



Studying the Microstructure and Mechanical Properties of (WC – TiC - Co) /ZrO₂ Composite Prepared by Powder Technology



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MANUFACTURE of composite materials has become an important issue in recent years due to their high mechanical properties that make them suitable for many applications which needs high wear resistance and high strength. In the present work, (WC-TiC-Co) with 3,6,9,12,15, and 20 wt. % ZrO₂ composites were prepared by mechanical milling. The mixed powders were pressed in a uniaxial press and sintered at 1450 °C for two different times 1.5 and 3 hrs. The results indicated that the relative density decreases gradually by increasing ZrO₂ percent for both sintering times. The microstructure of WC-TiC-Co/ ZrO₂ composites indicated the formation of needle shape particles from 0 – 9 wt. % ZrO₂ samples for 1.5 hr. sintering time and disappeared for the others sintered for 3 hrs. Hardness, compression strength, and transverse rupture strength decreased by increasing ZrO₂ percent for all samples, but both the wear resistance and fracture toughness increased gradually by increasing ZrO₂ wt. % up to 9 wt. % and then decreased for the higher percent's.

Keywords: (WC- TiC- Co), ZrO₂, Cutting tools, Micro structure, Physical properties, Mechanical properties

Introduction

In recent years, the manufacturing of unconventional cutting tools with super hardness and high wear resistance attracted the attention of engineering academics. Cemented carbides with rigid structure, high strength and high wear resistance over a broad range of contact parameters are widely exploited for many applications as cutting tools. Also, it plays an important role in resisting wear and corrosion either at ambient or at elevated temperatures. Tungsten carbide is known by its superior hardness and wear resistance, but unfortunately, it is a brittle material which is exposed to fracture easily [1, 2]. Addition of a ductile metals such as cobalt and/or nickel greatly

improves its toughness so brittle fracture can be avoided during the operation process [1]. WC-Co composite is the most common ceramic material used in manufacturing of cutting tools. It consists of a hard WC phase that has a volume fraction larger than 80%, and a ductile cobalt metal which protect the samples from any fracture. As volume fraction and elastic modulus of WC is higher than those of Co phase the most load is applied on the WC phase [3, 4]. Addition of small amounts of grain growth inhibitors carbides such as TiC, VC, Cr₃C₂, ZrC, NbC, or TaC to WC –Co enhances hardness and tribological properties and it is used as a protecting material from oxidation, but all these materials degrade the fracture toughness of cemented carbides [3, 5]. WC-TiC-Co alloy with

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Received 19/6/2019; Accepted 8/9/2019

DOI: 10.21608/ejchem.2019.13821.1854

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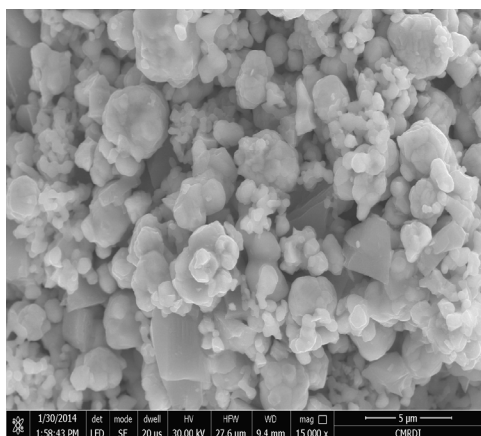
WC/TiC grain size above 0.8 has higher hardness because of the replacement of WC by TiC/(Ti,W) C core-rim phase of higher hardness[3]. WC-Co used as a cutting tools, but it has certain specific limitations because of the presence of metallic binder phase, which leads to softening induced failure at high temperature and sudden change in load. To overcome these disadvantages, researchers proposed a different combinations of metallic binder to achieve improvement of physical and mechanical properties. On the other hand the replacement of metallic binder by ceramic center – additive appears in a new trend [6]. Zirconium oxide (ZrO_2) considered one of the most important materials used as it has a marten site transformation. ZrO_2 is used to replace cobalt in densifying WC materials. Addition of ZrO_2 is expected to increase the fracture toughness due to

transformation toughening. The polymorphic t - m transformation in ZrO_2 leads to a finite amount of volume change and large shear strain [7]. The research aims at studying the effect of ZrO_2 addition by different percents on the mechanical, and physical properties of (WC – TiC – Co) composite using powder metallurgy technique.

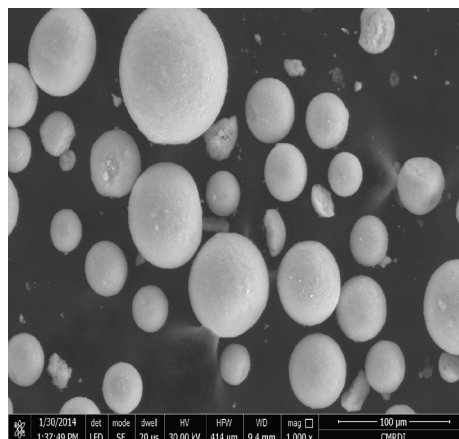
Materials and Experimental Procedures

Materials

(WC-TiC-Co) powder of purity of 99.97% and (0.5 – 1 μm) particle size was used. It is supplied by hart metal company. ZrO_2 powder with purity of 99.99% and (3- 5 μm), particle size respectively was used. It is supplied by El Nasr Company for Refractories and ceramics, Sornaga, Egypt show Fig. 1.



(a)



(b)

Fig. 1. FESEM micrographs of; (a) (WC-TiC-Co) powder, (b) ZrO_2 powder.

Experimental procedure

WC-TiC-Co composite powder is mixed with ZrO_2 by 3,6,9,12,15 & 20wt%. The mixtures are well mixed in a planetary mill model SPEX 8000 rpm mixer/ mill for 2 hours in the presence of 1.5 wt. % paraffin wax as a lubricant material. Ethyl alcohol was used as a process controlling agent [8, 9, 10, and 11]. The mixtures were dried at 140°C for one hour in the dry furnace. The resultant mixed powders were compacted, in a rectangular die using uniaxial hydraulic press, under load of 80 bar. The green density of the compacted samples was measured, and the samples were divided into two groups one of them sintered at 1450°C for 1.5

hr and the other for 3 hrs in a vacuum furnace. The first group of the green samples was sintered at 1450°C for 1.5 hrs with a rapid rate of 10 °C/min followed by cooling down to room temperature. The second group of the green samples was sintered by the same schedule but the holding time is 3 hrs. The heating cycle is shown in Fig. 2.

2.1.3 Composite characterization

The density of the sintered samples was estimated by Archimedes principal using water as a floating liquid according to MPIF standard 42, 1998, in which the sintered specimen was weighed in both air and distilled water.

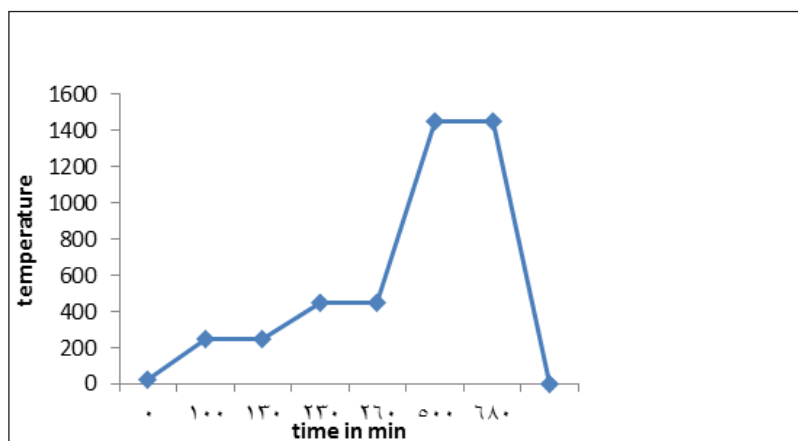


Fig. 2. Heating cycle of the sintering process.

The sintered samples were mounted and ground successively by SiC papers with 120- 3000 grades, then polished with 6 micrometer diamond paste. The specimen surface is prepared by standard grinding and polishing technique using a machine model “Buhlertm”. The microstructure of the polished specimens was evaluated by Field Emission – Scanning electron microscope (FE-SEM; QUANTAFEG250, Holland) equipped with energy dispersive X-ray (EDS) spectrometers, and secondary electron (SE) and backscattered electron (BSE) detectors for particle size, morphology and chemical composition determination. The diffraction pattern of sintered samples are achieved by x-ray diffraction analysis using x-ray diffractometer model x, pert PRO PAN with cu $k\alpha$ radiation ($\lambda=0.15406\text{nm}$).

Vickers micro hardness (VMH) was measured as the average of 5 readings along the cross section polished surface of the specimen using vickers hardness tester model 1600-4981 by applying 30 Kg load for 15 sec.

The fracture toughness was estimated using Vickers indentation technique, depending on crack length measurements of the radial crack pattern produced by HV_{30} indentations. The K_{IC} values were calculated according to the formula of Antic [12].

Compression strength of the investigated samples was measured using uniaxial SHIMADZU universal testing machine UH-F500KN. The applied cross-head speed of universal test machine used is 2mm/min. The compression test sample was conducted at ambient temperature (25 °C).

The rupture test was performed using compression

testing machine and attest fixture, according to MPIF Standard 4. The test bar was placed so that it is centrally located perpendicular to the supporting rods with the top up. The fixture with the test bar was placed between the plates of the compression testing machine and the load was applied with constant rate of 2.5 mm/ min, until the test bar fractured.

The transverse rupture strength for sintered samples was calculated according to the following expression:

$$TRS = 3P / 2T^2W \quad 2.1$$

Where TRS is the Transverse Rupture Strength in N/mm^2 , P is the Fracturing load (N), L is the distance between the supporting rods, and T is the thickness of sample in mm and W is the width of the sample in mm.

The wear tests of the sintered specimens were carried out using a pin-on-ring tribometer. Each specimen is ground using abrasive papers of 1200, 2000, 4000 grades respectively. Silicon carbide ring of diameter of 63 mm, speed of 78 rpm and surface roughness of 60 μm were used. For each sample the sliding distance was kept stable at room temperature without lubrication. The tested specimens have rectangular shape with 8*8*12 mm dimensions with a contact area of 64 mm^2 . The specimens were loaded against the ring under normal loads of 55 and 30 N at sliding speeds of 0.3 m/s. The abrasive wear rate is the weight loss of the specimen divided by the sliding distance. An electronic balance of 0.0001 g resolution was used to measure the loss weight.

Result and Discussion

Densification

The density variation and apparent porosity of (WC – TiC – Co) /ZrO₂ composites sintered at 1450°C for 1.5 and 3 hr are given in Figs. 3(a,b). It is clear for both sintering times that by increasing zirconia percent from zero up to 20 wt % a gradual decreases in the sintered density was achieved

. This is due to the lower density of ZrO₂ (6.05 g/cm³) than that of (WC – TiC – Co). Also the increasing of ZrO₂ at the expense of cobalt leads to decreasing of the formed liquid phases. This is in turn results in decreasing the cobalt percent to be not sufficient for closing all the pores due to the incomplete capsulation of all WC –TiC particles and thus prevents the full densification of the sintered samples [13].

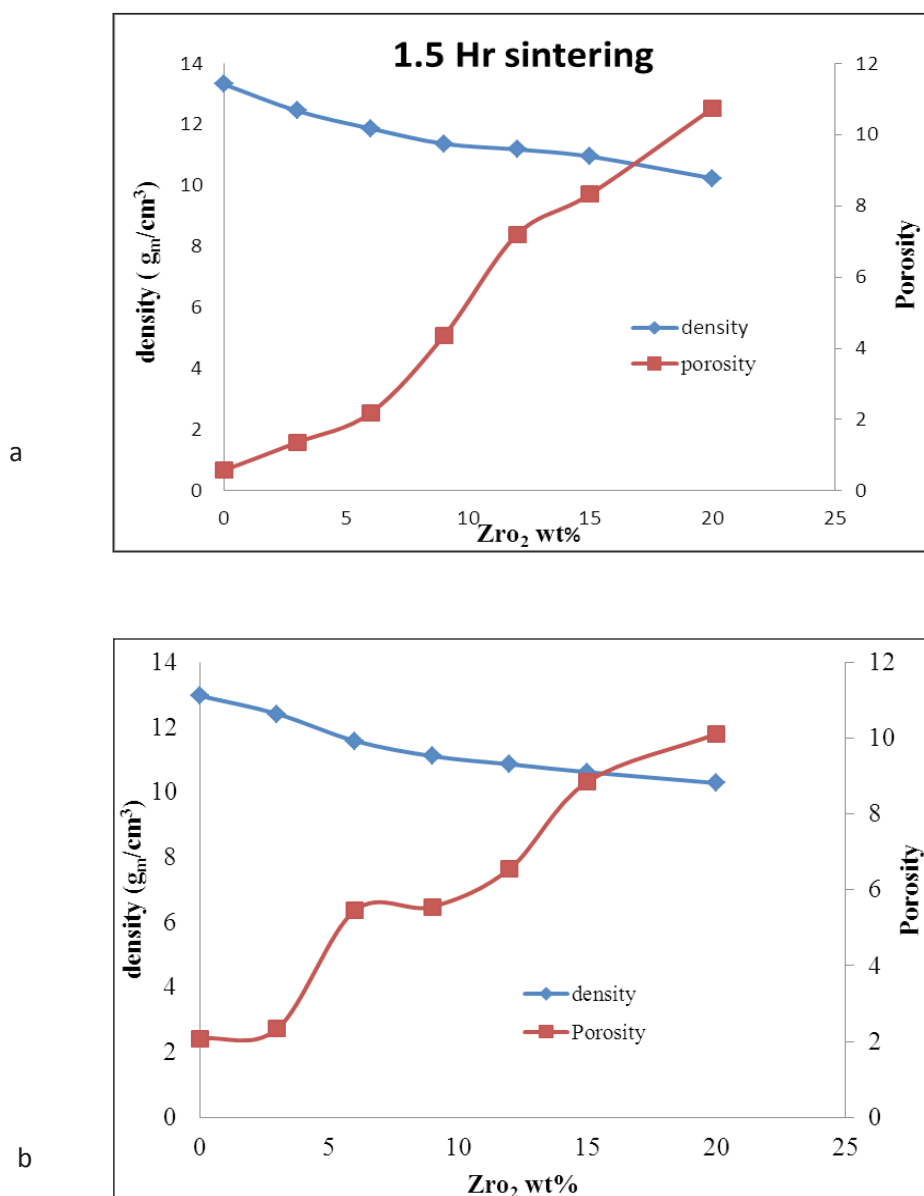


Fig.3. Density and apparent porosity for specimens sintered at 1450°C for (a) 1.5 hr, (b) 3hrs.

Phase constituent and microstructure.

X-ray diffraction patterns of the WC-TiC-Co/ZrO₂ composites sintered at 1450°C for 1.5hr and 3hrs are shown in Figs. 4(a,b). It is found that the composites are composed of WC as major phase and h- W₃Co₃C, TiC and t-ZrO₂, C as a minor phases. Although t-ZrO₂ content was increased from 3 wt. % to 20 wt. %, the intensity of t-ZrO₂ phase did not show any significant increases. This means that t-ZrO₂ was grounded to the nano

crystalline form during the milling process with WC, then it dissolved through the liquid Co phase binder and prevents grains from any connection or welding with each other's. The isolation of t-ZrO₂ grains inhibited their grain growth and decreases the crystallinity. It is worth to note that η- W₃Co₃C and C phases are revealed with the addition of zirconia up to certain limits. The appearance of C phase may be attributed to the formation of h- W₃Co₃C phase at the expense of both WC and TiC phases.

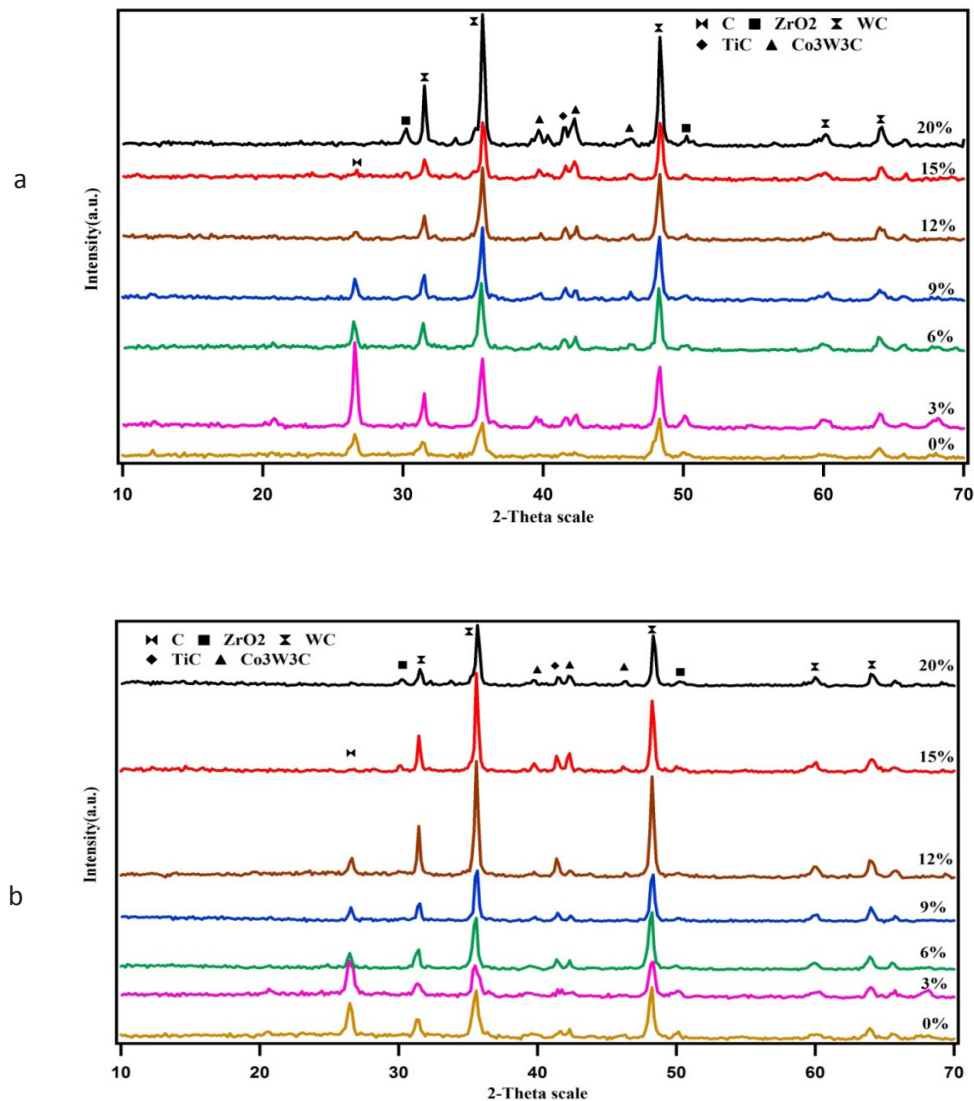
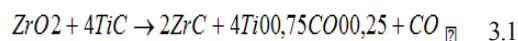


Fig. 4. XRD pattern for specimens sintered at 1450°C for (a) 1.5 hrs. and (b) for 3 hrs. as a function of ZrO₂.

The possibility of the presence of any type of reactions between TiC and ZrO₂ [12,13] at 1450°C resulting in the formation of amorphous oxy carbides through the following reactions which can be considered as one of the reasons contributed in the decrease of the content and the intensity of ZrO₂ phase.



On the other hand, as the sintering time increases from 1.5hr to 3 hrs, the intensity of t-ZrO₂ phase decreased and become very weak compared by the specimens sintered at 1.5hr. This can be understood in term of the consumption of zirconia in its reaction with TiC as a function of time. This means that ZrO₂ disappears completely if there is a sufficient sintering time and stoichiometric amounts of TiC. Consequently, ZrO₂ added to the specimens sintered at 1450°C for 1.5hr did not completely disappear through reaction because the time is not sufficient, while the ZrO₂ content in the specimens sintered at 1450°C for 3hrs disappeared because the time seems to be sufficient for the reaction of zirconia with TiC. The appearance of zirconia in the specimens contains high content of ZrO₂ (>9wt. %) can be attributed to the insufficient amount of TiC.

Microstructure investigation is an important tool to assess the particle size, shape and configuration of all particles, as this affects greatly on the mechanical properties of the produced composite. Fig. 5. And 6 show the field emission scanning electron microscope (FESEM) of WC-TiC/Co specimens sintered at 1450°C for 1.5hr and 3hrs as a function of ZrO₂ content. A uniform distribution of WC-TiC (rods/needles shape) and ZrO₂ (rounded to sub-round) grains embedded in liquid phase are seen. These needles and rods are a maximum in the free zirconia specimens sintered at 1450°C irrespective to time. WC-TiC in the specimens sintered at 1450°C for 1.5hr maintains its morphology with increase of the zirconia content up to 9wt. % then, it converted into regular and irregular shapes with the further increase of zirconia. This variation in the morphology can be back to Co binder content, and the reaction of ZrO₂ with TiC. In the free zirconia specimens, Co binder (>9 wt. %) forms liquid phase with WC and the viscosity of this liquid decreases to some extent allowing the formation of rods/needles from WC-TiC. The presence of TiC seems to be the support and the controller in the orientation of WC to form rodes/needles. With the increase of the sintering time, the viscosity of the liquid formed in 3hrs becomes lower than that formed in 1.5hr. With addition of zirconia at the expense of the Co binder in the composites, the viscosity of the liquid formed in

the specimens sintered at short time (1.5hr) seems to be decreased as a result of the decrease of the liquid content relevant to Co and the oxy carbide phases. However, the liquid chemistry and its quantity seems to still have viscosity allow to the formation of WC-TiC rode/needles. The disappearance of the rods/needles shape of WC-TiC with further increase of zirconia content (>9wt. %) can be rationalized by the change of the liquid phase chemistry and its content as result of the decrease of Co content and the developed oxy carbide amorphous phase from the reaction of TiC and ZrO₂, and in turns the decrease of the TiC to some extent which cannot be considered as support to the formation of rodes/needles. On the other hand, the increase of the sintering time to 3hrs led the conversion of the morphology of WC-TiC with addition of zirconia. This can be explained based on the formation of low viscous liquid phase relevant to Co in 3hrs compared by the liquid phase formed in 1.5hr. This transient liquid facilitated and strengthened the reaction of TiC and zirconia to proceed toward the formation of amorphous oxy carbide. This in turn led to the significant decrease of TiC and significant change of the liquid chemistry. It is possible to report that needles or rods shape to be formed in the investigated composites should have a specific amount of TiC. This amount of TiC can be considered as a critical concentration. Also, the liquid phase-based WC-Co chemistry must be kept to some extent to allow the formation of rods or needles. It can be concluded that the sintering time, TiC and ZrO₂ of WC-TiC/Co composites are the key factor controlling the WC morphology. Also, the particle size of the specimens sintered at 1450°C for 3hrs is higher than those sintered at 1450°C for 1.5hr. This difference can be attributed to the neck formation among the grains and in turn the grain growth as a result of the soaking time. ZrO₂ phase grains was maintaining its morphology in all photomicrographs while its size showed a significant increase with the increase of sintering time as a result of the grain growth.

Also, pores and voids were seen in FESEM micrographs. They are located along the contact area among the particles as well as some of them within the particles. This can be rationalized by:

- 1- The increase of the mean free path by zirconia preventing the matrix constituents to become close to each other and in turn incompleteness of the sintering process occurred. The addition of ZrO₂ at the expense of Co binder decreases the liquid phase content and become insufficient for filling the voids between the particles
- 2- The expected evaporation of Co-produced from the reaction of ZrO₂ and TiC.

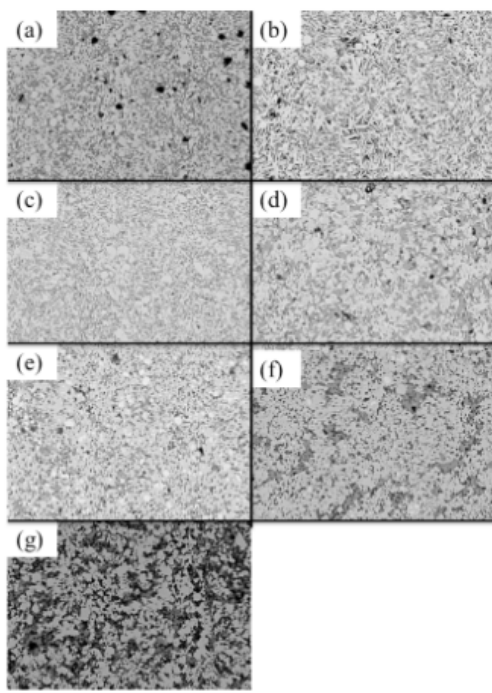


Fig.5. FESEM images of specimens sintered at 1450 °C for 1.5 hr. a, b, c, d, e, f and g represent 0,3,6,9,12,15 and 20 wt.% of ZrO_2 respectively.

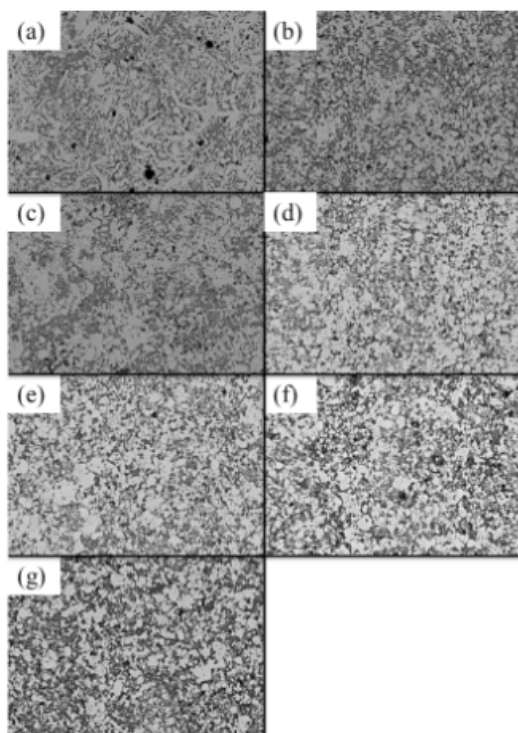


Fig. 6. FESEM images of specimens sintered at 1450 °C for 3 hrs. a, b, c, d, e, f and g represent 0,3,6,9,12,15 and 20 wt.% of ZrO_2 respectively.

Mechanical properties of the sintered samples

Hardness test

The mechanical properties are highly depends on both density and particle size. Vickers hardness of WC –TiC – Co cemented carbides reinforced with zirconia content from 0wt% to 20 wt % was measured at applied load of 30 Kg for both samples sintered at 1450°C for 1.5 hr and 3hr. Fig. 7. Shows that the hardness of the sintered samples decreases gradually by increasing ZrO_2 percent for both sintering times. But there are obvious decreases in the hardness values of the samples sintered for 3 hrs than those sintered for 1.5 hr this may be attributed to the longer sintering time that suitable for appreciable grain growth [16] that decreases the hardness according to Hall Petch equation. The grain size of primary WC particles has great influence on hardness as clear from equation. 3. 3 [17].

$$HV = 550 + 23.5 / \sqrt{d_{WC}}$$

3. 3

Where HV is the hardness, and d_{WC} is the particle size of primary WC particles. As the initial particle of primary WC decreases, the hardness of the composite increases. As the grain size of WC is smaller, so more WC particles are dissolves in the cobalt binder and the hard phase distributes uniformly in all cemented carbide matrixes which increases the bind strength of hard phase [18, 19]. The grain growth phenomenon was confirmed by the FE - SEM micrographs. It is also clear from the figure that the highest hardness value measured was about 17.22 Gpa for ZrO_2 -free sample compared with previous work [6] and decreases to 15.78 G Pa for 3 wt % and the lowest hardness value was 9.96 GPa for 20 wt % Zirconia sample. This behavior of hardness in both cases may be attributed to the small increase of porosity and slight decreases in bulk density that confirmed by FE- SEM. These values are in good agreement with the densification behavior of these composite. Also, the hardness of (WC – TiC – Co) sintered sample was higher than that of WC – TiC – Co / ZrO_2 samples, for both sintering times. This is due to the lower hardness value of ZrO_2 than that of WC – TiC – Co.

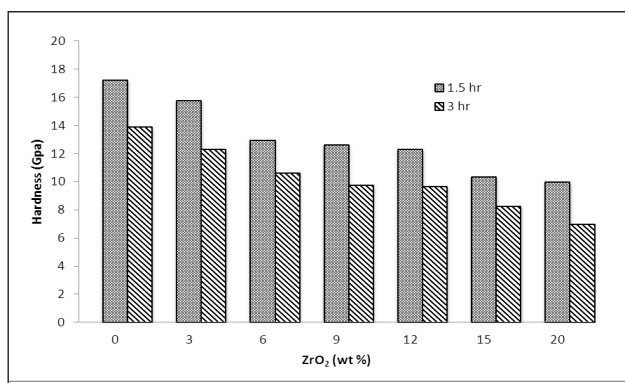


Fig. 7. Hardness of specimens sintered at 1450°C for 1.5hr and 3hrs.

Compressive strength measurement

The behavior of the axial compressive strength as a function of zirconia content for (WC- TiC – Co) composite sintered at 1450°C for 1.5 & 3 hrs were shown in the figs. 8(a,b). & 9. The results show two behaviors, the compressive strength decreases by increasing ZrO₂ percent from 0, 3 up to 20wt% for both sintering times, while it decreases in case of 3 hr sintering time lower than those at 1.5 hr sample. These results are in good agreement with hardness and densification results. This may be attributed to the formation of weak η phase W₃Co₃C and the increasing of porosity by increasing ZrO₂ percent, in which pores are considered as nuclei for crack propagation. The ZrO₂ free sample sintered for 1.5&3 hrs have the

highest value in the mechanical strength which was about 1768 M Pa in case of 1.5 hr sintering and 1398 Mpa in 3 hr sintering time. From Fig. 8(a,b). it was obvious that there is a decrease in the compressive strength value from ZrO₂ free sample to 3 wt % ZrO₂ and then increasing for 6 wt % this for 1.5 hr sintering time samples. This may be attributed to the formation of rod shape which increases for 6 wt % than 3 wt % sample and affects greatly on the compressive strength, Where the rod particles are enter locked with each other which enhances the strength. But for 3hrs sintering time samples the compressive strength values decreases gradually by increasing ZrO₂ percent that can be rationalized by increasing the porosity and particle size that facilitates the crack & the disappearance of the needle particles.

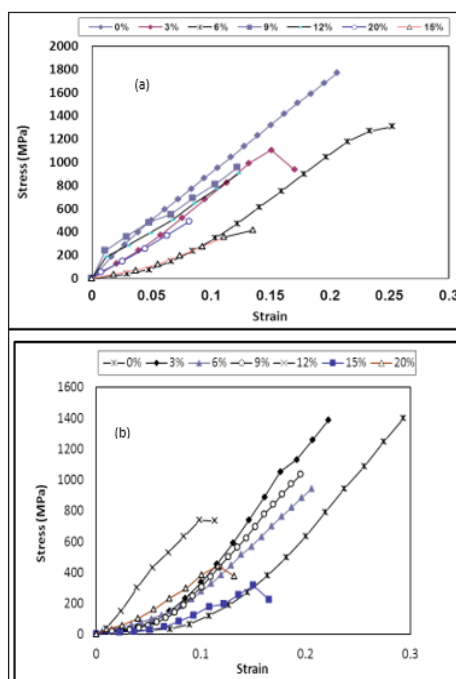


Fig. 8. Stress-strain curves for specimens sintered at 1450°C for (a) 1.5hr, (b) 3hrs.

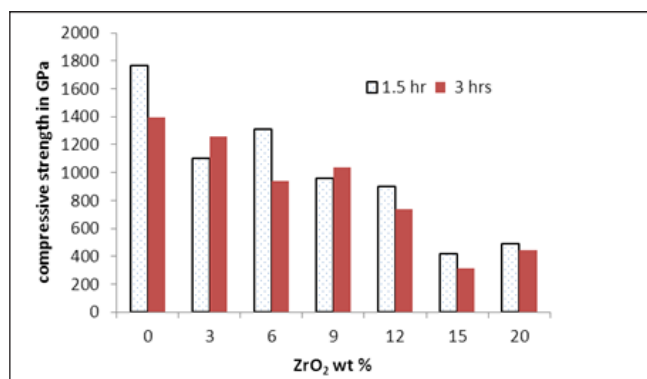


Fig. 9. Compression strength for specimens sintered at 1450°C for 1.5hr and 3hrs.

Transverse rupture strength test (TRS)

The strength of the materials fabricated by PM technique usually determined by the TRS as bending test is one of the most traditional and common tests for measuring the strength of a brittle ceramic materials. It is low-cost and versatile method to assess the strength and quality of a material [20]. Many applications such as strength and wear resistance depend greatly on the crack resistance. The transverse rupture strength this widely estimated in cemented carbides to evaluate their ability to bear an external load. Therefore, TRS of cemented carbides is sensitively dependent on two major factors. The first is an extrinsic flaw where the fracture is initiated and the second factor is an intrinsic resistance to propagate the crack. The effect of these flaws on the transverse rupture strength is dependent on the loading condition during the test because it is affected not only by flaw size, but also by the location and distribution of flaws. The effect of the size and location of flaws on the transverse rupture strength was analyzed by Suzuki and Hayashi [20]. Fig. 10. Represents the effect of ZrO₂ percent on the rupture strength of

WC–TiC - Co composites sintered at 1450°C for 1.5&3 hrs. Generally, the commercial WC-(3–15) wt% Co generally show brittle fracture behavior [21]. The TRS decreases by increasing ZrO₂ content for both series of samples. This can be explained by the increasing of the porosity in the sample and decreasing in the densification as the presence of pores represent weak centre for the rupture process to occur. A second phenomenon is the decreasing of TRS values for the samples sintered at 1450°C for 3 hrs lower than that sintered for 1.5 hrs. This may be due to the presence of rod shape particles of WC that interfered with each other & makes type of electrostatic bonds between the different particles that strengthen the matrix & increase the resistance for rupture. Also, the greater particle size of the samples sintered for 3 hrs in which rupture of a massive part has large particle size is easier than that has smaller one where the small particles interact and gives denser object.

For both two sintering times small WC – TiC particles on the fracture surface with no sign for powder particle separation.

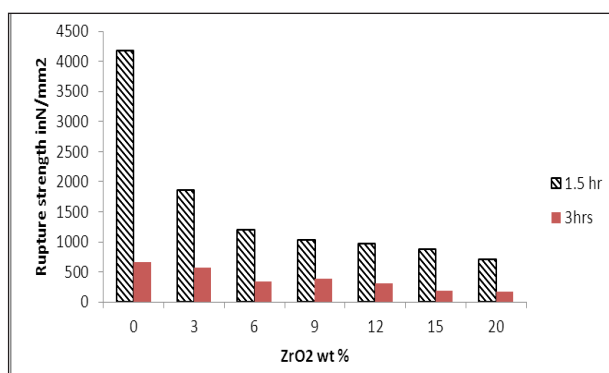


Fig. 10. The Transverse rupture strength as a function of ZrO₂% for samples sintered at 1450°C for 1.5 and 3hrs.

Fracture toughness test

As it is well-known that most cemented carbide components rely primarily on the material's hardness, however, a number of application relevant properties, such as strength and wear resistance, strongly depend on the crack resistance. Hence easy access to the fracture toughness is desirable for alloy development and quality control. By applying the indentation on the polished surface of WC-TiC-Co/ZrO₂ sintered at 1450°C for 1.5 & 3 hrs, two types of crack patterns were developed and treated based on C/a ratio to determine the K_{1C}. The investigated specimens gave two crack patterns, palm Quist and half-penny as given in Table1. Fig. 11. Shows K_{1C} of WC-TiC-Co/ZrO₂ specimens produced from the indentation test at an applied load of 30 Kg. In general, the fracture toughness of both series decreases with the increase of ZrO₂ content at the expense of Co. This may be attributed to the increase of the porosity as results of the decrease of the wetting of WC by Co. Although the addition of ZrO₂ to WC-TiC-Co did not give highest values for K_{1C} compared by the specimen's free zirconia but there are other important issues must be handled to judge if zirconia addition has positive reflection on these composites or not. Based the published works, the addition of Co metal to WC is an attractive binder because of its excellent carbide wetting and adhesion properties as well as its capillary action during sintering which allows the achieve high densities. However, the increase of Co addition to WC has a negative reflection on the cost of the production of WC and its characteristics. It is worth noting that the production of fully dense self-bonded WC (i.e. binderless) is a good cutting tool candidate, but this route is still difficult to be applied because of the formed covalent bond between W and C. In this frame, the scientists and academician have been tried to find an alternative for Co binder taken into consideration this question: how can compromise the fracture toughness value with other mechanical properties such as wear and strength? For example, the production of WC with reasonable fracture toughness, hardness, strength with high wear resistance can be met with targeted application. Among these trials ZrO₂ was added to WC. Several techniques included conventional and recent trends were used to process fully dense WC- ZrO₂. The K_{1C} value recorded does not exceed 5.4–4.4 and 11–12 MPa m^{1/2} [21,6] where the maximum K_{1C} of WC-Co and WC-TiC-Co reaches 13 MPa m^{1/2} and 11 MPa m^{1/2}, respectively.

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This means that the decrease of K_{1C} of WC with the addition of ZrO₂ at the expense of cobalt is expected. In this investigation, the fracture toughness of specimens fired at 1450 oC for 1.5 h and 3h decreased from 13 to 5 m^{1/2} and 11 to 6.5 m^{1/2} respectively. However, the attractive recorded issue herein is the remarkable improvement of K_{1C} of the specimens sintered at 1450 °C for 3hrs compared by the specimens sintered for 1.5h as shown in Fig. 12. K_{1C} of the WC-TiC-Co specimen without ZrO₂ decreased by 16.6% with increasing the sintering time. This negative effect of sintering time can be attributed to the formation of glass and grain growth seen in the microstructure. With addition of ZrO₂ content up to 12 wt. %, K_{1C} of WC-TiC-Co increased and recorded improvement reached to ~35% then started to decrease to 22.6% with the increase of ZrO₂ content to 20wt. %. Despite the sintering time has badly effect on the WC-TiC-Co fracture toughness without ZrO₂ but it has a positive effect with the addition of ZrO₂ because the increase of sintering time contributed to enhance the densification by decreasing the porosity of the specimens. On the other hand, uniform distribution of sintered ZrO₂ inhibits the grain growth of WC and TiC grains. The decrease of K_{1C} relevant to the increase of ZrO₂ above 12 wt. % can be explained in terms of the binder phase mean free path. It seems that the mean free path of the binder phase (ZrO₂) reaches to critical value, i.e. the thickness between WC-TiC grains increased. This means that the influence of ZrO₂ appeared at high temperature and its optimum value recorded with the addition of 12 wt. % through the conventional techniques (pressureless sintering).

Although the recorded decrease of K_{1C} values of the specimens compared by the WC-TiC-Co specimens but these values is higher than that of WC- ZrO₂. This means that the processing of WC-TiC-Co with zirconia gave a good fracture toughness. This product is considered cost-effective.

The mean free path is defined as the average thickness of the binder between the WC

Grains and is dependent on the cobalt content and the size of the WC grains.

As well as the density & increasing the porosity of the samples. Also, the good distribution of ZrO₂ particles in WC matrix which prevents the grain growth, and the presence of cobalt melts

that dispersed in the matrix preventing or reduced the fracture in the samples.

Zirconia free sample has fracture toughness of $13 \text{ MPa m}^{1/2}$ at 1450°C for 1.5 hr. & by addition of 3 & 6 wt % zirconia the fracture toughness value didn't change greatly. But by increasing zirconia content more than 6 wt % fracture toughness decreases. It was expected that fracture toughness increases by increasing zirconia content, but it decreases the result was around 5 -13 $\text{MPa m}^{1/2}$ which is more than WC-ZrO₂ which is around (5.4 – 4.4) $\text{MPa m}^{1/2}$ [22]. This means that the presence of cobalt enhances fracture toughness, and by decreasing cobalt percent the fracture toughness was decreased. The effect of m- ZrO₂ phase formation on the fracture toughness is not

significant as hardness. The decreasing in fracture toughness can be explained by many reasons, the first is the addition of ZrO₂ is expected to increase the fracture toughness due to the polymorphic tetragonal- monoclinic transformation which leads to a finite volume change and large shear strain. [23-25] But in this work the tetragonal ZrO₂ phase didn't transformed to the monoclinic one as indicated by XRD. The second is that the fracture toughness decrease with increasing yttria content from 2 to 3 wt % [26]. In this work ZrO₂ was stabilized by 5 mol % of yttria. Also amount and type of stabilizer controlling the number of particles transform [25] and as number of transformed particles increase the toughness increase [27].

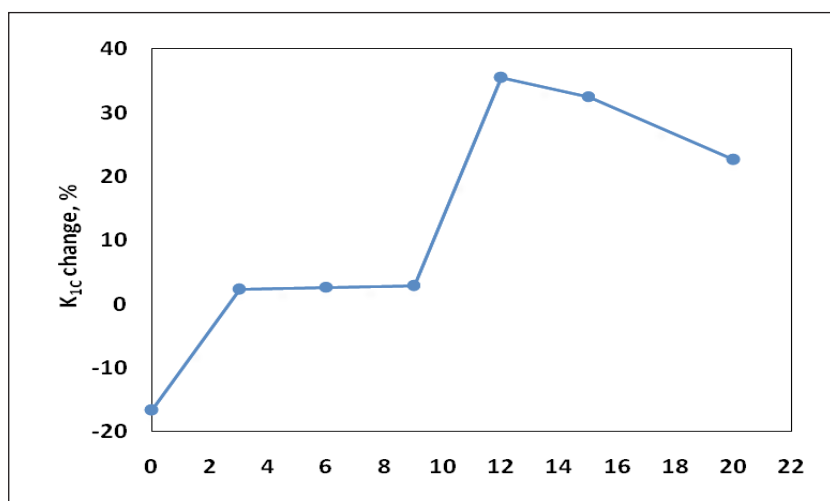


Fig. 11. K_{1C} change of WC-TiC-Co specimens sintered at 1450°C for a) 1.5 hr and b) 3 hrs as a function of ZrO₂ content .

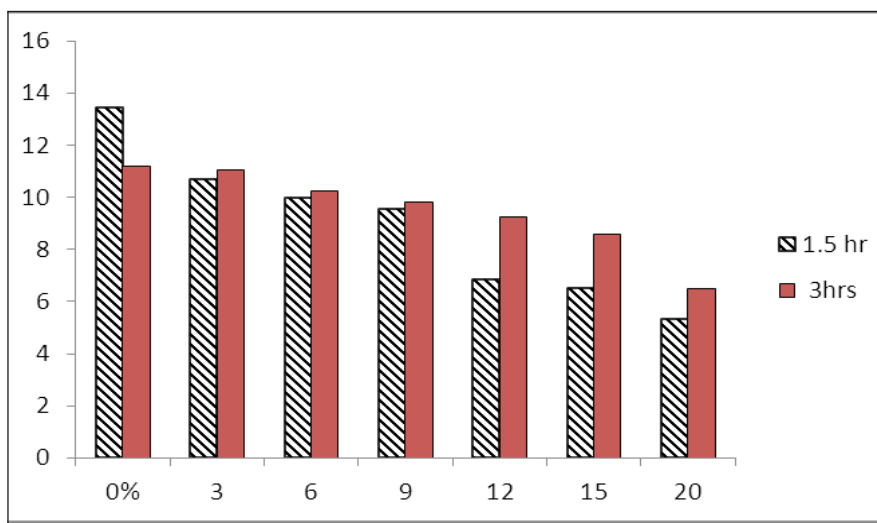


Fig. 12. Fracture toughness value for different wt% of ZrO₂.

TABLE. 1. Fracture toughness values for specimens sintered at 1450°C for 1.5hr and 3 hrs

ZrO ₂ wt %	Fracture toughness values in GPa for 1.5 h	Type of crack	Fracture toughness values in GPa for 3 hrs	Type of crack
0	13.45	PalmQuist	11.21	PalmQuist
3	10.7	PalmQuist	11.055	PalmQuist
6	9.98	PalmQuist	10.25	PalmQuist
9	9.54	PalmQuist	9.815	PalmQuist
12	6.819	PalmQuist	9.24	PalmQuist
15	6.49	PalmQuist	8.6	PalmQuist
20	5.3	HalfPenny	6.5	PalmQuist

Wear test

The important factors that affecting greatly on the performance of cutting tools is the sliding speed, the loaded force, weight friction and homogenization between the matrix and the reinforcement. Figs. 13(a,b). show the variation of wear rate of WC –TiC – Co specimens as a function of ZrO₂ composites with two different loads of 55&75 N applied by sliding speed of 0.3m/s. It is clear from that in case of 1.5 hr sintering the wear rate decreases in both loads regularly up to 9 wt % zirconia sample and then increases gradually by increasing the zirconia percent up to 20 wt% sample. This was attributed to the uniform distribution of zirconia particles in the matrix composite as seen in the microstructure which enhances the tribological behavior of the composite. Samples from 0- 9 wt % ZrO₂ are homogenously distributed and have needle shape which improves the toughness of the samples. This can be rationalized by two reasons

1. The formation of the needle particles which interact with each other by metallic bond and van der waals forces that enhances the densification and the interaction between the different particles in the composite, consequently improves the wear resistance.

2. Also, the formation of η phase W₃Co₃C that dispersed all over the matrix which resist the crack friction so enhances the resistance to wear. The formation of η phase in cemented carbide, improves both the bending strength and wear resistance [28]. Above 9wt% ZrO₂ sample the wear rate increases due to the disappearance of needle shape enspite of presence of η phase.

But in case of 3 hrs sintering time and 55 N load the wear rate decrease up to 6 wt% ZrO₂.

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But in case of the other load 75 N it decreases only for 3 wt % ZrO₂ sample after that, the wear rate increases continuously. The improvement in wear resistance may be attributed to the high indentation toughness due to the critical load of crack propagation which affected by toughness. Bhushan [29] stated that low toughness decreases the wear resistance by introduction of micro fracture at contact surface in sliding.

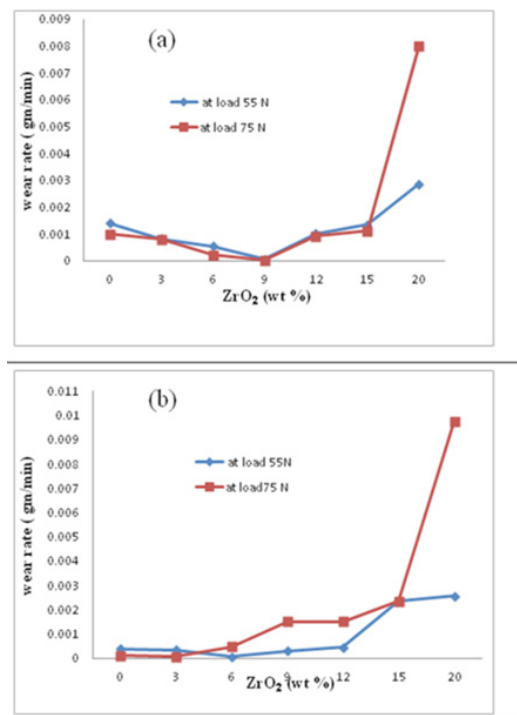


Fig.13. The wear rate as a function of ZrO₂ Wt% for specimens sintered at 1450 for (a) 1.5hr, and (b) 3hrs at 55N and 75N.

Acknowledgement

This research has been funded by the academy of scientific research in Egypt.

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