燃燒合成具多穩定相之金屬矽化物與硼化物

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摘 要

本研究係以自持傳遞高溫合成法(Self-propagating High-temperature Synthesis, SHS)，在氬氣環境下進行燃燒合成之 鈮矽(Nb-Si)介金屬、鈮硼(Nb-B)化合物以及鉬矽(Mo-Si)介金屬三 大部份之實驗研究，並於實驗中觀察各種不同莫爾比、試片密度 與預熱溫度對其火焰鋒面傳遞模式、燃燒溫度、火焰鋒面傳遞速 度之影響，並且詳細觀察燃燒合成產物與反應物元素當量比之關 係。 第一部份觀察各種不同莫爾比之鈮矽介金屬如：Nb3Si、 α-Nb5Si3、 β-Nb5Si3與NbSi2，以及複合材料Nb5Si3/Nb組成特性。 經由XRD分析其合成結果，在Nb：Si = 5：3其主要生成產物為 α-Nb5Si3；Nb：Si = 3：2其主要生成產物為β-Nb5Si3。而Nb：Si = 1：2除了生成NbSi2介金屬，尚殘留少許未反應之鈮與矽。於實驗 中搭配Nb：Si = 3：1發現無法利用此方法引起自持燃燒傳遞，因 而不加以探討。而實驗結果顯示出Nb：Si = 5：3其燃燒溫度與火 焰鋒面傳遞速度較其餘組態略高許多，並且比較所有組態之燃燒 溫度與火焰鋒面傳遞速度有相關一致性。在Nb5Si3/Nb複合材料方面，將鈮粉從5 mol%增加至15 mol%其燃燒溫度與火焰鋒面傳遞 速度都會隨著添加強化劑鈮粉的增加而降低，並且經由XRD分析 其主要生成產物為α-Nb5Si3以及少量未反應鈮粉殘留。根據組態5 ：3與1：2量測之燃燒溫度與火焰鋒面傳遞速度結果，計算出Nb5Si3 與NbSi2介金屬反應活化能約為259.2 kJ/mol與160.8 kJ/mol。 第二部份實驗為觀察各種不同莫爾比之鈮硼化合物組成特性 ，如：Nb3B2、NbB、Nb5B6、Nb3B4以及NbB2。經由XRD分析發 現，組態為1：1與1：2產物轉換率最佳，皆可合成出NbB與NbB2 。而組態為3：2、5：6以及3：4則會同時生成兩者或兩者以上之 鈮硼化合物(Nb3B4、NbB、NbB2)，並由實驗中發現無論搭配任何 組成皆無法合成出產物Nb3B2與Nb5B6。接著觀察Nb：B = 3：2燃 燒溫度與火焰鋒面傳遞速度偏低的原因，分析後發現是因為在燃 燒合成的過程中有大部份未反應的鈮粉殘留。再者，根據組態為1 ：1與1：2於預熱溫度200℃以上，火焰模式穩定平整的傳遞下， 量測之燃燒溫度與火焰鋒面傳遞速度結果，計算出NbB與NbB2反 應活化能約為151.8 kJ/mol與132.4 kJ/mol。 第三部份主要是觀察各種不同組態鉬矽介金屬，其中包含Mo3Si、Mo5Si3 以及MoSi2。產物合成結果在Mo：Si = 1：2 產物 轉換率最佳，能夠完美的合成出MoSi2 介金屬。而Mo：Si = 3：1 與5：3 並無法利用此方法引起自持燃燒傳遞，因而不加以探討。 於實驗中搭配Mo：Si = 2：3 與1：1 觀察其燃燒合成產物與反應 物元素當量比之關係，其同時生成產物MoSi2 與Mo5Si3 介金屬以 及未反應的鉬粉殘留。實驗結果顯示出Mo：Si = 3：2 與1：2 火 焰鋒面傳遞速度較Mo：Si = 1：1 略快，其燃燒溫度也較高。根 據組態1：2 於實驗中量測之燃燒溫度與火焰鋒面傳遞速度結果， 計算出MoSi2 介金屬反應活化能約為34.9 kJ/mol。

關鍵詞 : 鈮矽介金屬，鈮硼化合物，鉬矽介金屬， 自持傳遞高溫合成，活化能，預熱溫度，X 光粉末繞射分析儀

目錄

參考文獻

[1] 李弘斌, “ 高溫材料之自行燃燒合成反應的參數探討, ” 行政院國 家科學委員會, NSC 85-2216-E-228 – 001, 1996.

[2] 方建智, 謝誌鴻, 陳建忠. “ 低溫燃燒合成介金屬之機構探討 ” 中華民國材料年會, 台北市國立台灣大學, 2002.

[3] 朱世富 “ 材料科學與工程, ” 新文京開發出版股份有限公司, pp.327-329, 2002.

[4] 李弘斌, “ 粉末冶金的新發展－自行燃燒合成反應, ” 美國辛辛那 提大學國際微熱研究中心.

[5] K.Morsi., “ Review:reaction synthesis processing of Ni-Al intermetallics materials, ” Mater. Sci. Eng., A, Vol.299, pp. 1-15, 2001.

[6] M.N. Mungole, R. Balasubramaniam, A. Ghosh., “ Oxidation behavior of titanium aluminides of high niobium content, ” Intermetallics, Vol. 8, pp. 717-720, 2000.

[7] B.M. Warnes., N.S. DuShane, J.E.Cockerill., “ Cyclic oxidation of diffusion aluminide coatings on coalt base super alloys, ” Surface Coatings

Technol., Vol. 148, pp. 163-170, 2001.
[8] V. Gauthier, B F. ernard, E. Gaffet, D. Vrel, M. Gailhanou J.P. Larpin, “ Investigation of the formation mechanism of nanostructured NbAl3 via MASHS reaction, ” Intermetallics, Vol. 10, pp. 377-389, 2002.
[9] C. Nishimura, C.T. Liu, “ Reaction sintering of Ni3Al to near full density ” Scripta Metall. Mater., Vol. 26, pp. 381-385, 1992.
[10] Z.A. Munir, U. Anselmi-Tamburini, “ Self-propagating exothermic reaction:the synthesis of high-temperature materials by combustion, ” Mater. Sci. Rep., Vol. 3, pp. 277-365, 1989.
[11] A.G. Merzhanov, “ History and recent development in SHS, ” Ceram. Int., Vol. 21, pp. 371-379, 1995.
[12] J.J. Moore, H.J. Feng, “ Combustion synthesis of advanced materials:Part Ⅰ, ” Mater. Sci., Vol. 39, pp. 243-273, 1995.
[13] P. Mossino, “ Some aspects in self-propagating high-temperature synthesis, ” Ceram. Int., Vol. 30, pp. 311-332, 2004.
[14] P. Zhu, J.C.M. Li, C.T. Liu, “ Reaction mechanism of combustion synthesis, ” Mater. Sci. Eng. A, Vol. 329, pp. 57-68, 2002.
[15] A. Biswas, S.K. Roy, K.R. Gurumurthy, N. Parbhu, and S. Banerjee, “ A study of self-propagating high-temperature synthesis of NiAl in thermal explosion mode, ” Acta. Mater. Vol. 50, pp. 757-773, 2002.
[16] 李弘斌, “ 利用固體燃燒的材料製成法:自行傳播燃燒反應, ” 1996.
[17] J.J. Moore, H.J. Feng, “ Combustion Synthesis of Advanced Materials:Part I. Reaction Parameters, ” Progress in Mater. Sci., Vol. 39, pp. 243-273, 1995.
[18] J.J. Moore, and H.J. Feng, “ Combustion Synthesis of Advanced Materials:Part II. Classification, Applications and Modeling, ” Progress in Mater. Sci., Vol. 39, pp. 275-316, 1995.
[19] Makino, “ Fundamental Aspects of the Heterogeneous Flame in the Self-propagating High-temperature Synthesis （SHS） Process, ” Progress in Energy and Combust. Sci., Vol. 27, pp. 1-74, 2001.
[20] U. Anselmi-Tamburini, F. Maglia, G. Spinolo, S. Doppiu, M. Monagheddu, G. Cocco., “ Self-propagating reactions in the system Ti-Si:a SHS-MASHS comparative study, ” J. Mater. Syn. Proc., Vol. 8, pp. 377-383, 2000.
[21] C.L. Yeh, C.C. Hsu, “ An experimental study on Ti5Si3 formation by combustion synthesis in self-propagating mode, ” J Alloys Comp., Vol. 395, pp. 53-58, 2005.
[22] J.D. Rigney, P.M. Singh, J.J. Lewandowski, “ Environmental Effects on Ductile-Phase Toughening in Nb5Si3-Nb Composites, ” J Organomet. Chemie., Vol. 36, pp.36-41, 1992.
[23] M.G. Mendiratta, J.J. Lewandowski, D. Dimiduk, “ Microstructures and mechanical behavior of two-phase Nb silicide-Nb alloys, ” Mater. Res. Soc. Symp. Proc., Vol. 133, pp. 441-446, 1989.
[24] M.G. Mendiratta, D.M. Dimiduk, “ Phase relations and transformation kinetics in the high Nb region of the Nb-Si system, ” Scripta Metall., Vol. 25, pp. 237-242, 1991.
[25] J.J. Lewandowski, D. Dimiduk, W.R. Kerr., M.G. Mendiratta, “ Microstructural Effects on Nb-Nb Silicide Composite Properties, ” Mater. Res. Soc. Symp. Proc., Vol. 120, pp. 103-108, 1990.
[26] M.G. Mendiratta, J.J. Lewandowski, D. Dimiduk, “ strength and ductile-phase toughening in the two-phase Nb/Nb5Si3 alloys, ” Metall. Trans. A., Vol. 22A, pp. 1573-1583, 1991.
[27] S. Gedevanishvili, Z.A. Munir, “ Field-activated combustion synthesis in the Nb-Si system, ” Mater. Sci. Eng. Vol. A211, pp. 1 – 9, 1996.
[28] A.R. Sarkisyan, S.K. Dolukhanyan, I.P. Borovinskaya, “ Laws of the combustion of mixtures of transition metals with silicon and the synthesis of silicides, ” Combust. Explos. Shock Waves, Vol. 15, pp. 112-115, 1979.
[29] M.E. Schlesinger, H. Okamoto, A.B. Gokhale, R. Abbaschian, “ The NbSi (Niobium-Silicon) System, ” J. Phase Equilib., Vol. 14 pp. 502-509, 1993.
[30] A. Feng, Z.A. Munir, “ Field-Assisted Self-Propagating Synthesis of β-SiC, ” J. Appl. Phys., Vol. 76, pp. 1927, 1994.
[31] A. Feng, Z.A. Munir, “ The effect of an electric field on self-sustaining combustion synthesis part 1:modeling studies, ” Metall. Mater. Trans., Vol. 26B, pp. 581-586, 1995.
[32] A. Feng, Z.A. Munir, “ The effect of an electric field on self-sustaining combustion synthesis part 2 : field-assisted synthesis of β-SiC, ” Metall. Mater. Trans., Vol. 26B, pp. 587-593, 1995.
[33] S. Gedevanishvili, Z.A. Munir, “ Field-assisted combustion synthesis of MoSi2 ± SiC composites, ” Scripta Metall. Mater., Vol. 31, pp. 741, 1994.
[34] I.J. Shon, Z.A. Munir, “ Synthesis of TiC and TiC-Cu composites and TiC-Cu functionally-graded materials by electothermal combustion, ” J. Amer. Ceram. Soc., Vol. 81, pp. 3243, 1998.
[35] A.G. Merzhanov, “ Solid flames:discovery, concepts and horizons of cognition, ” Combust. Sci. Technol. Vol. 98, pp. 307-336, 1994.
[36] P. Mossino, “ Some aspects in self-propagating high-temperature synthesis, ” Ceram. Int. Vol. 30, pp. 311 – 332, 2004.
[37] S. Otani, M.M. Korsukova, T. Mitsuhashi, “ Floating zone growth and high-temperature hardness of NbB2 and TaB2 single crystals, ” J. Crystal Growth Vol. 194, pp.430-433, 1988.
[38] A.G. Merzhanov, I.P. Borovinskaya, “ Self-propagating synthesis of high-melting inorganic compounds, ” Dokl. Akad. Nauk USSR Vol. 204, pp.366-369, 1972.

[39] I.P. Borovinskaya, A.G. Merzhanov, N.P. Novikov, A.K. Filonenko, “ Gasless combustion of powder mixtures of the Transition metals with boron, ” Combust. Explos. Shock Waves Vol. 10, pp. 2-10, 1974.
[40] D.D. Radev, M. Marinov, “ Properties of titanium and zirconium diborides obtained by self-propagated high-temperature synthesis, ” J. Alloys Compd. Vol. 244, pp. 48-51, 1996.
[41] A.A. Zenin, A.G. Merzhanov, G.A. Nersisyan, “ The investigation of thermal wave structure in SHS processes on example boride synthesis, ” Dokl. Phys. Chem. Vol. 250, pp. 83-87, 1980.
[42] A.A. Zenin, A.G. Merzhanov, G.A. Nersisyan, “ thermal wave structure in SHS processes by the example of borides synthesis, ” Combust. Explos. Shock. Waves Vol. 17, pp. 63-71, 1981.
[43] T. Tsuchida, T. Kakuta, “ Synthesis of NbC and NbB2 by MA-SHS in air process, ” J. Alloys Comp. Vol. 398, pp. 67-73, 2005.
[44] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, “ Superconductivity at 39K in Magnesium Diboride, ” Nature Vol.410, pp.63-64, 2001.
[45] I. Zlotnikov, I. Gotman, E.Y. Gutmanas, “ Processing of dense bulk MgB2 superconductor via pressure-assisted thermal explosion mode of SHS, ” J. Eur. Chem. Soc. Vol.25, pp. 3517-3522, 2005.
[46] K. Przybylski, L. Stobierski, J. Chmist, A. Kolodziejczyk, “ Synthesis and properties of MgB2 obtained by SHS method, ” Physica C Vol. 387, pp. 148-152, 2003.
[47] K. Przybylski, J. Chmist, R. Zalecki, A. Kolodziejczyk, “ Effect of microstructure on properties of MgB2 synthesized by SHS method, ” Physica C Vol. 408-410, pp. 117-119, 2004.
[48] H. Takeya, A. Matsumoto, K. Hirata, Y.S. Sung, K. Togano, “ Superconducting phase in niobium diborides prepared by combustion synthesis, ” Physica C Vol. 412-414, pp. 111-114, 2004.
[49] A. Yamamoto, C. Takao, T. Masui, M. Izumi, S. Tajima, “ High-pressure synthesis of superconducting Nb1-xB2(x＝0-0.48) with the maximum Tc=9.2 K, ” Physica C Vol. 383, pp.197 – 206, 2002.
[50] P. de la Mora, M. Castro, G. Tavizon, “ Comparative of the electronic structure of alkaline-earth borides (MeB；Me＝Mg, Al, Zr, Nb and Ta) and their normal-state conductivity, ” J. Solid State Chem. Vol. 169, pp.168-175, 2002.
[51] C.A. Nunes, D. Kaczorowski, P. Rogl, M.R. Baldissera, P.A. Suzuki, G.C. Coelho, A. Grytsiv, G. Andre, F. Bouree, S. Okada, “ The NbB2-phase revisited:Homogeneity range, defect structure, Superconductivity, ” Acta Mater., Vol. 53, pp. 3679-3687, 2005.
[52] B.K. Yen, T. Aizawa, J. Kihara, “ Synthesis and formation mechanisms of molybdenum silicides by mechanical alloying, ” Mater. Sci. Eng., Vol. A220, pp. 8-14, 1996.
[53] C.D. Seetharama, N.T. Naresh, “ Reaction synthesis of high-temperature silicides, ” Mater. Sci. Eng., Vol. A192/193, pp. 8-14, 1996.
[54] Ch. Gras, D. Vrel, E. Gaffet, F. Bernard, “ Mechanical activation effect on the self-sustaining combustion reaction in the Mo-Si system, ” J. Alloys Comp., Vol. 314, pp. 240-250, 2001.
[55] S. Zhang, Z.A. Munir, “ Synthesis of molybdenum silicides by the self-propagating combustion method, ” J. Mater. Sci., Vol. 26, pp. 3685-3688, 1991.
[56] J.J. Petrovic, “ MoSi2-Base High-Temperature Structural Silicide, ” MAS Bull., Vol. XVIII, pp. 35, 1993.
[57] J.J. Petrovic, and A.K. Vasudevan, “ Overview of high temperature structural silicides, ” Mater. Res. Soc. Symp. Proc., Vol. 322, pp. 3, 1994.
[58] J.J. Petrovic, A.K. Vasudevan, “ A comparative overview of molybdenum disilicide composites, ” Mater. Sci. Eng., Vol. A155, pp. 1, 1992.
[59] J.J. Petrovic, “ Mechanical behavior of MoSi2 and MoSi2 composites, ” Mater. Sci. Eng., Vol. A192/193, pp. 31-37, 1995.
[60] S.W. Jo, G.W. Lee, J.T. Moon, Y.S. Kim, “ On the formation of MoSi2 by self-propagating high-temperature synthesis, ” Acta Mater., Vol. 44, pp. 4317-4326, 1996.
[61] M. Eslamloo-Grami, and Z.A. Munir, “ Effect of Nitrogen Pressure and Diluent Content on the Combustion Synthesis of Titanium Nitride, ” J. Amer. Ceram. Soc. Vol. 73, pp. 2222-2227, 1990.