 65,7 | 16,0 | -- | 68,4 | 51,4 |
| Ti | - | 2,43 | 28,2 | 84,0 | - | 31,6 | 10,8 |
| Nb | 100 | 57,07 | 5,91 | - | 100 | - | 37,8 |
| O | - | - | - | - | - | - | - |

**Figure 6:** EDS Analyses of C3 Sample.

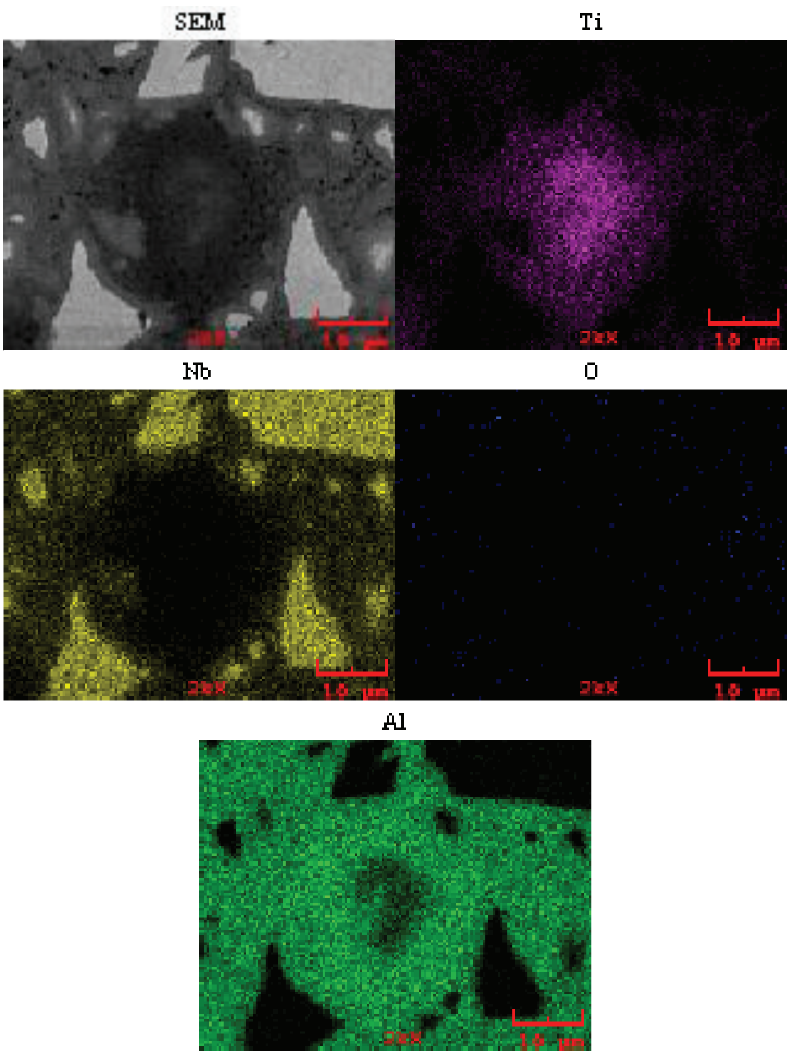



**Figure 7:** SEM-Map Analyses of C3 sample.

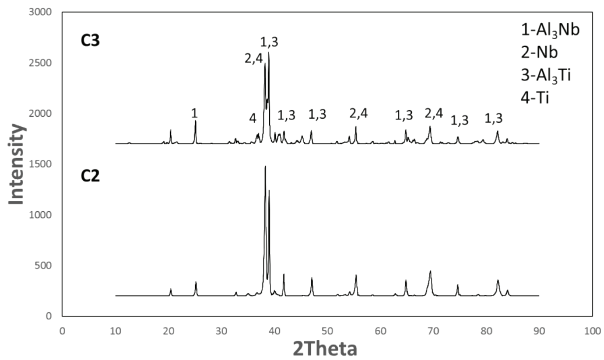



**Figure 8:** XRD Analyses of C2 and C3 sample.

the intermetallic phase. For C3 sample, as the temperature increased, niobium phase became more reactive and the formation of intermetallic phase increased. Increasing with the intermetallic phase the composites hardness also increased from 120±25 HV to 411±65 HV. This high hardness value can be attributed to dense structure of intermetallic composite. The different hardness values for the different production conditions indicate the strong effect of microstructure variations on the mechanical behavior [22].

TiAl intermetallic compound was approximately 200 HV [22]. Depends on the production conditions intermetallic usually contain pores. This pores result decreasing the hardness values.

It is possible to increase the amount of Nb in the work to be done in the future and decrease the amount of Ti so that the aluminum reacts with the niobium before the titanium so that more niobium is consumed and the hardness is increased.

## 4 Conclusion

The following results can be derived from the present study:

$NbAl_3$ and $TiAl_3$ based intermetallic compound coatings produced by the one-step pressure-assisted electric current- activated sintering (ECAS) method have a low porosity in open atmosphere for 90 s. The phases formed in the composite included $NbAl_3$, $TiAl_3$ and Nb, Ti as major phases and some other intermetallic phases also detected such as TiAl, $Nb_2Al$ in SEM-EDS analyses. These findings were confirmed by XRD analysis. Peritectical reaction has not completed for 90 s. Some unreacted ductile niobium particles has remained in the body. Thus it can be succeed to produce metallic reinforced in situ intermetallics by resistive sintering. The Vickers micro-hardness values for intermetallic composites increases from 120 ± 20 HV to 450 ± 65 HV by increasing the holding time in the process by ensuring the formation of a higher proportion of intermetallic phases

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**Conflict of interest:** Authors state no conflict of interest.

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