1. Introduction

Metal matrix composites (MMCs) provide good combinations of metal and ceramic characteristics. The ceramic reinforcement particles such as Al₂O₃, SiC, and TiC enhanced their strength, stiffness and wear resistance. Among them, TiC reinforced ferrous composites are characterized for being chemically stable, greatly improving hardness and wear-resistant properties. In addition to commercially available reinforcement particles, in-situ processes are often employed to prepare MMCs. Das et al. later reviewed various in-situ synthesizing routes of TiC and demonstrated their advantages and disadvantages while added into ferrous based composites.

The TiC particles used in commercial tool steels are often as large as microns in size and angular in shape which are both detrimental to mechanical properties. Nanosize and spherical TiC particles are clearly preferable for applications in the MMCs. Ye and Quan showed that fine TiC could be synthesized by mechanical alloying (MA). According to El-Eskandarany, MA was a process for fabrication of many advanced materials and alloys at room temperature and was also effective in synthesizing compounds. For example, Lee et al. successfully synthesized TiC strengthening particles in-situ by reacting titanium and carbon.

In this study, we intended not only to synthesize TiC but also to consolidate TiC containing MMCs via sintering processes that were not explored before. Powder metallurgy was a cost-effective processing route for making steel-ceramics composites because a wide range of reinforcement volume fraction could be added and the distribution of embedded particles was relatively uniform. Bolton and Gant showed that TiC containing tool steels could be sintered by vacuum sintering process. Abenojar et al. also demonstrated atmospheric sintering could achieve good densification in stainless steels containing hard particles. On the other hand, the major commercial process used for making TiC containing tool steel was a combination of encapsulation and hot isostatic pressing (HIP) as shown by Pagounis et al. Pagounis and Lindross demonstrated that the sintered body such formed could achieve full densification. The encapsulation process was costly and time-consuming from manufacturing point of view. The present study intended to investigate the possibility of eliminating encapsulation process prior TiC-tool steel powder sintering. The concept was to combine MA and to explore more cost-effective powder metallurgy processes. Manufacturing cost might be reduced simultaneously by using in-situ formed TiC and non-capsulated sintering process.

2. Experimental Procedures

Elemental Ti (10 μm, purity 99.9%) and nano-carbon powders (30 nm, purity 99.8%) were used as raw materials and mixed to give composition of Ti–50at%C. Commercial tool steel powders (40 μm) with compositions of 1.7C–8Si–0.3Mn–18Cr–1Mo (in wt%) were used as matrix.

The milling process for TiC was carried out at room temperature using high-energy planetary ball mill (Retsch PM100, Germany) in protected atmosphere. The jar (50 mL)
and balls (10 mm in diameter) were made of stainless steel. The ball-to-powder weight ratio (BPR) was 10:1. The materials were milled at 100–400 rpm for 0–16 h. X-Ray diffraction (XRD) with CuKα radiation was used to identify the phases of powders after ball milling. The Raman spectra were recorded in the range between 200 and 1 800 cm⁻¹. Scanning electron microscopy (SEM; Hitachi S-4700) operated at 15 kV was used to observe morphological changes of the powders after different milling times at 400 rpm. The crystal structure of self-synthesized TiC powders milled for 16 h at 400 rpm were confirmed by selected area diffraction using transmission electron microscopy (TEM; JEOL F-2100) operated at 200 kV.

Tool steel powders were milled for 2 h at 450 rpm before sintering with TiC. Composite powders containing 0 to 44 vol% TiC were prepared using TiC powders milled at 400 rpm for 8 h. Densification processes included vacuum sintering (1 543 K, 1 h) or dual process combining vacuum sintering and subsequently HIPping (1 523 K, 120 MPa, 2 h). Heat treatments were performed by austenitizing the specimens at 1 373 K for 1 h, quenching in nitrogen, tempering twice at 753 K for 3 h, and furnace cooling afterwards. Microstructure of composites was observed by SEM. The bulk density of the composites was determined by Archimedes’ principle according to ASTM C830-00(2006)e1 standard. The density of powder mixtures before sintering is measured using a Micromeritics AccuPyc-1330 pycnometer. The apparent porosity of sintered sample is then estimated from the value [(wet weight−dry weight)/(wet weight−weight in water)/density of water×100%] using water as the immersion medium. The hardness test was performed using a Rockwell hardness tester (INDENTEC 8150SK) according to ASTM E18-08b. The flexural strength was measured by three point bending test according to ASTM C1161-02c(2008)e1 at crosshead speeds of 0.5 mm/min.

3. Results and Discussion

3.1. TiC Synthesizing Processes

3.1.1. The Influence of Ball Milling Parameters

The XRD patterns of Ti and C mixtures ball milled at 100, 200, 300 and 400 rpm for 16 h are illustrated in Fig. 1. For all Ti and C powders milled at 100–300 rpm for 16 h, only Ti and C peaks are observed. Peaks of C are much weaker due to the great difference between the mass absorption coefficients of Ti and C, which are 208 and 4.6 m²/g⁻¹. As rotation speed increases to 400 rpm, Ti and C peaks disappear and only TiC peaks retain.

By fixing the rotation speed at 400 rpm, the effects of milling time are further studied. Figure 2 shows the XRD spectra of 400 rpm ball milled Ti–50at%C powders with varied MA durations. With 6 h or shorter milling time, only Ti peaks are observed. When milling time further increases to 8 h, Ti peaks disappear and TiC peaks emerge. The TiC is formed by the mechanically induced self-propagating reaction at a temperature of 1 373 K for 1 h, quenching in nitrogen, tempering twice at 753 K for 3 h, and furnace cooling afterwards. Microstructure of composites was observed by SEM. The bulk density of the composites was determined by Archimedes’ principle according to ASTM C830-00(2006)e1 standard. The density of powder mixtures before sintering is measured using a Micromeritics AccuPyc-1330 pycnometer. The apparent porosity of sintered sample is then estimated from the value [(wet weight−dry weight)/(wet weight−weight in water)/density of water×100%] using water as the immersion medium. The hardness test was performed using a Rockwell hardness tester (INDENTEC 8150SK) according to ASTM E18-08b. The flexural strength was measured by three point bending test according to ASTM C1161-02c(2008)e1 at crosshead speeds of 0.5 mm/min.

3.1.2. Raman Spectroscopy of Synthesized Powders

Figure 3 shows Raman spectra of raw powders. The spectra of carbon display two peaks at approximately 1 320 and 1 590 cm⁻¹. The titanium powders can not produce a Raman spectrum, since titanium has no Raman active vibrational modes. Lohse et al. showed that, in the spectra of commercial TiC, three major peaks are present at approximately 260, 420 and 605 cm⁻¹. The Raman spectra of the Ti–50at%C powders milled for varied rotation speed for 16 h are shown in Fig. 4. Figure 4(a) shows the Raman spectra of Ti–50at%C powders milled at 100 rpm for 16 h. The Raman spectrum demonstrates weak peaks at approximately 260, 420, 605, 1 320 and 1 590 cm⁻¹ that correspond to C and TiC. With increasing rotation speed, the intensities of TiC peaks increase while the intensities of carbon peaks decrease. The Raman spectrum of powders milled at 400 rpm demonstrates broadened peaks and a reduction in peak intensity. This is probably due to that, at 400 rpm, the ratio of Ti and C in synthesized TiC becomes closer to stoichiometry which decreases Raman peak intensity. The Raman spectra of ball milled Ti–C mixtures apparently confirm that TiC is formed successfully in current study.
3.1.3. Structures of Powders

**Figure 5** shows the bright field image (BFI) and the corresponding selected area diffraction pattern (SADP) of the Ti–50at% C powders milled at 400 rpm for 16 h. The SADP is identified as a single phase of NaCl-type TiC. The same Debye–Scherrer rings corresponding to TiC were also reported by El-Eskandarany.¹⁴) Nanocrystalline TiC is thus confirmed to form.

SEM analyses were performed to understand the morphological changes of synthesized powders during MA process. SEM micrographs of the starting Ti–50at% C powder mixtures milled for varied milling time at 400 rpm are shown in **Fig. 6**. The original Ti powders are bulky with irregular shape. After milling for 2 h, the powders are flattened and cold welded (**Fig. 6(b)**). By increasing the milling time to 6 h, the cold welded particles are fractured into small particles (**Fig. 6(d)**). SEM shows that the TiC powders made by milling for longer than 8 h at 400 rpm consist of very fine powders about 1 μm in size. In **Fig. 6(f)**, these TiC powders have characteristically spherical shape and are apparently clustered by nano-size particles in correspondence with TEM observations in **Fig. 5**.

### 3.2. Composite Densification

**3.2.1. Microstructures**

Microstructures of the vacuum sintered composites containing 0–44 vol% TiC are shown in **Fig. 7** where the dark
regions are TiC particles. It is observed that the fine TiC particles distribute uniformly within the tool steel matrix. Porosity appears to increase slightly with the content of TiC. Meanwhile, in Fig. 7(a)–7(d), gray areas are shown to have good bonding surfaces with matrix. These gray areas are analysed to consist of chromium carbide by energy dispersive spectroscopy (EDS). These spherical shaped carbides are probably formed due to local liquid phase sintering during the 1543 K vacuum sintering process.

HIP process is then applied upon the vacuum sintered composites to further improve densification. Figure 8 shows microstructures of the composites containing 0–44 vol% TiC after dual densification process by vacuum sintering and subsequently HIPping. Porosity appears to decrease in comparison with the vacuum sintered microstructures shown in Fig. 7.

The apparent porosity and relative density of composites sintered by different processes are presented in Fig. 9 and Fig. 10, respectively. The apparent porosity of vacuum sintered composites is lower than 1.4% and that of HIPped specimen is below 0.2%. It shows that TiC reinforcements hinder densification and increase the internal voids during
Fig. 7. Microstructures of vacuum sintered composites containing (a) 0; (b) 15; (c) 26; (d) 35; (e) 44 vol% TiC.

Fig. 8. Microstructures of vacuum sintered and HIPped composites containing (a) 0; (b) 15; (c) 26; (d) 35; (e) 44 vol% TiC.
vacuum sintering process. However, the subsequent HIP process is very effective in reducing internal voids by closing up TiC-steel interfaces (Fig. 9). The relative density formed by dual step densification is increased from 98.8% to over 99.5% (Fig. 10).

3.2.2. Hardness Test

Figure 11 shows that the hardness increases linearly with volume percentage of strengthening phase or TiC content. However, the hardness of 0 vol% TiC containing tool steel demonstrates a lower value differentiating from the linear relation. In 0 vol% TiC containing specimen, carbon concentration in matrix decreases due to chromium carbide formation which causes the hardness to drop to under 40 HRC. The chromium carbide is formed after the vacuum sintering process as shown in Fig. 7.

Composite hardness over 71 HRC is achieved by adding 44 vol% TiC. The hardness of composites reinforced with synthesized TiC in current study are no less than 65.8 HRC as reported by Chen et al. in commercial TiC containing composites sintered by encapsulated HIPping. The dual process combining vacuum sintering and HIPping also gives slightly higher hardness than vacuum sintering. It confirms that HIPping is effective in reducing internal voids as reported by Rizzo and Conway. Hardness obtained by the two processes become almost the same when TiC content increases to over 40 vol%. With over 25 vol% TiC addition, the effects of porosity on reduction of hardness are apparently overwhelmed by the great amount of TiC.

3.2.3. Flexural Strength Test

Figure 12 shows the flexural strength test results of three different densification processes. Three factors appear to cause the differences in flexural strengths. First, the flexural strength decreases linearly with TiC content with or without HIP. Second, a large difference between the traditional HIPped material and the dual processed non-TiC added
specimens is observed due to the formation of chromium carbide. And the third, by comparing the flexural strengths of non-HIPped and HIPped specimens (Fig. 12), HIPping can greatly increase the flexural strength by almost twice with <1.5% reduction in porosity. It is clear that the porosity plays an important role in reducing the flexural strength. Apparently, the porosity, chromium carbide formation, and strengthening TiC particles are all detrimental to flexural strength.

When the volume content of TiC increases over 25%, the flexural strengths become comparable in vacuum sintered and in vacuum sintered and HIPped specimens (Fig. 12). This means that the content of TiC particles become a more dominant factor in flexural strength of composites with high strengthening phase content. Either porosity or chromium carbide only affects very slightly under this situation. This observation is consistent with that in the changes of hardness with TiC content (Fig. 11).

It is further observed that the dual process (vacuum sintering + HIPping) utilized in current study is more advantageous than the traditionally encapsulated HIPping process in improving the scattering of mechanical properties. In the traditionally encapsulated and HIPped composites, micro-sized and irregularly shaped TiC particles are employed as strengthening phases. These particles easily become stress concentrators. The scattering in strength is thus more pronounced (Fig. 12). On the other hand, the self-synthesized nanosize TiC particles have improved interface with the tool steel matrix especially after HIPping. The sensitivity of flexural strength upon particle shape is therefore reduced.

4. Conclusion

TiC powders are successfully synthesized by mechanical alloying elemental Ti and nano-carbon for over 8 h at 400 rpm. TiC forms at an instant via a mechanically induced self-propagating reaction. Vacuum sintering and HIPping are applied to consolidate the composite compacts. HIPping is clearly beneficial in reducing internal voids of vacuum sintered composites and thus increases composite hardness and flexural strength. Up to 99.9% sintering density is achieved without encapsulation. Composite with hardness as high as 71.6 HRC is obtained. Both the mechanical properties and their scattering in tool steel composites currently investigated are superior to those made by traditional encapsulated HIP process. The observations also show that the dependence of mechanical properties upon porosity becomes less influential as TiC content increases over 25 vol%.

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