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Solid State Recycling of Waste Ti Chips: Effect of Wet and Dry Grinding on Synthesis of Ti-Tic Composite Powder during Planetary Milling

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Abstract

The present investigation aims at recycling of waste Ti chips to synthesize Ti-TiC metal matrix composite (MMC) by planetary milling. The synthesis of Ti-TiC MMC powder mixture by both wet milling (12 hours) and dry milling (3 hours) of initial Ti chips/powder and graphite powder has been reported. The structural and morphological characterization of Ti-TiC milled powder have been studied by X-Ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The apparent density tap density and flowability of powders have been investigated. Higher level of contamination (Fe, Cr and Ni) is observed in case of 12 hours wet milling than 3 hours dry milling of Ti-TiC composite. The formation of Ti-TiC nanocomposite after 3 hours of dry milling has been established.

Keywords: Recycling; Ti-TiC composite; Planetary milling; Wet and dry milling; Microscopy

Introduction

Titanium and Ti-alloys are widely used in automobile, aerospace, biomedical and chemical industries as they have high specific strength, low density, high corrosion resistance and good biocompatibility. A large amount of chips is generated during machining of pure Ti and Ti alloys. Thus, effective methods for recycling and re-use of waste Ti should be established, since Ti is very expensive. In general recycling, the metal chips are melted and then casted. During this process, the materials are subjected to oxidation and degradation. Besides, melting is a low efficiency process which requires additional costs such as energy consumption, cost of labor, harmful gas emission etc. In this present study, as an alternative to melting, a novel method of recycling has been introduced for production of Ti-TiC composite materials by powder metallurgy. The proposed method utilizes only waste Ti metal chips which are cheap in comparison with metallic powders. So, this method is an economical and environmentalist approach for utilization of waste. Powder metallurgy is defined as the method or technique used to produce metal powders by compressing the metal with or without addition of other material and heating them just below the melting temperature to solidify or strengthen the material [1].

There have been considerable efforts to produce titanium alloys/composite powders by mechanical milling/alloying. Shaibani et al. [2] prepared powders from gray cast iron chips by target jet and conventional ball milling. Afshari et al. [3] recycled bronze machining chips into bronze powder by jet milling and subsequently compared with ball milling technique. Soufiani et al. [4] fabricated Ti-6Al-4V powders from machining scraps by both planetary and shaker milling route. Lui et al. [5] studied the effect of chip conditions on the solid-state recycling of Ti-6Al-4V machining chips. They recycled five different types of chips obtained by turning or milling with or without the application of coolant by equal channel angular processing (ECAP). Dikici et al. [6] studied the effects of disc milling parameters during recycling of Ti-6Al-4V powders. Shial et al. [7] synthesized Ti powder by planetary milling of Ti chips for 2.5 hours and further they milled the prepared Ti powder and graphite powder (Ti/C weight ratios of 100/6 and 48/12) for 12 hours in planetary mill under wet condition (toluene) using stainless steel jars and balls. They observed that produced Ti-TiC composite powder was contaminated with Fe and oxidation occurred due to prolong milling. Verma et al. [8] recycled steel chips to nanostructured steel compact by planetary milling followed by conventional sintering. Razavi et al. [9] synthesized of TiC-Al_2O_3 nanocomposite powder from impure Ti chips, Al and carbon black by mechanical alloying. They observed formation of TiC after 10 hours of milling. Razavi et al. [10] also synthesized nanocrystalline TiC powder from impure Ti chips by mechanical alloying for 15 hours.

Some research groups have directly converted various metals and alloys waste chips into bulk product through severe plastic deformation (SDP) like hot extrusion and ECAP without melting. Luo et al. [11,12] recycled both commercial pure Ti (CP Ti) and Ti-6Al-4V chips by SPD technique without melting. Peng et al. [13] also recycled Ti chips by ECAP processing and studied microstructure and mechanical properties. Topolski et al. [14] recycled commercial purity (cp) titanium Grade 2 chips obtained by turning, and to produce a solid bulk material. Shi et al. [15] recycled Ti-6Al-4V and Ti-15V-3Cr-3Al-3Sn machining chips obtained from conventional turning (CT) and ultrasonically assisted turning (UAT) by ECAP process. Recently, Wan et al. [16] reviewed the solid-state recycling techniques like ECAP, hot extrusion, severe plastic deformation (SPD) and high-pressure torsion of Al chips. Sherafat et al. [17] recycled Al7075 alloy chips by fabricating Al7075-Al composite by hot extrusion via powder metallurgy. Hu et al. [18] recycled AZ91D magnesium alloy by solid state route using compaction of chips into billets and then hot extrusion of billets into rods. Mindivan et al. [19] recycled pure magnesium chips by cold press and hot extrusion processes.

From the thorough literature study, it has been observed that several researchers have attempted to recycle expensive Ti/Ti-alloy chips either through powder metallurgy route or severe plastic deformation process using ECAP or hot extrusion. However, none of them studied the effect of wet and dry milling during recycling of Ti chips by using planetary milling. Hence, the present study aims at recycling of waste Ti chips by powder metallurgy, where Ti chips are initially converted into Ti powder and then synthesis of Ti-TiC composite by planetary milling has been studied. The effect of dry and wet grinding during fabrication of Ti-TiC composite powder is investigated.

Experimental

Synthesis of Ti-TiC composite powder by planetary milling

The starting material used was commercially available pure machined titanium scrap (CP Ti) chips. Planetary milling of Ti chips was carried out in a specially designed high energy dual-drive planetary mill (DDPM). The details of mill design are available elsewhere [20]. The stainless-steel jars of volume 1 L each and high chrome steel balls of 8 mm diameter were used as grinding media. The chips were cut into small pieces and then cleaned ultrasonically using acetone to remove the surface impurities. The balls and Ti chips were loaded into a stainless-steel jar and milling was conducted under toluene (wet milling) to prevent oxidation. An amount of 100g chips and the required amount of balls were used in each of jars. Mill was run continuously for 30 minutes and proper care was taken to prevent contamination of the charge while loading and unloading. After milling for 3 hours, powder was taken out from the mill for characterization.

The Ti powder obtained after wet milling of Ti chips with BPR 10:1 was used as starting material for Ti-TiC composite fabrication. The milled obtained Ti powder and graphite powder (Loba Chemie, India, purity: 98 %, size: 60 mesh) again milled in a steel jar using same steel ball. Titanium and graphite powder were taken in 50:50 atomic ratio and the ball to powder weight ratio of 10:1 was maintained. The powders were initially wet milled using toluene for 12 hours. Details of Ti-TiC composite powder fabrication processes are reported in our previous paper [7]. It has been observed that there is huge contamination of iron in fabricated Ti-TiC composite powder after prolonging wet milling (12 h). The iron contamination comes from two stages of wet milling:

a) 1st stage- during preparation of Ti powder from Ti chips by milling

b) 2nd stage- during preparation of Ti-TiC composite powder (milling of Ti powder and graphite powder)

Hence, in the present study, Ti chips and graphite powders were milled in dry condition by purging Ar gas to prepare Ti-TiC composite powder by single stage grinding. All the milling parameters were kept same as wet grinding (BPR: 10:1, steel ball dia. 8 mm, Ti chips/graphite wt. ratio- 50:50). It is to be noted here that the main idea is to reduce the grinding time to minimize iron contamination. Milling was carried out for a total period of 3 hours at the intervals of 30 minutes. At each interval, argon gas was purged without opening steel jar. Stearic acid of 1 wt. % was added as process control agent (PCA). Finally, powder was taken out from the mill for characterization.

Characterization of milled Ti-TiC composite powder

The milled powders were characterized by X-Ray diffractometer (Model: Philips) using CuKα target to analyze phase evolution during milling. The morphology and size of the powders were observed under SEM (Model: JEOL JSM-6084LV) and FESEM (Model: FEI Nova NanoSEM 450) with EDX facility. The internal morphology of the powders was characterized by TEM (Model: FEI Tecnai G2 F 30 Super Twin operated at 300 kV). The apparent and tap density of both Ti and Ti-TiC composite powders were studied by Electrolab (Mumbai, India) bulk density tester (Model: EV-02) and Electrolab tap density tester (Model: ETD-1020X). The Hausner ratio and Carr index were calculated from measured apparent and tap density of powder to correlate the flowability of milled powder.

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Results and Analysis

Phase analysis

Figure 1 shows the XRD spectrum of the Ti chips and graphite powders after wet milling for 12 hours and dry milling for 3 hours respectively. It has been seen from XRD spectrum that Ti_2C is formed along with anatase and TiO. In our previous paper [8], we showed that TiC was formed when wet milling of Ti and graphite powder was conducted for 12 hours. As formation of titanium carbide from Ti and graphite is self-propagating and exothermic in nature, hence dry milling of Ti chips and graphite powder only for 3 hours is enough to initiate the reaction as compared to 12 hours of wet milling. In dry milling, collision between chips, powder and ball results in comparatively higher temperature than wet milling. On the other hand, milling was carried out under toluene in case of wet milling and hence rise in temperature is less. The high heat helps in initiation the reaction between Ti and graphite for formation of TiC in dry milling easily. Moreover, the TiC peaks obtained after 12 hours wet milling are weak as compared to Ti_2C peaks obtained after 3 hours of dry milling. It is also observed that peaks are broad, due to particle refinement and increase of lattice strain. Zhu et al. [21] also prepared TiC by mechanical alloying of Ti and graphite powder. They showed milling temperature increased slowly in the initial milling period, but when milling time reached 115 minutes, the temperature of the vial increased abruptly.

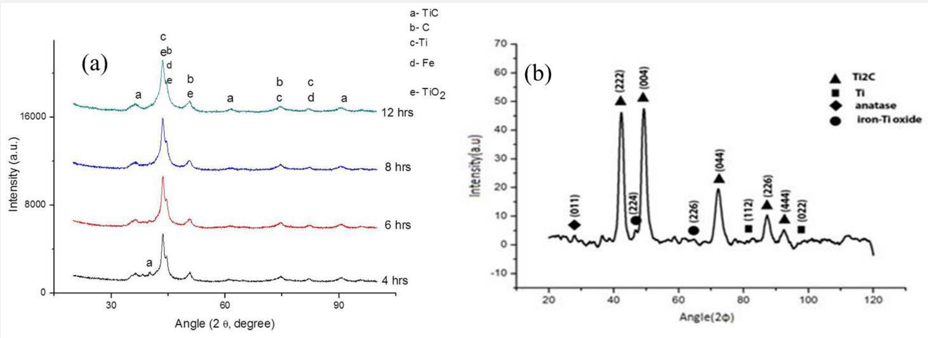

Figure 1: XRD Spectrum of Ti and Graphite Powder after Wet Milling for 12 Hours and Ti Chips and Graphite Dry Milling for 3 Hours respectively.

Microstructure study

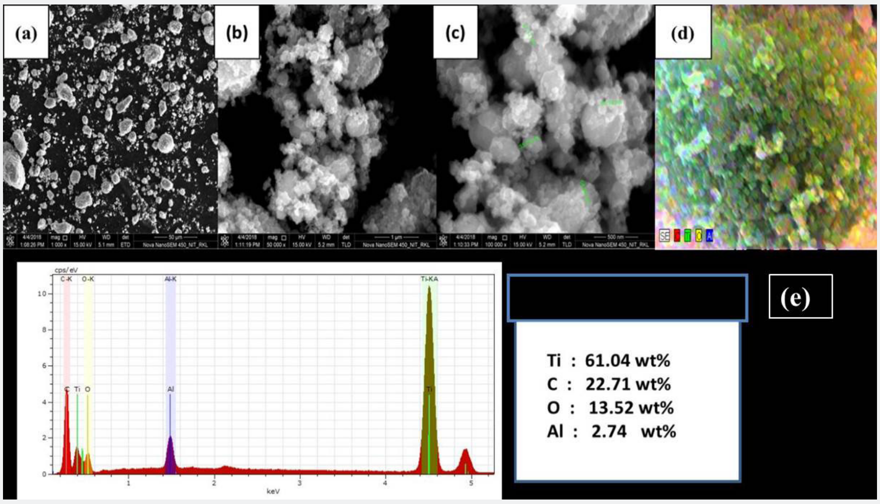

Figure 2: (a-e): FESEM Micrographs, Elemental Mapping, EDS Spectra and Quantitative Elemental Analysis of Ti Chips+ Graphite Powder after Dry Milling for 3 Hours.

Figure 2a-2e show the FESEM micrographs, elemental mapping, EDS spectra and quantitative EDS analysis of Ti chips + graphite powder obtained after dry milling for 3 hours. The micrographs (Figure 2a-2c) show that powder particles size vary from nanometric size (<100 nm) to micrometer range (10μm). The elemental mapping and EDS spectra show the presence of Ti, C along O2 and Al (impurity). Although inert gas argon was used during milling, still oxidation could not be prevented completely

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due to high oxidative nature of Ti. It is also evident from elemental mapping that Ti and C are uniformly distributed throughout the particles. Figure 3 shows the SEM micrographs, EDS spectra and quantitative elemental analysis of Ti chips+ graphite powder dry milled for 3 hours, and Ti+ graphite powder wet milled for 12 hours respectively. It has been found the higher amount of Fe contamination in case of wet milling (27.36 wt. %) as compared to dry milling (3.94 wt. %). The reason is due to prolong wet milling of 12 hours than only 3 hours of dry milling. The abrasion of balls against the ball and jar surface is higher in wet milling than dry milling. During dry milling, steel balls and jar surface are coated with Ti and graphite powder and hence abrasion is comparatively less.

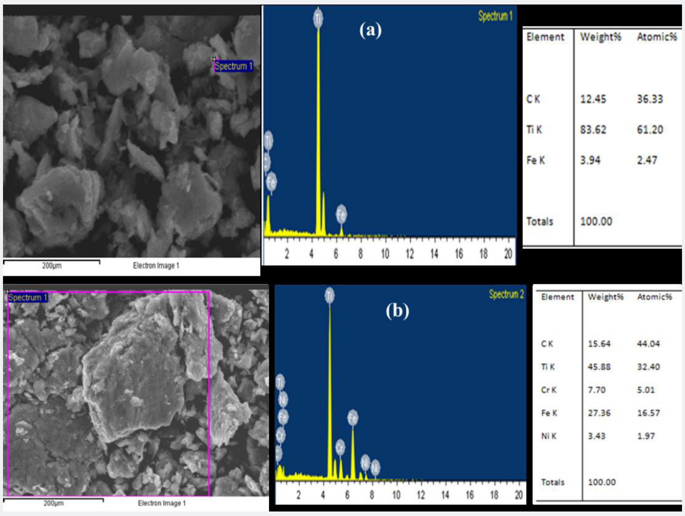

Figure 3: SEM Micrographs, EDS Spectra and Quantitative Elemental Analysis of (a) Ti Chips + Graphite Powder after 3 H of Dry Milling (b) Ti Powder + Graphite Powder after 12 h of Wet Milling.

Figure 4 shows the bright field TEM micrograph and corresponding SAED patterns of Ti chips + graphite powder dry milled for 3 h and Ti powder + graphite wet milled for 12h respectively. The powder particle size of <100 nm can be observed from both TEM micrographs. The diffraction patterns in both cases show the presence of HCP Ti, TiC, unreacted graphite and Fe. The ring patterns are also indexed in both cases.

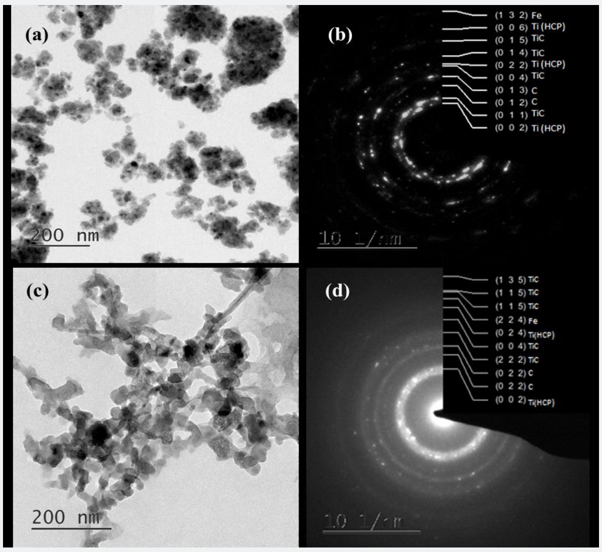

Figure 4: Bright Field TEM Micrograph and Corresponding SAED Patterns of (a,b) Ti Chips + Graphite Powder Dry Milled for 3 H (c,d) Ti Powder + Graphite Wet Milled for 12 h.

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Figure 5 shows the HAADF TEM micrograph, elemental mapping EDS spectrum of Ti chips + graphite powder dry milled for 3h. From HAADF image, the morphology of powder particles is clearly seen. The elemental mapping exhibits the existence of Fe along with presence of Ti and graphite. It is also observed that Ti and graphite are uniformly distributed. The EDS spectrum also reveals the presence Ti and C with Fe. Figure 6 shows the high resolution TEM micrographs and enlarged view of the micrographs. The micrograph shows the evidence of crystallites with size 4-7nm (Figure 6 a). Some unreacted amorphous graphite resulted from high energy milling are also clearly seen from the micrographs. The enlarged view shows the interplanar spacing of TiC. The interplaner spacing as shown in figure (Figure 6c, 6d) are 0.271 and 0.269 nm respectively. The standard interplanar spacing of (111) FCC TiC is 0.266 nm (JCPDS file no: 02-0942), which matches with the values as shown in figure.

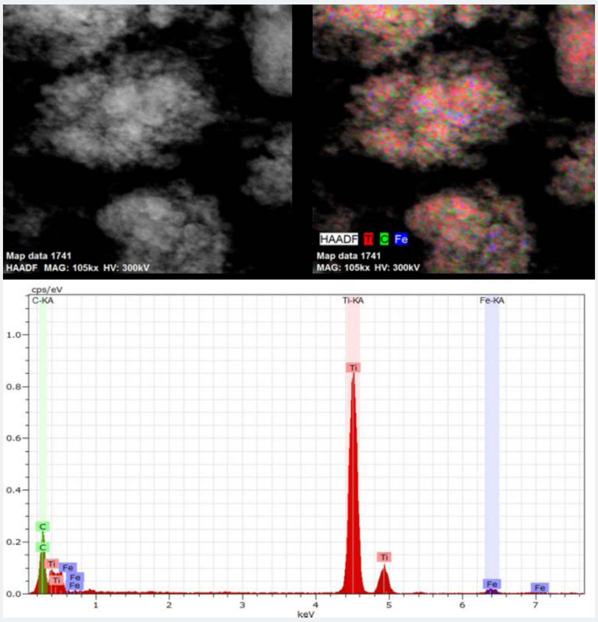

Figure 5: HAADF TEM Image, Elemental Mapping and EDS Spectrum of Ti Chips + Graphite Powder Dry Milled for 3 h.

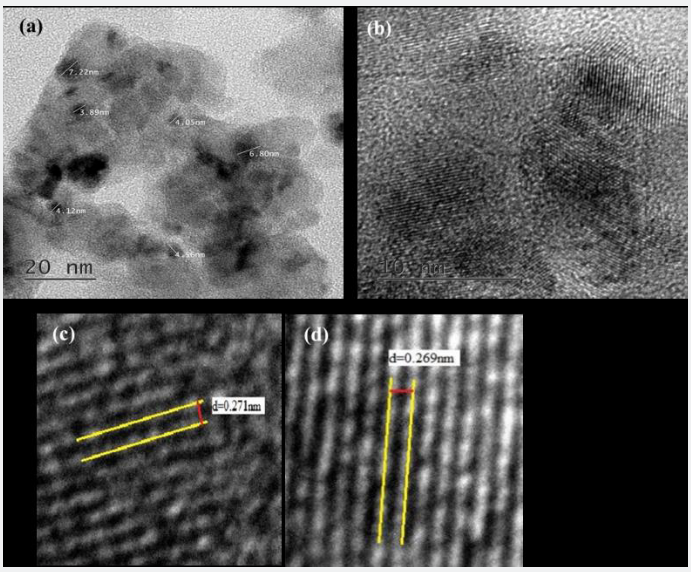

Figure 6(A-D): High Resolution TEM Micrographs and Enlarged view showing Interplanar Spacing of Tic.

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Apparent density, tap density and flowability study of Ti-TiC composite mixture

Table 1 shows the apparent density, tap density and flowability of Ti-TiC powder obtained after dry and wet milling. It has been observed that dry milled powder exhibits slightly higher apparent and tap density than wet milled powder. This is due to generation of higher fraction of smaller powder particles in dry milling. The dry milled fine powder particles accommodate in the void space among the large particles and particles occupy less volume during tapping. However, there is not much variation in flowability as calculated by Hausner ratio and Carr index.

Table 1: Flow Characterization of the Ti-TiC Composite Powder.

Serial No.	Milling Technique used	Bulk Density (g/cc)	Tap Density (g/cc)	Hausner Ratio	Carr Index
1	Wet Milling	2.8	3.45	1.23	18.9
2	Dry Milling	2.9	3.56	1.22	18.6

Discussion

The synthesis of TiC from Ti and graphite powder/chips by planetary milling is mechanically activated self-propagating high temperature synthesis process. Hence, ignition temperature and time are critical for the reaction to initiate. Long milling time of 12 hours is required in wet milling, whereas only 3 hours is required in dry milling for the reaction. In dry milling, reaction can be initiated easily due to abrupt rise in temperature after critical milling time. But in case of wet milling, the rise in temperature is less and delayed, hence it takes more time to initiate the reaction. The contamination level is higher (Fe-27.36, Cr-7.70, Ni-3.43, all in wt.%) in case of prolong high energy wet milling of 12 hours, whereas a low level of contamination (Fe-3.94 wt. %) is found in case of 3 hours dry milling. In dry milling, powder coats the steel balls and jar surface and hence it reduces the contamination level. On the other hand, no such coating happens in case of wet milling. As stainless-steel jars and high chrome balls are used during planetary milling, hence there is maximum contamination of iron along lesser amount of Cr and Ni.

Conclusion

The following conclusions can be made from the present investigation:

a) A higher amount of contamination (Fe-27.36, Cr-7.70, Ni-3.43, all in wt. %) was observed when the powders were wet milled for 12 hours as compared to dry milled for 3 hours (Fe-3.94 wt. %). The dry milling reduces contamination by forming a coating of powders on the balls and jar surface. But no such coating on ball and jar surface takes place in case of wet grinding.

b) The formation of TiC is fast in dry milling of Ti chips and graphite powder as compared to wet milling.

c) The study confirmed the formation of Ti-TiC composite nanoparticles (<100 nm) just after 3 hours of dry milling.

Acknowledgement

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