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Synthesis, microstructure, and mechanical properties of WC–TiC–Co ceramic composites

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Abstract

A ceramic composite constituting the formula 78 wt% WC–16 wt% TiC–6 wt% Co denoted as the 78WC–16TiC–6Co ceramic composite was fabricated using a powder metallurgy process, by utilising commercially available WC and Co powders, and laboratory produced TiC powders. TiC powders were produced from machining chips of Grade 4 Titanium. Five different procedures were followed for the manufacturing process by altering the amount of the binding agent (stearic acid) and/or compacting pressure and/or sintering regime (temperature and time) and/or mixing process (dry mixing and mechanical alloying). Characterisation investigations conducted on the sintered samples revealed that stearic acid as the binding agent resulted in the decrease of the relative density while mechanical alloying (MA) induced finer microstructures. The 78WC–16TiC–6Co composites manufactured from commercially available and laboratory produced TiC powders using similar process procedures (including MA) exhibited similar characteristics in terms of relative density, hardness, and wear performance.

Keywords: Composites; Powders-solid state reaction; Carbide; Hardness; Wear resistance

1. Introduction

Cemented carbides represent a group of hard and wear-resistant refractory materials, in which hard carbide particles are bound together by a ductile binder matrix.[1–5] They combine the high hardness and strength of the carbides (WC, TiC, TaC) with the toughness of the ductile binder (Co, Ni, Fe).[2–5] In this respect, cemented carbides can also be named as ceramic composites. The application area of the cemented carbides or ceramic composites is extremely widespread and includes metal cutting, machining of woods, plastics, composites and soft ceramics, mining, construction, and military components.[1–6]

WC–Co based ceramic composites are especially attractive in the machining of ferrous and non-ferrous alloys.[2,7,8] WC is hard (able to resist cutting, abrasion, penetration, bending, and stretching) but brittle; Co is soft but tough (able to withstand great strain without tearing or breaking).[2–8] These composites benefit from improvements with the addition of metallic carbides such as TiC, TaC and NbC. Metallic carbides enhance the hardness and wear resistance of WC–Co based ceramic composites by inhibiting WC grain growth during sintering.[2,3,4,8,9,10,11]

Commercial-grade WC–Co composites comprise WC contents in a range between 50% and 97% (along with other metallic carbides), and Co between 3% and 16%.[7,12–15] The content of Co as the binding metal depends on the specified use. For cutting tools, when the major use is for coarse machining, the binding-metal content is higher, to provide increased toughness, while for finish machining, the binding-metal content is lower.[7,13,15–23] Table 1 illustrates the commercial-grade WC–Co composites along with their physical properties. According to the ISO application codes, WC–Co composites illustrated in Table 1 are classified in three groups symbolised using P, M and K. The composite with the symbol P is used to machine steels; M is used for multiple purposes, including machining of steels, nickel-based super alloys, and ductile cast irons; K is used for cutting gray cast iron, non-ferrous metals, and non-metallic materials.[7,18,23]

The present study focuses on the production and characterisation of WC–TiC–Co ceramic composites with an ISO code

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Table 1
Physical properties of WC–Co composite grades for machining by ISO application code.[2]

ISO code	Composition (%)				Density (g/cm^3)	Hardness (HV)
	WC	TiC	Ta (Nb)C	Co		
P01	50	35	7	6	8.5	1900
P05	78	16	–	6	11.4	1820
P10	69	15	8	8	11.5	1740
P15	78	12	3	7	11.7	1660
P20	79	8	5	8	12.1	1580
P25	82	6	4	8	12.9	1530
P30	84	5	2	9	13.3	1490
P40	85	5	–	10	13.4	1420
P50	78	3	3	16	13.1	1250
M10	85	5	4	6	13.4	1590
M20	82	5	5	8	13.3	1540
M30	86	4	–	10	13.6	1440
M40	84	4	2	10	14	1380
K01	97	–	–	3	15.2	1850
K05	95	–	1	4	15	1780
K10	92	–	2	6	14.9	1730
K20	94	–	–	6	14.8	1650
K30	91	–	–	9	14.4	1400
K40	89	–	–	11	14.1	1320

of P05, which is extensively used in machining steels. Commercially available WC and Co powders were used as starting materials. The TiC powder, which is a potential material for high temperature applications because of its high melting point and the low density,[23] was obtained from machining chips of the Grade 4 Titanium as illustrated in Fig. 1.[24]

2. Experimental

The WC and Co powders utilised in this study were the commercial products of Dr. Fritsch (Germany) and Eurotungtene (France), respectively. Both powders had spherical morphology with an average grain size of 1 μm. The TiC powders added to the mixture of WC–Co powders were manufactured from machining chips of Grade 4 Titanium in laboratory scale, by following the route illustrated in Fig. 1.[24] The XRD pattern and the grain size distribution of the TiC powders are illustrated in Fig. 2.[24] The appearance of no other peaks but those of TiC on the XRD pattern (Fig. 2a) indicates the quality of the TiC powders obtained from machining chips of Grade 4 Titanium (Fig. 1). According to Fig. 2b, the grain size of TiC powders varied in a broad range between 0.1 μm and 50 μm, with an average size of 3.4 μm.

In the scope of this study, an attempt has been made to fabricate the 78WC–16TiC–6Co ceramic composite with an ISO code of P05 (Table 1) using a powder metallurgy process, following five different procedures as depicted in Fig. 3. In summary, the amount of the binding agent (stearic acid) and/or compacting pressure and/or sintering regime (temperature and time) and/or mixing process (dry mixing and mechanical alloying) were the main variables of the process. 0, 3 and 5% stearic acid were used as the binding agent. Powders were mixed and homogenised in a T2C Turbula (WAB^{TM}, Basel, Switzerland) blender for 2 h. MA processes were carried out in a vibratory ball mill (Spex^{TM} 8000 D Mixer/Mill, New Jersey, USA) using hardened WC balls (6.35 mm diameter), in a WC vial (50 ml capacity), with a ball-to-powder weight ratio of 10:1 for 6, 9, and 12 h. The powder mixtures were compacted by cold pressing (MSE^{TM}, Kocaeli, Turkey) at different pressures (200 MPa, 400 MPa and 625 MPa). Compacts were sintered using a high temperature controlled atmosphere furnace (Linn^{TM}, Eschenfelden, Germany) at two different sintering regimes (1500 °C for 8 h and 1550 °C for 9 h) under different atmospheres (argon and vacuum).

After sintering, characterisation investigations including microhardness tests, density measurements, microstructural examinations, and wear tests were conducted on the samples. Microstructural characterisations were carried out using a TM1000 (Hitachi^{TM}, Tokyo, Japan) scanning electron microscope (SEM). The hardness measurements were made using a microhardness tester (Schimadzu^{TM}, Tokyo, Japan) under an indentation load of 1 kg on the Vickers hardness (HV) scale. Densities of the samples were measured according to the Archimedes' method by using a precise balance (Precisa^{TM}, Dietikon, Switzerland). Wear tests were performed on a recip-

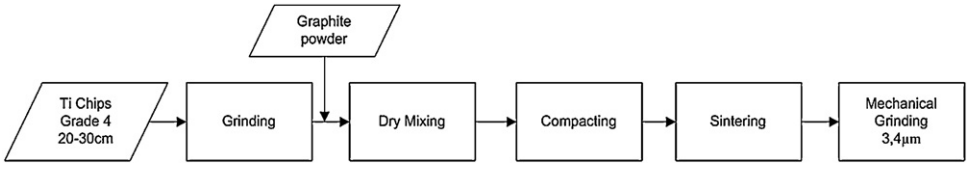

Fig. 1. Fabrication route of TiC powder used in this study. Starting material was the machining chips of Grade 4 Titanium.[24]

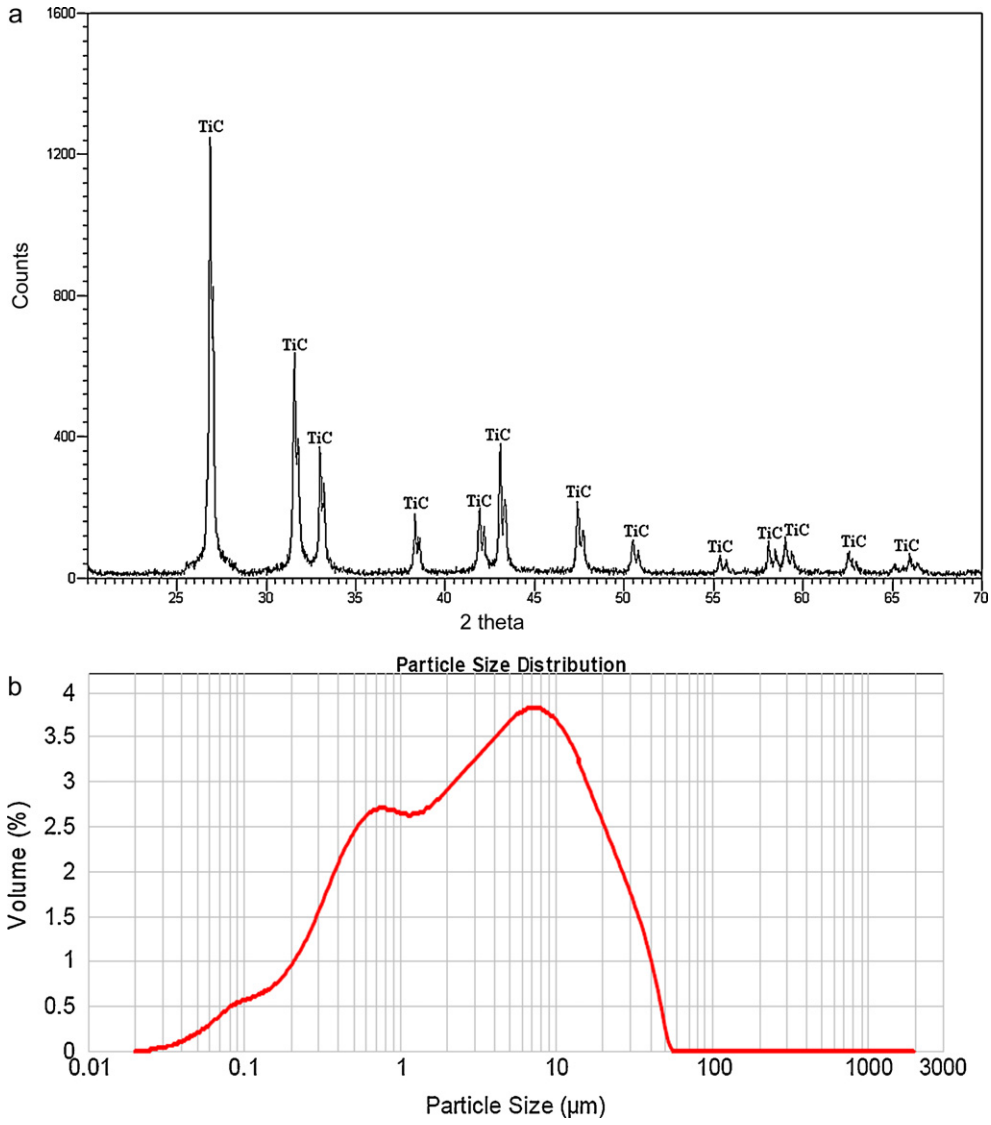

Fig. 2. (a) The X-ray diffraction pattern and (b) the particle size distribution graph of the TiC particles used in the present study according to Fig. 1.[24]

rocating wear tester (Tribotester^{TM}, Clichy, France) under a load of 5 N. Al_2O_3 balls having a 6 mm diameter rub on the surfaces of the samples with a sliding speed of 10 mm/s. The stroke of the Al_2O_3 balls was 2 mm for the total rubbing cycle of 2.5×10^3. Frictional force and the coefficient of friction were continuously recorded throughout the wear tests. Contact surfaces of the samples were examined using a surface profilometer (Dektak^{TM} (6 M), Newyork, USA) and an optical microscope (Leica^{TM} (CTR 6000), Wetzlar, Germany).

3. Results and discussion

Table 2 lists the results of the average density and hardness measurements. Low relative density values were obtained from the samples, where stearic acid was added to the powder mixtures as the binding agent (Process Procedure Nos. 1 and 2 of Fig. 3). The samples manufactured by following Process Procedure Nos. 3–5 of Fig. 3 (without addition of binding agent) exhibited relative densities between 78 and 80%.

According to the results of hardness measurements, composites having relative density values higher than 71% yielded higher hardness levels (between 1963 and 2057 HV). Considering the scatter of the hardness data (Table 2), the hardness of the composites having relative densities between 71 and 80% (produced by following Process Procedure Nos. 2–5 of Fig. 3) can be approximated to 2000 HV, which is higher than that of the composite produced by standard powder metallurgy routes (1608

Table 2
Relative density (%) and hardness values (HV) of 78WC–16TiC–6Co composites manufactured in this study.

Process procedure No.	Relative density (%)	Hardness (HV)
1	63	1797 ± 159
2	71	1963 ± 213
3	78	2057 ± 100
4	79	1973 ± 228
5	80	1989 ± 127

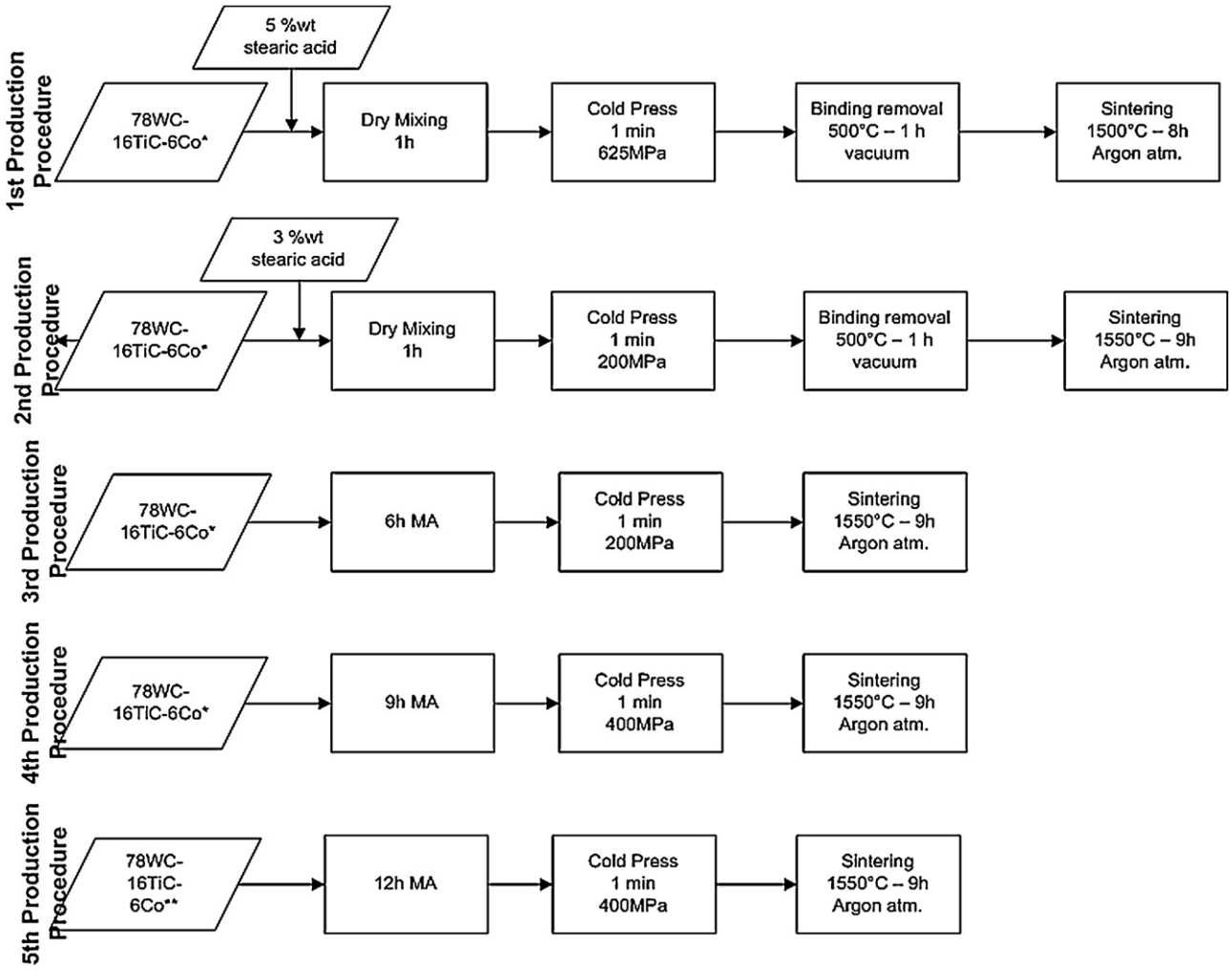

Fig. 3. The flow chart of the process procedures followed in this study to fabricate 78WC–16TiC–6Co ceramic composites.

HV)[25] and commercial-grade ceramic composite (Table 1) with an ISO code of P05 (1820 HV). It should be noted that hardness levels higher than measured in the present study were reported in literature for the hot isostatic pressed WC–15TiC–10Co composites (about 2200 HV).[23]

The SEM micrographs obtained in the back-scattered mode (Fig. 4) revealed the chemical gradients within the microstructures of the samples fabricated in this study. In general, the microstructures were composed of TiC (dark areas in Fig. 4), Co (gray areas in Fig. 4) in WC matrix (light areas in Fig. 4) having continuous skeleton form, which is the characteristic appearance for TiC containing WC–Co composites [26]. Porosities were also detected in the microstructures (shown by arrows in Fig. 4). Compared with the Process Procedure Nos. 1 and 2 in Fig. 3, Process Procedure Nos. 3–5 in Fig. 3 tended to refine the microstructure, while reducing the amount of visible porosities. This observation can be attributed to the milling of powder mixtures (MA process), which also provided a final relative density of about 80% after sintering (Table 2).

The highest amount of porosity (Fig. 4) observed and the lowest hardness measured (Table 2) in the sample fabricated by following Process Procedure No. 1 in Fig. 3 can be correlated with literature reporting the dependence of the mechanical properties (hardness, modulus, toughness, etc.) of engineering ceramics on the porosity content.[27–29] Even so, the sample fabricated by following Process Procedure No. 2 in Fig. 3 contained some visible porosities (Fig. 4b) and yielded a hardness value (1963 ± 213 HV) in the range of the samples, where the porosities were not clearly identified during SEM examinations (Fig. 4c–e). This observation suggests that the hardness reached a saturation value of 2000 HV for the studied ceramic composites in the event that the relative density is higher than 71%.

In the scope of the present study, a new 78WC–16TiC–6Co composite was manufactured by utilising a commercially available TiC powders (average grain size 2.7 μm – 99.5% purity) supplied by Alfa Aesar. After following the Process Procedure No. 4 in Fig. 3, relative density and hardness were measured as 76% and 1939 ± 390 HV, respectively. These values were in the same range with those of the samples fabricated by utilising laboratory produced TiC powder according to Process Procedure No. 4 in Fig. 3 (Table 2).

Following the wear tests, measurable wear tracks were not detected on the surfaces of the samples fabricated according to Process Procedure No. 4 in Fig. 3. Friction curves of the samples

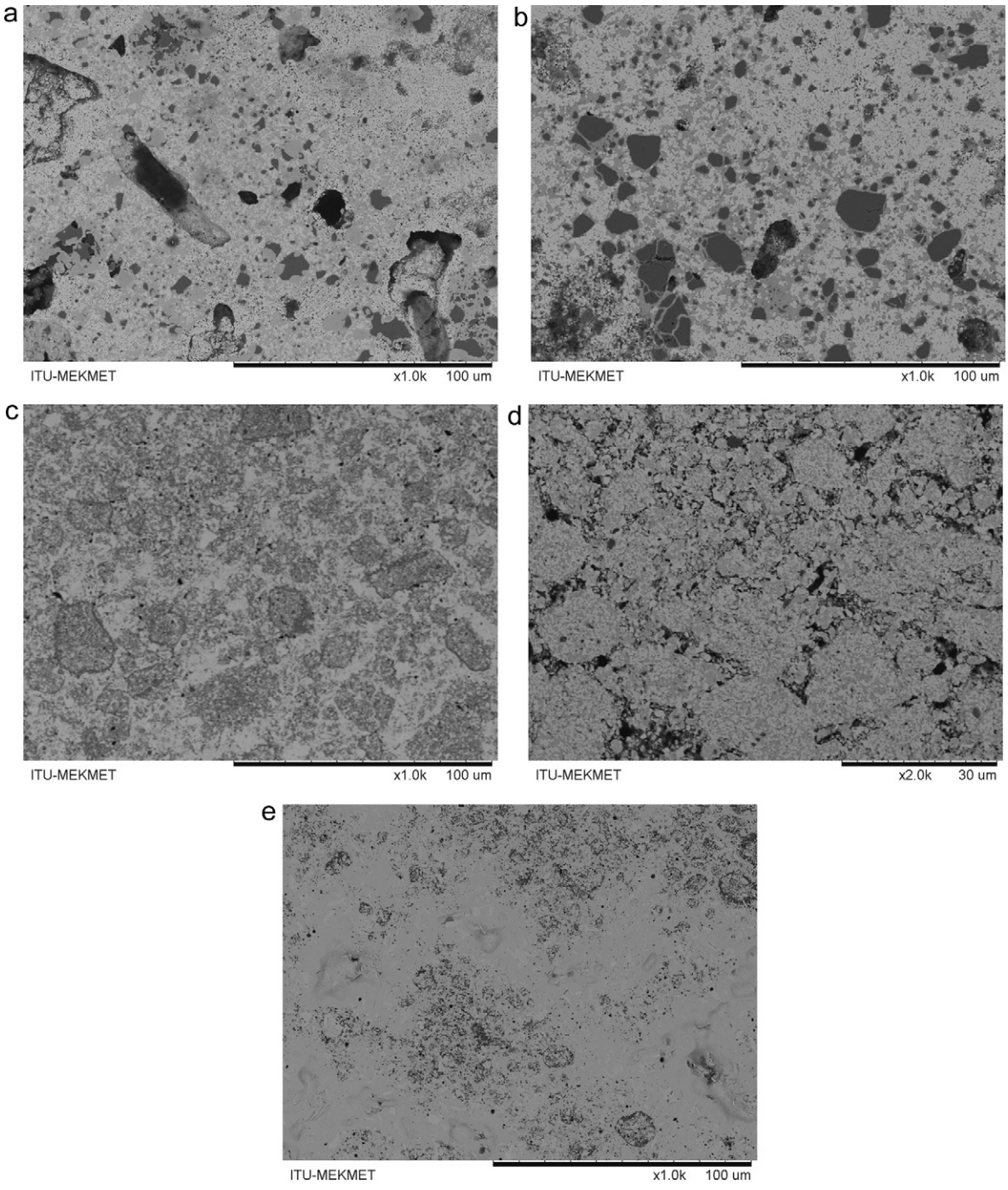

Fig. 4. SEM micrographs of the 78WC–16TiC–6Co composites manufactured by following process procedures: (a) No. 1 (b) No. 2 (c) No. 3 (d) No. 4 and (e) No. 5 (arrows show the porosities).

against Al_2O_3 ball are depicted in Fig. 5. The friction coefficient of the sample fabricated with the addition of the laboratory produced TiC powders remained at its initial value of about 0.2 throughout the testing period (Fig. 5a). On the other hand, the friction coefficient of the sample fabricated with the addition of commercially available TiC powders tended to increase to a value of about 0.3 by the end of the test after reaching about 0.15 at the initial stage (Fig. 5b). The increase of the friction coefficient (from 0.15 to 0.3) during wear testing can be associated with micro-ploughing at the contact surfaces.[30] It should be noted that no attempt has been made in the present study to identify the effect of micro-ploughing on wear, except the examination of the contact surfaces by a 2-D profilometer and an optical microscope. In broad scale, the results of the wear tests suggest wear-less friction between 78WC–16TiC–6Co ceramic composite and the Al_2O_3 counter facing ball with an average friction coefficient of about 0.2. In this respect, wear performances of the ceramic composites fabricated with the addition

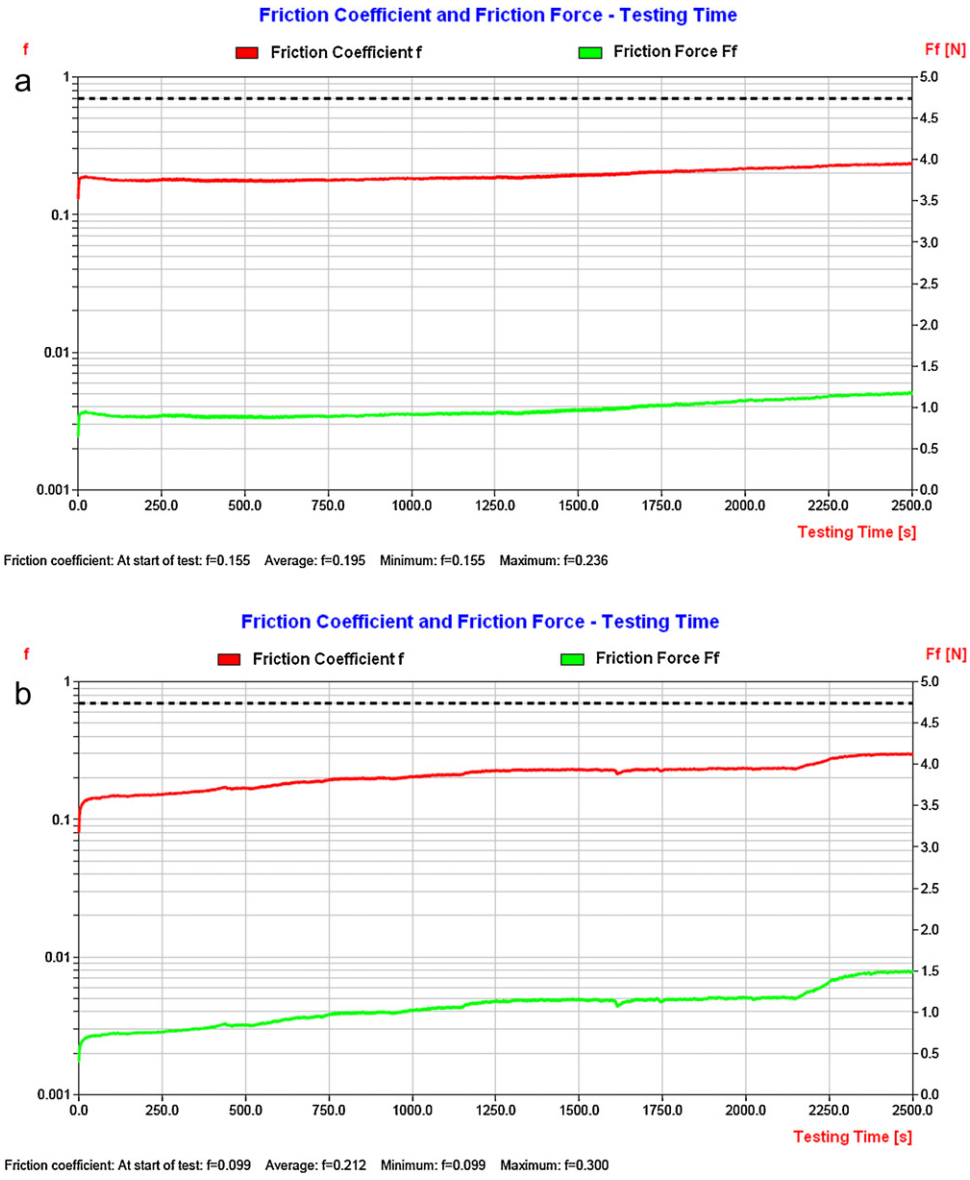

Fig. 5. The friction curves of the 78WC–16TiC–6Co produced in the present study by utilising: (a) laboratory produced and (b) commercially available TiC powders.

of commercially available and laboratory produced TiC powders were comparable, similar to the results of density and hardness measurements (Table 2).

4. Conclusions

Stated below are the observations and conclusions obtained based on the characterisation tests conducted on the 78WC–16TiC–6Co ceramic composites fabricated by the powder metallurgy process.

1. The addition of stearic acid as the binding agent to the mixture of WC, TiC, and Co powders caused relatively high porosity and low relative density.
2. The application of the MA process during preparation of powder mixtures refined the microstructure, reduced the porosity, and increased the relative density, while yielding a hardness value higher than that of conventional grade 78WC–16TiC–6Co ceramic composite with an ISO code of P05.
3. The density, hardness, and wear performance of the ceramic composites did not change remarkably with the type of TiC powder (commercially available or laboratory produced) added to the mixture of WC and Co powders.
4. TiC powders produced from machining chips of Grade 4 Titanium possibly have technological potential to be used in the fabrication of commercial grade WC–Co composites for machining applications.

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