Investigation the Effect of Titanium on Adhesive Wear and Hardness of NiAl-Y2O3 Composite Material

Haydar Al-Ethari¹, Ali Hubi Haleem¹, Kawthar Y. AL-Dulaimi¹
¹University of Babylon, Babylon governorate, Iraq
Email: draletharihah@yahoo.com, alialihhhobi@yahoo.com, kawthar_al.dulaimi@yahoo.com

Abstract. In the present study, the nickel aluminide NiAl-based composite, reinforced with yttrium oxide Y₂O₃ with addition of titanium, was prepared by sintering at 1350 °C for one and a half hours under argon gas atmosphere. Brinell hardness test was carried out according to (ASTM E140 – 12b). Titanium addition leads to an increase in hardness of (NiAl-Y₂O₃) composite. The increase in hardness is mainly due to increased NiAl-Y₂O₃ mechanical resistance when titanium is added by the solid-state solution strengthening, as well as by the high density (5.7514 g/cm³) and very low porosity (1.93%) of the final samples. The addition of 2 wt % Ti to the NiAl compound increases the hardness of the compound material (90NiAl-10Y₂O₃) to 295 HB and then increases to 330 HB by adding 2.5 wt. % Ti and continues to increase to 378 HB by adding (3 wt. % Ti). Wear test is carried out to find the wear characteristics of the composites developed by powder metallurgy route. The results revealed that the addition of titanium leads to a decrease in the wear-rate of NiAl-Y₂O₃. Addition of 2 wt. % Ti to (70NiAl-30Y₂O₃) leads to a reduction in adhesion-wear rate from (7.611 * 10⁻⁶ g/cm) to (5.81* 10⁻⁶ g/cm) and to (5.47*10⁻⁶ g/cm) by adding 2.5 wt. % Ti. The adhesion-wear ratio continues to decrease to 4.77 * 10⁻⁶ g/cm by adding 3 wt. % Ti.

1. Introduction:
The requirements of modern industry have led to the appearance of new structural materials as substitutes for Ni-Superalloys. Future aircraft will be required: a better fuel efficiency, high propensity to weight ratio, long service life, and lower cost. In order to reach these requirements, the materials must be light, strong and rigid, and have the ability to keep these properties at harsh environments and high temperatures when employed in the structural framework or in the engines, as the supreme essential feature here is the lower weight. The automotive industry faces technological challenges because of the need to enhance reduce emissions, fuel efficiency, enhance performance, and increase safety, as well as choosing improved methods and enhancing quality. These qualities can be partly recognized by reducing the weight of the engine, especially the reciprocating parts [1, 2].

Intermetallic compounds can be defined as a regular alloying phase, formed up of two or more chemically different metallic elements to create a new phase with new crystalline structure and new features. These compounds can have the properties of both ceramic and metallic materials, also their properties are intermediate the properties of metals (which are generally more ductile and softer) and the properties of ceramic materials (generally brittle and hard). Intermetallic can be ordered into two categories: the first includes intermetallic compounds with a variable structure such as NiAl, while the second with a fixed structure such as MoSi₂ [3, 4].
Numerous studies have been directed on nickel aluminide NiAl since 1990 which resulted in their usage as a structural material for applications operating in hard environments and high temperature due to its unique mechanical and physical properties, which has prepared it to be a competitor to the traditional nickel-based alloys. It has a low density (5.90 g/cm³) (approximately 2/3 that of typical super alloys density), higher melting point of about 2000 °C of the melting point of these alloys. Their resistance to corrosion and oxidation is very high because of the high content of aluminum. The possession of thermal conductivity is more about 4-8 times for those owned by the Ni-alloys [5, 6].

Reinforced nickel aluminide (NiAl) has much better mechanical properties than that of the nickel aluminide compound, which is mostly used for wear coatings, specifically in gas turbine blades. While numerous important challenges still remain, excellent progress has been made in many areas, and the prediction for using NiAl alloys as high-temperature structural materials is promising [7].

Intermetallic compounds in common are brittle and very hard to machine. The ductility of polycrystalline NiAl is approximately zero below about 500 K. Still, as NiAl exists over a varied range of stoichiometries, it is possible to use appropriate alloying additions (such as Ta, Nb, Ti, Mn, Co, Cr, Hf, W, Zr) in order to develop its mechanical properties. Alloying additions are used to raise the number of independent slip systems by reducing the antiphase boundary (APB) energy in different ways [8]. Tian Li, et. al. [9] have studied the effects of Ti alloying addition on room temperature compression deformation behaviour and the microstructure of a NiAl–Cr(Mo)–Hf near eutectic alloy. According to previous studies, Ti is predicted to have a strong preference for Al sites in the B2 crystal structure of NiAl [10]. The current research topic is mainly focused on the wear characterization of particulate reinforced NiAl-Y₃O₃ composite and investigates the effect of Ti with various weight percentages (2, 2.5, and 3 wt. %) on the microstructure, hardness, and wear performance of NiAl-Y₃O₃ composite.

2. Materials used:
Table (1) shows the basic powders used in the preparation of the samples in the current study with their purity and particle size.

The preparation of intermetallic nickel aluminide NiAl and its composite required various steps. The first includes the preparation of the powder mixture, which involves component configuration by determining the weight percentages of nickel and aluminum powders in the composition of NiAl compound and its composite with Y₂O₃ and Ti. At the second step, the mixed ingredients were carried out via planetary ball mill type (FRITSCH Pulverisette-Germany) using alumina balls with a weight of (38 g). Alcohol was used with 10 wt. % to prevent oxidation of the mixed ingredients. After this step, dry compacting at ambient temperature was carried out with a uniaxial compacting pressure of 190 MPa using a double-impact steel die via a hydraulic press to obtain green samples with a diameter of 13 mm and a height of 4 mm. The sintering of this green compact was carried out at a temperature of 600 °C for 15 hours to form the nickel aluminide compound. Argon gas was used during sintering. The samples were cooled to room temperature inside the furnace. The planetary ball mill was used for grinding of the sintered samples for two hours in order to prepare the NiAl powder.

| Powder          | Average particle Size (µm) | Purity  | Source                                      |
|-----------------|---------------------------|---------|---------------------------------------------|
| Nickel powder   | 37.53                     | 99.9 %  | India/CDH fined chemical/Central Drug House (P) Ltd. |
| Aluminum Powder | 20.14                     | 99.8 %  | India/CDH fined chemical/Central Drug House (P) Ltd. |
| Yttrium Powder  | 14.23                     | 99.5 %  | India/CDH fined chemical/Central Drug House (P) Ltd. |
| Titanium Powder | 24.17                     | 99.9 %  | India/CDH fined chemical/Central Drug House (P) Ltd. |
To prepare the intermetallic composite (NiAl-Y2O3) and also NiAl-Y2O3 with additions of (Ti) the same mixing process was used. Dry pressing technique was used with a double-effect die and a compacting pressure of 770 MPa for 4 minutes setting time to produce cylindrical green samples with a diameter of 13 mm and a height of 4 mm for the purpose of hardness and adhesive wear rate tests. This level of the compacting pressure was determined experimentally based on the constancy of the green density. Constant loading rate of 0.3 kN/sec was used for all compacting processes with duration of 4 minutes. Sintering of the composite samples was done at 1350 °C for one and a half hour under an atmosphere of Argon gas with a pressure of (2 bar). A heating rate of (10 °C / min.) was used from 25 °C to 800 °C with duration of 3 hours at this temperature, while 5 °C / min. was used for heating from 800 °C to 1350 °C. Brinell hardness test was carried out according to (ASTM E140 – 12b) [11] using hardness testing machine type (Wilson-BUEHLER). The ball indenter diameter is (10 mm standard ball) with applying load of (3000Kgf) after the grinding and polishing processes of all samples. The hardness was recorded as an average of three measurements in three different places on the specimen. The final density and porosity of the samples was determined by using Archimedes method. The samples were weighed in a sensitive balance (with ± 0.0001g accuracy) after drying in a hot dryer and then calculating the density of the samples using the Archimedes principle by employing density kit measurement. Density of the sample is determined for the three weights taken for each sample using the following formula [12]:

\[ \rho_c = \frac{W_{\text{air}} \times \rho_{\text{liquid}} (W_{\text{soaked}} - W_{\text{liquid}})}{\Delta W} \]…………………(1)

Where, \( \rho_c \) = Density of the composite (g/cm^3), \( W_{\text{air}} \) = Weight of the sample in air (g), \( W_{\text{liquid}} \) = Weight of the sample in liquid (g), and \( W_{\text{soaked}} \) = Weight of the sample soaked in liquid for 2 hours (g).

Table (2) shows the powders used in the synthesis of the basic samples of nickel aluminate with and without additives. The concentrations of titanium selected for this study follow from the compositions of NiAl alloys produced by casting methods to allow for a more meaningful discussion of the properties of NiAl- Y2O3 composites obtained herein by powder metallurgy.

Adhesive wear test was carried out to find the wear characteristics of the composites developed by powder metallurgy route. The pin-on-disk device type (PIN ON DISK TRIBOMETER model MT/60/H) equipped with a diamond indenter was used. It consists of an electric motor at a constant rotary speed of 490 rpm and conveyor rollers. In this test, (20 mm diameter and 10 mm diameter) with a fixed load of 10 N for half an hour have been used. The rate of wear of these samples was calculated at room temperature from the following relationship [13]:

\[ W_k = \frac{\Delta W}{SD} \]……………………………………..(2)

Where: (\( W_k \)) is the rate of wear (g/cm) and (\( \Delta W \)) change in the weight of samples after the experiment, and (SD) Sliding distance (cm), calculated on the basis of (SD=SS*t), where: (SS) Sliding speed (cm / sec) and (t) operating time (min).

| Sample number | Weight percent of Powder (wt. %) |
|---------------|---------------------------------|
| I             | 55Ni-50Al                       |
| II            | NiAl-10 Y2O3                    |
| III           | 88NiAl-10 Y2O3-2Ti              |
|               | 87.5NiAl-10 Y2O3-2.5Ti          |
|               | 87NiAl-10 Y2O3-3Ti              |

|               | 55Ni-50Al                       |
|               | NiAl-30 Y2O3                    |
|               | 68NiAl-30 Y2O3-2Ti              |
|               | 67.5NiAl-30 Y2O3-2.5 Ti         |
|               | 67NiAl-30 Y2O3-3Ti              |
3. Results and Discussion:

3.1 Microstructure Analyses:
The developed interfacial microstructure before the sintering process between aluminum and nickel can be depicted in order to investigate the mechanisms of the formation of Ni–Al intermetallics during heat treatment. Figure (1) shows the beginning of the bonding process between the Ni and Al particles during the first step of sintering (600 °C for 10 hours), while Figure (2) shows the structure composition during this step. The figure indicates the presence of Ni$_2$Al$_3$ only without NiAl, NiAl$_3$ and Ni$_3$Al intermediates. Nickel aluminide Ni$_2$Al$_3$ peaks were compared to the standard XRD card No. 14-0648.

![Figure 1. SEM image of Bonding Process between Ni and Al Particles during Sintering at 600 °C for 10 hours.](image1)

![Figure 2. XRD Shows the Structure Composition after Sintering Process at 600 °C for 10 hours.](image2)
The diffusion of nickel through Al will continue and leads to increase in percentage formation of NiAl as shown in Figure 3. During the long time of sintering (12 hours) the number of nickel atoms decreases gradually, due to Ni consumption, the formation of NiAl alone remains approximately constant (Figure 4). The Al diffusion rate is larger than Ni, aluminum rich intermetallics, namely Ni$_2$Al$_3$, has formed at the interface between aluminum and nickel powders by the solid state interdiffusion. The five phases, Ni$_2$Al$_3$, NiAl, Ni$_3$Al, Al and Ni, co-exist, however, Ni$_3$Al grow at the expense of Ni$_2$Al$_3$, Ni and Al. When the time reaches 12 hours, the Al and Ni$_2$Al$_3$ peaks are completely replaced by those corresponding to NiAl and Ni$_3$Al, and the Ni peaks weaken. Nickel aluminide Ni$_3$Al and NiAl$_3$ peaks were compared to the standard XRD cards No. 21-0008 and 02-0416.

![Figure 3. The Beginning of NiAl Formation Process (Sintering at 600 °C for 12 hours).](image1)

![Figure 4. EDS Analysis Results Showing NiAl Peaks (70NiAl-30 Y$_2$O$_3$) (Sintering at 600 °C for 12 hours).](image2)
As the sintering time increases to 14 hours at 600 °C, peaks related to the formation of NiAl and Ni$_3$Al in addition to the presence of Ni$_2$Al$_3$ and NiAl$_3$, while the Ni and Al peaks weaken. Nickel aluminide NiAl peaks were compared to the standard XRD card No. 44-1188. As the sintering time is raised to higher than 15 hours at 600 °C, the Ni peaks almost disappear and the NiAl becomes the major phase, only minor Ni$_3$Al phase exists. For this stage of sintering process, Figure (5) shows the XRD results. Sintering process at 1350 °C for 1.5 hours was carried out to obtain NiAl phase alone. For this stage of sintering process, Figure (6) shows the XRD results. All peaks in pervious figures were substantially identical to standard X-ray diffraction measurement tables (JCPDS) for nickel and aluminum powders. The increase in the sintering time is the result of most Ni$_3$Al nickel aluminide converted to NiAl by giving sufficient time to Ni$_3$Al nickel atoms to propagate and thus to interact with each atom with one aluminum atom to form NiAl nickel instead of Ni$_3$Al which forms from the interaction of three atoms with one aluminum atom (Figures 7 and 8).

**Figure 5.** XRD shows the Structure Composition after Sintering Process at 600°C for 15 hours (NiAl-30 Y$_2$O$_3$).
Figure 6. XRD Shows the Structure Composition after Sintering Process at 1350°C for 1.5 hours.

Figure 7. Surface Appearance of NiAl intermetallic compound at (1350°C for 1.5 hours: a) 500x, and b) 1.99kx.
3.2 Effect of Titanium on the Hardness of NiAl-Y_2O_3 Composite:

Titanium addition leads to an increase in hardness of (NiAl-Y_2O_3) composite as shown in Figure (9). An addition of 2 wt. % Ti to the composite material (90NiAl-10Y_2O_3) increases its hardness to 295 HB, while adding 3 wt. % Ti increases the hardness to 378 HB. The increase in hardness is mainly due to increased NiAl-Y_2O_3 strength when titanium is added by the solid-state solution strengthening, as well as by the high density (5.7514 g/cm³) of the final samples (Figure 10). The density decreases with increasing the percentage of added Y_2O_3. This is due to the low density of yttrium oxide (5.01 g/ cm³) compared to NiAl (5.86 g/ cm³) [14]. As the density increased, the NiAl porosity decreased, so the addition of Y_2O_3 to NiAl will enhance its hardness. Nickel aluminide NiAl exhibits feature of transgranular characteristics. Based on comparison of the fracture behavior, it can be concluded that Ti addition may be beneficial to the enhancement of the NiAl-Y_2O_3 interface. In view of the better deformation ability of bcc (Ti) solid solution phase, (Ti) solid solution can accommodate more applied stress on loading and thus contribute to suppression of the intergranular fracture [9].
3.3 Effect of Titanium on Adhesive Wear of NiAl-Y₂O₃ Composite:

The results shown in Figure (11) revealed that the addition of titanium leads to a decrease in the wear-rate of NiAl-Y₂O₃. Addition of 2 wt. % Ti to (70NiAl-30Y₂O₃) leads to a reduction in adhesion-wear rate from (7.611 * 10⁻⁶ g/ cm) to (5.81* 10⁻⁶ g/ cm) and to (5.47*10⁻⁶ g/ cm) by adding 2.5 wt. % Ti. The adhesion-wear ratio continues to decrease to 4.77 * 10⁻⁶ g/ cm by adding 3 wt. % Ti. The development of tough NiAl-Y₂O₃ composites based on the addition of particulate titanium having extraordinary wear resistance, this is due to high hardness resulting from the addition of titanium. As the hardness increased, the wear rate decreased. Microstructural refinement modifies the wear behavior. Grain boundary strengthening increases the hardness of the material, thus generating an enhancement of the wear resistance [1].
Figure 11. Effect of Titanium on the Adhesive Wear of NiAl-Y₂O₃ Composite.

4. Conclusions:
1. The NiAl intermetallic compound can be prepared with reactive sintering technique for nickel-aluminum powder at 600 °C for 15 hours under the atmosphere of argon gas. Increasing the reactive sintering time to more than 10 hours increases the accessibility of the NiAl phase alone.
2. The addition of titanium to the composite material (NiAl-Y₂O₃) affects the direction of increasing its mechanical resistance and increasing its hardness as well as its wear performance.
3. The increase of the added Y₂O₃ percentage in NiAl-Y₂O₃ affects the rise of the hardness of the intermetallic material.

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