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PREPARATION AND QUASI-STATIC MECHANICAL PROPERTIES OF ZR/W/PTFE GRANULAR COMPOSITES

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Summary: Zirconium/tungsten/polytetrafluoroethylene (Zr/W/PTFE) granular composites with mass ratios of Zr:W:PTFE of 16:66.5:17.5 were fabricated using a hot-pressing sintering method, and the quasi-static compressive behavior of the composite was experimentally investigated using a Materials Testing System pressure machine (MTS) at room temperature. Through the scanning electron microscope (SEM), a microscopic test analysis was carried out on the samples before and after loading. The composite's stress-strain curve under quasi-static loading presented elastic-plastic characteristics due to the nonlinear PTFE matrix, and it could be obviously divided into elastic deformation region, inelastic deformation region and strain softening region. The composite displayed significant strain rate hardening effect, and its compressive strength was about 43 to 50 MPa at a strain rate range from 10^{-4} to 10^{-2} s^{-1}. Results show that the density and strength of Zr/W/PTFE composite will be reduced when the sintering temperatures are lower at 370 ^{o}C or higher at 390 ^{o}C, because the PTFE can not melt sufficiently at low temperatures and its decompose rate will increase at high temperatures. The metal particles-PTFE matrix separation phenomenon can be clearly observed on the fracture surface and the compressive failure of the composite is caused primarily by the PTFE matrix fracture. According to the failure strength with strain rate and visco-elastoplasticity, a constitutive relation of the composite at low strain rates was established, which could accurately describe the quasi-static compressive mechanical properties of Zr/W/PTFE composite.

1 INTRODUCTION

Reactive materials are a special category of energetic materials, which are being intensively studied for many applications such as military, prppellant, welding, fireworks and oil fields [1-3]. They are usually composed of several non-explosive solid materials and pressed or sintered or bonded by other method to form an energetic structural composite. The

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composite normally stays inert and must be stable to survive launch, however, it will react rapidly with generating a high amount of chemical energy under a sufficiently strong impact. The requirements are a high density, high strength, high energy density and exothermic reaction initiation upon impact. There are many kinds of materials possessing the required properties, such as thermites, intermetallic compounds, metal-polymer mixtures, metastable intermolecular composites (MIC), matrix materials, and hydrides [1].

Due to the high activity, accessibility of aluminium (Al), and outstanding properties of Teflon (PTFE): low friction coefficient, high thermal stability, high electrical resistance, high chemical inertness, high melting point (327 ^{o}C), high thermal energy release when decomposed, and the easiness to deform. PTFE/Al is one of the reactive materials which is widely studied. Its preparation method was firstly disclosed by Davis [4] and several researchers improved the forming process that was prepared by cold pressing and sintering [4,5]. In recent years, metal-polymer received extensive attention due to their special response to high impact and/or thermal loading, whose reaction or phase change may be caused by shock waves [6-13]. Cai et al. made a series of research on the mechanics properties of un-sintered PTFE/Al/W granular composites [14-19]. They carried out lots of experiments (quasi-static, Hopkinson bar and dropped-weight) to investigate the effect of different molding pressures and particle size on the compressive strength. For reactive materials, the primary focus is on the impact initiated properties and energy release behavior under highly dynamic loads. Metal-polymer subjected to shock compression has been investigated by using a gas gun and/or Taylor anvil-on-rod impact tests [20-25]. W has been found to participate in the exothermic reactions and quantified in several studies, including those involving falling particles [26], particle clouds [27], piles of nanoparticles [28], and pyrotechnic mixtures [29,30]. In this paper, our approach is to use the hot-pressing sintering method to make Zr/W/PTFE composite where W is used to increase the density and the energy density.

This paper considers the mechanical properties of Zr/W/PTFE composite sintered at different temperatures. Quasi-static tests were employed to find stress-strain relationships and SEM was used to identify microstructure fracture characteristics. It is evident that the samples sintered at 380 ^{o}C have better performance and its compressive strength has significant strain rate effect at low strain rates.

2 EXPERIMENTAL

The Zr/W/PTFE composite was prepared using hot-pressing sintering; the preparation process chart is shown in Figure 1. There two types of initial PTFE powder: 5 μm (Tianyuxiang, type A02) and 25 μm (3M, type TFM 1700), whose composition and distributions are given in Table 1.

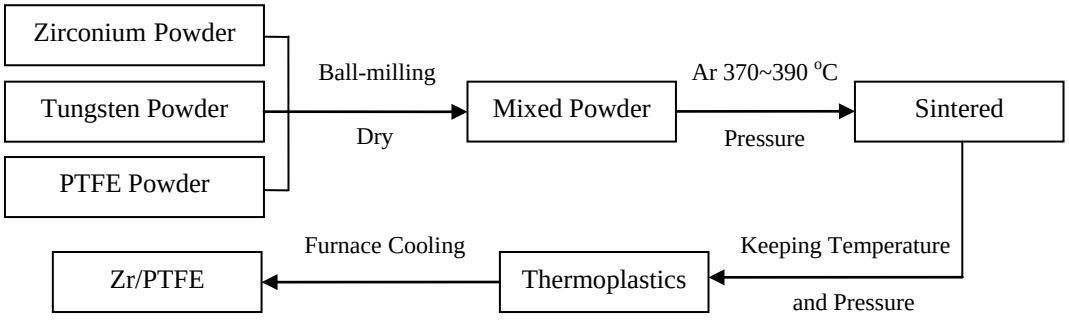


Figure 1: The preparation process chart for Zr/W/PTFE using hot-pressing sintering.

Powder	Mass fraction (%)	Average particle size (μm)
Zr	16	37
W	66.5	3
PTFE-1	17.5	5
PTFE-2	17.5	25

Table 1: Composition and distributions.

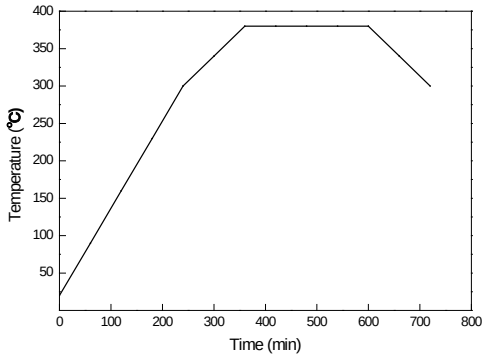


Figure 2: Typical sintering cycle for Zr/W/PTFE at 380 °C.

The individual powders were weighted at desired mass ratios and ball milled for 2 h with absolute ethyl alcohol. The powder mixtures were dried at 55°C in a vacuum oven for approximately 24 h prior to sintering. Next, the Zr/W/PTFE mixtures were loaded into a graphite die and hot-sintered under Argon atmosphere with the pressure of 20 Mpa. The temperature history of the typical sintering cycle is shown in Figure 2.

Sintering temperature (°C)	Density (g/cm^3)	TMD (%)
370	6.32	89.77
380	6.52	92.61
390	6.00	85.23

Table 2: The relation between sintering temperature and Zr/W/PTFE-1 density.

X-ray diffraction was performed on the Zr/W/PTFE mixtures before and after sintering in order to detect the presence of reaction products which are shown in Figure 3. We observed that all peak value positions of the two curves completely overlapped, which demonstrates no new substance was formed.

PTFE is a linear chain thermoplastic polymer, whose melting point is 327 °C and crystallinity is largely influenced by the sintering temperature. The density of Zr/W/PTFE-1 samples sintered at different temperatures is shown in Table 2, suggesting that the density of the samples sintered at 380 °C is 6.52 g/cm^3, which is significant higher than the other two groups. The density change may be: PTFE matrix couldn't melting mix sufficiently under the condition of the sintering temperature was 370 °C, and low crystallinity resulting in decreased the density of sample; when the sintering temperature reached 390 °C, the decomposition rate of PTFE increased, which resulting in the production of a small amount of tetrafluoroethylene, hexafluoropropylene and octafluorocyclobutane, etc. These gases caused much more voids within the samples sintered at 370 and 390 °C than that sintered at 380 °C, as shown in Figure 4.

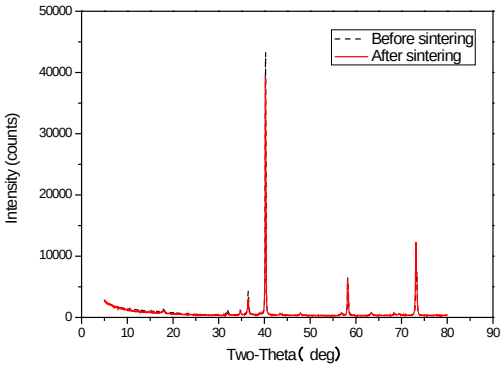
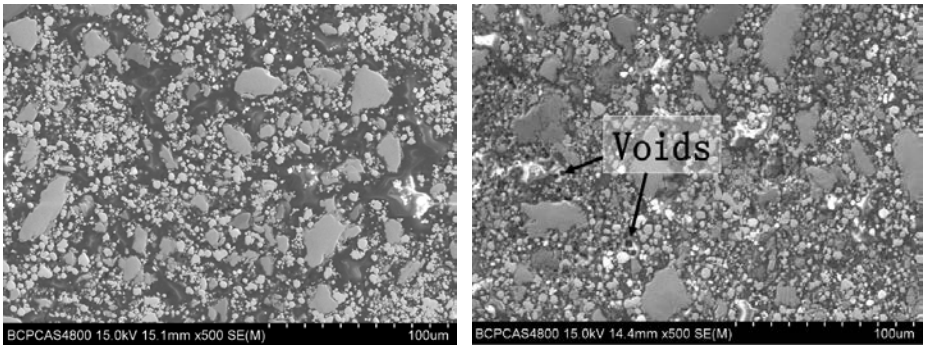


Figure 3: X-ray diffraction spectrum for sample before and after sintering.



(a) (b)

Figure 4: SEM images of 380 °C (a) and 390 °C (b)Zr/W/PTFE-1 sample.

Quasi-static compression tests with MTS (Model WDW-300) were carried at a strain rate range from 10^{-4} to 10^{-2} s^{-1} and these stress-strain curves are shown in Figure 5. All samples had identical initial dimensions of 10 mm diameter and 10 mm height.

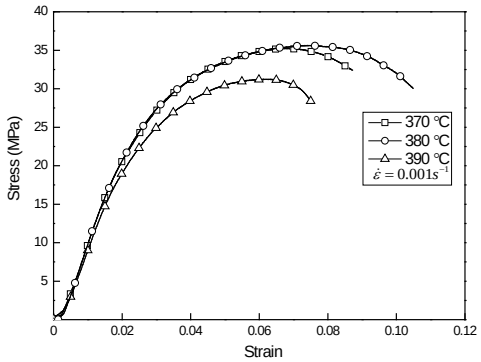


Figure 5: Compressive stress-strain curves of Zr/W/PTFE-1 sintered at different temperatures.

The mechanical behaviors of Zr/W/PTFE mainly depend on the matrix and quality of the interfaces between matrix and particles. PTFE sintering process is a phase transition process, during which crystal structures will turn into amorphous structure when the temperature is higher than 327 °C and recrystallize when the temperature is lower than 327 °C. Because of the lower crystallinity, the compressive strength of samples sintered at 370 °C was slightly

lower than that at 380 ^{o}C. The samples sintered at 390 ^{o}C had high porosity, many inner-flaw and relatively weak bond interface, which led to a significant reduction in the compressive strength of the composite.

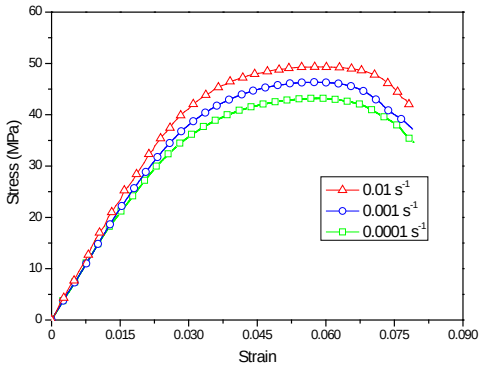
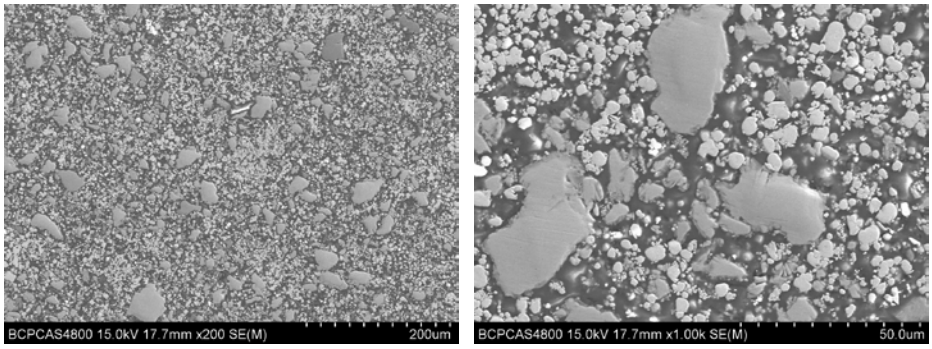


Figure 6: Stress-strain curves of Zr/W/PTFE-2 in quasi-static compression tests.

The stress-strain curves of the Zr/W/PTFE-2 composite indicate that the compressive strength exhibit a distinct strain rate effect, whose value increases from 43 MPa to 50 MPa with increasing strain rate, while the critical strain and Young's modulus are not sensitive to strain rate (Figure 6). The curves presented the typical elastoplasticity with no yield point and they can be broadly divided into elastic deformation region, inelastic deformation region and strain softening region.

3 RESULTS AND DISCUSSION

The initial microstructure of the composite is shown in Figure 7. The SEM images show that the Zr and W particles are evenly distributed in PTFE as the continuous matrix. The Zr particles can be distinguished because of its irregular shape with larger particle sizes of 37 μm. The W particles as bright features because of their high atomic number, which also can be distinguished.

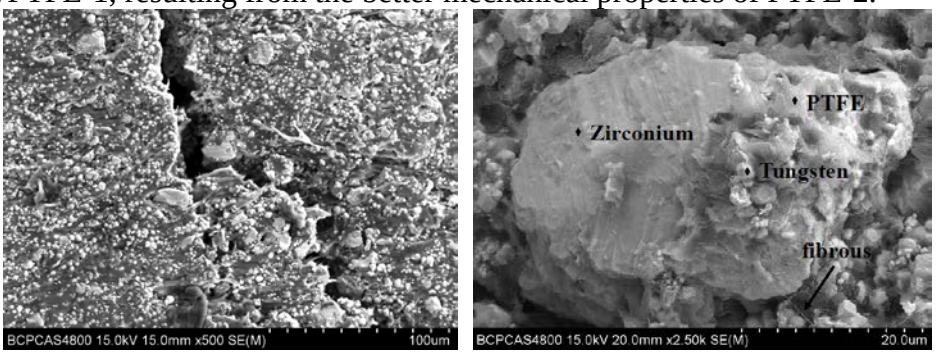


(a) (b)

Figure 7: SEM images of initial compact configuration at: (a) lower magnification; (b) higher magnification.

The side crack microstructure of the Zr/W/PTFE-2 sample after compression test is shown in Figure 8 (a). Large tensile deformations of the PTFE without transgranular fractures in the Zr particles and undeformed W particles can be observed near the cracks. The failure starts at the particles-PTFE interfaces and these tensile deformations prevent any further inward extension of cracks. Observation of a fracture surface shows the three constituents in

a clearer fashion (Figure 8(b)). The larger W particles are surrounded by W and PTFE, and some fibrous PTFE which tends to enhance the resistance to a propagating crack, can be found with a length of 5 μm. The Zr/W/PTFE-2 samples have higher compressive strengthen than Zr/W/PTFE-1, resulting from the better mechanical properties of PTFE-2.



(a) (b)

Figure 8: SEM images of the Zr/W/PTFE-2 sample after the quasi-static compression test: (a) overall view of side crack; (b) detail of fracture surface.

The stress-strain curves of the composite at different strain rates have the same change tendency. The compressive strength of the composite increases with increasing strain rate, while there is no obvious strain rate effect for critical strain and its value is almost a constant 0.06. The destruction of the sample is controlled by strain and a normalized method was adopted to study its constitutive. The normalized stress $\tilde{\sigma}$ is as follows:

$$\tilde{\sigma} = \sigma / \sigma_c \tag{1}$$

where, σ , σ_c are the compressive stress and compressive strength for the samples, respectively. The stress-strain curves of the composite at different strain rates after normalized are nearly coincide with each other, as is shown in Figure 9.

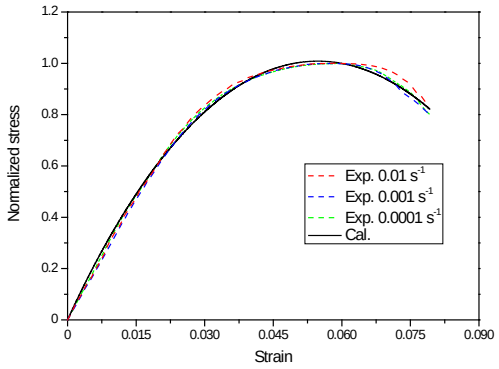


Figure 9. Stress-strain curves after stress normalized.

The normalized curves can be expressed using an elastic-viscoplastic model which is descibed as follows:

$$\tilde{\sigma} = A\varepsilon + B\varepsilon^n \tag{2}$$

The first item in the above equation characterizes the elastic stage features, and the second item represents the viscoplastic stage features. The parameters were obtained by

fitting the curves in Figure 8, and A=39.44, B=-268.33, n=1.876.

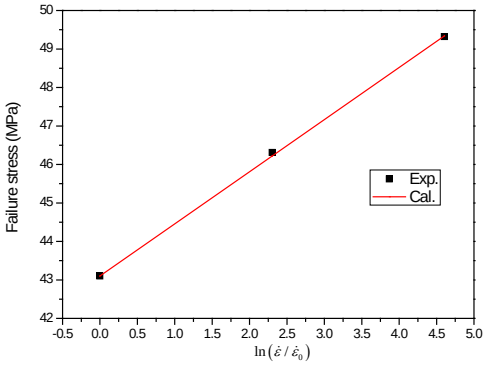


Figure 10: Relation between failure stress and logarithmic strain rates.

Figure 10 shows the relation between failure stress of quasi-static compression test and logarithmic strain rates. The linear fitting equation is as follows:

$$\sigma = \sigma_0 \left[1 + C\left(\dot{\varepsilon} / \dot{\varepsilon}_0\right)\right] \tag{3}$$

where, reference strain rate $\dot{\varepsilon}_0 = 10^{-4} s^{-1}$, $\sigma_0 = 43.1MPa$ and C=0.03144 by fitting the experimental results.

With consideration of the strain rate hardening effect, the quasi-static compressive mechanical behavior of Zr/W/PTFE composite can be described using the following formula:

$$\sigma = \sigma_0 \left(A\varepsilon + B\varepsilon^n\right)\left[1 + C \ln\left(\dot{\varepsilon} / \dot{\varepsilon}_0\right)\right] \tag{4}$$

The constitutive relation fit to quasi-static compressive data for the composite at different strain rates is illustrated in Figure 11. As can be seen from Figure 11, the elastic-viscoplastic constitutive relation has been established as Eq. (4), which can well describe the Zr/W/PTFE composite compressive mechanical behavior at low strain rates.

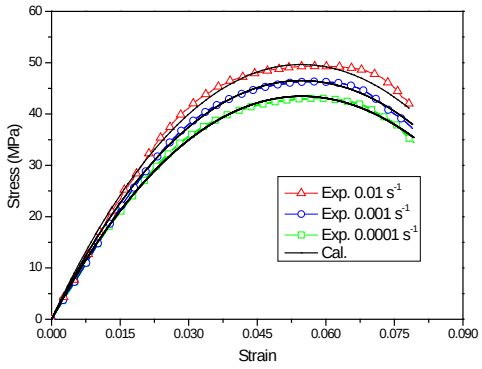


Figure 11: Comparison of experimental and constitutive relation results.

4 CONCLUSIONS

The Zr/W/PTFE granular composites were fabricated using the hot-pressing sintering

method without new products. The samples sintered at 380 ^{o}C have better performance, while higher or lower sintering temperaturem will result in lower density and reduced compressive strength. The composite displayed significant strain rate hardening effect and the stress-strain curves resulted from the quasi-static loading present elastic-plastic characteristics due to the nonlinear PTFE.

SEM images showed that the compressive failure of the composite was caused primarily by the PTFE fracture and interfacial debonding. The mechanical behaviors of the composite mainly depend on the matrix and quality of the interfaces between matrix and particles.

Finally, a normalized method was adopted and an elastic-viscoplastic constitutive relation with consideration to the strain rate hardening effect is established. The results showed that the equation can accurately describe the Zr/W/PTFE composite quasi-static compressive mechanical behavior.

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