Rare Metal Materials and Engineering
Volume 48, Issue 2, February 2019
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2019, 48(2): 0406-0410.

ARTICLE

Effect of Y_2O_3 Crucible on Purification of Ni_3Al-Based Superalloy Scraps

Bai Peng, Zhang Huarui, Li Yiming, Kong Bin, Zhang Hu

Beijing Key Laboratory for Advanced Functional Material and Thin Film Technology, Beihang University, Beijing 100191, China

Abstract: The effect of Y_2O_3 crucible on the purification of Ni_3Al-based superalloy IC21 scraps during vacuum induction melting was investigated. Different purification results were compared between using MgO crucible and Y_2O_3 crucible. The results indicate that Y_2O_3 crucible is more effective in reducing the content of hydrogen, nitrogen and oxygen. Contents hydrogen, nitrogen, and oxygen using Y_2O_3 crucible are about 50%, 80%, and 80% lower than that using MgO crucible, to 0.5, 1 and 2 μg/g in IC21 scraps, respectively. When the melting temperature is above 1550 °C or the reaction time exceeds 5 min, these two parameters have a limited impact on the dehydrogenation and denitrification process when using Y_2O_3 crucible. When melting at 1750 °C for 5 min or melting at 1650 °C for 30 min, the content of oxygen reaches the highest level of 6 μg/g.

Key words: Y_2O_3 crucible; superalloy; deoxidation; thermodynamics

Ni_3Al-based superalloy has become one of the most important materials in combustion engine because of its high melting point (T_m>1300 °C) and superior high-temperature performance[1-3]. Recently, Ni_3Al-based single crystal superalloy IC21, as a new generation of superalloy for turbine blades, has been extensively studied[4,5]. Solid solution strengthening and precipitation strengthening elements like Re and Ta are added into the alloy to improve the strength and toughness at high temperatures, which results in high cost of the IC21 superalloy. During mass production, a large amount of scraps, including sprues, casting riser and scrap castings etc, result in the low process yield (20%~40%) of the Ni_3Al-based superalloys[6]. Most of these scraps have not been successfully reused, and plenty of the rare metal resources are wasted. Accordingly, fewer scraps are expected during the melting. Besides that, scraps from the producing process should be recycled.

The contaminant content in the scraps is higher than that in the normal parts, including the rising content of some minority elements like hydrogen, nitrogen and oxygen. Moreover, more non-metallic inclusions exist in it[7]. Hydrogen can lead to pores and hydrogen embrittlement[8]. TiN inclusions may form due to the high content of nitrogen in the superalloy. As a result, the mechanical properties and high-temperature performance of the parts will be greatly influenced[9]. Oxygen will cause an increase in oxide inclusions in the matrix. Such inclusions can be the crack sources during the deformation process, which may have a significant influence on mechanical properties[10,11].

Therefore, in order to promote the recycling of Ni_3Al-based superalloy scraps, the most significant step is to reduce the content of H, N and O. An appropriate crucible has a vital influence on purification. MgO, CaO, Al_2O_3 and Y_2O_3 are commonly used materials for crucibles [12-16]. MgO crucible is widely used for melting carbon steel and some nonferrous metals because of its low cost and high erosion resistance. However the thermal stability of MgO is not sufficient to melt at the temperature higher than 1600 °C [12]. CaO crucible shows a good thermal stability, and can be used under high vacuum. Moreover, CaO has a significant effect on the desulfurization of melting pure iron and superalloy[13]. However, CaO is easily hydrated and has a reaction with active elements like Al, Ti, Hf and Nb at high temperatures[14]. Al_2O_3 crucible is low in cost and high in strength. However, the thermal stability of Al_2O_3 is lower than that of CaO and it

---

Received date: February 28, 2018
Foundation item: National Science & Technology Pillar Program of China (2013BAB11B04); National Natural Science Foundation of China (51404017)
Corresponding author: Zhang Huarui, Ph. D., School of Materials Science and Engineering, Beihang University, Beijing 100191, P. R. China, Tel: 0086-10-82339256, E-mail: huarui@buaa.edu.cn

will react with alkaline molten slag[15,16].

Y_2O_3 shows extraordinary high-temperature stability, as an important candidate material for the production of crucible, which has been investigated and used in highly reactive Ti-Al-based alloys[17-21]. However, only limited research has been conducted to study the performance of melting Ni-based superalloy or Ni_3Al-based superalloy scraps when using Y_2O_3 crucible [22]. Such investigations will not only be used to improve the purification level of superalloy scraps, but also to design and optimize materials of crucible during vacuum induction melting (VIM) processes.

Accordingly, the purpose of this study is to investigate the effect of Y_2O_3 crucible on dehydrogenation, denitrification and deoxidation of IC21 scraps at different temperatures and reaction time during VIM process. By contrast, MgO crucible was introduced under the same conditions.

1 Experiments

Y_2O_3 crucible was prepared by a cold isostatic pressing method. The inner layer was composed of a powder with a diameter of 5 μm. The sintering pressure was 20 MPa, and the sintering temperature was 1650 °C.

IC21 scraps were obtained from the waste during the production of turbine blades. Scraps were well cleaned by ultrasonic cleaning bath. The main chemical composition of the master alloy is given in Table 1. Then VIM process was then carried out for 5 min with MgO and Y_2O_3 crucible at 1550 °C under a pressure of 3×10^{-3} Pa. The melt was poured into a graphite mould which was preheated to 900 °C. The contents of H, N and O were tested by heating-melt method in an inert gas (LECOONH836, USA). The measurement accuracy of this method was ±1 μg/g.

In addition, experiments with different melting temperatures and reaction time were carried out using Y_2O_3 crucible, and the corresponding parameters are listed in Table 2. To explain the corrosion process between the superalloy melt and Y_2O_3 crucible, a wetting experiment was conducted by a sessile drop method [23]. The IC21 superalloy was cut into 3 mm×3 mm×3 mm cubes and ground to remove the oxide layer. The Y_2O_3 ceramic substrates with a diameter of 20 mm were mechanically sanded using SiC sandpaper, and then ultrasonically cleaned in acetone. The detailed description of this wetting experiment can be found in Ref. [24].

Table 1 Nominal element composition of IC21 superalloy (wt%)

Al	Mo	Ta	Cr	Ni
7.6~8.3	9.0~13.0	2.4~4.0	1.5~2.5	Bal.

Table 2 Parameters of melting with Y_2O_3 crucible

Temperature/°C	1550	1650	1750	1850
Reaction time/min	5	5, 10, 20, 30	5	5

2 Results and Discussion

2.1 Effect of crucible materials on purification

Fig.1 shows the results of impurity content when melting using MgO and Y_2O_3 crucibles. It can be seen that all the contents of H, N and O in the case of using Y_2O_3 crucible are lower than in the case of using MgO crucible at 1550°C for 5 min. Particularly, the O content shows a significant difference, which is decreased by 80%, from 10 μg/g to 2 μg/g, compared with using MgO crucible,. H is reduced by 0.5 μg/g and N is reduced by 4 μg/g.

The results indicate that Y_2O_3 crucible is more effective in reducing impurity elements than MgO crucible. The reaction of metallic oxide under high temperature and high vacuum degree can be expressed as follows:

$$\frac{1}{y}M_xO_y(s)=\frac{x}{y}M(g)+[O] \tag{1}$$

The Gibbs free energy change is

$$\Delta G^{\theta}=-RT\ln K^{\theta}=-RT\ln\frac{p_{[M]}^{\frac{x}{y}}\cdot a_{[O]}}{a^{\frac{1}{y}}{}_{M_xO_y}} \tag{2}$$

$$a_{[O]}=w_{[O]}\cdot f_{[O]} \tag{3}$$

where $a_{[O]}$ and $a_{[M_xO_y]}$ are the activity of [O] and M_xO_y, respectively. $p_{[M]}$ is the partial pressure of metal gas, $w_{[O]}$ is the equilibrium concentration of oxygen, and $f_{[O]}$ is the activity coefficient.

According to Eqs.(1~3), when the reaction reaches equilibrium, the content of oxygen in the melt is low, and accordingly $f_{[O]}\approx 1$, $a_{M_xO_y}$=1.

Therefore,

$$w_{[O]}=a_{[O]}=101325\frac{\exp(-\frac{G^{\theta}}{RT})}{p_{[M]^{\frac{x}{y}}}} \tag{4}$$

And because of the existence of C in the melt,

$$[C]+[O]=CO(g) \tag{5}$$

The effect of MgO and Y_2O_3 on the deoxidation can be

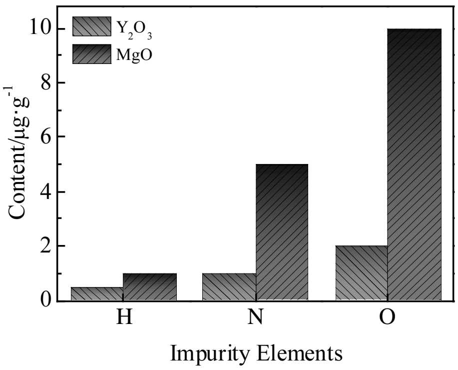

Fig.1 H, N, O content after melting at 1550 °C, under 3×10^{-3} Pa for 5 min

expressed as follows:

$$MgO(s)+[C]=Mg(g)+CO(g) \tag{6}$$

$$Y_2O_3(s)+3[C]=2Y(g)+3CO(g) \tag{7}$$

So the ratio of Mg partial pressure to CO partial pressure is 1:1, and the ratio of Y partial pressure to CO partial pressure is 2:3.

Thus,

$$p_{\mathrm{Mg}} = \frac{1}{2} p_{\mathrm{system}}\ ,\quad p_{\mathrm{Y}} = \frac{2}{5} p_{\mathrm{system}} \tag{8}$$

According to Eqs.(4~7), $w_{[O]}$ is obtained while melting with MgO and Y_2O_3 crucible.

$$w_{\mathrm{MgO,[O]}} = a_{\mathrm{MgO,[O]}} = 202650\frac{\exp(25.03-\dfrac{74811.64}{T})}{p_{\mathrm{system}}} \tag{9}$$

$$w_{\mathrm{Y_2O_3,[O]}} = a_{\mathrm{Y_2O_3,[O]}} = 187639\frac{\exp(20.61-\dfrac{93304.91}{T})}{p^{\frac{2}{3}}_{\mathrm{system}}} \tag{10}$$

At 1550 °C,

$$w_{\mathrm{MgO,[O]}} = \frac{0.228}{p_{\mathrm{system}}} \tag{11}$$

$$w_{\mathrm{Y_2O_3,[O]}} = \frac{10^{-8}}{p^{\frac{2}{3}}_{\mathrm{system}}} \tag{12}$$

So the theoretical thermodynamics relation between the equilibrium concentration of oxygen and the vacuum degree (p_{system}) is expressed as Fig.2.

Theoretically, at 1550 °C, MgO would decompose and oxygen would diffuse into the melt when the vacuum degree is below 50 Pa. During the VIM process, the saturated vapor pressure of Mg increased while the solubility of Mg declined. As a result, Mg would volatilize in the chamber and MgO would provide [O] according to Eq.(6). So the contaminants of oxygen were supplied by MgO crucible. However, Y_2O_3 crucible has a much higher stability and only starts to decompose when the pressure is lower than 10^{-4} Pa. Thus, the oxygen content melted with Y_2O_3 crucible is much lower than with MgO crucible at 1550 °C.

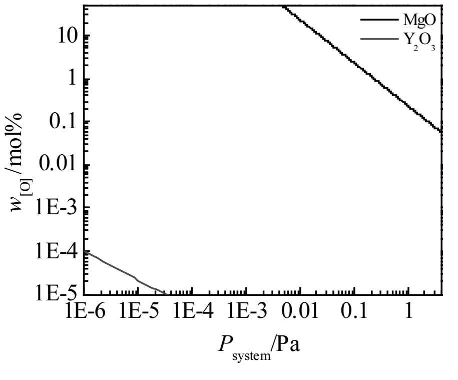

Fig.2 Relations between the equilibrium content of oxygen and the vacuum degree of MgO crucible and Y_2O_3 crucible at 1550 °C

On the other hand, as a surface active element, O preferred to stay at the layer of liquid-gas interfaces and occupied some positions of N. It prevented the reaction of denitrification. Therefore some of the nitrogen stayed in the melt due to the growth of oxygen content.

As for the content of H, the results between MgO crucible and Y_2O_3 crucible were nearly the same. The solubility of H at 1550 °C under 3×10^{-3} Pa was relatively small and it is hard to form compounds. So it is only less than 1 μg/g of H in both crucibles that remained in ingots.

2.2 Effect of melting temperature and reaction time when using Y_2O_3 crucible

Different melting temperatures were selected to find the appropriate process parameters for dehydrogenation, denitrification and deoxidation when using Y_2O_3 crucible. The melting pressure was maintained at 3×10^{-3} Pa and the reaction time was 5 min. Fig.3 indicates that with the increasing temperature, there is a rising tendency for O content, while the H and N contents show a slight change.

According to Eq.(12), when the pressure of the system is 3×10^{-3} Pa, the relation between equilibrium concentration of oxygen and temperature using Y_2O_3 crucible can be calculated, as shown in Fig.4.

The decomposition of Y_2O_3 hardly happened at 1550 °C. However, it would increase with the rise of temperature,

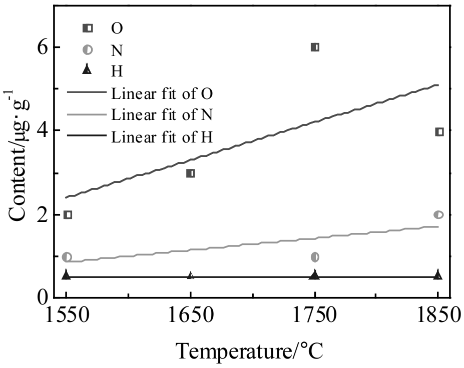

Fig.3 H, N and O content after melting at 1550~1850 °C for 5 min

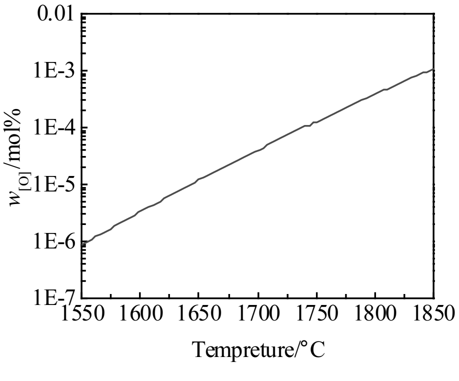

Fig.4 Relation between equilibrium concentration of oxygen and temperature using Y_2O_3 crucible at 1550~1850 °C

because the Gibbs free energy dropped. At 1850 °C, $w_{[O]}$ was 1000 times higher than that at 1550 °C. Therefore there was an increasing tendency of O content with the rise of temperature. Whereas, the content of oxygen was still in a ultra-low level (less than 6 μg/g). As for the H and N content, no other contamination sources were found, and the contents of hydrogen and nitrogen remained about the same.

Fig.5 also shows a growth trend of the O content at 1650 °C with the increase of reaction time. The contents of H and N remain unchanged. The results are similar to those melting at 1550~1850 °C.

The O contamination was caused by Y_2O_3 when some Y_2O_3 particles were separated from the crucible by the erosion action of the melt. According to the results from wetting experiments in Fig.6, the contact angle between the IC21 superalloy and the Y_2O_3 ceramics is about 83°. It is the wetting system, and the microstructure of the surface of Y_2O_3 crucible is shown in Fig.7. There are capillaries on the surface of Y_2O_3 ceramics, and the molten IC21 will fill some of the capillaries due to its good wettability, as shown in Fig.8. Different linear shrinkage rates at different parts of the surface make the Y_2O_3 produce microcrack easily. Driven by the electromagnetic force, the melt mixed as well as scoured the crucible surface, leading to the spalling of Y_2O_3 particles. Therefore, more Y_2O_3 particles are likely to be introduced into the alloy with a longer melting time and result in an increase in the total oxygen content.

To explain the growth of oxygen content, more experiments were taken, and the content of yttrium in the alloy was measured. As shown in Fig.9, the content of yttrium increases with extending the melting time, which displays a similar tendency to the oxygen in Fig.5. According to the results of TEM (Fig.10), the solid solutions of yttrium are found in the matrix. So the spalling and dissolution of Y_2O_3 particles are the main reason that causes the increase of oxygen content.

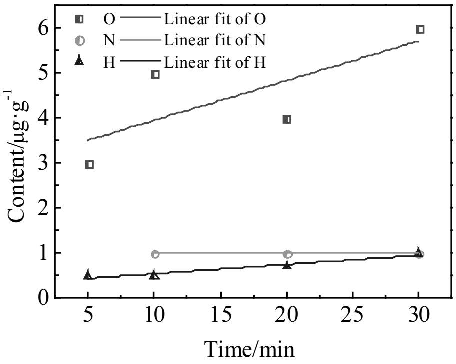

Fig.5 H, N, O content at 1650 °C for different reaction time

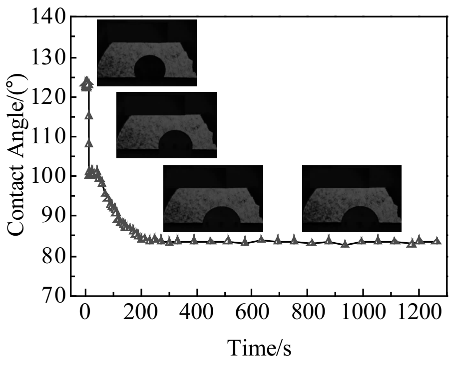

Fig.6 Contact angle between IC21 melt and Y_2O_3 ceramics at 1600 °C

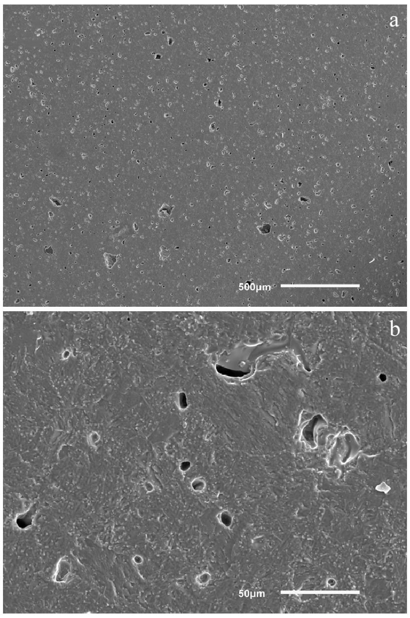

Fig.7 Microstructures of the surface of Y_2O_3 crucible

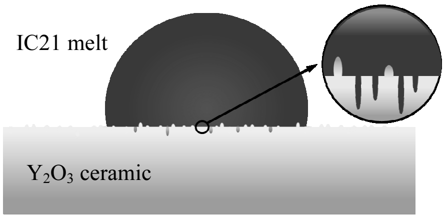

Fig.8 Process of filling capillaries with IC21 melt on the surface of Y_2O_3 ceramics

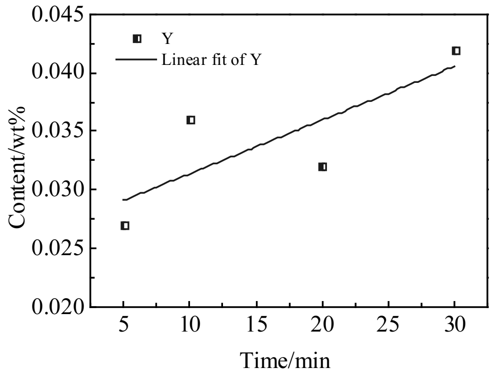

Fig.9 Y content after melting at 1650 °C for different time

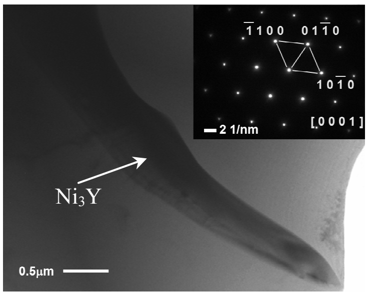

Fig. 10 Solid solutions of yttrium in matrix

3 Conclusions

1) Y_2O_3 crucible shows a higher thermodynamic stability at 1550 °C, which leads to a lower content of hydrogen, nitrogen and oxygen of 0.5, 1 and 2 μg/g, respectively, compared with using MgO crucible.

2) The melting temperature and melting time have a limited effect on dehydrogenation and denitrification above 1550 °C or after 5 min.

3) Higher temperature and longer melting time can introduce a trace amount of O contamination lower than 6 μg/g, when melting at 1750 °C for 5 min or melting at 1650 °C for 30 min. However, O content is still in an ultra-low level compared with using MgO crucible.

References

1 Zhao Wenyue, Liu Yuzhuo, Li Shusuo *et al. Oxidation of Metals*[J], 2014, 81(5-6): 631
2 Mi Guofa *et al. Rare Metal Materials & Engineering*[J], 2008, 37(7): 1144
3 Zhang Haixia, Li Shusuo, Gong Shengkai *et al. Material Research Innovations*[J], 2015, 19(S4): S98
4 Xu Xiaojing, Wu Qiong, Gong Shengkai *et al. Materials Science Forum*[J], 2013, 748(s1-2): 582
5 Li Hui, Li Fuli, Li Shusuo *et al. Materials Science Forum*[J], 2013, 748: 659
6 Huang Xuebing, Zhang Yun, Hu Zhuangqi. *Metallurgical & Materials Transactions A*[J], 1999, 30(7): 1755
7 Durber G L R, Osgerby S, Quested P N. *Metals Technology*[J], 1984, 11(1): 129
8 Morgan M J. *Thesis for Doctorate*[D]. Philadelphia: University of Pennsylvania, 1986
9 Niu Jianpin, Sun Xiaofeng, Yang Kenu *et al. Transactions of Nonferrous Metals Society of China*[J], 2002, 18(1): 11
10 Mennicke C, He M Y, Clarke D R *et al. Acta Materialia*[J], 2000, 48(11): 2941
11 Zhang Lina, et al. *Rare Metal Materials & Engineering*[J], 2001, 30(7): 971 (in Chinese)
12 Kostov A, Friedrich B. *Computational Materials Science*[J], 2006, 38(2): 374
13 Sakamoto K, Yoshikawa K, Kusamichi T. *Transactions of the Iron & Steel Institute of Japan*[J], 1992, 32(5): 616
14 Opila E J, Jacobson N S, Myers D L *et al. JOM*[J] , 2006, 58(1): 22
15 Zhang Huarui, Tang Xiaoxia, Zhou Chungen *et al. Journal of the European Ceramic Society*[J], 2013, 33(5): 925
16 Zhang Huarui, Tang Xiaoxia, Zhou Lei *et al. Journal of Materials Science*[J], 2012, 47(17): 6451
17 Lapin J, Gabalcová Z, Pelachová T. *Intermetallics*[J], 2011, 19(3): 396
18 Liu Aihui, Li Bangsheng, Nan Hai *et al. Rare Metal Materials & Engineering*[J], 2008, 37(6): 956
19 Wagner C. *Acta Metallurgica*[J], 1973, 21(9): 1297
20 Cui Renjie, Tang Xiaoxia, Gao Ming *et al. Materials Science & Engineering A*[J], 2012, 541(16): 14
21 Ma Limin, Tang Xiaoxia, Wang Bin *et al. Scripta Materialia*[J], 2012, 67(3): 233
22 Bai Hongbo, Zhang Huarui, Weng Junfei *et al. Material Research Innovations*[J], 2015, 18(S4): 357
23 Ellefson B S, Taylor N W. *Journal of the American Ceramic Society*[J], 2010, 21(6): 193
24 Ran Chao, Zhang Huarui, Zhang Hu *et al. Acta Metallurgica Sinica*[J], 2017(5): 1

氧化钇坩埚对 Ni_3Al 基高温合金返回料纯净化熔炼的影响

白 鹏，张花蕊，李一鸣，孔 玢，张 虎
(北京航空航天大学 特种功能材料与薄膜技术北京市重点实验室，北京 100191)

摘 要：研究了 Y_2O_3 坩埚对 Ni_3Al 基高温合金返回料纯净化熔炼的影响，并对使用 Y_2O_3 坩埚和 MgO 坩埚进行真空感应熔炼的结果进行了对比。结果表明：使用 Y_2O_3 坩埚对 N3Al 基高温合金 IC21 返回料进行纯净化熔炼有利于降低返回料中的 H、N 和 O 含量，和使用 MgO 坩埚相比分别降低了 50%、80%和 80%，最低可以达到 0.5、1 和 2 μg/g 的数值。当精炼温度高于 1550 ℃或精炼时间超过 5 min 时，精炼参数对纯净化熔炼的效果影响很小。

关键词：Y_2O_3 坩埚；高温合金；脱氧；热力学

作者简介：白 鹏，男，1992 年生，硕士生，北京航空航天大学材料科学与工程学院，北京 100191，电话：010-82339256，E-mail: baipeng_1992@buaa.edu.cn