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ARTICLE

Fabrication of Tungsten-Tin Alloy Powder and Its Explosive Consolidation

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Abstract: The preparation tungsten-tin alloy powder and its explosive consolidation were studied. In order to obtain tungsten-tin alloy powder, weldability between tungsten and tin was studied at first. Then, tungsten-tin alloy powder was prepared by heating tungsten powder and tin powder in strong alkali solution. Finally, the explosive consolidation of tungsten-tin alloy powder was carried out, and the detonation velocity of the explosive used in the experiment was measured with a continuous velocity probe. The results show that the detonation pressure of the explosive is about 3.24 GPa calculated by the measured detonation velocity. The density of the consolidated tungsten-tin alloy block is 16.017 g.cm^{-3}. The hardness (HV) values of the tungsten-tin alloy block are in the range of 2100~2470 MPa.

Key words: explosive consolidation; tungsten-tin composite; welding; powder metallurgy

Tungsten and tungsten alloys possess superior properties, such as low thermal expansion, good wear resistance, and good corrosion resistance. Therefore, these materials are widely used in aerospace, military equipment, electronics, and chemical engineering[1-4]. Existing studies focus on tungsten alloys containing refractory metal[5], whereas despite their advantages[6], few reports are centered on tungsten alloys that contain low-melting-metal. Tungsten-tin alloys are categorized under tungsten alloys with low-melting metal. The use of tin, a binder phase that combines high-hardness tungsten particles together, facilitates the acquisition of high-tungsten-content alloy. Tungsten tin alloys hold broad applications. This material can be used to prepare penetrators or shape-charges[7]. In shape-charges made of tungsten tin alloys, tin melts during the jet process. This occurrence prevents the tungsten particle stream from dispersing. To lower the negative impact on the environment, some scholars proposed using tungsten tin alloy bullets to replace lead bullets[8,9]. Tungsten tin alloy can also be used as a co-solvent in ore smelting or material sweating. To produce tungsten-tin block materials, this paper proposes a processing technique, which is simple and consumes low energy. The tungsten-tin alloy particles were prepared at first, the bonding of tungsten and tin before the explosive consolidation could improve the strength of the tungsten-tin block, then explosive compaction was used to fabricate tungsten-tin block. The tungsten-tin alloy block density reaches 96.5% of the theoretical density.

1 Experiment

1.1 Weldability between tungsten and tin

Tungsten-tin alloy holds broad application prospects, but the traditional method of melting cannot produce tungsten-tin alloy (the melting points of tungsten and tin are 3410 °C and 232 °C, respectively, and the boiling point of tin is 2260 °C). Currently, some methods, such as mechanical alloying[10], sintering above 900 °C[11], and sintering above 930 °C under a hydrogen atmosphere[12], are used to produce tungsten-tin alloy. This paper presents a new method for welding tungsten and tin, as described by the following steps. First, a tungsten plate was covered with tin powder in an alumina crucible. Then, alkaline solution was poured into the alumina crucible. Finally, the alumina crucible was sintered to above 600 °C under an argon atmos-

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phere. The microstructure of a diffusion-bonded joint was observed by scanning electron microscopy (SEM) (Fig.1a). The bright areas correspond to tungsten particles, where as the relatively dark areas correspond to tin. The result shows the presence of tungsten particles in the tin.

The diffusion zone of tungsten and tin sintered at 600 °C is shown in Fig.1b. This finding was acquired through elemental Sn mapping, by electron probe micro-analyzer (EPMA) mapping of the cross section of the interface zone. Test result indicates that the interface zone of tungsten and tin diffusion-bonded joint includes a transition region on the tungsten side, a mid-diffusion region, and a transition region on the tin side. The mid-diffusion region is about 2 μm. The diffusion zone of tungsten and tin sintered at 800 °C is presented in Fig.1c. The mid-diffusion region in this specimen is wider than that of the specimen sintered at 600 °C. Unsintered and sintered (800 °C) tungsten plates are compared in Fig.1d. The plate on the right side is the sintered tungsten plate. The tungsten plate sintered in alkaline solution is encapsulated by tin, which is thinner than that of the unsintered plate. The diffusion of tungsten in tin accounts for the thinning of the tungsten plate. Analysis suggests that tungsten and tin can be welded under the proposed technology.

1.2 Manufacturing tin-encapsulated tungsten particles

The raw materials used in this study were tungsten and tin powders, and both had a particle size less than 74 μm. Fig.2 shows a schematic of the encapsulating process. The mass ratio was 9:1 (tungsten:tin), and the mixed powder composed of 90% tungsten and 10% tin was high-energy ball milled at a milling speed of 200 r/min for 1 h in a QM-BP planetary ball mill. The mass ratio for the steel balls and mixed powder was 1:1. The particles of tungsten and tin were mixed well during ball milling.

Alkaline solution was prepared using NaOH and KOH. Their mass ratio was 1:1. This alkaline solution was placed in an alumina crucible with the mixed powder, and the alumina crucible was sintered in an alumina tube furnace at 300 °C under an argon atmosphere. The heating rate was 5 °C/min, and the temperature was maintained for 1 h when it reached 300 °C. The mixed powder was then cooled in the furnace.

After sintering, tungsten-tin alloy particles were obtained, but the powder was impure. That is, alkali particles and alkali-soluble salt were present in the metal powder. Hence, the powder was washed several times with water to remove impurities and then dried in air.

The mixed powder was sintered at 800 °C without the alkaline solution. The succeeding steps were similar to the procedure described in the previous sections.

1.3 Explosive consolidation of tungsten-tin composite particles

Explosive consolidation is a method of preparing powder metallurgy materials. This method is a high-speed impact produced by detonation or explosive energy, acting on the

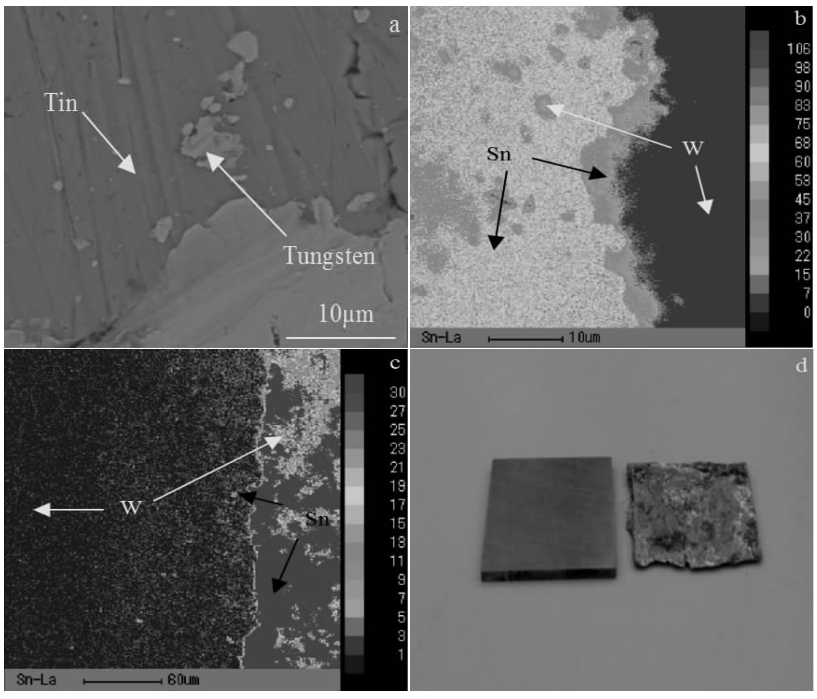


Fig.1 SEM microstructures of the diffusion-bonded joint (a); Sn mapping of interface zone for the cross-section specimens sintered at 600 °C (b) and 800 °C (c) by EPMA; unsintered and sintered (800 °C) specimens (d)

powder in the form of shock waves that make the powder compact and be sintered into a dense solid[13-15].

Some calculation methods for the minimum pressure (P_{min}) were used in explosive consolidation. We chose the Carroll-Holt model to simulate the P_{min}[16, 17]. The minimum pressure is determined by the following formula:

$$P_{min} = \frac{2}{3}\sigma_s \ln\left(\frac{\rho_0}{\rho_0 - \rho}\right) \quad (1)$$

Where σ_s is yield strength of particle material, ρ is bulk density after explosive consolidation, and ρ_0 is density of solid substance.

The relationship between pressure and density is shown in Table 1. The hardness (HV) of material is about $3\sigma_s$.

It can be seen that the hardness (HV) of the material is very important to explosive consolidation. But there is no data on the hardness (HV) of tungsten-tin material. In order to obtain the hardness (HV) of the tungsten-tin material, we used explosive consolidation to consolidate the tungsten-tin alloy powder.

The schematic illustration of explosive consolidation is shown in Fig.3. The initial density of the tungsten-tin alloy powder is 11.62 g.cm^{-3}. The inner diameter of the steel tube is 38 mm and the thickness of the steel tube is 2 mm, and the thickness of the explosive is 20 mm around the steel tube. The explosive used in the experiment is a ammonium nitrate fuel oil (ANFO) with a density of 0.8 g·cm^{-3}. The detonation velocity was measured by a continuous velocity probe[18]. The distance-time curve of detonation wave is shown in Fig.4. The curve shows that the detonation velocity ($D_{C\text{-}J}$) is not a fixed value, which increases gradually, and eventually reaches 3654 m/s. The detonation pressure ($P_{C\text{-}J}$) is determined by the following formula:

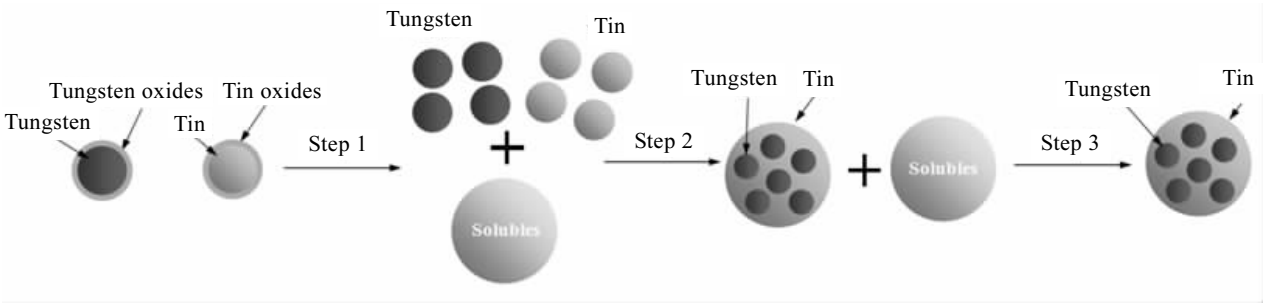
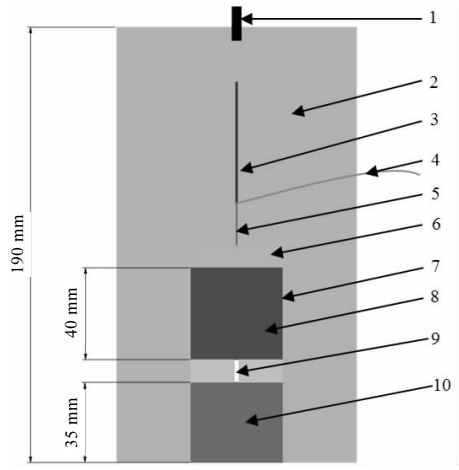


Fig.2 Schematic of the encapsulating process

Table 1 Relationship between pressure and density

ρ/ρ_0/%	P_{min}
95	$2.00\sigma_s$ (0.67HV)
99	$3.07\sigma_s$ (HV)
99.9	$4.61\sigma_s$ (1.54HV)



1 detonator; 2 explosive; 3 continuous velocity probe; 4 wire; 5 support structure of continuous velocity probe; 6 steel; 7 steel tube; 8 tungsten-tin alloy particles; 9 venthole; 10 steel block

Fig.3 Schematic illustration of explosive compaction

$$P_{C\text{-}J} = \frac{1}{K+1}\rho_e D_{C\text{-}J}^2 \quad (2)$$

Where ρ_e is density of ANFO, K value of ANFO is 2.3. $P_{C\text{-}J}$ is approximately 3.24 GPa.

2 Results and Discussion

2.1 Theoretical analysis of manufacturing tungsten-tin composite particles

Welding between tungsten and tin is the basis of the production of tin-encapsulated tungsten particles. Tungsten and tin powders are encapsulated with a layer of oxide in air as shown in Fig.5. The oxide layer prevents the welding between tungsten and tin. The oxide layers on the tungsten and tin surfaces are removed by alkaline solution in Step 1. The oxides then react with the alkaline solution and generate an alkali-soluble salt. In Step 2, the powder and alkaline solution are heated above the melting point of tin, turning tin into liquid. Atomic motion accelerates between the tungsten-tin interfaces at the specified temperatures. As a result, tungsten particles are encapsulated by tin. The water in the alkaline solution is evaporated during the heating. Hence, the alkali-soluble salt and small alkaline particles become incorporated into the metal powder. In Step 3, the

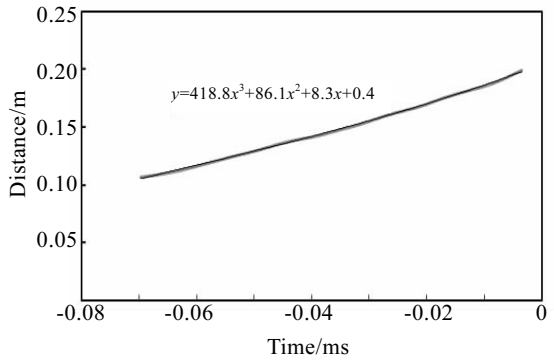


Fig.4 Distance-time curve of the detonation wave

powder is washed by water. Water can dissolve the alkaline particles, and the alkaline solution can dissolve the alkali-soluble salt.

The powder is washed several times and then dried in air. Finally, a pure tin-encapsulated tungsten particle powder is obtained. The main reaction equations are as follows (3)~(6):

$$WO_3 + NaOH \xrightarrow{300\ ^\circ C} Na_2WO_4 + H_2O \quad (3)$$

$$WO_3 + KOH \xrightarrow{300\ ^\circ C} K_2WO_4 + H_2O \quad (4)$$

$$SnO_2 + NaOH \xrightarrow{300\ ^\circ C} Na_2SnO_3 + H_2O \quad (5)$$

$$SnO_2 + KOH \xrightarrow{300\ ^\circ C} K_2SnO_3 + H_2O \quad (6)$$

2.2 Experimental analysis of manufacturing tungsten-tin composite particles

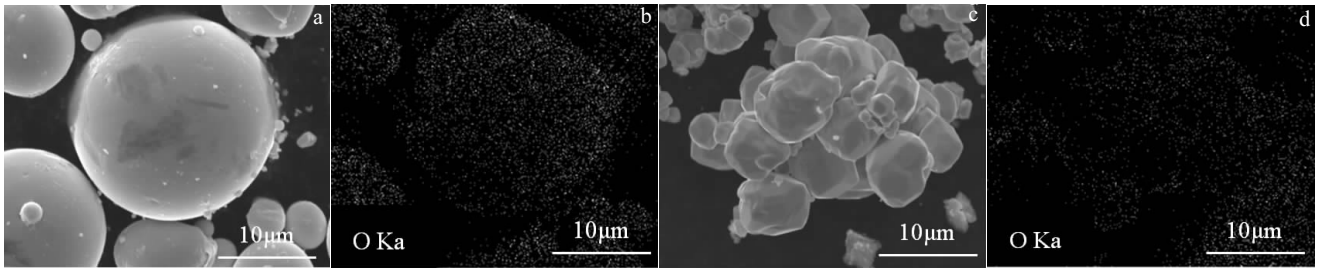


Fig.5 SEM image of tin particles (a); O mapping of tin particles (b); SEM image of tungsten particles (c); O mapping of tungsten particles (d)

In Fig.6, X-ray diffraction (XRD) analysis shows that the specimen sintered at 300 °C is pure. The microstructural characteristics of the sintered specimens were analyzed by SEM (Fig.7a~7d). As shown in Fig.7a, the tungsten particles are encapsulated by tin. The bright areas correspond to tungsten particles, and the relatively dark areas correspond to tin. Separation is not apparent at the interface zone (Fig.7b), indicating the strong bonding between tungsten and tin. The specimen sintered without alkaline solution is presented in Fig.7c and 7d. The images reveal that tungsten and tin do not bond thoroughly and remain numerous cracks. This poor bonding is due to the oxide layer on the metal powder surface, implying the need for an alkaline solution. The experiment verifies that the sintering temperature of tin-encapsulated tungsten particles (300 °C) is lower than that of tin-encapsulated tungsten plate (600 °C). This discrepancy may be mainly due to the much higher surface energy and the thinner oxide layer of the powder compared with the plate. Given these attributes, the powders bonded more easily than the plate at low temperatures.

2.3 Experimental analysis of explosive consolidation

The specimen after explosive consolidation is shown in Fig.8. The specimen length is 42 mm and the diameter is 32 mm. Fig.8b shows the cross-section of the specimen. The center of the specimen is not well compacted. The specimen was meas-

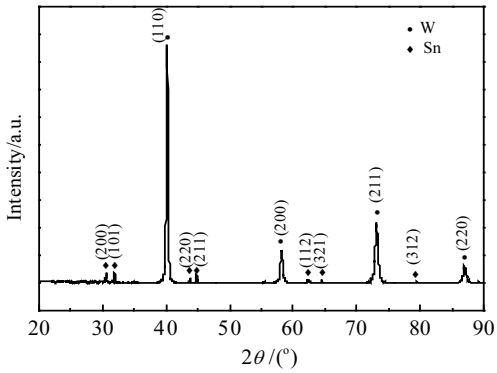


Fig.6 XRD pattern of tungsten-tin composite powder sintered at 300 °C with alkaline solution

ured by Archimedes' method, the mass of specimen was denoted as M_1, and the mass of the specimen measured in the water was denoted as M_2. The density of the specimen was obtained by the following equation:

$$\rho = \frac{M_1}{M_2}\rho_{water} \quad (7)$$

Density of the specimen is shown in Table 2.

Fig.9 shows SEM image of the prepared specimen. There are no cracks in the specimen, but some voids can be seen.

Hardness is an important performance index of metallic materials. It can be understood as the ability of a material to resist elastic deformation, plastic deformation, or damage, and can also be expressed as the ability of a material to re sist residual deformation and damage. Fig.10 shows a general view of the sample containing Vickers indentations, which were made under an indenter load of 500 g. The hardness (HV) values of the tungsten-tin alloying block are in the range of 2100~2470 MPa. The indentation pressure on the pores affects the microhardness of the sample. The hardness of the sample is more discrete because of the existence of pores. The Vickers hardness test results show that the hardness of tungsten-tin dense material is more than 2470 MPa. According to Carroll-Holt model, in order to obtain 99% of the theoretical density tungsten-tin bulk material, the P_{min} in the experiment needs more than 2.47 GPa.

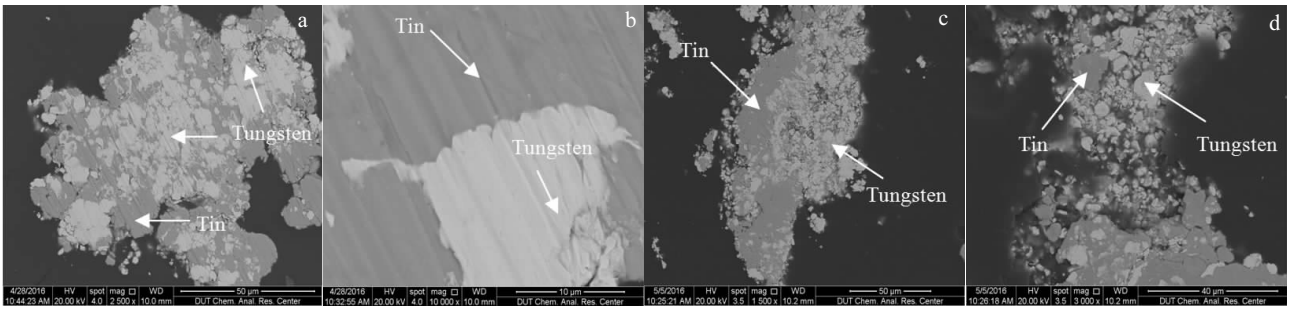


Fig.7 SEM images of specimen sintered at 300 °C with alkaline solution (a, b) and at 800 °C without alkaline solution (c, d)

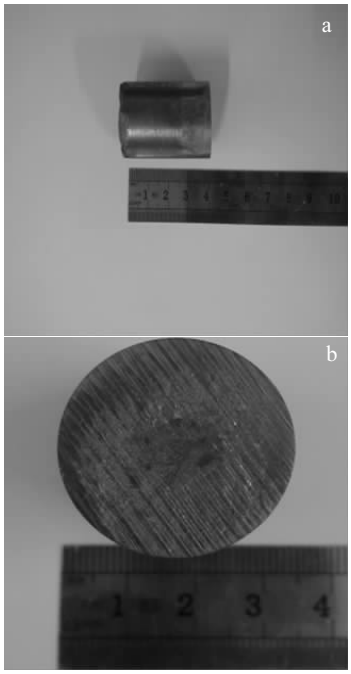


Fig.8 Size (a) and cross-section (b) of specimen after explosive consolidation

Table 2 Density of the specimen

M_1 / g	M_2 / g	ρ_{water} / g·cm^{-3}	Measured density/ g·cm^{-3}	Theoretical density/ g·cm^{-3}	Relative density/ %
325.673	20.333	1.0	16.017	16.598	96.5

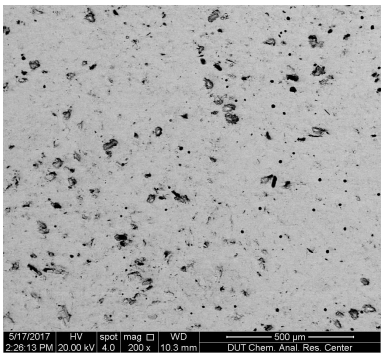


Fig.9 SEM image of prepared specimen

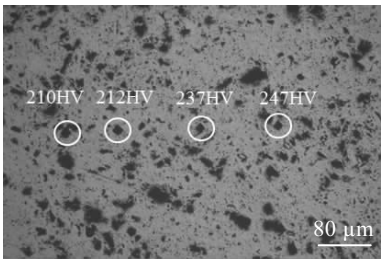


Fig.10 Variations of microhardness of the specimen

The $P_{C\text{-}J}$ of the explosive is 3.24 GPa that meets the pressure requirement of Carroll-Holt model, but the density of the tungsten-tin bulk material is only 96.5% of the theoretical density. The reason of the low density may be that

the Carroll-Holt model is just a simplified model, and the actual explosive consolidation process is very complex. In this experiment the density of the material is very high. When the voids between particles close, they absorb energy, the pressure becomes lower near the axis of the sample, so the center of the sample is not well compacted.

3 Conclusions

1) Welding tungsten plate with tin in alkaline solution below 600 °C proves the weldability of tungsten and tin. Microanalysis indicates that the welding type produced is under diffusion welding, and the diffusion region widens with the rise of sintering temperature.

2) A processing technology for producing tungsten-tin alloy particles is proposed. In the process, the oxide layers on the surfaces of the tungsten and tin powders are removed by an alkaline solution. Moreover, the tin encapsulates tungsten particles at 300 °C. The tungsten-tin alloy particles produced by this process technology are pure.

3) Tungsten-tin block is fabricated by explosive consolidation, a continuous velocity probe is introduced to measure the detonation velocity. The density of the sample is 16.017 $g\cdot cm^{-3}$. The hardness (HV) values of the tungsten-tin block are in the range of 2100~2470 MPa.

References

1 Gao H, Chen W, Zhang Z. *Materials Letters*[J], 2016, 176: 181

2 Hasegawa A, Fukuda M, Yabuuchi K *et al*. *Journal of Nuclear Materials*[J], 2016, 471: 175

3 Xu Yuxin, Han Xuguang, Zhao Xiaoxu *et al. Rare Metal Materials and Engineering*[J], 2016, 45(1): 122 (in Chinese)

4 Du Chengxin, Du Zhonghua, Zhu Zhengwang. *Rare Metal Materials and Engineering*[J], 2017, 46(4): 1080 (in Chinese)

5 Shen J, Li S, Zhai D *et al. Materials and Manufacturing Processes*[J], 2013, 28: 1240

6 Mohammed K S, Rahmat A, Ahmad K R. *Journal of Materials Science & Technology*[J], 2013, 29: 59

7 Shekhar H. *Central European Journal of Energetic Materials*[J], 2012, 9(2): 155

8 Thomas V G, Roberts M J, Harrison P T. *Ecotoxicology and Environmental Safety*[J], 2009, 72: 1031

9 Kalinich J F, Vergara V B, Emond C A. *Military Medicine*[J], 2008, 173: 754

10 Xia Z P, Shen J J, Shen Y Q *et al*. *Journal of Alloys and Compounds*[J], 2008, 448: 210

11 Saadat A R, Nishikawa O. *Journal of Applied Physics*[J], 1976, 47: 4726

12 Petrunin I E, Grzhimal'skii L L. *Metal Science and Heat Treatment*[J], 1969, 11: 24

13 Wang J X, Zhou N, Li B M *et al. Combustion, Explosion, and Shock Waves*[J], 2011, 47(3): 369

14 Prümmer R. *Materialwissenschaft and Werkstofftechnik*[J], 1989, 20(12): 410

15 Wang Zhanlei, Wang Huiping, Hou Zhonghua *et al. Rare Metal Materials and Engineering*[J], 2014, 43(5): 1051 (in Chinese)

16 Carroll M M, Holt A C. *Journal of Applied Physics*[J], 1973, 44(10): 4388

17 Vorozhtsov S, Vorozhtsov A, Kudryashova O *et al. Powder Technology*[J], 2017, 313: 251

18 Li K B, Li X J, Yan H H *et al*. *Measurement Science and Technology*[J], 2018, 29(11): 115901

钨锡复合粉末的制备与爆炸压实

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摘　要：研究了钨锡合金粉末的制备及其爆炸压实。首先，研究了钨与锡之间的可焊接性，从而为制备钨锡合金粉末提供了依据。然后，通过在强碱溶解中加热钨粉和锡粉制备出了钨锡合金粉末。最后，对钨锡合金粉末进行爆炸压实，并使用连续压导探针测量实验中所使用炸药的爆速。结果表明：使用测得的爆速计算出炸药的爆压约为 3.24 GPa。对爆炸压实后得到的钨锡块体进行表征，测得其密度为 16.017 $g\cdot cm^{-1}$，维氏硬度在 2100~2470 MPa 之间。

关键词：爆炸压实；钨锡复合材料；焊接；粉末冶金

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