Study on Oxidation Behavior of (W,Mo)Si_2 Powders in Air at 400, 500 and 600ºC

Feng Peizhong[1,a], Qu Xuanhui[1,b], Wang Xiaohong[2,c] and Akhtar Farid[1,d]

[1]School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, P. R. China
[2]School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou 221008, P. R. China
[a]fengroad@163.com, [b]quxh@mater.ustb.edu.cn, [c]matinbow@163.com, [d]faridmet22@hotmail.com

Abstract

The oxidation of (W,Mo)Si_2 powders has been investigated at 400, 500 and 600ºC for 12.0 hours in air. It was shown that the low temperature oxidation resistance of (W,Mo)Si_2 was worse than that of $MoSi_2$, and they showed great changes in mass, volume and colour. Especialy at 500ºC, the amount of volume expansion of (W,Mo)Si_2 was as high as about 7~8 times and color changed from black to yellow after 4.0h with MoO_3, WO_3, (W,Mo)O_3 and amorphous SiO_2 as main reaction products. The mass gain and oxidation rate were relatively slower at 400ºC and 600ºC than that at 500ºC.

Keywords : Molybdenum disilicide, Molybdenum-tungsten disilicide, Low temperature oxidation, Accelerated oxidation

1. Introduction

$MoSi_2$ has been regarded as the most promising high-temperature structural materials [1,2]. Besides low fracture toughness at room temperature and low strength at high temperature, poor oxidation resistance of $MoSi_2$ at low temperatures limits its structural applications. At around 500ºC, disintegration happens after a certain period of exposure in air, which was first discovered by Fitzer in 1955 and termed 'pest oxidation'.

It is confirmed that (W,Mo)Si_2 synthesized by SHS is composed of solid solutions of $MoSi_2$ and WSi_2 from the atoms of Mo and W replaced each other during synthesis. And WSi_2 can strengthen $MoSi_2$ at high temperature [3]. $MoSi_2$ reinforced with WSi_2_heating element are produced by world known Kanthal Co. Ltd, and the high-temperature properties of this heating element are improved.

Over the past years, some pest oxidation research about $MoSi_2$ was carried out. The main reason was to understand the non-selective oxidation of Mo and Si, and take measures to suppress pest oxidation were considered [4]. However, the reports on low temperature oxidation of (W,Mo)Si_2 are still limited. The aim of this work is to investigate the low temperature oxidation behavior of (W,Mo)Si_2 powders synthesized by SHS, focusing on the mechanism of low temperature accelerated oxidation and the influence of tungsten.

2. Experimental and Results

(W,Mo)Si_2 prepared by SHS_was crushed and ball milled to about 1.0μm sizes. The powders about 1.0g were placed in porcelain crucible, set in a porcelain boat and loaded into a box furnace, which was stabilized at a predetermined temperature. The temperature of the furnace was controlled within ±3ºC. Oxidation tests were conducted at 400ºC, 500ºC and 600ºC in air for 12.0 hours. The mass gain of sample was evaluated through measuring the mass gain of porcelain crucible with (W,Mo)Si_2 powders by analytical balance (Precision 0.1mg). For comparison, pure $MoSi_2$ sample prepared from the same technology route was oxidized at 500ºC for 12.0h. Phase identification was made by a Rigaku Dmax-RB X-ray diffraction (XRD).

The obvious volume expansion accompanied with great changes in mass and color of (W,Mo)Si_2 and $MoSi_2$ samples were noted to occur at three different temperatures after 12.0h. Especially at 500ºC, a significant amount of volume expansion about 7~8 times was observed, almost the whole (W,Mo)Si_2 sample was oxidized after only 4.0h with the mass gain of 160.69%, and it need about 8.0h to $MoSi_2$. The samples oxidized at 400ºC and 600ºC were noted to have less mass gain and color changes than that at 500ºC. The oxidation of all samples was fast in the first 0.5h at all temperatures, and then the rate of mass gain was decreased with test time. The end mass gain of (W,Mo)Si_2 at 400, 500 and 600ºC were 133.15%, 161.83% and 139.77% (Fig. 1), respectively. And that of $MoSi_2$ at 400 and 600ºC were 119.57% and 134.62%, respectively [5]. Thus it can be preliminary concluded that the low temperature oxidation resistance of (W,Mo)Si_2 was less than that of $MoSi_2$. The effect of tungsten was similar to the results of Zhang [6].

Fig. 2shows the X-ray diffraction patterns of the samples before and after oxidization. At 500ºC, MO_3 (M means Mo, W or Mo+W) and amorphous SiO_2 with few residual (W,Mo)Si_2 were the main reactive products. At 400ºC, mainly (W,Mo)Si_2 with a little MO_3, M_5Si_3 and SiO_2 were the final products. (W,Mo)Si_2, MO_3 and SiO_2 were the eventual reactionproducts of 600ºC oxidation. M_5Si_3 was not found at 500ºC and 600ºC conditions.

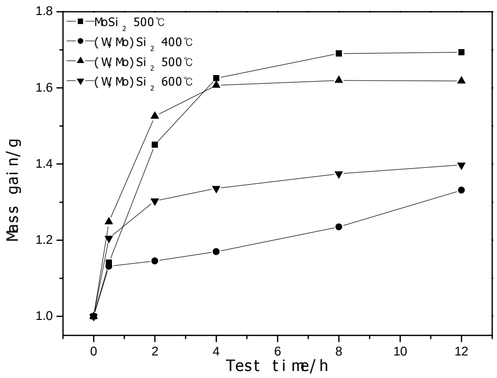

Fig. 1. Oxidation kinetics of (W,Mo)Si_2 and $MoSi_2$ powders at different temperature.

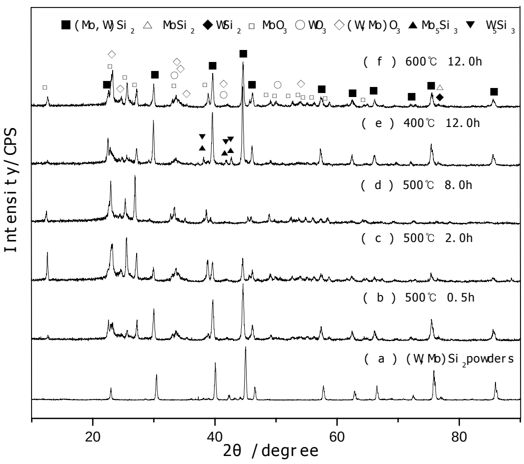

Fig. 2. XRD diffraction patterns of (W,Mo)Si_2 powders oxidized at different temperature.

It might be that the low temperature accelerated oxidation behavior of WSi_2 was worse than that of $MoSi_2$, and the addition of tungsten to $MoSi_2$ could change the lattice parameters of raw materials, and resulted in the change of mechanism of low temperature oxidation and accelerated the oxidation rate. At 400ºC, the oxidation rate during first 0.5h was very fast, but it was the least amongst three temperatures. And the oxidation layer could arise some selective oxidation with M_5Si_3. Temperature was the main factor controlling its oxidation behaviour at 400ºC. The nonselective oxidation of Mo, W and Si was the governing mechanism at 500ºC, Mo_5Si_3 could not be observed from XRD patterns, and the intermediate products Mo_4O_{11} might emerge at this temperature. The oxidation rate might be increased at 600ºC, but the effect of the volatilization of MO_3 could exceed that of oxidation, which would encourage the formation of protective silica glass and restrain the further oxidation.

3. Summary

The low temperature oxidation resistance of (W,Mo)Si_2 was less than that of $MoSi_2$ at 400ºC, 500ºC and 600ºC, which might result from the doping of WSi_2 and high sensitivity of Mo_5Si_3 to oxygen. The (W,Mo)Si_2 samples were taken great changes in volume, mass and colour after 12.0h oxidation in air at all test temperatures. The oxidation rate was low at 400ºC. The amount of volume expansion was as high as 7~8 times and the color changed from black to yellow at 500ºC after 4.0 hours, and the maximum mass gain was about 161.94% with MoO_3, WO_3, (W,Mo)O_3 and amorphous SiO_2 as main reaction products. The volatilization rate of reactants Mo and W was increased at 600ºC, which promoted the formation of protective silica glass film and restrained the diffusion of molybdenum and oxygen and further accelerated oxidation. The oxidation resistance of (W,Mo)Si_2 at 400ºC and 600ºC was better than that at 500ºC.

4. References

1. A. K. Vasudevan and J. J. Petrovic, Mater. Sci. Eng., **A155,** 1(1992).
2. J. J. Petrovic, Intermetallics, **[8]**, 1175(2000).
3. J. Subrahmanyam and R. R. Mohan, Mater. Sci. Eng., **A183**, 205(1994).
4. C. G. Mckamey, P. F. Tortorelli, J. H. Devan and C. A. Carmichael, J. Mater. Res., **7[10]**, 2747(1992).
5. P. Feng, X. Qu, S. H. Islam and X. Du, J. Univ. Sci. Technol. Beijing, in press, (2006).

H. Zhang, C. Long and X. Liu, Chin. J. Rare. Metals (in Chinese)., **26[3]**, 202(2002).