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DEVELOPMENT OF NANOGRAINED Ti-Al-GRAPHITE (Ni-P) BY MECHANICAL ALLOYING ROUTE

ROZWÓJ PRODUKCJI NANOKRYSTALICZNYCH PROSZKÓW Ti-Al-GRAFIT (Ni-P) METODĄ MECHANICZNEJ SYNTEZY

TiAl base intermetallic is one of a new materials for high temperature applications due to, high strength to weight ratio and high melting temperature, high stiffness and modulus of elasticity, good oxidation and corrosion resistance, positive dependence of strength on temperature (T< 873 K). However, it encounters limitation, like brittleness at room temperature and this effect may be reduced or eliminated if nanosized grains are produced.

In this work, an attempt has been made to produce intermetallic compound of TiAl based nanocomposite by using mechanical alloying method. Electroless Ni-P coated graphite powder has been mixed with titanium and aluminium powders to study the effect of this addition. The effect of grain size on the process parameters like weight percentage on time of milling (up to 50h) and rotation per minute (rpm) of the milling (up to 400) are studied. The morphology of the grains is characterized by XRD, SEM and TEM.

Związki międzymetaliczne TiAl należą do nowych materiałów stosowanych na elementy żaroodporne i żarowytrzymałe ze względu na ich wysoką wytrzymałość, twardość i moduł sprężystości jak również wysoką temperaturą topnienia, odporność na korozję oraz żarowytrzymałość zwłaszcza w zakresie temperatur (T< 873 K). Jednak podstawową wadą spiekanych stopów TiAl jest ich kruchość w temperaturze otoczenia. Powyższe zjawisko może być wyeliminowane poprzez zastosowanie bardzo drobnoziarnistych proszków o wielkości ziarna rzędu „nano" tzw. nanoproszków. W niniejszej pracy przedstawiono metodę wytwarzania związków międzymetalicznych TiAl na bazie nanoproszków produkowanych w wyniku procesu mechanicznej syntezy. Proszek grafitu powlekany bezprądowo (Ni-P) był mieszany z proszkiem tytanu i aluminium. W toku eksperymentów badano wpływ powlekanego (Ni-P) proszku grafitu na własności stopów TiAl. Analizowano również wpływ czasu mielenia (aż do 50h) i prędkości obrotowej młyna (aż do 400 obrotów na minutę) na stopień rozdrobnienia proszków. Kształt i wielkość ziarna proszków kompozytowych Ti-Al- grafit (Ni-P) była przeprowadzona za pomocą mikroskopu skaningowego (SEM) oraz transmisyjnego (TEM).

1. Introduction

Titanium Aluminides are being pursued for the high temperature applications due to high strength to weight ratio, high melting temperature, positive dependence of strength on temperature (T< 873 K) (1). By Powder Metallurgy (PM) technique it is possible to produce finished, near net shaped intermetallic products from elemental powders through mechanical alloying in a single step.

TiAl suffers from limited ductility at ambient temperatures and poor oxidation resistance at elevated temperatures (2–5). So research efforts are focused towards improving the room temperature ductility and elevated temperature creep resistance by the addition of alloying elements. Such an improvement can be achieved by the addition of selected alloying elements such as V (6), Nb, Cr, Mo, B (7), Ni (6,8) etc. Addition of nickel to γ TiAl is expected to improve the oxidation resistance by replacing Ti in the sub lattice. TiAl based intermetallic with nickel is found to develop a lamellar ($\alpha_2+\gamma$) structure. In particular, rapid solidification (RS) techniques are often used to reduce segregation and to refine microstructure. γ TiAl containing 0.5% Ni produced by splat-quenching followed by annealing at 900°C can enhance the room temperature ductility (6). The carbon reinforcement in TiAl and Ti_3Al, as matrixes has shown better recrystallization characteristics (9–11). The phosphorus addition can enhance the oxidation resistance of the titanium aluminide by reducing the number of oxygen vacancies (12). Electroless, EL coating is an efficient method to

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incorporate nickel and phosphorus in the alloy produced by the P/M process. It is reported that by producing nanometer-size grains of the aluminides, even 5% elongation can be achieved (13). There are different methods to improve the mechanical properties of TiAl like Thermo Mechanical Treatment (TMT), alloying addition and mechanical alloying (14). In the case of mechanical alloying technique mechanical properties are improved by reducing the grain size through high energy milling which has an advantage of a low temperature requirement for processing.

In this study, an attempt has been made to improve the room temperature ductility of titanium aluminides by addition of Ni and oxidation resistance by the addition of phosphorus. It is difficult to add the metalloid, phosphorus into the intermetallics; therefore EL coating technique of Ni-P was used to coat the graphite powders by which all the alloying addition could be incorporated. The Ti, Al and Ni-P coated graphite powders are mechanically alloyed in a controlled atmosphere using high energy milling. The initial powders and the advanced materials thus developed are analyzed by XRD, SEM and TEM.

2. Experimental

To start with the graphite powder of size in the range of 100–150 μm was weighed and subjected to account for the bath loading factor (the ratio of surface area of the substrate to the volume of EL coating bath) of ~25% as recommend by Agarwala (15). The surface preparation of the substrate material (graphite powder) was carried out after degreasing of the porous bag containing powder by dipping the bag in acetone to ensure good adhesion of the EL coatings. Then the powders were sensitized and activated by dipping in 0.1% stannous chloride solution for 2 minutes and dipping in 0.01% palladium chloride solution for 2 minutes respectively followed by allowing them to dry using hot air. Alkaline EL bath was used to produce Ni-P coated graphite powder. The bath temperature and pH were maintained at 90 ± 2°C and 9 ± 0.25 respectively. The coated graphite powder was characterized by SEM, XRD and TEM.

The mechanical alloying of powders was carried out in a high energy ball mill. The parameters studied are weight percentage of graphite (1 to 4 wt. %), time of milling (up to 50 hours) and RPM (up to 400) of milling.

Phases present and the size of the grains were determined by XRD studies using copper target with filtered Kα radiation. The variation of b/h ratios obtained from the XRD patterns with different milling conditions during mechanical alloying were analyzed to see the variation in the grain size. SEM and TEM studies were carried out to confirm the above.

3. Results and discussion

The SEM micrographs of uncoated graphite powder and Ni-P coated graphite powder are shown in Fig. 1(a and b). The graphite powder under SEM appeared bright due to electron charging from the surface of the specimen in Fig. 1a. The quality of coating is satisfactory since the entire surface of graphite powder seem to have been coated by Ni-P as could be seen from SEM micrographs. The white patches on the surface are outer layers of Ni-P coating (Fig. 1b). It can also be observed that the Ni-P coating penetrates into the fractured surface of the graphite powder. The coated graphite powder shows typical Ni-P globules over the catalytic surface.

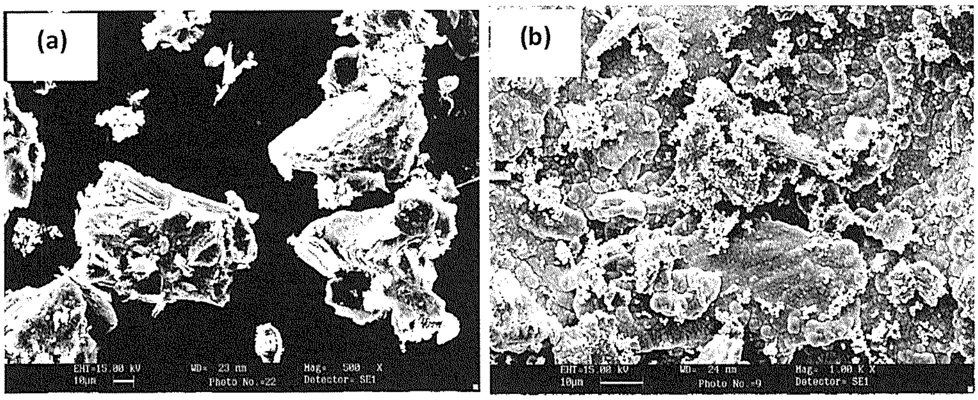

Fig. 1. SEM micrographs a) Graphite powder and b) graphite powder coated with Ni-P

The XRD patterns for the Ni-P coated graphite powders are shown in Fig. 2. The diffraction pattern of Ni-P coated graphite powder shows the peaks corresponding to both Ni and graphite. Sharma et al also reported similar XRD pattern for the uncoated carbon fiber (16). It can be stated that the peaks of Ni confirms the feasibility of developing the EL Ni-P coatings on graphite powder. The phosphorus goes into the lattices of Ni, hence lattice distortion occurs and attributes to the broadening of diffraction peak of Ni at ~44 (2-theta) angle.

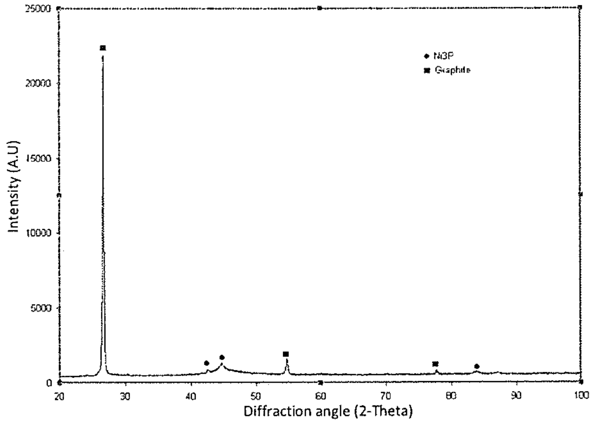

Fig. 2. XRD analysis of Ni-P coated graphite

The elemental titanium and aluminium powders used for the mechanical alloying were of size 150 microns and 220 microns respectively. Milling time has two basic effects on the powder, first the powder breaks into finer particles and then the particles join together due to cold welding by diffusion bonding by the pressure developed due to the impact of moving balls in the ball mill. Such cycle continues throughout the milling.

The XRD analysis show that the complete dissolution of aluminum in titanium takes place at a grain size of about 15 nanometer after 10 h of milling at 400 rpm. Broadening of peaks are seen with increase of the time of milling and it depicts the refinement of grains. The grain size analysis of mechanically alloyed powder was analyzed from the XRD patterns using Sherrer's formula,

$$B = 0.9\lambda/(t \cos \theta), \qquad (1)$$

where B is Broadening of diffraction line measured at half the maximum intensity in radians, t is the size of grain and θ is the Bragg's angle. The peak broadening B is calculated as:

$$B \times B = Bm \times Bm - Bs \times Bs, \qquad (2)$$

where Bm is the width of maxima at the base and Bs is the width at half of maximum intensity.

From the measured width of the maxima at the base and at the half maximum intensity of the XRD patterns B was calculated (from eqn. 2) and the grain size was calculated (using eqn. 1). XRD patterns of MA powders milled at 400 rpm for different extents of time from 2–10 h are shown in Fig. 3 (a). The peak broadening 'B' with the increasing time is observed and the grain size is calculated. It is observed that the grain size decreases with increasing in milling time as shown in Fig. 3 (b).

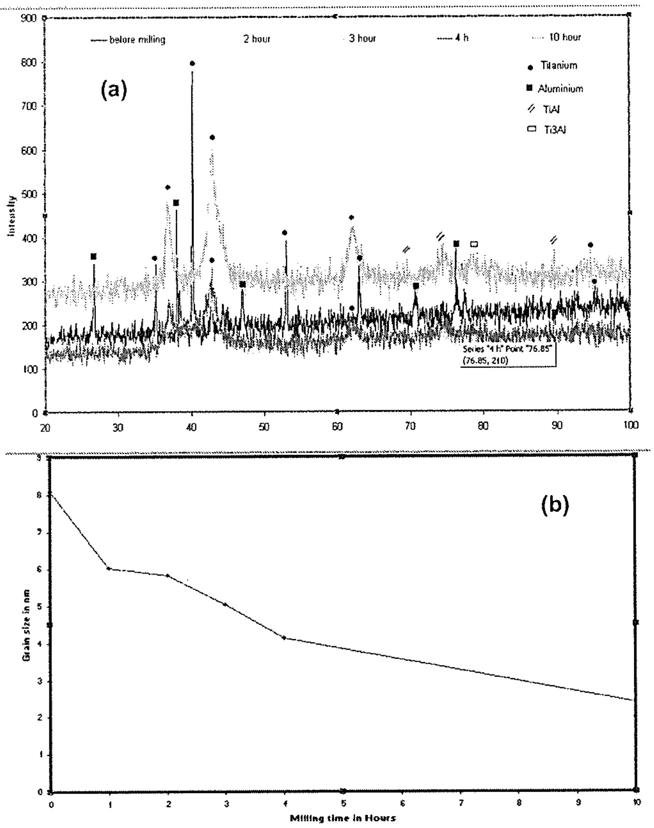

Fig. 3. MA powders milled at rpm = 400 for different extents of time. (a) XRD analysis and (b) effect of grain size on the milling time

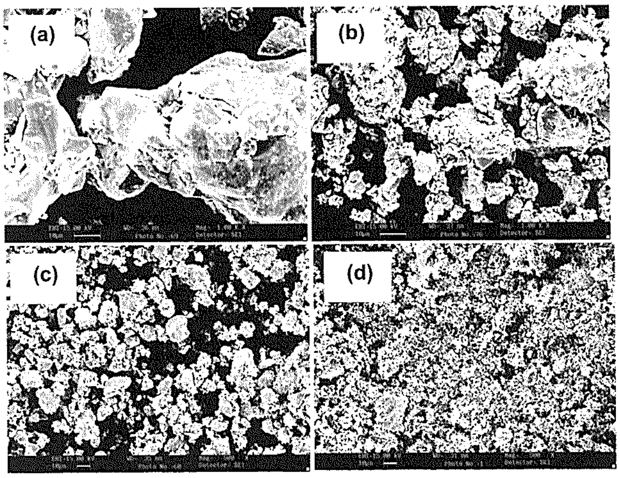

Fig. 4. SEM micrograph of Ti-Al powders (a) before milling and after milling at 400 rotation rate for (b) 1 h, (c) 4 h and (d) 10 h

With an increase in milling time, particles gets stressed due to deformation and fracturing. The particles undergo cycles of fracture and cold welding to form a continuous solid solution, Figs. 4 (a–d), confirm that the grain refinement is enhanced by graphite addition.

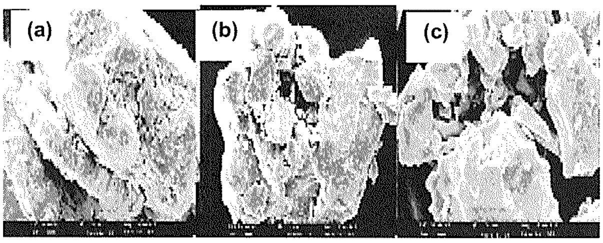

Fig. 5. Mechanically alloyed TiAl-3 wt% graphite (coated with Ni-P) for 20 h with different rpm, (a) 260, (b) 430 and (c)750

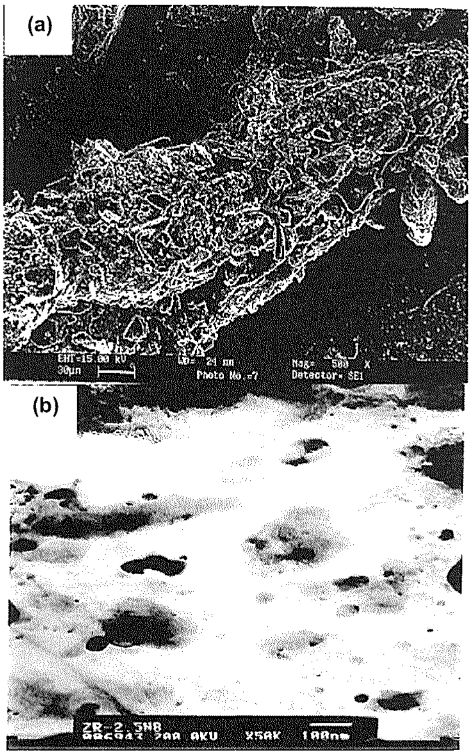

Fig. 6. Micrographs of Milled Ti-Al powders at 100 rpm for 50 hours. (a) SEM and (b) TEM micrograph of milled Ti and Al powder interface

Fig. 5 show SEM micrographs of Ti and Al powders mechanically alloyed at various rotation rate. In this case the TiAl-3 wt% graphite (coated with Ni-P) are mechanically alloyed for 20 h with different rpm of 200, 400 and 600. It is seen that at lower rate the cold welded strained interfaces are present while at higher rpm, fragmented finer particles (less than 1 μ size) are observed due to the fracture of the strained interfaces. The variation of b/h ratio obtained by XRD studies with different milling times during mechanical alloying at various rotation per minute (rpm) confirmed the reduction of size of grains with an increase of the milling speed. It was estimated that 100 nm grain size is formed by MA at 200 rpm for 60 h. TEM analysis of mechanically alloyed Ti-Al-Gr (3wt%) at 100 rpm for 50 h, showed various phases at the Ti and Al particles interface. Fig. 6a shows only the agglomerated particles under SEM. Fig. 6b shows various phases which might be α(Ti) -Ti_3Al -TiAl- $TiAl_3$-α(Al) under TEM suggesting that this region could be the interface between α(Ti) and α(Al) or TiAl particles. Such phases are also seen in as-pressed Ti and Al materials produced by reaction synthesis (RS), the highly non-homogeneous material contain phases like Al_3Ti, Ti_3Al, Al_2Ti, AlTi and Ti (17). This can be explained by the phase diagram (Fig. 7), which starts from the titanium rich end and proceeds towards aluminum rich end.

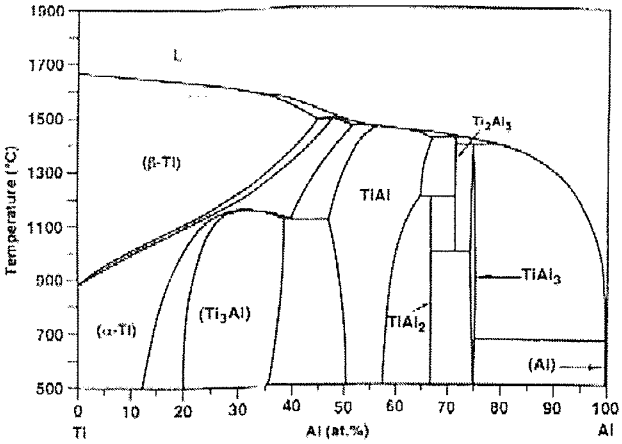

Fig. 7. Binary Ti-Al phase diagram

4. Conclusions

1. Ni-P coating on graphite powders is feasible using alkaline EL bath and can be used to develop uniform coating of on the irregular and fractured surfaces of graphite powder.
2. The mechanical alloying is highly effective process for the production of nanograined powders by controlling the time and rpm of the milling.

Acknowledgements

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