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Self-assembled, aligned TiC nanoplatelet-reinforced titanium matrix composites with outstanding compressive properties

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TiC nanoplatelet-reinforced titanium composites were synthesized through a novel fabrication approach that combines a resol nanosphere (10–30 nm) coating with conventional powder metallurgy. The TiC nanoplatelets, 28–130 nm thick, are self-assembled, well aligned in each individual prior-β grain but randomly orientated throughout the microstructure. The resultant Ti–TiC composites exhibit outstanding compressive properties, with ultimate strength = 2.54 GPa, yield strength = 1.52 GPa and strain to fracture = 44.4%, stronger than all other advanced Ti materials reported to date.

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Titanium and its alloys are advanced structural materials that have found critical applications in aerospace, marine engineering, chemical processing, offshore drilling, defence and other industries. However, the inadequate stiffness and wear resistance of Ti materials have restricted their wider applications in some degree. To overcome these deficiencies, Ti metal matrix composites (MMCs) reinforced with stiff ceramic phases have been developed [1,2]. These efforts have resulted in successful industrial applications of Ti MMCs, most notably the Ti–TiB and Ti–TiC MMCs [3,4], where TiB and TiC are identified to be the two most suitable reinforcements for Ti [4].

Both Ti–TiB and Ti–TiC MMCs are currently reinforced with micrometric TiB or TiC reinforcements. Nanometric ceramic reinforcements, including nanoparticles, nanotubes, nanofibres and nanoplatelets, have the potential to further noticeably improve the mechanical

properties of the MMCs at a smaller volume fraction compared to micrometric reinforcements [5–8]. This has been demonstrated in the case of nanometric aluminium MMCs vs. micrometric Al MMCs [9].

However, to date, neither in situ nor ex situ conventional ingot metallurgy or powder metallurgy routes have proved to be promising in the fabrication of nanometric Ti–TiB or Ti–TiC MMCs [2,10,11]. Liu et al. [12] managed to fabricate nanometric Ti–TiC MMCs under some extreme conditions. They consolidated Ti powder and graphite powder blends at 900–1200 °C for 5 min under a pressure of 2.5–7.5 GPa, heated at 450 °C min^{−1} and cooled at ~18,000 °C min^{−1}. The effort resulted in nanometric TiC particles of 15–35 nm in the Ti matrix and therefore an increase in hardness. Gu et al. [13] have recently applied selective laser melting to powder blends of 50 nm TiC spheres and Ti powder and obtained nanometric Ti–TiC MMCs containing ~93 nm thick TiC nanoplates. The hardness and wear resistance of the Ti MMCs fabricated were considerably increased. However, the TiC nanoplates produced this way showed no particular orientations in the microstructure [13].

Along with reinforcement dimensions, volume fraction and dispersion, the alignment of the reinforcements

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in the matrix has long been recognized to be another key issue that affects the strengthening efficiency [5,14,15]. Consequently, a number of techniques have been used to align or orient fibre- or platelet-like reinforcements, including hot working [15], weaving [16], laminating with aligned fibres or platelets [7,17] or applying a magnetic field [18]. In general, it is challenging to achieve both dispersed and aligned nanometric fibres or platelets, especially when they are introduced as ex situ reinforcements, due to the high van der Waals interaction [13,19]. However, it is desirable to achieve locally aligned but macroscopically randomly orientated nanometric reinforcements in a ductile matrix. Such novel nanometric microstructures are expected to exhibit isotropic mechanical properties, though with much improved load-bearing capacity due to the locally aligned reinforcements.

This work reports on the fabrication and characterization of a nanometric Ti MMC which contains locally aligned but macroscopically randomly orientated TiC reinforcements through a novel approach which combines conventional powder metallurgy with nanochemistry. The resulting as-sintered nanometric Ti–TiC MMCs show outstanding compressive properties, superior to all other advanced Ti materials reported to date, including Ti-based bulk metallic glasses [20–26].

Hydride dehydride (HDH) Ti powder (particle size: <150 μm , purity 99.4%, supplied by Kimet Special Metal Precision Casting Co., Ltd., China) was used. Reagents Pluronic® F127 (EO₁₀₆PO₇₀EO₁₀₆, Mw = 12,600, EO = ethylene oxide, PO = propylene oxide), formaldehyde, phenol and sodium hydroxide from Sigma–Aldrich were employed in the coating process to introduce nanometric carbon precursors on the Ti powder surfaces. The coating was applied as follows. HDH Ti powder was first treated in a 1 M NaOH solution at 60 °C for 6 h, assisted with gentle stirring, to activate the surface TiO₂ layer. The powder was then thoroughly rinsed with Mill Q water and redispersed in a 10% F127 aqueous solution by gentle stirring for 36 h to form a slurry. Finally, the slurry was centrifuged and the sediment was dispersed in a pH 9 NaOH solution, followed by the addition of resol oligomer, which was prepared by condensation polymerization of formaldehyde and phenol [27,28]. The mixture was placed in a 66 °C water bath for 72 h to enable further polymerization of resol into phenolic resol spheres on the Ti powder surfaces. After polymerization, the polymer-coated Ti powder was collected by centrifugation and dried in an oven at 70 °C. Coated and uncoated Ti powders were then blended and finally

uniaxially pressed at 800 MPa into small cylinders (diameter: 10 mm; height: 3–10 mm). Isothermal sintering was conducted at 1350 °C for 1 h in vacuum (10^{-3} – 10^{-2} Pa), heated and cooled both at 4 °C min⁻¹.

The morphology of the coated and uncoated Ti powders was examined using scanning electron microscopy (SEM, Zeiss Neon 40EsB; Philips XL30) equipped with an energy-dispersive X-ray spectrometer. The sintered density was measured using the Archimedes' method [29]. Samples for microstructural characterisation were polished and finished using colloidal silica with 3 vol.% hydrogen peroxide and etched with Kroll's etchant. The microstructure was studied using SEM (Philips XL30; FEI Helios NanoLab 600). The average size of prior- β grains was measured from ~200 grains using the lineal intercept method. Transmission electron microscopy (TEM; Tecnai F20, operated at 200 kV) was used to determine the orientation of the TiC nanoplatelets in the α -Ti matrix. TEM samples were prepared using a focused ion beam instrument (FEI Helios NanoLab 600). The nitrogen and oxygen contents were analysed using a Leco TC 136 analyser and the carbon content was determined using a CS 444 instrument. Vickers hardness was measured under a 2.5 kg load with a duration of 15 s. Cylinders of 6 mm in both diameter

Figure 1. SEM images of (a) the starting HDH Ti powder particles and (b) HDH Ti particles coated with polymer. The inset is an enlarged view of the polymer coating.

Figure 2. Microstructure of the TiC nanoplatelet-reinforced titanium composite. SEM images showing (a) TiC nanoplatelets dispersed in Ti matrix, (b) TiC nanoplatelets aligned within each prior- β grain with orientations varying from one grain to another, (c) TiC platelets exposed by deep etching in Kroll's solution for 20 min, and (d and e) the thickness of typical TiC nanoplatelets. (f) A low-magnification TEM image showing four aligned TiC nanoplatelets, with the corresponding electron diffraction patterns of the phases indicated by the small square. The sample was synthesized from the powder blends containing 50 wt.% polymer-coated Ti powder.

Table 1. Sintered density (1 h at 1350 °C), microstructure, impurity content and hardness of fabricated Ti–TiC composites with different compositions.

Powder mixture (wt.%)	Density (g cm ⁻³)	Microstructure constituent	Grain size (μm)	HV2.5 (MPa)	Impurity (ppm)		
					O	C	N
100 Ti	4.21 ± 0.01	α-Ti	67.2	1660 ± 320	3400	120	180
30 coated Ti + 70 Ti	4.42 ± 0.00	α-Ti + TiC nanoplatelets	46.8	2480 ± 340	–	–	–
60 coated Ti + 40 Ti	4.43 ± 0.01	α-Ti + TiC nanoplatelets	42.6	3126 ± 245	5400	440	200
100 coated Ti	4.44 ± 0.01	α-Ti + TiC nanoplatelets + TiC microparticles	38.6	4175 ± 284	–	–	–

Figure 3. Microstructure of an as-sintered Ti–TiC sample reinforced with both nanoplatelets and micrometric particles of TiC. The sample was sintered from 100 wt.% polymer-coated Ti powder compact.

and height were machined from as-sintered samples and compressed on an Instron tester (Model 5584) at room temperature at a crosshead speed of 0.5 mm min⁻¹.

Figure 1 shows the morphology of the uncoated and coated HDH Ti powder particles. Resol nanospheres of 10–30 nm in size were uniformly deposited on the particle surfaces (Fig. 1b). Figure 2 shows the microstructural features of a sample sintered from the blend of coated and uncoated Ti powders with a weight ratio of 1:1. Figure 2a is a low-magnification view of the as-sintered microstructure. The TiC reinforcements form as parallel platelets in each grain (see Fig. 2b and c). However, the orientations of these TiC reinforcements vary from grain to grain (see Fig. 2a), namely, they are locally aligned but macroscopically randomly orientated. Detailed observations indicate that these TiC platelets are about 28–130 nm thick (see Fig. 2d and e). The as-sintered Ti MMC samples also show a much smaller prior-β grain size than the Ti samples sintered

from the uncoated Ti powder (see Table 1). This indicates that some carbide particles existed in the microstructure during isothermal sintering at 1350 °C, which restricted prior-β grain growth.

TEM revealed that the matrix is hexagonal α-Ti (matrix) and the reinforcement is non-stoichiometric TiC_x (x ≈ 0.65), consistent with reports by others [30,31]. The nanoplatelets show strong orientational relationships with the Ti matrix. A typical case is shown in Figure 2f with an identified orientational relationship of (0001)_{α-Ti}//(021)_{TiC} and [0110]_{α-Ti}//[600]_{TiC}.

The Ti–TiC MMC shows microstructural similarities to the lamellar Fe–Fe₃C eutectoid. However, Ti–C is not a eutectoid system; rather, it is a peritectoid system. Previous efforts of introducing carbon in the form of carbon black nanoparticles (86 nm), nanodiamonds (4–6 nm) or multi-walled carbon nanotubes all resulted in micrometric TiC particles [9,10,32]. The introduction of carbon precursor into Ti powder as dispersed resol nanospheres by wet chemical coating appears to be critical for the formation of TiC nanoplatelets. In addition, it has been found that increasing the percentage of the coated Ti powders in the powder blends (from 10 to 100 wt.% investigated) can change the morphology of the TiC reinforcement from nanoplatelets to micrometric particles, as shown in Figure 3. The local carbon concentration affects both the morphology and size of the TiC reinforcements formed in the microstructure. TiC nanoplatelets formed predominantly with the use of about 50 wt.% coated Ti powder.

The Ti–TiC MMCs fabricated show outstanding mechanical properties and an extended linear hardening regime beyond the high yielding strength under compression, as illustrated in Figure 4a. Depending on the reinforcement fraction and/or its morphology (summarized in Table 1), the yield strength reached 1.24 GPa in the TiC nanoplatelet-reinforced sample (No. 3) and

Figure 4. (a) Compressive stress–strain (engineering) plots of fabricated Ti–TiC composites with different compositions. Sample Nos. 1 and 2 did not fracture under the load applied. The sintered density and microstructural parameters of these samples are summarized in Table 1. (b) A comparison of the compressive properties of Ti–TiC MMCs fabricated in this study: ultrafine-grained Ti, nanostructured Ti MMCs, Ti-based bulk metallic glass (BMG), and Ti BMG-based composites. The compressive yield strengths ($\sigma_{0.2}$) of CP-Ti (Grade III), Ti–6Al–4V and Ti–10V–2Fe–3Al are included as colour strips.

1.52 GPa in the TiC nanoplatelet and micrometric particle co-reinforced sample (No. 4, see microstructure in Fig. 3), compared to 480 MPa for the unreinforced commercially pure (CP)-Ti. Moreover, the samples underwent significant work hardening beyond the yielding point, leading to ultimate compressive strength up to 2.54 GPa (No. 3) or 2.48 GPa (No. 4) and a large strain to fracture up to 44.4% (No. 3) or 34.5% (No. 4). Linear work hardening is a well-established phenomenon for the deformation of another hexagonal metal, magnesium, due to athermal hardening by accumulation of dislocations [33,34]. An immediate benefit of this is an extremely high maximum strength (in compression) of up to 2.54 GPa. Such a level of strength and ductility makes these as-sintered novel Ti–TiC composites competitive with all other advanced Ti-based materials, including ultrafine-grained Ti obtained by severe plastic deformation [20], as-cast hypereutectoid Ti alloys [21], composites [22], Ti bulk metal glasses (BMGs) [23,24] or BMG-based composites [26], and nanostructured Ti MMCs [25]. Figure 4b compares the compressive properties of all these Ti materials. The Ti–TiC composites fabricated in this study show both outstanding strength and ductility under compression.

The ultrahigh strength of the novel Ti–TiC composites arises from the interstitial content and grain refinement, as well as the locally aligned TiC nanoplatelets. Their contributions can be estimated based on the hardness increment (1466 MPa) from samples Nos. 1–3 (see Fig. 4a and Table 1). The hardness (Brinell) due to interstitials (C, N, and O) can be estimate using $HB = 196\sqrt{\%N} + 158\sqrt{\%O} + 45\sqrt{\%C} + 20\sqrt{\%Fe} + 57$ [35,36]. This gives ~300 MPa or ~20%, according to the N, O and C contents listed in Table 1, where the Fe content is 440 ppm in the powder. Refinement of prior-β grains from 67.2 to 42.6 μm was estimated to contribute to <250 MPa or <17%, according to previous studies [37,38]. Contribution from the locally aligned TiC nanoplatelets thus accounts for >60%. The predominant strengthening effect of TiC reinforcements in Ti MMCs has been justified in other studies too [9,39]. However, the locally aligned TiC nanoplatelets resulted in both outstanding strength and ductility under compression.

In summary, we have developed a new type of self-assembled, locally aligned TiC nanoplatelet-reinforced Ti matrix composites with outstanding compressive properties. The fabrication method consists of coating the Ti powder with resol nanospheres (10–30 nm), followed by conventional powder metallurgy. The method has great flexibility in controlling the morphology of the TiC reinforcements.

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