



Synthesis of hypoxia-high density TZM alloy based on mechanochemistry and particle size distribution theories

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ABSTRACT

Molybdenum powders were high-energy ball milled for 3, 6, 9 and 12 h respectively, using two ball milling methods: (1) dry milled in vacuum and (2) wet milled in mixed solution of ethanol-polyethylene glycol. The effect of high-energy ball milling on relative density of titanium-zirconium-molybdenum (TZM) alloy was investigated. Particle size distribution and calculated proportion in each size range were designed according to the Dinger-Funk model, reaching the dense packing state. The effects of three different kinds of carbon source (graphite, stearic acid ($C_{18}H_{36}O_2$) and carbon nanotubes (CNTs)) on oxygen content and relative density were analyzed. The effects of carbon source on oxygen content were studied. After high-energy milling, fine molybdenum alloy powder particles and large amounts of dislocations and vacancies are helpful to improve TZM alloy density during solid sintering process. Doping carbon nanotubes (CNTs) into the TZM alloy as carbon source can improve its density and decrease oxygen content, which is more effective than graphite or stearic acid as carbon sources. Higher TZM alloy relative density results in lower oxygen content.

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1. Introduction

Titanium-zirconium-molybdenum (TZM) alloy contains 0.5–0.8 wt % titanium, 0.08–0.1 wt % zirconium, 0.01–0.04 wt % carbon and molybdenum balance. TZM has follows molybdenum characteristics, such as high melting point, elastic modulus, thermal and electrical conductivity, and temperature stability, along with low thermal expansion coefficient. Due to solution and precipitation strengthening achieved by additive elements, TZM alloy has high hardness and creep resistance at high temperature. Nowadays TZM alloy is highly desirable in astronautics, metallurgy, electronics and military applications [1–4].

However, oxygen on the surface and in the TZM alloy easily binds with the alloying elements, forming larger size metal oxide particles. Oxygen presence in TZM alloys increases the probability of carbide transforming into oxide, prevents even alloying elements

dispersion and causes cracks initiation. In addition, high oxygen content in TZM alloy increases the ductile-to-brittle transition temperature, reduces recrystallization temperature and toughness [5–8]. Thus, oxygen is the impurity element, which needs to be controlled in TZM alloy manufacturing.

Preparation of TZM alloys commonly uses melting and powder metallurgy methods. The grains of alloys fabricated by melting are coarse and large, resulting in low hardness and strength, which is unacceptable for special service conditions. On the contrary, the grain size of TZM alloys fabricated by powder metallurgy is fine and the mechanical properties are much better. However, TZM alloys fabricated by powder metallurgy have high porosity. Lots of voids exist in the alloy, where oxygen aggregates and cannot diffuse out of the alloy. This leads to increased oxygen content, degrading mechanical properties of TZM alloys. In addition, TZM alloys are commonly used at high temperature and pressure service conditions. With the expansion of the blow holes and voids, some of them may coalesce into larger voids, ultimately leading to cracks formation. In addition, some isolated voids can shrink, forming closure cavities, causing stress concentration.

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Based on the previous studies [9–12], particle size distribution theory of powder metallurgy is considered in this paper to investigate hypoxia-high density TZM alloy preparation by high energy ball milling. TZM alloy density and oxygen content are also discussed.

2. Experimental procedure

2.1. Design composition of TZM alloy

Chemical composition of the TZM alloy is listed in Table 1. Molybdenum, titanium and zirconium powders are at least 99.99% pure. TiH_2 and ZrH_2 in place of pure elemental components have been used as the starting materials for the TZM alloy preparation. Carbon in sample 1 came from graphite powder with a minimum purity of 99% and 400 mesh particle size. Stearic acid was utilized instead of graphite powder in sample 2 using liquid-solid doping method for adding carbon into the alloy. Sample 3 was prepared with carbon nanotubes (CNTs) as the carbon source.

2.2. High energy ball milling

The alloy powders were milled in a planetary ball mill (QM-1SP4, China) for 3, 6, 9 and 12 h. The labels of ball milling samples are listed in Table 2. To prevent iron contamination due to steel balls and jar, the milling balls and jar were made of stainless steel with high chromium content. The size of the balls was $\Phi 2$ mm, $\Phi 5$ mm and $\Phi 10$ mm, respectively. It contained the mixture of balls and powder with a ball to powder weight ratio of about 5:1. The milling speed was 135 rpm. Dry milling in vacuum and wet milling in a mixture solution of ethanol and polyethylene glycol (PEG) were used.

2.3. Particle size distribution

Based on the dense packing Dinger-Funk equation [13–16], molybdenum powder proportion and particle size distribution were calculated to achieve dense packing state. Molybdenum powder starting material was screened by the particle size from fine to coarse. Molybdenum powder in each particle size class was weighed according to the calculated dense packing.

2.4. Mixing materials

Comparative tests were performed with graphite, stearic acid and CNTs as carbon source. Sample 1 used solid-solid way to mix molybdenum, TiH_2 , ZrH_2 and graphite powders. The alloy powder was mixed for 2 h in the three-dimensional mixer. Sample 2 used solid-liquid mixing. First, TiH_2 and ZrH_2 powders were mixed into molybdenum starting material and then fully dissolved stearic acid crystals in ethanol were added. The mixture was dried for 4 h at 70 °C in a dryer. Sample 3 mixture was similar to sample 1, but CNTs in sample 3 were used in place of graphite as carbon source (graphite, stearic acid and CNTs had equal molar ratio).

Table 1
Design composition of TZM alloys in wt%.

No.	Ti	Zr	C (graphite)	C (Stearic acid)	C (CNTs)	Mo
1	0.5	0.08	0.06	—	—	Bal.
2	0.5	0.08	—	0.3	—	Bal.
3	0.5	0.08	—	—	0.06	Bal.

Table 2
Ball milling sample labels.

Medium	3 h	6 h	9 h	12 h
Air	A ₃	A ₆	A ₉	A ₁₂
$\text{CH}_3\text{CH}_2\text{OH} + \text{PEG}$	C ₃	C ₆	C ₉	C ₁₂

2.5. Powders reduction, compression molding and sintering

Reduction was performed for 4 h at 950 °C in a reduction furnace under hydrogen atmosphere. Powder was filled into the die mold, and pressed using the vertical 500 tons YT79-500 hydraulic press (Tianjin Tianduan Hydraulic Co., Ltd., China) with 180 MPa for 5 s. Sintering was performed in the HM3002 intermediate frequency induction furnace (Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, China). Sintering was done in the 99.99% pure hydrogen environment to expel air from the furnace, along with adsorbed gases, including water vapor and oxygen produced during the heating process, low melting temperature impurities and hydrogen generated during titanium hydride and zirconium hydride heating. Sintering temperature was held at 2100 °C for 4 h and the whole sintering process had 4 temperature plateaus.

2.6. Characterization

Oxygen content was tested by magnetomotive oxygen content analyzer (TC306, China) with 8 KVA power, 120–180 s analysis time and ± 0.5 ppm accuracy. Morphology, particle size, microstructure and element mapping of milled powder and alloy sheets were studied by scanning electron microscope with energy dispersive spectroscopy (SEM-EDS, JSM6700, Japan). TZM alloy density and porosity were calculated based on the Archimedes principle.

3. Results and analysis

3.1. Effect of ball milling and holding time on the state of molybdenum powder

Powders milled by dry milling in vacuum and wet milled in ethanol + PEG mixture solution were studied, respectively. The effects of the different ball milling methods and milling time of 3 h, 6 h, 9 h and 12 h on TZM alloy oxygen content were investigated. Fig. 1 shows SEM images of molybdenum powder morphology obtained via different ball milling time in vacuum and ball milling with ethanol + PEG for 9 h.

There are great changes in molybdenum powder particle morphology seen in Fig. 1. Alloy particle size has been refined with milling time increase. Serious lattice distortions happened in grains, leading to a large amount of defects, such as dislocations and vacancies. During solid phase sintering, fine particles and defects interact with each other and could improve alloy densification.

During milling, alloy powder particles have been subjected to impact, friction and compression from grinding balls, causing nearby particles to form surface cracks, resulting in particles size refinement. Particles are constantly broken and refine with milling time. However, particles can not get finer with more milling in case they reach the minimum size limit. This happens because the newly-formed cracks are usually smaller, requiring higher fracture stress. At a certain point fracture stress can exceed plastic deformation stress and particles will deform plastically instead of breaking. Thus, excessive milling time is meaningless, and would only lead to increased energy consumption. As seen in Fig. 1(b) through 1(e), particles size gets finer from 3 to 9 h milling time.

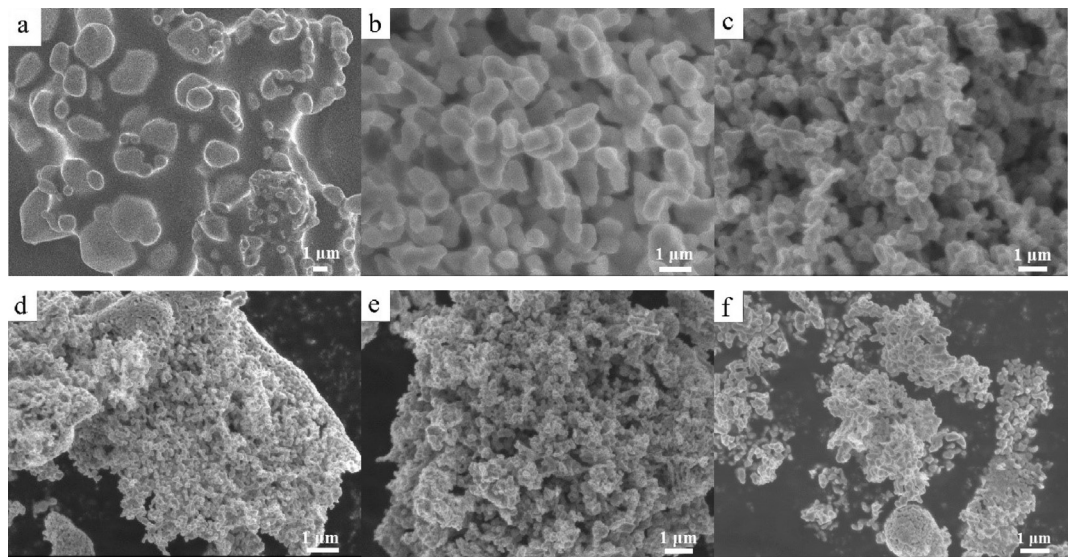


Fig. 1. Morphology of molybdenum powder obtained via different milled time in vacuum: a) not milled; b) 3 h; c) 6 h; d) 9 h; e) 12 h dry milled and f) 9 h milled with ethanol + PEG.

Comparing Fig. 1(d), (e), the change in particles size is not obvious. This shows that particles size reach a size limit and extending milling time plays a minor role in particles thinning when the milling time reached 9 h.

During milling in vacuum, surface energy of the particles increases and particles have high surface activity accompanied by the agglomeration phenomenon. The surface of powder particles can be easily oxidized, which can increase oxygen content of the TZM alloy. Adding organic solvent with smaller surface tension can help disperse powder particles, reduce powder agglomeration. Organic solvent coated on the surface of the particles can also prevent powder particles oxidation.

By comparison, powder particles agglomeration in Fig. 1(d) is more significant than in Fig. 1(f). Adding polyethylene glycol electrolyte dispersant to powders and vacuum dry grinding of alloy powder particles effectively reduce particles agglomeration.

3.2. Particle size distribution effect on TZM alloy density

Dinger and Funk introduced finite small particle size and modified the Andreasen equation:

$D = D_S$ (1)

$\frac{CPFT}{100} = 0$ (2)

$D = D_L$ (3)

$\frac{CPFT}{100} = 1$ (4)

$\frac{CPFT}{100} = \frac{\left(\frac{D}{D_L}\right)^n - \left(\frac{D_S}{D_L}\right)^n}{\left(\frac{D_L}{D_L}\right)^n - \left(\frac{D_S}{D_L}\right)^n}$ (5)

$\frac{CPFT}{100} = \frac{(D^n - D_S^n)}{(D_L^n - D_S^n)}$ (6)

here, CPFT is the accumulation volume fraction less than a certain size in %, D is each class characteristic particle size, D_S is the minimum particle size, D_L is the maximum particle size and n is distribution module.

In this study, after ball milling of the alloy powder the following values were taken: D_L = 74 μm and D_S = 27 μm, according to the 4 levels 27–37 μm; 37–48 μm; 48–74 μm and >74 μm. Characteristic particle sizes at all levels were obtained as 66 μm; 48 μm; 37 μm and 32 μm. According to the theory of continuous size distribution of particles, the value of n is in the range of 0.33–0.55, and the porosity of the actual distribution is the smallest. In the present study, n was obtained as 0.33; 0.37; 0.41; 0.45; 0.49; 0.53 and 0.57. The conditions are as follows: the material is the same raw material, the material density is basically unchanged before and after ball milling, and the mass and volume fractions of the material are all the same.

By using the Dinger-Funk equation, the theoretical formula of the particle size distribution of the TZM alloy powder was calculated. The calculation results are shown in Table 3. Theoretical calculation results of different n values correlation with the particle size composition are shown in Fig. 2.

As seen from Fig. 2, when the particles size is 48 μm and >74 μm, n value increases with particles volume fraction. When the value of n is 0.33, 48 μm particle volume fraction is 38.6%, when the value of n increases to 0.57, the volume fraction increases to 40.44%. When the n value is 0.33, the volume fraction of >74 μm particles is 9.05%,

Table 3
The proportion of each particle size distribution class.

D _n ~ D _{n-1} /μm	n						
	0.33	0.37	0.41	0.45	0.49	0.53	0.57
>74	9.05	9.21	9.35	9.5	9.66	9.81	9.89
48–74	38.6	38.94	39.28	39.61	39.94	40.27	40.44
37–48	25.21	25.12	25.03	24.94	24.85	24.75	24.7
27–37	27.69	26.67	26.27	25.88	25.49	25.1	24.93

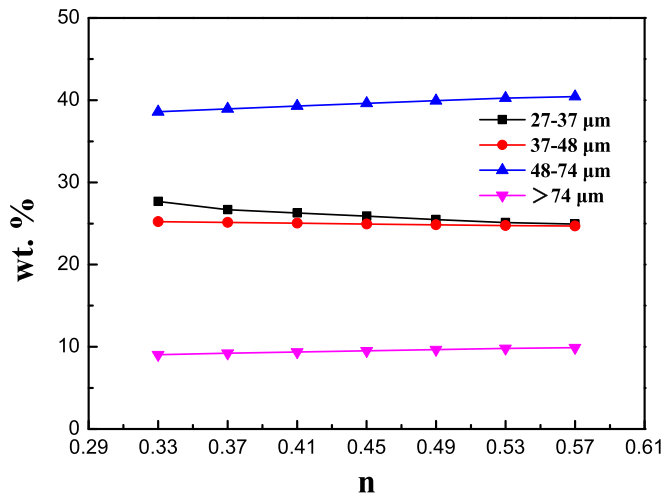


Fig. 2. Results of particle size distribution calculation for different n values.

and the n value increases to 0.57 when the volume fraction increases to 9.89%. For the particles in the 37–48 μm range the volume fraction of 25% does not change much with the n value. The particle volume fraction of in the 27–37 μm size range decreases with the n value. When the n value is 0.33, the volume fraction is 27.69%, and when the n value increases to 0.57, the volume fraction decreases to 24.93%, a decrease of about 3%. The change of the particles volume fraction with the n value is small, on the order of 2–3%, and for the 27–37 μm volume fraction range is less than 1%. For the particle size of 48–74 μm and >74 μm , large particles size fraction is about 50%, and for the 37–48 μm and 27–37 μm particle size, the sum of large and small particles volume fraction is about 50%. Large particles are uniformly distributed in the alloy, accounting for about 50% of the alloy mass. Medium and small particles are distributed in the gaps between adjacent larger particles, according to “drill gap” theory, decreasing alloy porosity. As a result, the internal structure of the alloy is more compact, and the relative density of the alloy is increased.

Archimedes principle is used to test the measured density of different TZM alloys, and the ratio of the measured density to the theoretical density of the alloys is calculated. Thus, the relative density of the alloy is obtained. The relative density is used to evaluate the density of the alloy. Oxygen content of the TZM alloy was tested by the TC306R oxygen analyzer, listed in Table 4. Relative density and oxygen content are shown in Figs. 4 and 5.

Fig. 3 shows that when the distribution modulus n value is near 0.37, the relative density of the alloy reaches the maximum value, and the system reaches the most closed packed state with continuous distribution of the maximum particle density. The highest degree of densification of alloy is reached and the alloy porosity is the lowest.

Fig. 4 shows that when the n value is near 0.37, oxygen content of the alloy reaches the minimum value. TZM alloy has high degree of densification, and in the nucleation process, the grains are closely

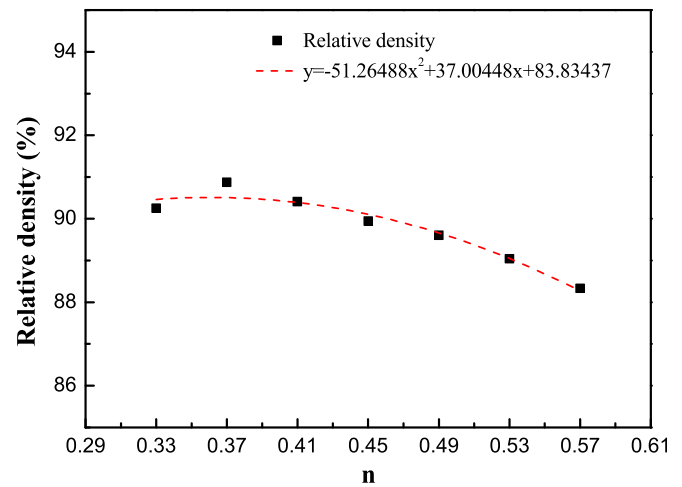


Fig. 3. Relative density of TZM alloy prepared by particle size distribution proportion calculated for different n values.

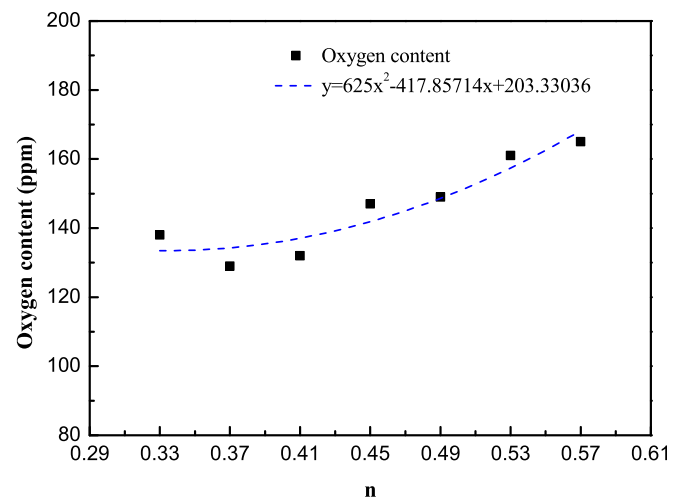


Fig. 4. Oxygen content of TZM alloy prepared by particle size distribution proportion calculated for different n values.

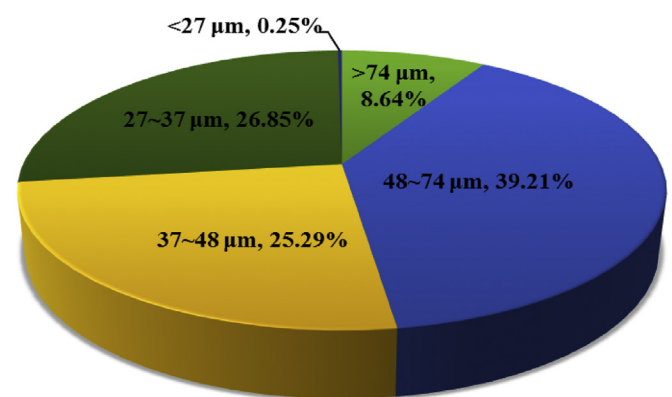


Fig. 5. Optimum proportion of particle size distribution.

Table 4
Relative density and oxygen content of TZM alloy prepared by particle size distribution proportion calculated for different n values.

Result	n						
	0.33	0.37	0.41	0.45	0.49	0.53	0.57
Relative Density, %	90.25	90.87	90.41	89.94	89.6	89.04	88.33
Oxygen content, ppm	138	129	132	147	149	161	165

arranged with compact internal structure, lower number of pores and holes, and thus reduced free oxygen content in the alloy. Therefore, the degree of TZM alloy densification has a great influence on the oxygen content of the alloy. The denser the alloy, the

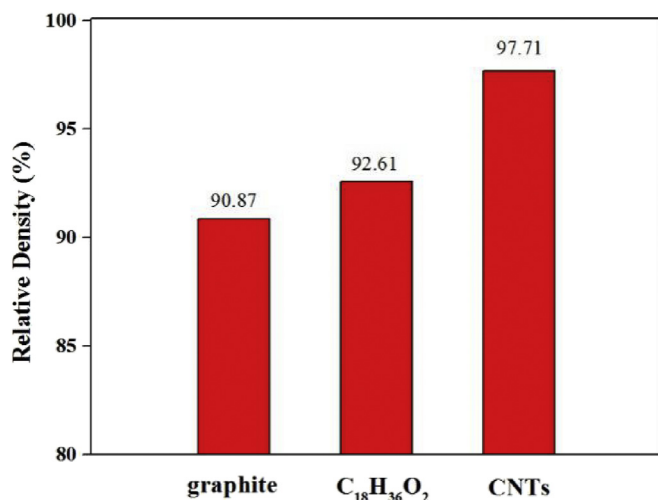


Fig. 6. Relative density of TZM alloy prepared with three kinds of carbon sources.

lower the porosity of the alloy with less pores and holes and lower free oxygen content. On the contrary, more porous structure has higher oxygen content.

Research results show that for the modulus of distribution, $n = 0.37$, TZM alloy is most dense with lowest oxygen content, according to the accumulation system of particle gradation optimization model and the Dinger-Funk equation. The best matching ratios of particle sizes are shown in Fig. 5.

The relative density of TZM alloy prepared by the traditional technology is about 75%, and oxygen content is about 500–600 ppm. According to particle gradation ratio of ingredients, TZM alloy relative density reached 90.87% maximum with 15% increase in relative density and lowest 129 ppm oxygen content. Oxygen content was reduced by more than 400 ppm compared with traditional TZM alloy. It can be seen that the particle size distribution can significantly improve the relative density of the alloy, and can greatly reduce the oxygen content of the alloy.

3.3. Effects of different carbon sources on the densification degree of TZM alloy

Graphite, stearic acid ($C_{18}H_{36}O_2$) and carbon nanotubes (CNTs) were used as the carbon source. Effects of different carbon source on the density and oxygen content of the alloy were studied. Fig. 6 compares the relative density of TZM alloy prepared with three

different forms of carbon source.

TZM alloy relative density increases from graphite to stearic acid, to carbon nanotubes as carbon sources in Fig. 6. Compared with graphite, using stearic acid as the carbon source increased the relative density of the alloy by 1.7%–92.61%. Using carbon nanotubes as the carbon source improved by the alloy relative density by an additional 6.8%, to 97.71%. Graphite has hexagonal layered structure, and its adsorption ability is weak with larger 30–40 μm powder particles. Graphite and molybdenum powders cannot be closely arranged, and there is a large gap between the particles, thus the degree of the alloy densification is low.

When stearic acid solution was used as the carbon source, the alloy powder was fully infiltrated, and the contact area between the stearic acid and the alloy powder was increased with uniform distribution of the stearic acid molecules in the alloy. Stearic acid is an organic saturated fatty acid with a certain viscosity conducive to the bonding between the particles, which can reduce the gap between the powder particles. However, as the solid phase sintering was carried out, the organic acid was heated and decomposed. Part of carbon was dissolved into the matrix to form metal carbide particles, and the other part was discharged in the form of CO_2 and H_2 . Gasses discharge could cause voids in the alloy.

Carbon nanotubes were also used as the carbon source because the surface area and the surface activity of the carbon nanotubes are high. The surface of the carbon nanotube powder had strong adsorption capacity, allowing close packing of CNTs with the alloy powder. The particle size range of carbon nanotubes in 2–100 nm, and they can fill the gaps between the alloy powder particles, significantly improving alloy density and microstructure.

Fig. 7 shows SEM images of the TZM alloy prepared with stearic acid and CNTs, respectively. Fig. 7(a) shows many holes and voids with added stearic acid. These holes are from the initial stage, where the gaps between the adjacent particles were not filled completely. During the solid phase sintering process, the organic acid in the matrix is heated and decomposed to form volatile gas, forming holes. The presence of these holes degrades mechanical properties and causes free oxygen aggregation, followed by internal holes surface oxidation.

Fig. 7(b) shows the surface of the TZM alloy with carbon nanotubes and lower number of holes and cracks. Carbon nanotube powder better fills the gaps between the alloy particles, resulting in more compact structure. The melting point of the carbon nanotubes is 3593 $^{\circ}C$, and they cannot be decomposed into volatile gas during the solid phase sintering process. At the same time, carbon nanotubes have larger surface energy, which significantly speeds up the formation of bonds between the particles, thus increasing the alloy density.

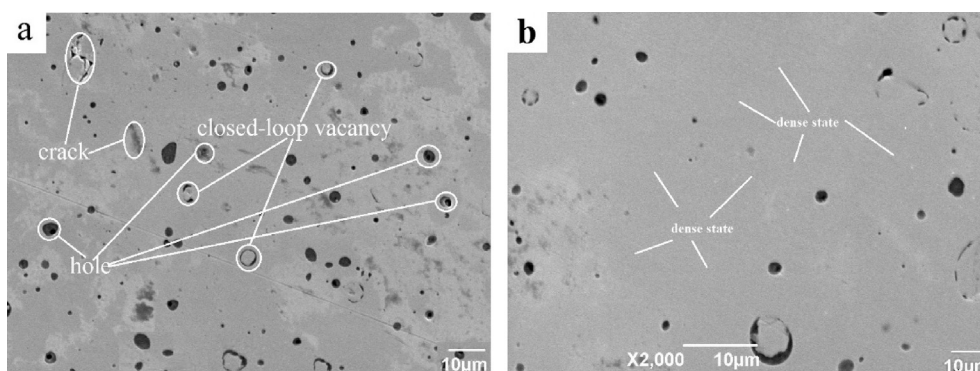


Fig. 7. SEM photograph of TZM alloy prepared with: a) stearic acid and b) CNTs.

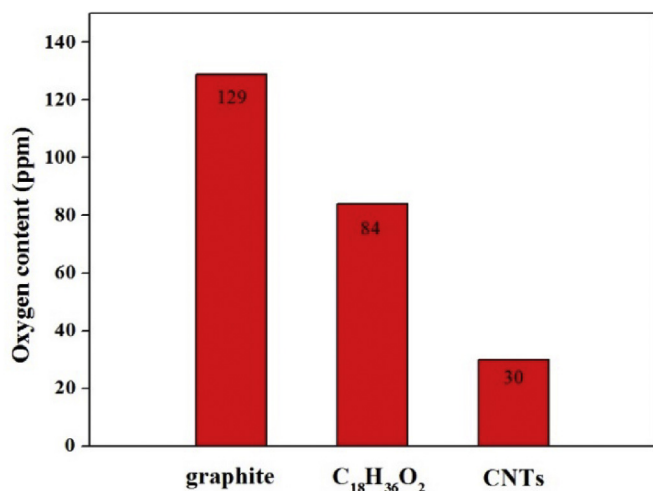


Fig. 8. TZM alloy oxygen content test result for different kinds of carbon source.

3.4. Effect of different carbon sources on oxygen content of TZM alloy

After the process of ball milling and particle size grading, TZM alloys with three different carbon sources were prepared by adding corresponding amounts of graphite powder, stearic acid and carbon nanotube powder according to Table 2. Oxygen content of three kinds of TZM alloys was tested by the TC306R oxygen analyzer, and the results are shown in Fig. 8.

In Fig. 8 can see that the oxygen content of stearic acid and carbon nanotubes can be below 100 ppm. Oxygen content of TZM alloy with carbon nanotubes as carbon source was only 30 ppm. Compared with the TZM alloy prepared by the other two kinds of

carbon sources, the oxygen content was significantly decreased. When using stearic acid as the carbon source, the oxygen content of the alloy was 84 ppm. Oxygen content of TZM alloy prepared by graphite as carbon source was the highest at 129 ppm.

Element distribution of TZM alloy using stearic acid and carbon nanotubes as carbon source was analyzed by energy dispersive spectroscopy, shown in Figs. 9 and 10.

Irregular shape carbon and titanium elements distribution is visible Figs. 9 and 10. It is inferred that the alloy solid solution is formed during the sintering process of carbon, titanium and molybdenum matrix, and the solid solution is mainly found at the grain boundaries. Distribution of oxygen is similar to carbon and titanium. This is due to the presence of oxygen in the alloy, mainly in the form of titanium and zirconium oxides. In addition, there is a small amount of free oxygen in the alloy internal pores.

The reason for the difference of the oxygen content of the TZM alloy, which used two kinds of carbon sources is that carbon distribution is uniform in the TZM alloy with added carbon nanotubes, while carbon distribution is concentrated in the TZM alloy with added stearic acid. Stearic acid is heated to decompose during the solid state sintering process, and the alloy is discharged through the pores, forming volatile gas. The number of carbon atoms in the TZM alloy with stearic acid as carbon source is less than with carbon nanotubes. As a result, the loss of carbon atoms in the metal oxide can be reduced in some of the alloys. In the solid phase sintering process, carbon nanotubes will not decompose into volatile gases. Carbon nanotube powder has a large number of active atoms, which reduces the activation energy of alloy surface atoms, thereby reducing oxygen content in the alloy.

4. Conclusions

After ball milling, the particles are refined. Refinement of particles and large number of internal defects in the solid phase

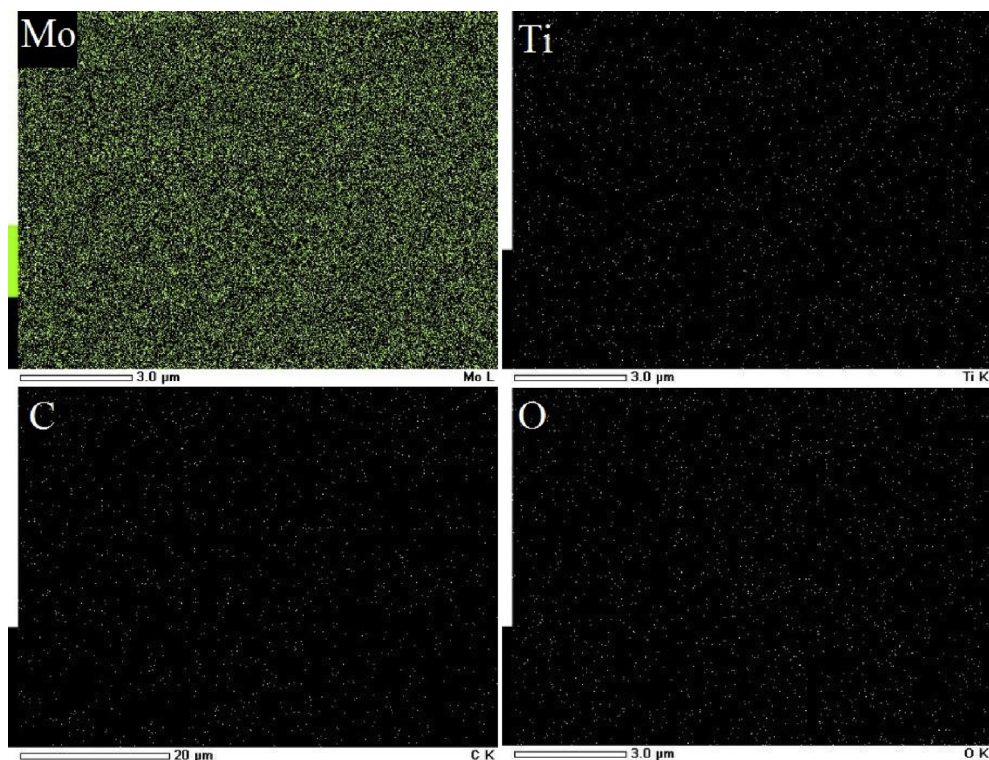


Fig. 9. Element mapping analysis of TZM alloy made with stearic acid as the carbon source.

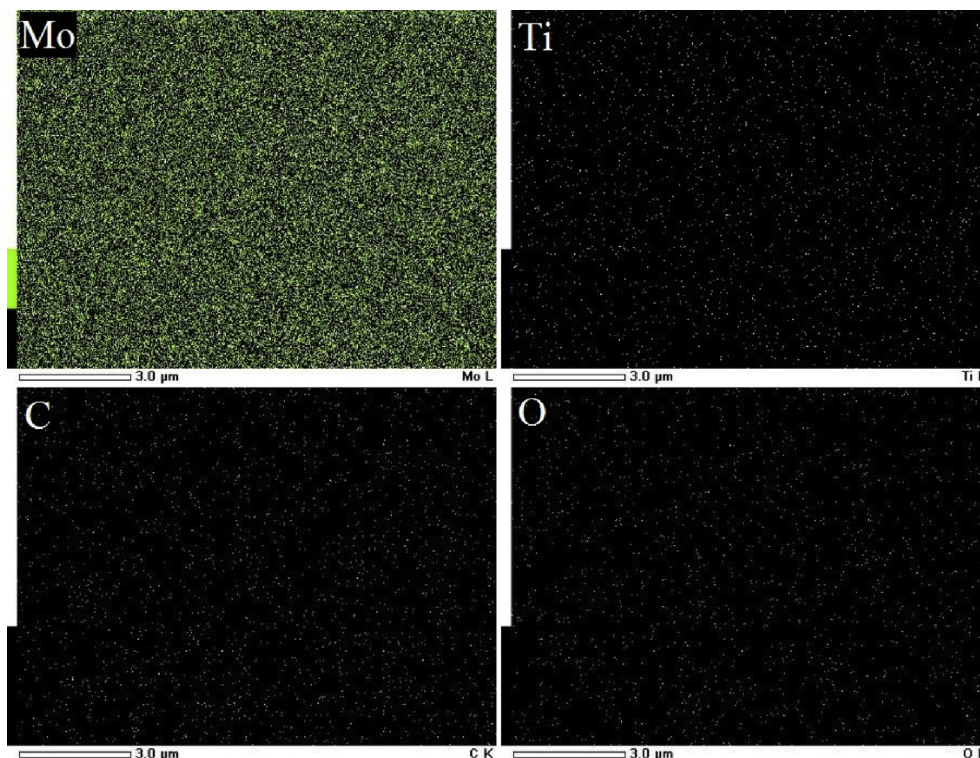


Fig. 10. Element mapping analysis of TZM alloy made with CNTs as carbon source.

sintering process help to improve the density of the alloy. When the minimum particle size is reached, the ball milling time is increased, and the powder particles cannot be further refined. The best ball milling time for the TZM alloy is 9 h. Relative alloy density can be increased by more than 15% with the addition of carbon nanotubes as carbon source compared with the traditional graphite process.

The distribution modulus n is in the vicinity of 0.37, in accordance with the accumulation system of particle gradation optimization model and the Dinger-Funk equation. Calculated TZM alloy particle gradation ratio of ingredients allows reaching 90.67% relative density and 129 ppm oxygen minimum content. The theoretical ratio of the best particle size is: 9.21% ($>74 \mu\text{m}$): 38.94% (48–74 μm): 25.12% (37–48 μm): 26.67% (27–37 μm).

Different ways of introducing carbon leads to different density and the oxygen content of the alloy. With graphite as the carbon source, the relative density of the TZM alloy was 90.67%. Using stearic acid as the carbon source, the relative density of the alloy was increased to 92.61%. Using carbon nanotubes as the carbon source, the relative density of the alloy can reach 97.71%. The denser the alloy, the lower the porosity with less holes and cracks lower oxygen content.

When the density of TZM alloy is high, the amount of voids and blow holes is low. Consequently, oxygen cannot diffuse into the alloy. Density has a significant effect on the oxygen content of TZM alloy. The higher TZM alloy density is, the less free oxygen exists in alloy, and the lower overall oxygen content is.

Conflict of interest

The authors declare that they have no conflict of interest.

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