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Thermodynamic simulation of oxidation process of the Mo_{ss}-Mo_3Si hypoeutectic alloy, doped with yttrium

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Abstract

In order to study the effect of yttrium additives on the oxidation of molybdenum silicide alloys, thermodynamic modeling of the interaction in the Mo-Mo_3Si-Y_5Si_3 system with dry and moist air was performed in the temperature range 25-2000 °C. To predict the composition of oxidation products and the sequence of the formation of phase components, the dependences on the temperature and consumption of oxidants – water vapor and oxygen of the air – are obtained. The calculations were performed using the HSC Chemistry 6.12 software, into the database of which the calculated missing thermochemical characteristics of $Y_2Si_2O_7$, Y_2SiO_5 silicates and yttrium molybdates $Y_2Mo_3O_{12}$, Y_2MoO_6 were entered. It is shown that, under equilibrium conditions, the oxidation process with dry and moist air proceeds almost equally, since the interaction of the components of the alloy with oxygen is thermodynamically preferable than with water vapor. According to the obtained thermodynamic models, the oxidation process of the Mo-5 wt. % Si alloy of the hypoeutectic composition doped with yttrium can be represented as a sequence of the following chemical transformations: firstly Mo and Y silicides oxidize forming Y_2O_3, SiO_2 and metallic Mo, then molybdenum is oxidized to MoO_2 and Y_2O_3 interacts with SiO_2 with the formation of silicates Y_2SiO_5 and $Y_2Si_2O_7$. As a result of the complete oxidation of the alloy, MoO_3 and $Y_2Mo_3O_{12}$ are added to the condensed product, and molybdenum oxide $(MoO_3)_n$ vapor appears in the gas phase. Based on the results of a complete thermodynamic analysis, the possibility of the formation of silicates and yttrium molybdate during the oxidation of the hypoeutectic alloy Mo-5Si-3Y (wt. %) was established. This can increase its oxidation resistance due to the formation of a protective film limiting the diffusion of oxygen into the alloy, which, of course, requires experimental confirmation.

References

[1] R. Mitra. Intermetallic Matrix Composites. Properties and Applications. Chapter 5 – Molybdenum silicide-based composites. *Woodhead Publishing*. **2018**. P.95-146.
[2] A.V. Larionov, L.Y. Udoeva, and V.M. Chumarev Thermodynamic simulation of phase formation in the Mo-Si, alloys doped with scandium or neodymium. *Butlerov Communications.* **2015**. Vol.43. No.9. P.84-88. DOI: 10.37952/ROI-jbc-01/15-43-9-84
[3] A.V. Larionov, L.Y. Udoeva, V.M. Chumarev, and A.N. Mansurova. Thermodynamic simulation of phase formation in the Mo-Si alloys doped with yttrium. *Butlerov Communications.* **2015**. Vol.43. No.9. P.89-96. DOI: 10.37952/ROI-jbc-01/15-43-9-89
[4] A.N. Mansurova, A.V. Larionov, S.N. Tyushnyakov, and L.A. Marshuk. Phase composition and microstructure of the obtained under nonequilibrium crystallization conditions Mo-Si alloys. *Butlerov Communications.* **2015**. Vol.43. No.9. P.97-101. DOI: 10.37952/ROI-jbc-01/15-43-9-97
[5] L.Yu. Udoeva, A.V. Larionov, V.M. Chumarev, A.N. Mansurova, and S.N. Tushnyakov. The phase formation study of the hypoeutectic Mo-Si alloys, doped with REM (Sc, Y, Nd). *Butlerov Communications.* **2016**. Vol.47. No.8. P.106-114. DOI: 10.37952/ROI-jbc-01/16-47-8-106
[6] L.Yu. Udoeva, V.M. Chumaev, A.V. Larionov, S.V. Zhidovinova, S.N. Tyushnyakov. Influence of Rare Earth Elements on the Structural-Phase State of Mo–Si–X (X = Sc, Y, Nd) in situ Composites. *Inorganic Materials: Applied Research*. **2018**. Vol.9. No.2. P.257-263.
[7] A.V. Larionov, R.I. Gulyaeva, L.Yu. Udoeva, V.M. Chumarev. Effect of Y and Sc on the thermal stability of silicide phase in Nb-Si and Mo-Si in-situ composites. *Book of Abstracts of the 16th IUPAC*

High Temperature Materials Chemistry Conference (HTMC-XVI), July 2-6, Ekaterinburg, Russia / Ural State pedagogical University. Ekaterinburg. **2018**. P.195

[8] P.J. Meschter. Low-Temperature Oxidation of Molybdenum Disilicide. *Metallurgical transactions A.* **1992**. Vol.23A. P.1763-1772.

[9] H.J. Grabke, G.H. Meier. Accelerated Oxidation, Internal Oxidation, Intergranular Oxidation, and Pesting of Intermetallic Compounds. *Oxidation of Metals*. **1995**. Vol.44. No.1/2. P.147-176.

[10] K. Yanagihara, T. Maruyama, K. Nagata. High-temperature oxidation of Mo-Si-X intermetallics (X = Al, Ti, Ta, Zr and Y). *Intermetallics*. **1995**. Vol.3. P.243-251.

[11] K. Yanagihara, T. Maruyama, K. Nagata. Effects of third elements on the pesting suppression of Mo-Si-X intermetallics (X=Al, Ta, Ti, Zr and Y). *Intermetallics*. **1996**. Vol.4. P.S133-S139.

[12] K. Yanagihara, K. Przybylski, T. Maruyama. The role of microstructure on pesting during oxidation of $MoSi_2$ and Mo(Si,Al)2 at 773 K. *Oxidation of Metals*. **1997**. Vol.47. No.3/4. P.277-293.

[13] K. Kurokawa, H. Houzumi, I. Saeki et al. Low temperature oxidation of fully dense and porous MoSi2. *Materials science and engineering*. **1999**. Vol.A261. P.292-299.

[14] Q. Zhu, K. Shobu, E. Tani et al. Oxidation behavior of $Mo_{\leq 5}Si_3C_{\leq 1}$ and its composites. *J Mat. Sci*. **2000**. Vol.35. P.863-872.

[15] G.N. Komratov, V.P. Kobyakov. Oxidation of SHS Mo-Si-C Materials in Air. *Inorganic materials*. **2000**. Vol.36. No.4. P.337-342.

[16] K. Hansson, M. Halvarsson, J.E. Tang et. al. Oxidation behavior of a MoSi2-based composite in different atmospheres in the low temperature range (400-550 ^{o}C). *Journal of the European Ceramic Society*. **2004**. Vol.24. P.3559-3573.

[17] T. Iizuka, H. Kita. Oxidation behavior and effect of oxidation on mechanical properties of Mo5Si3 particle-reinforced Si_3N_4 composites. *Materials Science and Engineering A*. **2004**. Vol.374. P.115-121.

[18] J.G. Gonzalez-Rodriguez, I. Rosales, M. Casales et al. Corrosion resistance of molybdenum silicides in aqueous solutions. *J. Solid state electrochem*. **2005**. Vol.9. P.691-697.

[19] J. Yan, H. Zhang, S. Tang et al. Cyclic oxidation behaviors of $MoSi_2$ with different relative density. *Journal of Wuhan University of Technology-Mater. Sci. Ed*. **2008**. P.699-703.

[20] A.A. Sharif. High temperature oxidation of $MoSi_2$. *J Mater Sci*. **2010**. Vol.45. P.865-870.

[21] L. Ingemarsson, M. Halvarsson, K. Hellstrom et al. Oxidation behavior at 300-1000 ^{o}C of a $(Mo,W)Si_2$-based composite containing boride. *Intermetallics*. **2010**. Vol.18. P.77-86.

[22] K. Hellström, P. Persson, E. Ström. Oxidation behaviors and microstructural alterations of a $Mo(Si,Al)_2$-based composite after heating at 1580 °C either in a furnace (ex-situ) or via alternating current (in-situ). *Journal of the European Ceramic Society*. **2015**. Vol.35. Iss.2. P.513-523.

[23] D.D. Titov, A.S. Lysenkov, Yu.F. Kargin et al. Low-Temperature Oxidation of MoSi2–Si3N4 Composites. *Inorganic Materials: Applied Research.* **2016**. Vol.7. No.4. P.624-629.

[24] M. Samadzadeh, C. Oprea, H. Karimi Sharif et al. Comparative studies of the oxidation of MoSi2 based materials: Low-temperature oxidation (300-900 ^{o}C). *International Journal of Refractore Metals and Hard Materials*. **2017**. Vol.66. P.11-20.

[25] M. Samadzadeh, C. Oprea, H. Karimi Sharif et al. Comparative studies of the oxidation of MoSi2 based materials: High-temperature oxidation (1000-1600 ^{o}C). *International Journal of Refractory Metals and Hard Materials*. **2017**. Vol.69. P.31-39.

[26] T.A. Parthasarathy, M.G. Mendiratta, D.M. Dimiduk. Oxidation mechanisms in Mo-reinforced Mo_5SiB_2(T2)– Mo_3Si alloys. *Acta Materiala*. **2002**. Vol.50. P.1857-1868.

[27] K. Yoshimia, S. Nakatanic, T. Sudac et al. Oxidation behavior of Mo5SiB2-based alloy at elevated temperatures. *Intermetallics*. **2002**. Vol.10. P.407-414.

[28] V. Supatarawanich, D.R. Johnson, C.T. Liu. Effects of microstructure on the oxidation behavior of multiphase Mo-Si-B alloys. *Materials Science and Engineering*. **2003**. Vol.A344. P.328-339.

[29] P. Mandal, A.J. Thom, M.J. Kramer et al. Oxidation behavior of Mo–Si–B alloys in wet air. *Materials Science and Engineering*. **2004**. Vol.A371. P.335-342.

[30] V.S. Dheeradhada, D.R. Johnson, M.A. Dayanada. Diffusional analysis of a multiphase oxide scale formed on a Mo-Mo3Si-Mo5SiB2 alloys. *Journal of phase equilibria and diffusion*. **2006**. Vol.27. No.6. P.582-589.

[31] S. Paswan, R. Mitra, K. Roy. Nonisothermal and Cyclic Oxidation Behavior of Mo-Si-B and Mo-Si-B-Al Alloys. *Metallurgical and materials transactions A*. **2009**. Vol.40A. P.2644-2658.

[32] I. Rosales, H. Martinez, D. Bahena et al. Oxidation performance of Mo_3Si with Al additions. *Corrosion Science*. **2009**. Vol.51. P.534-538.

[33] S. Burk, B. Gorr, M. Kruger et al. Oxidation Behavior of Mo-Si-B-(X) Alloys: Macro- and Microalloying (X= Cr, Zr, La2O3). *JOM*. **2011**. Vol.63. No.12. P.163-181.

[34] J. Das, R. Mitra, S.K. Roy. Oxidation behavior of Mo-Si-B-(Al, Ce) ultrafine-eutectic dendrite composites in the temperature range of 500-700 °C. *Intermetallics*. **2011**. Vol.19. P.1-8.

[35] S. Majumdar, D. Schliephake, B. Gorr et al. Effect of Yttrium Alloying on Intermediate to High-Temperature Oxidation Behavior of Mo-Si-B Alloys. *Metallurgical and materials transactions A*. **2013**. Vol.44A. P.2243-2257.

[36] M.A. Azim, S. Burk, B. Gorr et al. Effect of Ti (Macro-) Alloying on the High-Temperature Oxidation Behavior of Ternary Mo–Si–B Alloys at 820-1300 °C. *Oxid Met*. **2013**. Vol.80. P.231-242.

[37] T. Karahana, G. Ouyangb, P.K. Rayb et al. Oxidation mechanism of W substituted Mo-Si-B alloys. *Intermetallics*. **2017**. Vol.87. P.38-44.

[38] N.K. Kumar, B. Roy, R. Mitra, J. Das. Improvement of oxidation resistance of arc-melted $Mo_{76}Si_{14}B_{10}$ by microstructure control upon minor Fe addition. *Intermetallics*. **2017**. Vol.88. P.28-30.

[39] A. Roine. HSC 6.0 Chemistry. Chemical reactions and Equilibrium software with extensive thermochemical database and Flowsheet simulation. *Pori: Outokumpu research Oy*. **2006**. 448p.

[40] O. Kubaschewski, C.B. Alcock. Metallurgical thermochemistry. *Oxford: Pergamon press*. **1982**. 383p.

[41] T.B. Massalski. Binary Alloy Phase Diagrams, 2nd ed. ASM International. *Metals Park. Ohio.* **1990**.

[42] https://www.materialsproject.org/#apps/phasediagram

[43] L.Yu. Udoeva, A.V. Larionov, N.I. Selmenskikh, V.M. Chumaev , L.I. Leont'ev. The phase formation in the eutectic Nb-Si alloys, doped with yttrium. *Volga Scientific Bulletin*. **2014**. No.1. P.27-32. (russian)

[44] L.Yu. Udoeva, V.M. Chumaev, L.I. Leont'ev, N.I. Selmenskikh. Structural-phase state of Nb - Si eutectic alloys, doped by yttrium and scandium. *Non-ferrous metals.* **2014**. No. 8. P.59-65. (russian)

[45] E. Courcot, F. Rebillat, F. Teyssandier, C. Louchet-Pouillerie. Thermochemical stability of the Y_2O_3-SiO_2 system. *Journal of the European Society*. **2010**. Vol.30. P.905-910.

[46] E.N. Kulenko, B.I. Polyak. Sintering of the ceramics belonging to the $MoSi_2$-Y_2O_3 and $MoSi_2$-SiC systems. *Refractories.* **1989**. Vol.30. Iss.7-8. P.418-425.

[47] Y. Suzuki, P.E.D. Morgan, K. Niihara. Improvement in Mechanical Properties of Powder-Processed $MoSi_2$ by the Addition of Sc_2O_3 and Y_2O_3. *J. Am. Ceram. Soc*. **1998**. Vol.81. P.3141-3149.

[48] I.L. Shabalin. Ultra-High Temperature Materials I. Chapter 7: Molybdenum. *Springer Science+Business Media Dordrecht*. **2014**. P.451-529.

[49] J.S. Mohammed. A study of high temperature reactions in oxide-dispersion-strengthened molybdenum at reduced oxygen partial pressures. A Thesis. *Georgia: Georgia Institute of Technology*. **2004**. P.15.

[50] O. Fabrichnaya, H.J. Seifert, R. Weiland et al. Phase Equilibria and Thermodynamics in the Y_2O_3-Al_2O_3-SiO_2 System. *Z. Metallkd.* **2001**. Vol.92. Iss.9. P.1083-1097.

[51] H. Mao, M. Selleby, O. Fabrichnaya. Thermodynamic reassessment of the Y_2O_3-Al_2O_3-SiO_2 system and its subsystem. *Computer Coupling of Phase Diagrams and Thermochemistry*. **2008**. Vol.32. P.399-412.