

利用固相置換反應於燃燒合成硼化鉬與其複合材料之研究

許瑋升、葉俊良

E-mail: 9607731@mail.dyu.edu.tw

摘要

本實驗研究係以自持傳遞高溫合成法 (Self-propagating High temperature Synthesis, SHS) 於充滿氫氣環境燃燒室中燃燒合成硼化鉬 (MoB) 並結合 MoO₃ 與硼的固相置換反應進行硼化鉬 Mo₂B、MoB₂、Mo₂B₅、MoB₄ 四種化合物的燃燒合成，並探討其燃燒反應之特性，研究其在氫氣壓力 0.136 MPa、試片密度為 40% 最大理論密度時，其火焰鋒面傳遞模式、火焰鋒面傳遞速度、燃燒合成溫度以及合成產物之影響與其複合材料各組態硼化鉬與氧化鋁、MoB-MoSi₂ 與 MoSi₂-Al₂O₃ 三種複合材料之結合，探討其燃燒反應之特性。實驗結果顯示以 SHS 合成 MoB 之燃燒反應，其火焰鋒面為平整穩定地傳遞模式，而藉由影像觀察之結果顯示出火焰鋒面於預熱溫度較高的情形下試片會產生二次燃燒的現象，並且在預熱溫度越高的情形下其火焰鋒面傳遞速度會有逐漸增加地趨勢，而合成 Mo₂B、MoB₂、Mo₂B₅、MoB₄ 之燃燒反應其火焰傳遞模式為一平整的火焰鋒面穩定地向下傳遞，而藉由影像觀察之結果發現試片會有明顯的膨脹現象與煙霧狀物質產生。而其火焰鋒面傳遞速度皆隨著試片中硼化鉬組態之莫耳分率的提高，而有逐漸下降的趨勢，這是因為在相對情形下置換反應中 MoO₃ 含量相對遞減的情形下，反應放熱能量變小，使其鋒面傳遞速度也隨著下降。而燃燒反應之最高燃燒溫度也隨著試片中硼化鉬莫耳分率的下降，而有逐漸上升的趨勢，與火焰鋒面傳遞速度有相對應的關係。四種組態中最高燃燒溫度最高的為 MoB₂，其次則為 Mo₂B 最低的是 Mo₂B₅ 而 MoB₄ 的實驗反應因為產物的生成大部分為 Mo₂B₅ 所以其燃燒溫度與 Mo₂B₅ 的實驗接近。利用 XRD 分析產物的結果中我們可以知道利用置換反應在生成 MoB₂ 與 Mo₂B₅ 兩種產物的成果最好，而在生成 Mo₂B 方面則會有大量的 Mo 殘留與生成些許的 -MoB，而於合成 MoB₄ 方面，雖然提高其莫耳分率但主要產物卻都是 Mo₂B₅，僅能生成少許的 MoB₄，三種產物的生成皆會有隨著莫耳分率的提高而有逐漸變好的趨勢。

關鍵詞：自持傳遞高溫合成法，置換反應，火焰鋒面傳遞模式，火焰鋒面傳遞速度，燃燒合成溫度

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參考文獻

- [1] D.R. Askeland, P.P. Phule, "The Science and Engineering of Materials Fourth Edition," 2005.
- [2] Z.A. Munir, U.A. Tamburini, "Self-Propagating Exothermic Reactions; The Synthesis of High-Temperature Materials by Combustion," Mater. Sci. Rep., Vol. 3, pp. 227-365, 1989.
- [3] Y. Choi, S. Rhee, "Effect of Precursors on the Combustion Synthesis of TiC-Al₂O₃ Composite," J. Mater. Res., Vol. 9, No. 7, pp. 1761-1766, 1994.
- [4] 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, NSC85-2216-E-228-001, 1996.

- [5] 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.
- [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 coal base super alloys,” *Surface Coatings Technol.*, Vol. 148, pp. 163-170, 2001.
- [8] A. G.,Merzhanov, “Solid Flames: Discoveries, Concepts, and Horizons of Cognition,” *Combustion Science and Technology*, Vol. 98, pp. 307-336, 1994.
- [9] J. J. Moore, and H. J. Feng, “Combustion Synthesis of Advanced Materials: Part I. Reaction Parameters,” *Progress in Materials Science*, Vol. 39, pp. 243-273, 1995.
- [10] J. J. Moore, and H. J. Feng, “Combustion Synthesis of Advanced Materials: Part II. Classification, Applications and Modeling,” *Progress in Materials Science*, Vol. 39, pp. 275-316, 1995.
- [11] A. Makino, “Fundamental Aspects of the Heterogeneous Flame in the Self-propagating High-temperature Synthesis (SHS) Process,” *Progress in Energy and Combustion Science*, Vol. 27, pp. 1-74, 2001.
- [12] H. Kudo, O. Odawara, “Characteristics of Self-Propagating Reaction in TiN Combustion Synthesis,” *J. Mater. Sci.*, 24, pp. 4030-4033, 1989.
- [13] A.G. Merzhannov, and I. P. Borovinskaya, “Self-Propagation High- Temperature Synthesis of Refractory Inorganic Compounds,” *Doklady Akademii Nauk USSK*, Vol. 204, No. 2, pp. 366-369, 1972.
- [14] 李弘斌, “利用固體燃燒的材料製成法:自行傳播燃燒反應,” 1996.
- [15] B. Aronsson., T. Lundstrom., and S. Rundqvist, *Borides, Silicides and Phosphides: A Critical review of their Preparation and Crystal Chemistry*.Metheun and Co., Ltd, London. 1965.
- [16] R.A. Cutler., ‘ ‘Ceramics and Glasses-Engineered Materials Handbook’ ’. Vol. 4. ed. S. J. Schneider, Jr, ASM International: Materials Park. USA. 1991, p. 787.
- [17] A.C. Silva, and M. J. Kaufman, ‘ ‘Synthesis of MoSi₂- boride composites through in situ displacement reactions’ ’ *Intermetallics*, Vol 5, pp 1-15, 1997.
- [18] A.W. Weimer (Ed.), *Carbide, Nitride and Boride Materials Synthesis and Processing*, Chapman and Hall, London, 1997, p. 3.
- [19] L. L. Wang, Z. A. Munir, Y. M. Maximov, ‘ ‘Review Thermite reactions: their utilization in the synthesis and processing of materials’ ’ *J. Mater. Sci.*, Vol. 28 pp. 3693-3708, 1993.
- [20] R. Subramanian, C.G. McKamey, L.R. Buck, J.H. Schneibel, ‘ ‘Synthesis of iron aluminide – Al₂O₃ Composites by in-situ displacement reactions’ ’ *Mater. Sci. Rep.*, Vol. A239-240 pp. 640-646, 1997.
- [21] C.H. Hanager, Jr., J.L. Brinhall, L.N. Brush, ‘ ‘Tailoring structure and properties of composites synthesized in situ using displacement reaction’ ’ *Mater. Sci. Rep.*, Vol. A195 pp. 65-67, 1995.
- [22] 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.
- [23] C.D. Seetharama, N.T. Naresh, “Reaction synthesis of high-temperature silicides,” *Mater. Sci. Eng.*, Vol. A192/193, pp. 8-14, 1996.
- [24] C.h. 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.
- [25] S. Zhang, Z.A. Munir, “Synthesis of molybdenum silicides by the self-propagating combustion method,” *J. Mater. Sci.*, Vol. 26, pp.3685-3688, 1991.
- [26] J.J. Petrovic, “MoSi₂-Base High-Temperature Structural Silicide,” *MAS Bull.*, Vol. XVIII, pp. 35, 1993.
- [27] J.J. Petrovic, and A.K. Vasudevan, “Overview of high temperature structural silicides,” *Mater. Res. Soc. Symp. Proc.*, Vol. 322, pp. 3, 1994.
- [28] J.J. Petrovic, A.K. Vasudevan, “A comparative overview of molybdenum disilicide composites,” *Mater. Sci. Eng.*, Vol. A155, pp. 1, 1992.
- [29] Y. Hitoshi, T. Kudoh, T. Suzuki, ‘ ‘Oxidation resistance of boronized MoSi₂’ ’ *Surface and Coatings Technology.*, pp169-170, 2003.
- [30] J.J. Petrovic, “Mechanical behavior of MoSi₂ and MoSi₂ composites,” *Mater. Sci. Eng.*, Vol. A192/193, pp. 31-37, 1995.
- [31] 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.