Rare Metal Materials and Engineering
Volume 46, Issue 9, September 2017
Online English edition of the Chinese language journal

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(9): 2389-2394.

ARTICLE

Effect of CNTs-Assisted Ball Milling on Morphology and Oxidation Behavior of Zr Powders

Kang Xiaoli[1,2], **Zhu Guoling**[2], **Yang Fan**[1], **Jiang Xiaodong**[1], **Yi Zao**[2], **Tang Yongjian**[1]

[1] Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang 621900, China; [2] Joint Laboratory for Extreme Conditions Matter Properties, Southwest University of Science and Technology and Research Center of Laser Fusion, CAEP, Mianyang 621900, China

Abstract: Morphology evolution and oxidation behavior of Zr powders milled with and without CNTs for different time were compared. XRD and SEM were used to determine the phase composition and morphology of obtained Zr and Zr/CNTs powders. Thermogravity (TG) analysis was applied to evaluate the thermal oxidation behavior of Zr and Zr/CNTs. Results show that the phase composition of Zr after milling is not influenced by adding CNTs, but the morphology and oxidation behavior of Zr are influenced. In case of milling without CNTs, particle size of Zr continues to reduce from more than 10 μm to about 2~3 μm when milling time increases from 1 h to 3 h. In case of CNTs-assisted milling, the particle size reduction of Zr is not obvious until milling time is prolonged to 3 h. This is because those CNTs adhered on the surface of Zr or CNTs-induced agglomerations among Zr prohibit the mechanical impact and fracturing effects of milling balls on Zr particles. Compared with direct milling of Zr, when the obtained Zr has similar particle size, adding CNTs lowers the onset oxidation temperature and peak exothermic temperature of Zr powders by 11~37 ℃, depending on milling time. This is ascribed to the high heat conductivity of CNTs which favors heat transfer between Zr particles. At the same time, oxidative mass gain of Zr/CNTs is slightly lower than that of the corresponding pure Zr when milling time is less than 2 h and then this trend reverses. The initial decrease in mass gain of Zr in Zr/CNTs mixtures under shorter milling time is related to two factors: one is CNTs-induced agglomerations of Zr, which prohibits the contact of Zr with oxygen and thus decreases the degree of oxidation, and the other is the delayed particle size reduction of Zr in Zr/CNTs mixtures. The subsequent reversal in mass gain for pure Zr and Zr/CNTs is due to the positive effect of particle size reduction of Zr in Zr/CNTs on its thermal oxidation just began, while the spontaneous oxidation-induced negative effect for well-refined pure Zr has become very obvious.

Key words: Zr powders; CNTs; ball milling; morphology; oxidation

Metal Zr has the advantages of high volumetric heat of combustion heat (77.77 kJ/cm^3), moderate ignition temperature (200~400 ℃) and good burning stability. These advantages make Zr powder an important component in energetic materials such as propellants and pyrotechnics[1-5]. Previous studies demonstrated that ignition and combustion properties of pure Zr and Zr-containing energetic compositions could be significantly influenced by particle sizes or types of Zr. Lee[6] found that Zr powders having fine particles (1~5 μm) and low purity (>94%) showed higher auto-ignition temperature (312 ℃ vs. 298 ℃) and activation energy of decomposition (77.9 kJ/mol vs. 70.1 kJ/mol) than Zr powders having coarse particles (1~23 μm) and high purity (>97%). Also, thermal behavior of Zr/KClO$_4$ compositions with these two types of Zr powders varied. C. Badiola[7] investigated ignition characteristics of microsized (50 μm) and nanosized (50~70 nm) Zr powders. Results showed that nanosized Zr powders had significantly low ignition

---

Received date: September 09, 2016
Foundation item: National Natural Science Foundation of China (51306165); Open Foundation of Joint Laboratory for Extreme Conditions Matter Properties, Southwest University of Science and Technology and Research Center of Laser Fusion, CAEP (12zxjk01); Science and Technology Foundation of CAEP (2013B0302052)
Corresponding author: Tang Yongjian, Ph. D., Professor, Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang 621900, P. R. China, E-mail: tangyongjian2000@sina.com

temperature (about 150~200 ℃) and the ignition time needed under the same heating power was shortened by several times. Therefore, tuning the reactivity of Zr powders to match different requirements is an important aspect in developing high-performance Zr-containing propellants and pyrotechnics. Besides changing the particle sizes or types of Zr, there are other solutions such as introducing external components to alter reactivity of Zr[8,9].

Recently, carbon nanotubes (CNTs) have been applied in energetic materials to modify the performance of either the pure energetic component or the energetic compositions. For example, as the initiator of the photo-acoustic effect, CNTs could realize optical ignition of energetic systems[10]; as the catalysts or catalyst support, CNTs could promote the thermal decomposition of NH_4ClO_4[11,12] or RDX[13,14]; as the flammable fuels, CNTs could react with oxidizer such as KNO_3 to produce high temperature [15]; as the additives, CNTs could control electrostatic discharge ignition sensitivity of composite energetic materials[16], delay performance of pyrotechnic delay composition[17] and thermal oxidation behavior of Al powders[18]. Particularly, the Ref. [18] reported that oxidation behavior of Al powders varied with the morphologies of Al/CNTs mixture, while morphologies of Al/CNTs mixture could be engineered by controlling milling time. This result may provide a new way to tailor oxidation of metal powders other than Al. However, there has been no more report on such kind of investigations.

In the present work, morphology evolution and thermal oxidation of Zr and Zr/CNTs milled for different hours were compared. The objective of this study is to understand the effect of CNTs on the morphology evolution of Zr during ball milling process and on the thermal oxidation behavior of Zr.

1 Experiment

Raw materials of Zr powders (38 μm) were purchased from General Research Institute for Nonferrous Metals, Beijing. CNTs used in this work was purchased from Shenzhen Nanotech Port Co. Ltd and used directly without other processing. They have diameters of 30~40 nm and lengths of a few μm. As seen in Fig.1, these CNTs were bent and tangled. Zr powders with or without CNTs were ball milled in ZrO_2 jars under ethyl alcohol protection. Milling balls were ZrO_2 balls of 6 mm in diameter and the ball-to-powder ratio was 10:1 in mass. The content of CNTs in the Zr/CNTs mixtures was 1.0% (wt%). Milling jars rotated at 150 r/min and the direction was reversed every 20 min with a break of 5 min in order for cooling. Samples were taken out and dried under vacuum when milling time accumulated to 1, 2, and 3 h. As a reference test, the physical mixture of Zr and CNTs mixed manually was prepared to compare with the ball milled Zr/CNTs.

Morphology of Zr or Zr/CNTs powders were characterized by SEM (scanning electron microscopy), and their phase structure was analyzed by XRD. Thermogravimetry (TG) measurement was used to study thermal oxidation of Zr or Zr/CNTs. In the TG test, powder samples of ~2 mg were heated under flowing air atmosphere from room temperature to 1000 ℃ at 20 ℃/min.

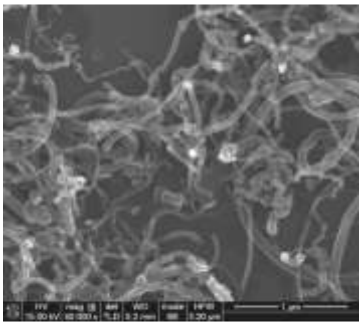

Fig.1 SEM image of CNTs used in this study

2 Results and Discussion

2.1 Structure and morphology analysis

Fig.2 and Fig.3 show XRD patterns of pure Zr and Zr/CNTs powders before and after milling, respectively. As seen in Fig.2, with prolonging milling time, peak intensities of the diffraction peaks gradually decrease, accompanied by the slight broadening of peaks, indicating the increasing defects in Zr particles during milling process. Fig.3 reveals that all diffraction peaks observed belong to Zr, so there is no new phase produced during CNTs-assisted milling. The diminished

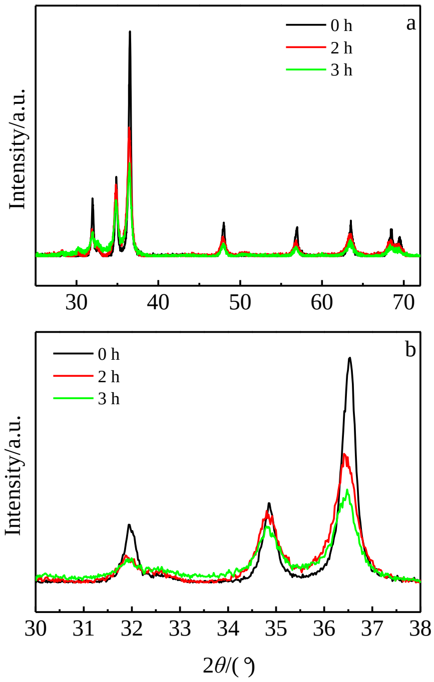

Fig.2 XRD patterns of pure Zr milled for different time: (a) full pattern and (b) partial enlarged pattern

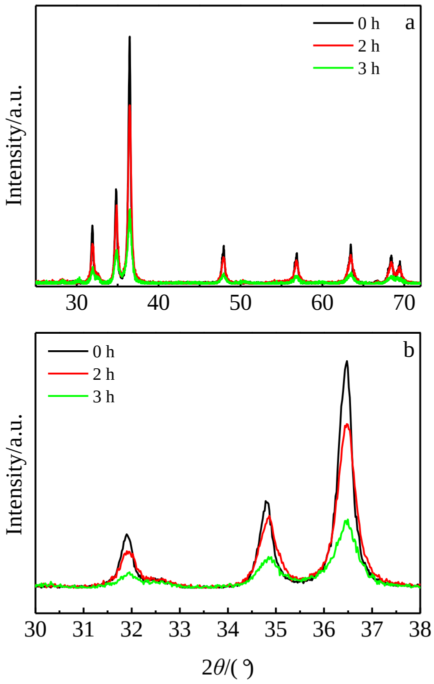

Fig.3 XRD patterns of Zr/CNTs milled for different time: (a) full pattern and (b) partial enlarged pattern

diffraction peaks for CNTs in the XRD patterns Zr/CNTs are probably because the content of CNTs is too low to be detected. The variation trend of peak intensities with milling time for Zr/CNTs mixtures is similar to that of pure Zr.

Fig.4 shows SEM images of pure Zr powders before and after ball milling. As seen in Fig.4a, particle size of raw Zr powders is not uniform, ranging from 1 μm to 20 μm. Their shape is irregular and the surface is rough. With the prolonging of milling time (Fig.4b, 4c), coarse Zr particles begin to break into small particles, and these newly generated small Zr particles tend to adhere on the surface of large particles. After milling for 3 h (Fig.4d), the mean particle size decreases to 2~3 μm, and the particle size distribution becomes more uniform than the short-time milled ones.

Fig.5 presents the morphology of Zr/CNTs mixtures obtained by ball milling. It could be observed that after milling for 1 h (Fig.5a), large agglomerations comprised of tangled CNTs and very fine Zr particles are formed, and the size of agglomerations ranges from 2 μm to 10 μm. These agglomerations are formed due to the electrostatic force between the CNTs and fine Zr particles. From the magnified picture in Fig.5b, one could see that the shape and length of CNTs keep nearly unchanged. After milling for 2 h (Fig.5c, 5d), the size of CNTs-Zr agglomerations decrease a little and the density of CNTs in the clusters also declines, indicating the improved dispersion of CNTs among Zr powders. When prolonging milling time to 3 h (Fig.5e, 5f), large agglomerations of

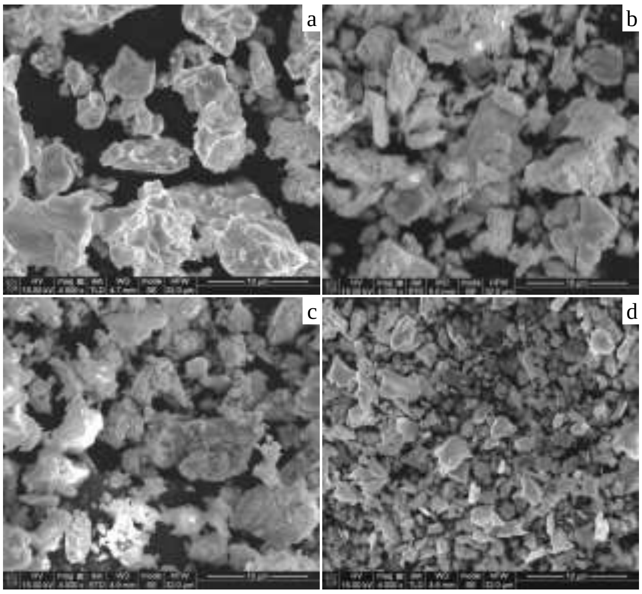

Fig.4 SEM images of pure Zr powders before milling (a) and after milling for 1 h (b), 2 h (c), and 3 h (d)

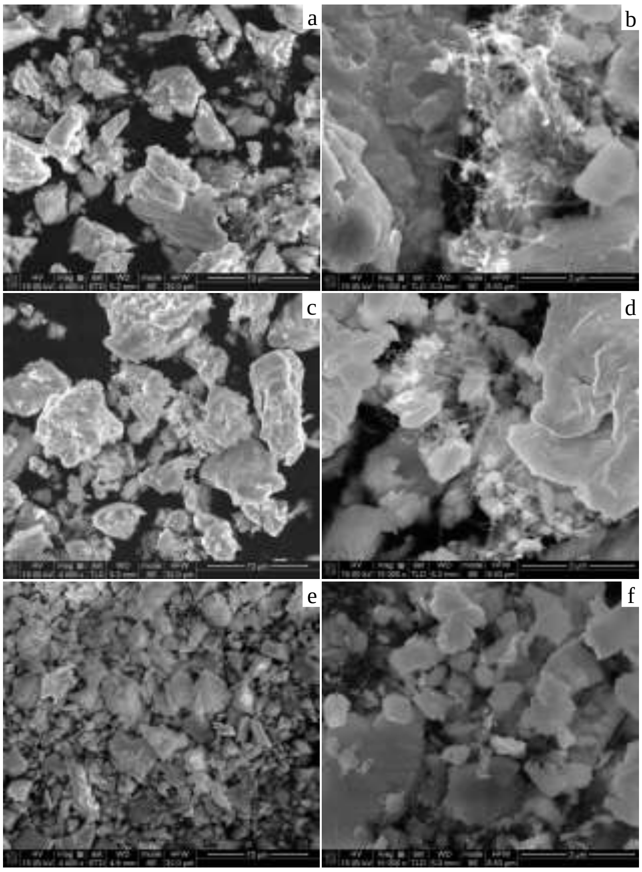

Fig.5 SEM images of Zr/CNTs mixtures after milling for 1 h (a, b), 2 h (c, d), and 3 h (e, f)

Zr/CNTs disappear, and the dispersion of CNTs in the mixture is further improved. At the same time, some of the CNTs in the mixture are found to be broken or shortened. Maybe due to the damage of CNTs, the binding of CNTs with Zr particle also changes. Despite those CNTs existing in the gaps of fine Zr particles, some of the shortened CNTs begin to adhere to the surface of coarse Zr particles, and some of the CNTs integrate with nano-scale Zr particles, leading to the increase in their diameter. Compared with the dispersion of CNTs in other metal powders such as Al [18] and Mg [19] through mechanical milling processing, the characteristic of CNTs dispersion in Zr powder is that it is difficult to let CNTs insert or embed into the Zr matrix. This is probably because the ductibility of Zr is worse than that of the soft metal like Al and Mg. Therefore, during low speed ball milling of Zr powders, the brittle fracturing process of coarse particles is dominated, and the plastic deformation is not obvious. Thus, CNTs only adhered on the surface of Zr or dispersed in the gaps of fine Zr particles but could not be embedded into the matrix.

In addition to the dispersion of CNTs in Zr powders, another question need to concern is the effect of adding CNTs on the morphology evolution of Zr powders. From Fig.4 and Fig.5, we could see that compared with pure Zr milled for the same time, particle size of Zr in Zr/CNTs mixtures looks larger, especially when milling time is shorter than 3 h. This result is different from the morphology evolution of Al/CNTs[18] and Mg/CNTs[19], where CNTs as a grinding aid favor the particle size reduction. Probable reasons for this difference are as follows: in case of Al/CNTs and Mg/CNTs, the promoting role of CNTs in particle size reduction occurs under the conditions that CNTs are heterogeneously dispersed and coat the surface of these metal particles, so the agglomeration and cold-welding of metal particles are prevented. However, in case of Zr/CNTs, as mentioned before, CNTs could not embed into the surface of Zr particles to form a coating. In contrast, in order to decrease the surface energy of each other, small Zr particles easily agglomerate with CNTs and form a lot of clusters. The existence of these clusters weakens the mechanical impact of milling ball on coarse Zr particles, so that the brittle fracturing and refining of Zr is restricted. When milling time is prolonged to 3 h, the dispersion of CNTs is improved, so the particle size reduction of Zr becomes obvious.

2.2 Thermal-gravity analysis

Fig.6 show TG curves of pure Zr and Zr/CNTs milled for different time. Fig.6a indicate that the onset oxidation temperature of Zr keeps decreasing when milling time is increased. On the other hand, the total mass gain first increases after milling for 1 h and then begins to decrease. The decrease in the onset oxidation temperature and the initial increase in mass gain after short-time milling could be easily understood by the particle size effect, which could be supported by the SEM images in Fig.4. While the subsequent reduction in mass gain is probably caused by the unavoidable spontaneous oxidation of fine Zr powders during milling process, because the ethanol-protection on oxidation during milling is very limited. As seen in Fig.6b, for Zr/CNTs mixtures, the variation of onset oxidation temperature and mass gain shows a similar trend with that of the pure Zr samples, except the maximum mass gain at the milling time equal to 2 h. This kind of difference in the variation of TG curves in Fig.6b is possibly caused by two reasons: first is the particle size effect of Zr in the Zr/CNTs mixtures during milling process, as mentioned in the SEM results; second is the special effect of CNTs. To declare the potential effect of CNTs, the detailed comparison in characteristic parameters in Fig.6a and Fig.6b are listed in Table 1.

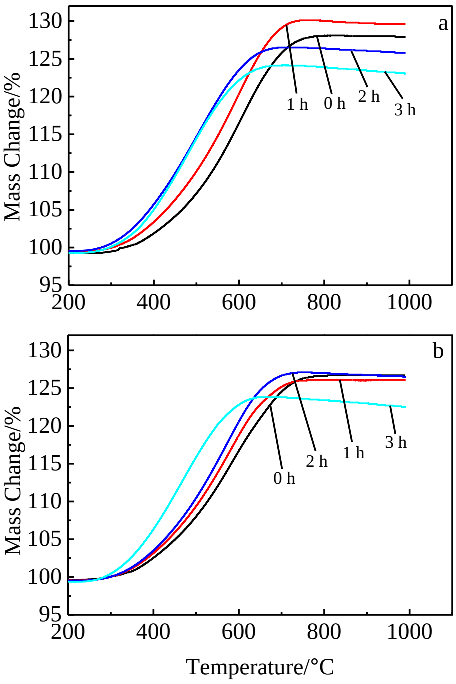

Fig.6 TG curves of pure Zr (a) and Zr/CNTs (b) milled for different time

It could be seen in Table 1 that the effect of adding CNTs during milling on the oxidation behavior of Zr powders is closely related to milling time, as could be reflected in the typical oxidation temperature and oxidative mass gain. Considering that during the heating of Zr/CNTs mixtures, the oxidative mass gain of Zr and the oxidative mass loss of CNTs simultaneously occurred, to strictly compare the degree of oxidation of Zr powders in the Zr/CNTs mixtures, the effect of oxidative mass loss of 1.0% CNTs was deducted when calculating the mass gain of Zr. It is found that when the milling time is set as 0, 1 and 3 h, the onset oxidation temperature in TG curve and peak temperature in DTG curve for Zr/CNTs are lower than that for pure Zr. That is, in most

Table 1 Summary of characteristic parameters obtained from TG curves

Time/h	T_{onset}/ ℃		T_{peak} in DTG/ ℃		Mass gain/%	
	Zr	Zr/CNTs	Zr	Zr/CNTs	Zr	Zr/CNTs
0	475	438	601	587	28.1	27.9
1	441	430	594	574	30.0	27.3
2	367	420	512	573	26.5	28.3
3	366	352	484	464	24.1	24.9

cases (except when the milling time is 2 h), the addition of CNTs favors the decrease in the oxidation temperature of Zr powders. This should be ascribed to the good thermal conductivity of CNTs, even though CNTs agglomerate seriously in the Zr/CNTs mixtures under short-time milling conditions. On the other hand, the oxidation ratio of Zr powders under CNTs-assisted milling is first decreased when milling time is shorter than 2 h, and then this trend reverses. By considering the SEM images in Fig.4 and Fig.5, it is inferred that this adverse effect of adding CNTs on oxidative mass gain of Zr/CNTs is related to two factors: (1) CNTs induced agglomeration of small Zr particles in Zr/CNTs mixtures, so that the oxygen diffusion into the inside of Zr particles is restricted and the active mass of Zr participated in the oxidation reaction is decreased; (2) after milling for the same time (1 h), particle size of Zr in Zr/CNTs mixtures is coarser than that of the pure Zr. The second aspect could also explain the abnormal increase in onset oxidation temperature and total mass gain for Zr/CNTs milled for 2 h when compared with its counterpart (seen in Table 1). In detail, though CNTs still play a positive role in the thermal conductivity of heat transfer during oxidation of Zr, when milling time is 2 h, the oxidation reaction of Zr/CNTs is more dependent on the particle size of Zr. In this stage, the particle size of pure Zr has been well refined, but the particle refining of Zr in Zr/CNTs just begins, so the onset oxidation temperature of Zr/CNTs is naturally high. At the same time, just because of the finer particle size of pure Zr, its spontaneous oxidation is more serious than the coarse Zr in the Zr/CNTs, which causes its lower mass gain than the corresponding Zr/CNTs. This kind of spontaneous oxidation also exists for the Zr in Zr/CNTs mixtures, but it is not obvious until the milling time is prolonged to 3 h.

In a word, the promoting effect of adding CNTs on lowering oxidation temperature of Zr is noticeable, while the potential adverse effect on decreasing reaction heat caused by agglomeration of CNTs in Zr/CNTs mixture needs further resolution.

3 Conclusions

1) CNTs-assisted ball milling is not beneficial to the particle size reduction of Zr. After milling for the same time, particle sizes of Zr in the Zr/CNTs mixture are larger than the Zr milled without adding CNTs.

2) CNTs could lower the onset oxidation temperature and peak exothermic temperature of Zr powders, even when CNTs seriously agglomerate in the Zr/CNTs mixtures under short-time milling conditions.

3) Agglomerations of CNTs themselves or agglomerations of Zr with CNTs are formed during milling, and the restriction effect of CNTs on particle size reduction of Zr has an adverse influence on the oxidative mass gain of Zr during thermal oxidation process, which means the potential loss in reaction heat of Zr.

4) It is suggested that by controlling the milling parameters and choosing appropriate size of both Zr and CNTs to improve the dispersion of CNTs in Zr powders, the adverse effect of CNTs on particle size reduction and oxidation reaction heat of Zr could be avoided.

References

1 Alekseev A P, Lempert D B, Nemtsev G G *et al*. *Russian Journal of Physical Chemistry B*[J], 2011, 5: 997

2 Lempert D B, Nechiporenko G N, Manelis G B. *Combustion, Explosion, and Shock Waves*[J], 2011, 47: 45

3 Pourmortazavi S M, Hosseini S G, Hajimirsadeghi S S *et al*. *Combust Sci Tech*[J], 2008, 180: 2093

4 Miyata K, Kubota N. *Propellants, Explosives, Pyrotechnics*[J], 1996, 21: 29

5 Byoung S M, Hyung S H. *Journal of Propulsion and Power*[J], 2012, 28: 211

6 Lee J S, Hsu C K. *Thermochimica Acta*[J], 2001, 367-368: 375

7 Badiola C, Dreizin E L. *Proceedings of the Combustion Institute* [J], 2013, 34: 2237

8 Kuwahara T, Kohno T, Wang C H. *Propellants, Explosives, Pyrotechnics*[J], 2004, 29: 56

9 Lv B L, Xu Y, Hou B *et al*. *Materials Research Bulletin*[J], 2008, 43: 2769

10 Manaa M R, Mitchell A R, Garza R G *et al*. *J Am Chem Soc*[J], 2005, 127: 13 786

11 Zhang X J, Jiang W, Song D *et al*. *Propellants Explosives Pyrotechnics*[J] 2009, 34: 151

12 Cui P, Li F S, Zhou J *et al*. *Propellants, Explosives, Pyrotechnics*[J], 2006, 31: 452

13 An T, Cao H Q, Zhao F Q *et al*. *Acta Phys-Chim Sin*[J], 2012, 28: 2202

14 Ren H, Liu Y Y, Jiao Q J *et al*. *Journal of Physics and Chemistry of Solids*[J], 2010, 71: 149

15 Guo R, Hu Y, Shen R Q *et al*. *Chemical Engineering Journal*[J], 2012, 211-212: 31

16 Poper K H, Collins E S, Pantoya M L *et al*. *Journal of Electrostatics*[J], 2014, 72: 428

17 Ren H, Jiao Q J, Chen S C. *Journal of Physics and Chemistry of Solids*[J], 2010, 71: 145

18 Jeong H Y, So K P, Bae J J *et al*. *Energy*[J], 2013, 55: 1143

19 Chen B H, Kuo C H, Ku J R *et al*. *Journal of Alloys and Compounds*[J], 2013, 568: 78

CNTs 辅助球磨对 Zr 粉形貌和氧化性能的影响

康晓丽 [1,2]，朱国灵 [2]，杨　帆 [1]，蒋晓东 [1]，易　早 [2]，唐永建 [1]
(1. 中国工程物理研究院激光聚变研究中心，四川 绵阳 621900)
(2. 西南科技大学-中国工程物理研究院激光聚变研究中心 极端条件物质特性联合实验室，四川 绵阳 621900)

摘　要：研究了不同球磨时间条件下 CNTs 辅助球磨对 Zr 粉形貌和氧化性能的影响。采用 XRD 和 SEM 分析了球磨过程中 Zr 粉的物相组成和形貌演变，采用热重（TG）法评估了 Zr 粉的氧化性能。结果表明：添加 CNTs 辅助球磨对 Zr 粉的物相组成没有影响，但是会影响 Zr 粉的形貌和氧化性能。不添加 CNTs 时，随着球磨时间的增加（1~3 h），Zr 粉粒径持续减小，球磨 3 h 后，Zr 粉粒径由十几微米减小到 2~3 μm。添加 CNTs 辅助球磨后，Zr 粉的颗粒细化过程滞后，球磨初期（1~2 h），Zr 粉粒径没有显著变化，直到球磨时间延长到 3 h 时，Zr 粉粒径才开始明显减小。这是因为 CNTs 在 Zr 颗粒表面的黏附和 CNTs 在 Zr 粉中的团聚阻碍了磨球对 Zr 颗粒的机械冲击和破碎作用。与直接球磨 Zr 粉相比，当所得 Zr 粉粒径相差不大时，添加 CNTs 辅助球磨使 Zr 粉的起始氧化温度和峰值氧化温度降低了 11~37 ℃，这是因为 CNTs 的良好导热性促进了 Zr 粉氧化过程中的传热。另一方面，球磨时间少于 2 h 时，Zr/CNTs 混合物中 Zr 粉的氧化增重量比纯 Zr 粉的增重量略有降低，但球磨时间超过 2 h 时，这种趋势出现反转。前者是因为短时间球磨时，CNTs 引起 Zr 粉的局部团聚，阻碍了团聚体中 Zr 粉与氧气的接触，并且混合物中的 Zr 粉颗粒还没有被明显细化，这都降低了 Zr 粉的氧化程度；随后的反转趋势是因为球磨时间增加后，混合物中的 Zr 粉开始明显细化，促进了其氧化反应的进行，但是纯 Zr 粉由于颗粒尺寸提前细化而发生了显著的自发氧化，降低了活性 Zr 的含量。

关键词：Zr 粉；球磨；CNTs；形貌；氧化

作者简介：康晓丽，女，1984 年生，博士，副研究员，中国工程物理研究院激光聚变研究中心，四川 绵阳 621900，电话：0816-2480903，E-mail: kangxiaoli515@126.com