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Araştırma Makalesi / Research Article

The Effect of Initial Compacting Pressure on the Production of Ti_3Al with Low Porosity

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Keywords
Titanium Aluminide; Volume Combustion Synthesis; Intermetallic; Powder Metallurgy

Abstract

Reaction synthesis, or combustion synthesis is a production technique in which the thermal activation energy required for the formation of a compound is sustained by exothermic reaction heat released in the reaction. Ti-Al alloys are promising materials for aircraft industry, and they could be produced by self-propagating high-temperature combustion synthesis. The purpose of the present study was to research the effect of high initial compacting pressures (420 MPa, 630 MPa and 850 MPa) on the porosity of Ti_3Al which produced by volume combustion synthesis. Microstructure examinations were carried out with optical microscope (OM) and scanning electron microscope (SEM). For phase analyses, X-ray diffraction device(XRD) was used. A considerable decrease in porosity was obtained because of the increase in the initial compacting pressure.

Başlangıç Presleme Basıncının Düşük Gözenekli Ti_3Al'nin Üretimine Etkisi

Anahtar Kelimeler
Titanyum Alüminit; Hacim-Yanma Sentezi; Metallerarası Bileşik; Toz Metalürjisi

Öz

Reaksiyon sentezi veya yanma sentezi, bir bileşiğin oluşumu için gerekli termal aktivasyon enerjisinin reaksiyonda açığa çıkan ekzotermik reaksiyon ısısı ile sürdürüldüğü bir üretim tekniğidir. Ti-Al alaşımları uçak endüstrisi için gelecek vaat eden malzemelerdir ve kendiliğinden ilerleyen yüksek sıcaklık yanma sentezi ile üretilebilirler. Bu çalışmanın amacı, yüksek başlangıç presleme basınçlarının (420 MPa, 630 MPa ve 850 MPa) hacimsel yanma sentezi ile üretilen Ti_3Al bileşiğinin gözenekliliği üzerindeki etkisinin incelenmesidir. Mikro yapı incelemeleri optik mikroskop (OM) ve taramalı elektron mikroskobu (SEM) ile yapılmıştır. Faz analizleri için ise X-ışınları kırınım cihazı (XRD) kullanılmıştır. Başlangıç presleme basıncındaki artışa bağlı olarak gözeneklilikte önemli bir azalma olduğu sonucu elde edilmiştir.

1. Introduction

Transition metal aluminides constitute a large group of intermetallic compounds that are of considerable interest due to their industrial importance. They possess a potentially attractive set of physical, chemical, and mechanical properties. Many of these compounds exhibit ordered structures, and are very stable due to their strong atomic bonding (Liu *et al.* 1990). Studies on intermetallic materials have been started by the US Air Force in the early 1960s to produce the alloy having regular hexagonal Ti_3Al phase.

In recent years, the Ti-Al alloys have received particular attention as a promising structural material for aerospace applications. Intermetallic compounds can be produced through a variety of

methods. However, processing and manufacturing of intermetallic compounds involve several difficulties. For example, there are limited possibilities for forming and shaping components from intermetallic compounds due to their low ductility. Among various other production methods, powder metallurgical techniques offer the possibility of near- net shape production, with relatively fewer limitations (Moore and Feng 1995, Moore 1995).

Combustion synthesis is a novel synthesis method which utilizes the exothermic heat of reaction to make the reaction propagate in a self-sustaining manner through the reactants. The method has been applied to prepare many inorganic materials including intermetallic compounds and their composites. (Merzhanov 1996, Holt and Dunmead 1991). In the volume combustion synthesis, the entire sample consisting of the reactant mixture is heated uniformly in a controlled manner up to the self-supporting ignition temperature that occurs in the volume, and the reactants spontaneously transform during the combustion. This mode of synthesis, also known as shock wave or thermal explosion, is a highly efficient method for weaker exothermic reactions that require pre-ignition preheating because it reaches an extremely high combustion temperature in a noticeably short time. Volume combustion synthesis depends on the rate of reaction heat released and the rate of heat varying with the environment. The effect of dynamic reactions (reaction rate, reaction mechanism) and the nature of the products (phase composition of composites and elemental distribution in solid solution) determine the domain during synthesis reactions (Ergin 2007). The main disadvantage for reaction is that the reaction product is typically porous and thus requires additional processing if a bulk form is desired. Several new processing techniques have been examined to incorporate densification along with the reaction to provide a dense product. Fig. 1 shows the Ti-Al binary phase diagram which is characterized by a number of stable intermetallic compounds such as $Ti_3Al(\alpha 2)$, $TiAl(\gamma)$, $TiAl_2$ and $TiAl_3$. TiAl and Ti_3Al play a prominent role in strengthening titanium alloys for structural applications at elevated temperatures, and they are the most extensively studied phases among Ti-Al compounds and their alloys (Baker 1992, Murray 1987).

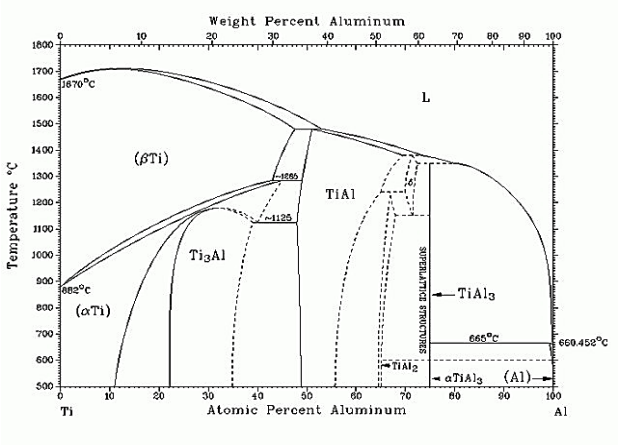


Figure 1. Al-Ti equilibrium phase diagram (Murray 1987)

Titanium aluminides can be produced using reactive synthesis, through both propagating as well as thermal explosion modes. However, due to the relatively low exothermicity of the reactions involved (Adeli *et al.* 2010), the thermal explosion mode is more suitable, particularly for industrial applications (Varma and Mukasyan 2002). In this study, combustion synthesis method was used to obtain titanium aluminide (Ti-26Al (at. %)) at 420 MPa, 630 MPa and 850 MPa compacting pressures. According to results of this study, it was observed that the combustion synthesis was partially realized in the 630MPa compacting pressure sample and traces of Titanium element were found, while the successful combustion synthesis process was realized for the sample pressed at 850 MPa compacting pressure.

Differential thermal analysis (DTA), used to measure heat flow into or out of a sample while it is being heated, can be used to determine onset temperatures and enthalpies of the reactions and phase transformations. Scanning electron microscopy is used for the characterization of microstructures and X-Ray powder diffraction technique is used for the phase characterization, crystalline structures.

2. Material and Experimental Method

Ti(at. 25%) Al samples were prepared using titanium powder (purity 99% and particle size 44 μm) and

aluminum powder (99.5%, 44 µm). Powder mixtures were prepared by making appropriate stoichiometric calculations for Ti_3Al.

Mixing powders were prepared by weighing with 0.0001 g balance in the vacuum chamber. Stainless steel vials and balls are used. Ti and Al powders were placed in vials together with the steel balls and mixed in the ball mill. Mixing was carried out at 250 rpm for 30 minutes. 3 grams of each powder mixture pressed in the hydraulic manual press. Compacting was performed in the steel molds each having and internal diameter of 10.1 mm and carried out under a pressure of 420, 630 and 850 MPa for 10 minutes. Ti_3Al intermetallic production from pressed samples was used with volume combustion synthesis (VCS) apparatus. The apparatus was prepared in the laboratory of Eskisehir Osmangazi University Metallurgical and Materials Engineering Department (Fig. 2).

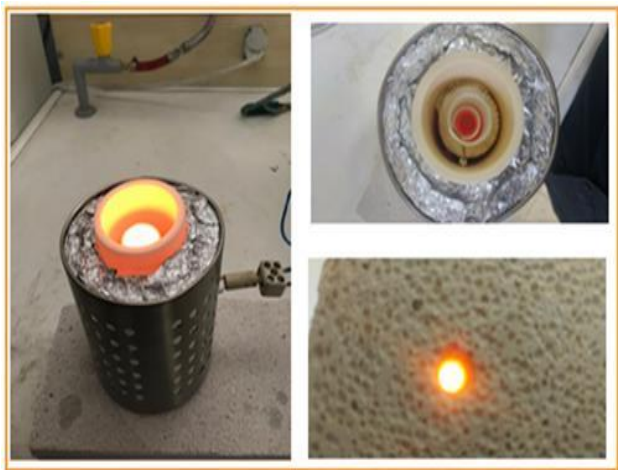


Figure 2. Combustion synthesis apparatus and synthesis stage of sample.

By analyzing DTA, the energy released by the exothermic reaction and the temperature required for preheating were determined in the synthesis of the powder mixture in the appropriate composition. Density values and porosity ratios of samples were calculated according to Archimedes Principle. In addition, microstructural studies of the samples were performed under optical microscope and scanning electron microscope (SEM) and phase analysis were performed with X-Ray diffraction device (XRD).

3. Results and Discussions

Thermodynamic calculations play an important role in selecting the appropriate method, especially for combustion synthesis. For this determination, adiabatic combustion temperature is primarily utilized in the combustion synthesis process. The reaction is

$$3\mathrm{Ti} + \mathrm{Al} \rightarrow \mathrm{Ti_3Al} \qquad (1)$$

The combustion reaction is carried out under adiabatic conditions, that is, the assumption that there is no heat loss is that all heat(Q) is used to heat the reaction product to a temperature called adiabatic combustion temperature (T_{ad}), and calculated as $\sim 1380°K$ by solving the following equation (Rogachev and Mukasyan 2014)

$$Q = -\Delta H^{\circ}_{298} = \int_{298}^{T_{ad}} C_p(product)dT \qquad (2)$$

where $C_p(product)$ is the specific heat of products as a function of temperature and ΔH°_{298} is heat of formation. In addition, the thermodynamic data (Lee 1999, Inoue *et al.* 2004, Han *et al.* 2005, Dunand 1995, Jokisaari *et al.* 1995) in Table 1 was used in the calculations. According to Merzhanov's suggestion (Merzhanov 1975), the reaction cannot become self-sustaining unless $T_{ad} > 1800°K$, meaning is weakly exothermic, and a pre-heat is required for the reaction. Therefore, it is decided to apply the method of volume combustion synthesis.

The change of the enthalpy in the system and the adiabatic combustion temperature after preheating were determined by solving the following equation:

$$-\Delta H^{\circ}_{298} + \int_{298}^{T_{ig}} C_p(reactants)dT = \int_{T_{ig}}^{T_m} C_{p(solid)}(product)dT + \Delta H_m + \int_{T_m}^{T_{ig}} C_{p(liquid)}(product)dT \qquad (3)$$

where ΔH_m is melting enthalpy, $C_p(reactants)$ is specific heat of reactants, T_{ig} and T_m are ignition temperature and melting temperature, respectively. The adiabatic temperature is calculated as $2363°K$.

Table 1. Thermodynamic Data

	ΔH_{298} (J/mol)	ΔH_m (J/mol)	T_m (K)	Cp (J/mol-K)
Al(solid)	0	-	933	$20.67+12.39*10^{-3}T$
Ti(α-solid)	0	-	1155	$22.1+10.04*10^{-3}T$
Ti(β-solid)	0	65870	-	$19.83+7.95*10^{-3}T$
Ti_3Al(solid)	67000	-	1873	$123.3+33.5*10^{-3}T-5.2*10^{6}T^{-2}$
Ti_3Al(liquid)	-100000	-	-	$42.362-5.86*10^{-3}T$

§ $C_p(Ti_3Al\ solid)$ was used in the 470-1425 °K temperature range.

DTA data for system involving titanium, which is relatively low melting transition metals, show that the combustion reaction can occur in the solid-state before aluminum starts melting. Aluminides were observed to form in these systems prior to the combustion reaction, indicating the importance of solid-state inter diffusion between the reactant elements.

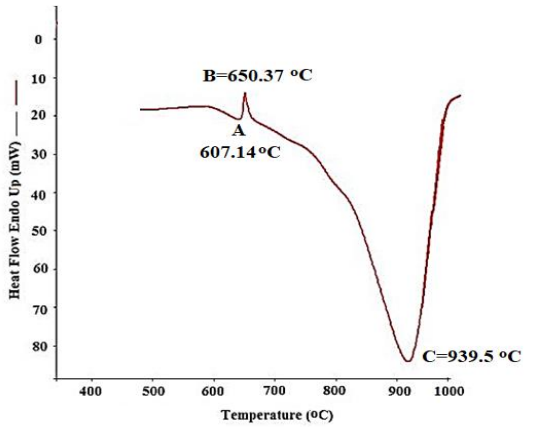


Figure 3. DTA heating curve of Ti-26Al (at.%) powder mixture.

Fig. 3 presents the DTA plot obtained for the Ti-26Al (at. %) powder compacts heated to 1000°C at 20°C min^{-1}. Samples were prepared using titanium and aluminum powders. During heating of samples, one endothermic peak and two exothermic peaks were observed. The small exothermic peak 'A', prior to the aluminum melting stage, can signify the formation of some intermetallic compounds due to the solid-state interdiffusion of reactants observed in several investigations. Especially $TiAl_3$ compound formed initially is a metastable phase which disappears on further heating through the reaction with unreacted titanium (Sina and Iyengar 2015).

The B peak (~650 °C) was found to be compatible with the literature as the melting temperature of Al (Wang *et al.* 2011, Školáková *et al.* 2018). The second big exothermic peak(B) is associated with the formation of titanium aluminides (Školáková *et al*. 2018). This peak corresponds to the combustion reaction occurring between titanium particles and molten aluminum (Školáková *et al*. 2020). However, the peak refers to the reaction between liquid Al and solid-Ti particles is at 939.5°C (1213 K). There were solid-Ti particles and liquid Al at this temperature. Observed adiabatic temperature in DTA was lower than the calculated one because of the use of powder mixture. Normally, the unavoidable heat losses cause lower values than the calculated values (Sanin *et al*. 2006).

Macroscopic images of intermetallic samples synthesized by volume combustion synthesis are given in Fig 4. For microscopic examinations, the samples were ground with 180, 600, 800, 1000 and 1200 mesh SiC papers and then polished with 3 µm diamond paste. The samples for porosity were examined after the polishing step.

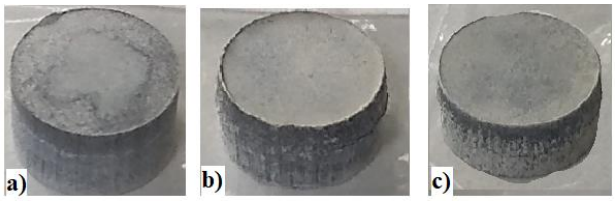


Figure 4. Ti_3Al samples after combustion respectively, a) pressed at 420 MPa, b) pressed at 630 MPa, c) pressed at 850 MPa.

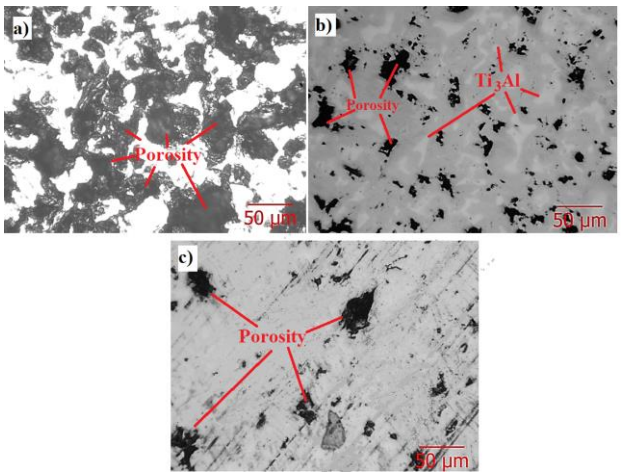


Figure 5. Optical microscope images of sample pressed at a) 420 MPa, b) 630 MPa, c) 850 MPa.

As can be seen from the optical microscope images given in Fig.5, the highest porosity ratio is observed at the lowest compacting pressure. Compaction of starting powders plays an important role in combustion synthesis reactions. Ti_3Al phase was also visualized as an light field in samples (Fig.5.b.) where the reaction was not completed. In the study carried out by Kurt *et al*. 2016, it was stated that the second phases in the interdendritic region have a bright contrast due to their higher atomic numbers compared to the Al element. According to the porosity values determined by Archimedes Method, porosity decreased for samples due to increased initial compacting pressure, see Fig. 6.

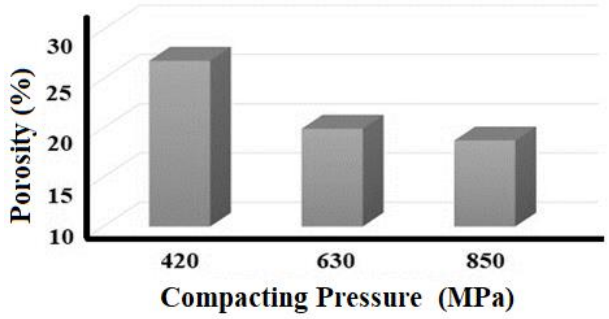


Figure 6. Porosity (%)-Compacting pressure diagram of synthesized samples.

In Fig. 7, SEM microstructure images of Ti_3Al intermetallic are given. The decrease in porosity is clearly seen due to the increased compacting pressure.

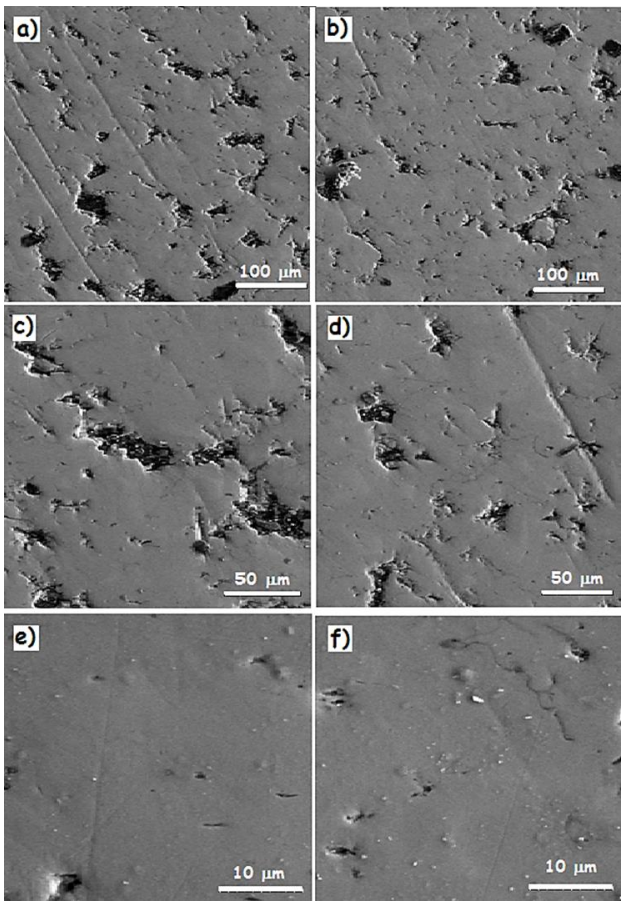
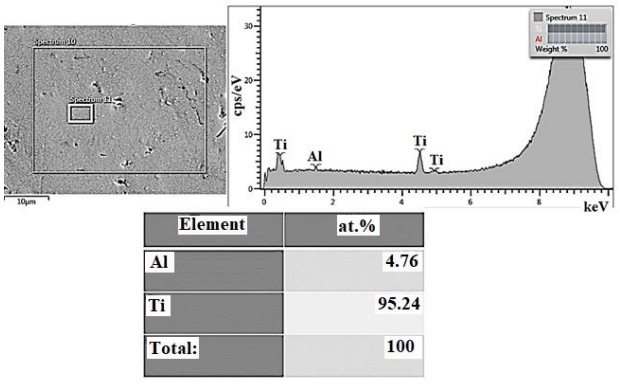


Figure 7. 200X, 500X, 2500X SEM microstructure images of Ti_3Al pressed at a-c-e) 630 MPa, b-d-f) 850 MPa.

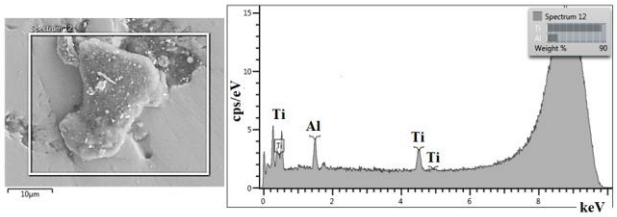
SEM images of sample pressed at 420 MPa were not studied due to the high porosity according to the optical image and Archimedes calculation. Ti_3Al and residual transition metal (Ti) products were observed from the EDX analysis values of pressed at 630 MPa, see Fig.8.



Element	at.%
Al	4.76
Ti	95.24
Total:	100

Figure 8. EDX analysis values of Ti_3Al pressed at 630 MPa.

According to results of the EDX analysis, stoichiometric ratios (at. 73.38% Ti, at. 26.62% Al) were reached for Ti_3Al pressed at 850 MPa, see Fig. 9.



Element	at.%
Al	26,62
Ti	73,38
Total:	100

Figure 9. EDX analysis values of Ti_3Al pressed at 850 MPa.

The XRD analysis shown in the Fig. 10, after compacting at 630 MPa compacting pressure, Ti-phase was obtained in the synthesized samples as well as Ti_3Al intermetallic phase. The presence of Ti indicates that the desired transformation in the synthesis cannot be completed.

The effect of the initial density on the ignition and propagation of the reaction depends on the balance between good particle interactions and should not cause excessive heat loss due to increased thermal conductivity (Moore and Feng 1995).

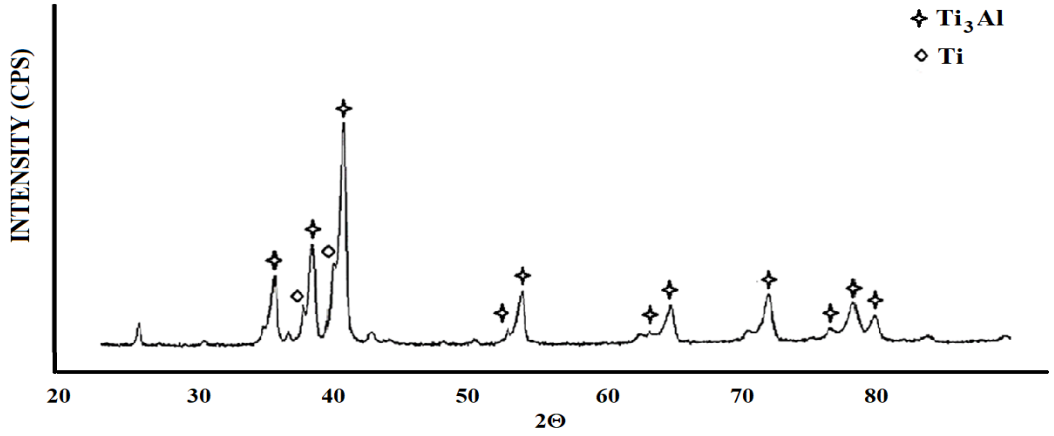


Figure 10. XRD data of sample pressed at 630 MPa.

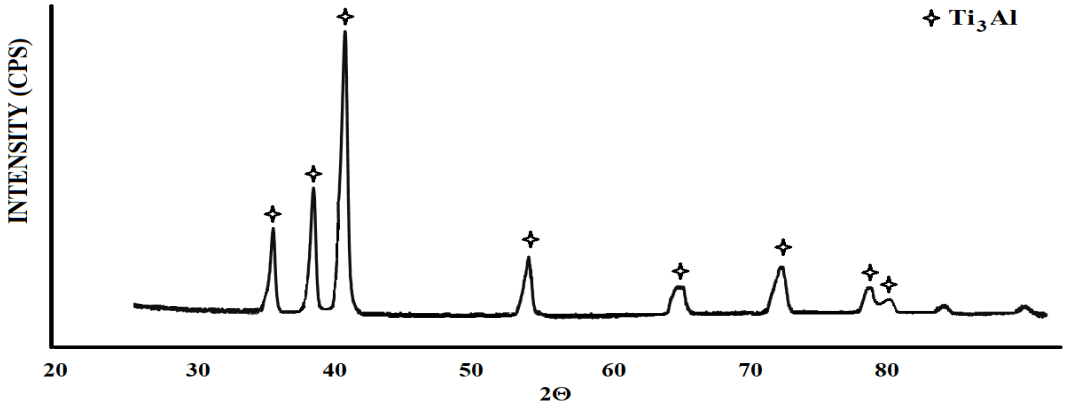


Figure 11. XRD data of sample pressed at 850 MPa.

The lowest porosity ratio was obtained for the Ti_3Al pressed with an initial compacting pressure of 850 MPa. According to XRD analysis, the desired Ti_3Al compound was obtained in these samples. Also, the best values in terms of reduction in porosity were obtained at 850 MPa compacting pressure. As the density increases, the close contact between the reacting particles increases then it results an increase in the thermal conductivity and accelerates the pre-propagation.

4. Conclusion

As a result of the material characterization made within the scope of the present study, the compacting pressure of 850 MPa was found to be the optimum value. Increasing the initial compacting pressure provides interfacial contact between the titanium particles and the aluminum melt, shorter diffusion distances, and better dissolution of solid titanium into liquid phases.

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