Improving the physical and mechanical properties of nickel by adding nano titanium oxide by powder technology

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Abstract: In the current article aims to study the effect of Nano construction on the physical and mechanical properties of nickel, samples were made from samples of nickel-based metal and supported with nano titanium oxide, with volumetric ratios of (0,5,10,15,20) %, where the matrix and the reinforcement were ground using a homemade microwave mill with milling times of (3, 6, 9) hours. After that the required weights were prepared and the powders were pressed at (100 bar) and for a time of one minute only. Then the samples resulting from pressing were thermally treated by means of oven and at 1200°C for a time of two hours, physical tests were carried out that included green density and bulk, true porosity, and mechanical properties are hardness, wear rate. The physical and mechanical tests gave the best results after sintering and at a milling time of 9 hours and reinforcement from (0-20) % where the green density decreased from (7.01-5.20) g/cm³, and the bulk density after sintering decreased from (8.43-7.20) g/cm³, porosity increased from (15.43-8.8)%. The mechanical properties increased the hardness from (99-240) Kg/mm², while the wear rate decreased from (4.03×10⁻⁷-6.59×10⁻⁸) g/cm. All these results indicate an improvement in nickel metal with an increase in the Nano composition ratio.

Keywords: Bulk Density, Composite Material, Green Density, Milling Time, Reinforcement.

1.Introduction:

Powder metallurgy is the technology of mineral preparation processes through which parts are produced with different shapes from metal powders, as the powders are pressed to obtain the desired shapes and then these parts are heated through a process called sintering in order to cause the bonding between the particles to obtain a coherent mass (Rigid Mass) [1]. The great industrial development has imposed on researchers in materials technology to find alternatives to materials that enter important industries that are resistant to shock and do not corrode easily and cheaply, and have other qualitative characteristics that make them the basis for achieving the desired development. A mixture of two parts of materials, one of which is called the matrix, and the other is called reinforced [2]. A composite material is a mixture of two or more substances closely related to each other, on the basis of which the material behaves as a single mass, so that it possesses intermediate properties for the properties of the components, meaning that the compound material consists of two phases, the first of which is: the base phase and the second is the phase of strengthening and the phases used are either metal materials or materials Ceramic or polymeric, and the strengthening phase is either minutes, fibers, filaments, or sheets [3,4]. With the scientific and technical development, materials have emerged that cannot be dispensed with or replaced with others, the most important of which is titanium oxide, which is one of the most important materials known to mankind due to its thermal, mechanical and chemical properties and features, friction coefficient and a low wear rate [5]. Although nickel metal has excellent thermal and electrical conductivity that qualifies it for use in many applications, it has a
relatively high wear and friction rate, so the current study aims to improve and reduce wear behavior as well as improves mechanical and physical properties by preparing a metal-based compound material. Nickel reinforcement by titanium oxide, for the purpose of use in many applications such as electric brushes, mechanical sliding bearings and other applications that require good mechanical and physical properties.

2. Procedure Part

2.1. Raw materials:

The base metal is nickel, which was of Swiss origin from Fluka, with a grain size of 50µm and a purity of 99.5%. As for the support material, it was of nano titanium dioxide with different support ratios and made by US Research Nanomaterials, Inc., of Chinese origin, with a 25nm grain size with a purity of 99.8%.

2.2. Preparation method:

The mix weights of each component were adjusted by following the volumetric ratios of the materials used mentioned in Table 1. The volumetric ratios were adopted due to the large difference in densities between the nan powders of nickel and titanium oxide. Weighing was done using a high precision (Sartorius) electric scale of Japanese origin with an accuracy of (0.0001) grams when weighing, then it was milled in three different times (3, 6, 9) hours using steel balls of 10 mm in diameter and the ratio (1:5) to weight the powder mixture [6]. When the grinding and blending process is completed and homogeneous powders are obtained, the samples are formed (pressed) by the method of uniaxial compression technology using a hardened steel mold. A hydraulic press was used (HONMAKSAN) of Turkish origin with a press capacity (20Ton). As the mixed mixture was placed inside the press mold, which was carefully and carefully placed in the piston in order to prevent any movement of the parts of the mold, which, in turn, causes the loss of the powder. Then a pressure of 100 bar was applied for one minute. This is to obtain cylindrical samples of 10 mm in diameter and 5 mm high. The sintering process was carried out using (CARBOLITE) furnace of English origin at a temperature of 1200°C. To prevent the models from being oxidized during the sintering process, they were covered with graphite powder and a cast iron sculpture in a special ceramic container. A layer of cast iron sculptor was placed at the bottom of the container with a thickness of 1 cm, then a layer of graphite of a thickness of 1.5 cm. The samples are paved on top of the graphite layer. Then the samples covered with another layer of 1.5 cm thick graphite powder, then another layer of 1 cm thick cast iron sculpture. Finally, the container with a layer of fire clay. After the samples out of the oven, they are ready for physical and mechanical checks.

Table 1 The volumetric ratios included in the composition of the prepared samples.

| Chemical composition % | Pure Nickel | Ni + TiO$_2$ | Ni + TiO$_2$ | Ni + TiO$_2$ | Ni + TiO$_2$ |
|-------------------------|-------------|--------------|--------------|--------------|--------------|
| Ni + TiO$_2$            | 100         | 95           | 90           | 85           | 80           |
| Ni + TiO$_2$            | 0           | 5            | 10           | 15           | 20           |

3. Measurements Used:

3.1. Bulk Density and Green Density:

It is defined as the ratio of the mass of a substance to its total volume, which includes the actual material and the open and closed pores. The volumetric density (after sintering) and greenness (before sintering) according to Archimedes' theory are calculated using the following relationship [7,8]:

$$B.D. = \frac{W_d}{W_s - W_l} \times \rho_w$$  (1)
\( \rho_w \): Density of water \((g/cm^3)\), \( W_d \): Weight of the Body While it is Dry \((g)\).

\( W_i \): The weight of the body suspended with water \((g)\), \( W_s \): The weight of the object which is saturated with water \((g)\).

### 3.2 True Porosity

The size of the closed and open pores represents the total volume of the body. The true porosity can be calculated from the following relationship \([8,9]\):

\[
T.P. = \frac{T.D. - B.D.}{T.D.} \times 100\% \tag{2}
\]

So: T.P.: The total porosity of the sintered body, B.D.: The volume density \((g/cm^3)\)

T.D.: Theoretical sintered body density \((g/cm^3)\).

### 3.3 Hardness Test

For the purpose of measuring the hardness of the manufactured models, the Brinell method was adopted to calculate the hardness, and a (WP 300 Universal Material Tester, 20KN) device manufactured by the German company (gunt hamburg) was used and used to measure a number of mechanical tests and to measure the hardness of any model five readings were taken in different areas to include the entire surface prepared for this purpose. Brinell hardness (HB) can be calculated by applying the following equation \([10]\).

\[
B.H. = \frac{2P}{\pi \times D \times \left( D - \sqrt{D^2 - d^2} \right)} \tag{3}
\]

As: \( D \): diameter of Bernel ball \((mm)\), \( d \): impact diameter \((mm)\), \( P \): test load \((Kg)\).

### 3.4 Wear Rate

The wear test was carried out and the force of friction measured using a Pin - on - Disc device, as the device places the sample with a disk moving at a certain rotational speed, and the weight of the sample is calculated before and after operating on the wear device, and there are different weights that can be placed on the sample to calculate the amount Weight loss of samples due to friction. And the conditions for wear variables are shown in Table 2. The wear rate was calculated from the following relationships \([11]\).

\[
\text{Wear Rate} = \frac{\Delta w}{S_d} \left( \frac{gm}{cm} \right) \tag{4}
\]

\[
\Delta w = w_1 - w_2 \tag{5}
\]

\[
S_d = 2\pi nt \tag{6}
\]

where: \( \Delta w \): The difference in weight of the sample before and after the test \((g)\), \( w_1 \): The weight of the sample before the test \((g)\), \( w_2 \): The sample weight after testing \((g)\), \( S_d \): The slip distance \((cm)\), \( t \): Test time \((\text{min.})\), \( r \): The radius from the center of the sample to the center of the disc \((\text{cm})\), \( n \): The number of turns of the disk \((\text{r.p.m.})\).
Table.2 Conditions for wear test variables

| Condition                                      | Value         |
|-----------------------------------------------|---------------|
| The rotational speed of the disk              | 950 r.p.m     |
| Test time                                     | 10 min        |
| load                                          | (10) N        |
| The diameter of the test tablet               | 65 mm         |
| Disk hardness                                 | 60 HRC        |

4. Results and discussions:

4.1. Effect of Reinforcement Content and Milling Time on green and Bulk Density

Figure 1 shows the relationship between the change in the volumetric ratios of the titanium oxide content and the milling time on the green density (before the sintering process), and it is noticed through the figure that an increase in the added volumetric ratios of the titanium oxide content at a 3-hour milling time led to a decrease in the density. Green, as the green density decreases from (6.034-4.500) g/cm$^3$, while at a 6-hour milling time, the green density decreases from (6.530-4.950) g/cm$^3$, and at a 9-hour milling time, it led to a decrease in the green density, as the density decreases. Green (7.01-5.20) g/cm$^3$ and all milling times at titanium oxide content from (0%) to (20%).

Figure 2 shows the relationship between the change in the volumetric ratios of the titanium oxide content and the milling time on the bulk density after conducting the sintering process at a temperature of 1200°C and a time of two hours. It is noticed through the figure that the increase in the volumetric ratios added to the titanium oxide content and the milling time at 3 hours led to a decrease in the bulk density, as the bulk density decreased after sintering from (8.12-6.69) g/cm$^3$, as for the milling time, at 6 hours. The bulk density decreased after sintering from (8.33-6.80) g/cm$^3$, as well as with a milling time of 9 hours, the bulk density decreased after sintering from (8.43-7.20) g/cm$^3$ and all the proportions at the titanium oxide content from (0%) to (20%). This decrease in green density and bulk density is due to the lower density of titanium oxide content (3.78) g/cm$^3$, when compared with the high density of nickel. Therefore, it is normal for a decrease in the green density and bulk density of the compound when titanium dioxide is added. It is also noticed that the density values after sintering have increased from the density values before it, due to the increase in the bonding strength between the nickel and the rest of the compound components as a result of the sintering temperature of 1200°C and for a time of two hours, which in turn helps to improve the interface of the composites and improve the bonding between the particles. That the decrease is due to the increase in the percentage of cold forming with the increase in the milling time and the accompanying increase in hardness and flow stress and a decrease in ductility, which is a standard for plastic formation, and this leads to an increase in the powder's resistance to compression and plastic formation with an increase in the milling time. The softening of the nickel particles also plays an important role in the decrease in the bulk density by increasing the milling time, and clumps form from it during grinding, as the decrease in particle sizes leads to an increase in the number and percentage of pores, and then the density decreases.
4.2. Effect of Reinforcement Content and Milling Time on True Porosity

Figure 3 shows the positive relationship between the change in the volumetric ratios of titanium oxide content and the milling time with the true porosity before sintering, unlike what was observed in the density relationship with a change in the titanium oxide content. It is noticed through the figure that an increase in the added volumetric ratios of the titanium oxide content has led to an increase. True porosity, as the percentage of true porosity increases from (18.21-24.88)% when milling 3 hours, while it increases from (16.72-22)% when milling time of 6 hours, and also increases from (13.56-19.78)% when milling time of 9 hours. All times of titanium dioxide content from (0%) to (20%). Figure 4 shows the positive relationship between the change in the volumetric ratios of titanium oxide content and the milling time with the true porosity after the sintering process at 1200°C. It is noticed from the figure that increasing the added volumetric ratios of titanium oxide has led to an increase in the true porosity as the true porosity percentage increases from (15.06-20.43)% at a 3-hour of milling time, and the porosity increases from (13.21-18.51)% at a 6-hour milling time, as well as the porosity increases from (15.43-8.8)% at 9 hrs. All times when the titanium oxide content is from (0%) to (20%). The reason for the increase in true porosity with the increase in titanium oxide content is attributed to the fact that the porosity is the opposite of the
density, and since the density decreases with the increase in the titanium oxide content, it is necessary that the pore ratio be high when the titanium oxide content increases, in addition to the lack of moisture between the base metal and the strengthening particles in addition to Failure of complete coalescence between particles of the composites before sintering [12]. As for the true porosity ratio after sintering and comparing it to its percentage before sintering, it is noted that the true porosity percentage has decreased after the sintering process, and this apparent decrease in the true pore ratio is due to the improvement of the adhesion between the base metal and the hardening particles during the sintering process in addition to the increase in the apparent density values. After sintering its values before sintering, as mentioned above, in addition to the hydrostatic stress that works to close the pores during the plastic distortion between nickel and the content of nano titanium oxide, as the sintering process has a major role in shrinking the size of the pores in the overlays and reducing it by increasing the fusion as a result of the diffusion process in the solid state [13].

**Figure 3** The relationship between the change in volumetric ratios of titanium oxide content and the milling time with the true porosity of the before sintering process.
Figure 4 The relationship between the change in volumetric ratios of titanium oxide content and the milling time with the true porosity of the after sintering process

4.3. Effect of Reinforcement Content and Milling Time on Hardness

Figure 5 shows the relationship between nanocomposite titanium oxide content and milling time with Brinell hardness of the nickel - titanium oxide compound before sintering. It is noticed in the figure that the increase in the milling time and the titanium oxide content led to a remarkable increase in the hardness values of the composite, as the Brinell hardness increased from (61-97) Kg/mm² at a milling time of 3 hours, while it increased from (68-101) Kg/mm². At a milling time of 6 hours, the hardness also increases from (76-116) Kg/mm² at a milling time of 9 hours, Figure (6) shows the relationship between Brinell hardness, titanium oxide content and milling time after performing the sintering process at 1200°C for only two hours Brinell hardness increased from (80-165) Kg/mm² at a milling time of 3 hours, while it increased from (91-187) Kg/mm² at a milling time of 6 hours, and the hardness increased from (99-240) Kg/mm² at the time of milling is 9 hours, all from (0-20%) TiO₂, as it is noticed that the sintering time has a very large effect on increasing the hardness value due to the action of high temperature, which increases the affinity of the atoms with each other and increases the mechanical entanglement that increases the hardness. This behavior can be attributed to several factors that reinforce each other in achieving this significant increase in hardness values. In the forefront is the smoothing of particles of all powders during grinding, and agglomeration of nickel particles formed as a result of cold welding due to the impact of the hammering of steel grinding balls, as both smoothing and agglomeration increase both the surface area and the area of contact of the particles and improve the bonding between them as a result of solid state diffusion during the sintering process and achieve a state of fusion. The increase in milling time also increases the percentage of cold forming and increases the involution density. During the sintering process, re-crystallization occurs within these particles, and the higher the cold forming ratio, the smoother the structure resulting from recrystallization, and with it the surface area of the crystalline boundary increases and the higher values the hardness is [14,15]. The increased milling time also leads to a homogeneous distribution of titanium dioxide particles in the compound, which leads to better bonding between the particles and higher hardness values, which is in agreement with [16].
Figure 5 The relationship between change in volumetric ratios of titanium oxide content and milling time with Brinell hardness before the sintering process.

![Graph showing the relationship between change in volumetric ratios of titanium oxide content and milling time with Brinell hardness before the sintering process.](image)

Figure 6 The relationship between change in volumetric ratios of titanium oxide content and milling time with Brinell hardness after the sintering process.

4.4. Effect of Reinforcement Content and Milling Time on Wear Rate

Figures 7 and 8 show the relationship between titanium oxide content and milling time with the wear rate before sintering and after sintering, respectively. It is noticed from these two figures that the rate of wear decreases with the increase of either the grinding time or the percentage of titanium oxide added in the compound, as the wear rate decreases before sintering from \((3.44 \times 10^{-5} - 9.43 \times 10^{-5})\) g/cm at a time of 3 hours. It also decreases from \((1.37 \times 10^{-5} - 6.93 \times 10^{-5})\) g/cm at a milling time of 6 hours, and the wear rate decreases from \((3.09 \times 10^{-6} - 2.54 \times 10^{-5})\) g/cm at a milling time of 9 hours. The Wear rate after sintering at 1200°C of \((4.56 \times 10^{-7} - 9.12 \times 10^{-7})\) g/cm at a milling time of 3 hours, and also less than \((2.79 \times 10^{-7} - 7.03 \times 10^{-7})\) g/cm at a milling time of 6 hours, the wear rate is reduced from \((6.59 \times 10^{-8} - 4.03 \times 10^{-7})\) g/cm at 9 hours, and all the time before and after sintering when the reinforcement ratio with nanocomposite titanium oxide is from (0-20)%.

The decrease in wear with increasing milling and cementing time in the nickel-titanium oxide complex can be attributed to the higher hardness of the composite by increasing the time of milling and cementing. In addition, increasing the hardness in the presence of titanium oxide reduces the wear rate according to the following equation [17]:

\[
W = K \frac{NS}{CH}
\]

where: \(W\): Loss in volume wear, \(K\): Wear constant, \(N\): Imposing vertical load, \(S\): Sliding distance, \(H\): Hardness of sample and \(C\): Engineering factor dependent on microstructure.
This wear behavior is also attributed to the degree of interconnection and cohesion that occurs between the particles of the base and support composite.

![Figure 7](image)

**Figure 7** The relationship between the change in the volumetric ratios of titanium oxide content and the milling time with the wear rate before the sintering process.

![Figure 8](image)

**Figure 8** The relationship between the change in the volumetric ratios of titanium oxide content and the milling time with the wear rate after the sintering process.

5. Conclusion:

The important conclusion in the current article is the possibility of making samples of Ni-TiO$_2$ with different support ratios from nano titanium oxide. The most important parameters were obtained with a physical and mechanical improvement, which is at a cementation ratio of 20% TiO$_2$. 
a thermal sintering of 1200°C, and a milling time of 9 hours. As it has been observed that there is an effect on the physical and mechanical properties of nickel during these parameters, so we find that the green and true density decreases with the increase of the support ratios, while the true porosity increases with the addition of the support ratios, while the mechanical properties there is a clear improvement during which we find a large increase in hardness and a decrease in the wear rate.

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