

HIGH-TEMPERATURE OXIDATION BEHAVIOR OF $\text{ReSi}_{1.75}$

K. Kurokawa, H. Hara, and H. Takahashi
Graduate School of Engineering, Hokkaido University
Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628
Japan

INTRODUCTION

It is well known that some refractory metal disilicides, for example MoSi_2 and WSi_2 , show excellent oxidation resistance at high temperatures which is due to the formation of a protective SiO_2 layer. In these disilicides, it is speculated high vapor pressure of metal oxide plays an important role in formation of a protective SiO_2 layer. That is to say, only SiO_2 , as a consequence of simultaneous formation of metal and silicon oxides at early stage of oxidation and evaporation of the metal oxide, may remain on the surface of the metal disilicide. In fact, MoSi_2 [1-3] and WSi_2 [4,5] form a protective SiO_2 layer above about 1100 and 1600 K, respectively. The high vapor pressure of Re_2O_7 must be also particularly advantageous for forming a SiO_2 layer. Thus, it is expected that Re silicides show excellent oxidation resistance.

The phase diagrams of the Re-Si binary system in literatures [6,7] indicate that a line-compound with the highest concentration of Si is $\text{ReSi}_{1.8}$ or ReSi_2 . However, the exact composition of the compound has not been clarified. In the present study, synthesis of a dense Re silicide with the highest concentration of Si was performed, and oxidation behavior of the Re silicide was investigated.

EXPERIMENTAL

In order to fabricate the Re silicide, a spark plasma sintering (SPS) method was applied. In this sintering method, the mixed powders consisting of elemental Re (average grain size: $40 \mu\text{m}$) and Si ($60 \mu\text{m}$) were packed in a graphite die under a compressive stress of 40 MPa, and then a pulsating current was passed through the mixed powders and the graphite die in an evacuated chamber of 6 Pa. The heating rate was 0.17 K/sec, and the maximum pulsating current was about 800 ampere to heat up to 1823 K. The sintered specimens were characterized by using X-ray diffraction (XRD) and an electron probe microanalyzer (EPMA).

Oxidation tests of the Re silicide were carried out in air at temperatures ranging from 773 to 1473 K. Oxidation kinetics was evaluated by measuring the mass change by oxidation. The oxidized specimens were characterized by using XRD, SEM, and EPMA.

RESULTS AND DISCUSSION

Synthesis of Re silicide

The previous work [6,7] proposed $\text{ReSi}_{1.8}$ or ReSi_2 as a compound with the highest concentration of Si. In order to clarify the exact composition of the Re silicide, the mixed powders of Re and Si with various atomic ratios of Si to Re, Si/Re=1.7, 1.75, and 1.8, were heated up to various temperatures. The Si phase in the composition of Si/Re=1.7 and the ReSi and Re_3S_3 phases in Si/Re=1.8 remained. On the other hand, the compact body synthesized from Si/Re=1.75 is consisting of a single phase. From these results, it was concluded that a compound with the highest concentration of Si was $\text{ReSi}_{1.75}$.

High-temperature oxidation behavior of $\text{ReSi}_{1.75}$

In oxidation of Re silicides, enough concentration of Si for the formation of a protective SiO_2 scale is required. In general, a silicide with the highest concentration of Si shows the best oxidation resistance. Therefore, oxidation tests of $\text{ReSi}_{1.75}$ were carried out at temperatures ranging from 773 to 1473 K in air. In the temperature region of 773 to 1173 K, the mass loss increased with increasing temperature. The mass loss was caused by the evaporation of a Re oxide (probably Re_2O_7), and it was the most severe at 1173 K. However, further increase in temperature led to the suppression of mass loss. In particular, the mass changes at 1373 and 1473 K were negligibly small, and this means that $\text{ReSi}_{1.75}$ has excellent oxidation resistance at temperatures above 1373 K.

To clarify the oxidation behavior of $\text{ReSi}_{1.75}$, the scale structures were observed. The scales formed at temperatures below 973 K appeared to be extremely fragile and porous. This may be due to less plasticity of SiO_2 . Though the scale formed at 1173 K appeared to be improved in brittleness, it had still high porosity. On the other hand, the scales formed at 1273 and 1473 K were very thin and dense. The XRD results showed that the scales formed at temperatures below 1273 K were consisting of amorphous SiO_2 , whereas those at 1373 and 1473 K were consisting of cristobalite SiO_2 . In all scales, any Re oxides were not detected in XRD experiments.

Based on the results of the oxidation behavior and the scale structures, an oxidation mechanism of $\text{ReSi}_{1.75}$ can be proposed. When $\text{ReSi}_{1.75}$ is exposed to an oxidizing atmosphere, in an initial stage of oxidation Re and Si must be simultaneously oxidized to form Re_2O_7 and SiO_2 . However, due to high vapor pressure of Re_2O_7 [8], only SiO_2 must be left on the substrate. In fact, a SiO_2 layer was formed on $\text{ReSi}_{1.75}$ at all temperatures. The scales formed in the low temperature region (773-1173 K) were fragile and porous, and the scale structure was maintained during oxidation, resulting in pronounced mass loss by the evaporation of Re_2O_7 . On the other hand, the scales formed at temperatures above 1273 K were thin and dense, that is, protective. Such difference in the scale structures probably depends on the plasticity of SiO_2 . In other words, pores or cracks introduced by the formation and the

subsequent evaporation of Re_2O_7 in the initial stage of oxidation can be healed by the plasticity of SiO_2 at higher temperatures. Once the substrate is covered with a protective SiO_2 scale, only SiO_2 grows in further oxidation. This is because the affinity of Re for oxygen is much lower than that of Si and hence oxidation of Re in the $\text{SiO}_2/\text{ReSi}_{1.75}$ interface is prevented.

Effect of vapor pressure of metal oxide on formation of a SiO_2 scale

It is well known that MoSi_2 and WSi_2 form a protective SiO_2 layer above about 1100 and 1600 K, respectively. In those disilicides, evaporation of the metal oxide plays an important role for the formation of a protective SiO_2 scale. The vapor pressure of Re_2O_7 (about 1 atm at 573 K) [8] is much higher than that of WO_3 and MoO_3 . Thus, a SiO_2 scale was formed on $\text{ReSi}_{1.75}$ even at temperatures as low as 773K. By considering the vapor pressures of WO_3 , MoO_3 , and Re_2O_7 , it may be concluded that a SiO_2 scale is formed, when the vapor pressure of the metal oxide reaches 10^{-4} atm. However, the formation of a protective SiO_2 scale was observed at temperatures as high as 1273K. Namely, the temperature for the formation of a protective SiO_2 scale in $\text{ReSi}_{1.75}$ was higher than that in MoSi_2 . Thus, a clear relationship between the value of the vapor pressure and the temperature for the formation of a protective SiO_2 scale was not found. The formation of a protective SiO_2 scale may depend on the plasticity of SiO_2 , and the plasticity may be affected by dissolution of a foreign oxide into SiO_2 .

CONCLUSIONS

In the present study, fabrication of dense $\text{ReSi}_{1.75}$ by a spark plasma sintering method and the oxidation tests of $\text{ReSi}_{1.75}$ at temperatures ranging from 773 to 1473 K were carried out. The following results were obtained.

- (1) Synthesis and sintering of $\text{ReSi}_{1.75}$ were simultaneously performed, and a compact body consisting of a single phase was fabricated.
- (2) A SiO_2 scale was formed on $\text{ReSi}_{1.75}$ in the temperature range from 773 to 1473 K, due to the evaporation of Re_2O_7 . However, the formation of a protective SiO_2 scale was observed at temperatures of 1273 K and above.

REFERENCES

- [1] Honingschmid O.: *Monatsh. Chem.*, **28**, 1017(1907).
- [2] Fitzer E.: *Proc. of the Second Plansee Seminar*, Springer-Verlag, Wien, 56(1955).
- [3] Cook J., Kahn A., Lee E., and Mahapatra R.: *Mat. Sci. Eng.*, **A155**, 183(1992).
- [4] Yefimenko L. N., Nechiporenko Y. P., and Pavlov V. N.: *Fiz. Metal. Metalloved.*, **16**, 931(1963).
- [5] Kurokawa K., Matsuoka H., and Takahashi H.: *Mater. Sci. Forum*, **251/254**, 885(1997).
- [6] in *Binary Alloy Phase Diagram*, *Ame. Soc. for Metals*, **2**, 1958.
- [7] in *Binary Alloy Phase Diagram*, *Ame. Soc. for Metals*, **3**, 3205.
- [8] Skinner H. B. and Searcy A. W.: *J. Phys. Chem.*, **77**, 1578(1973).