

探討置換型式與元素間之燃燒合成於金屬硼化物的製備

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摘要

本研究主要是探討利用燃燒合成技術嘗試生成不同金屬硼化物 (Ta-B、V-B、Cr-B、Nb-B、W-B) 之可能性，實驗分為二大部份：第一部份為單純利用純元素粉末，針對不同組態進行實驗；第二部份則為使用金屬氧化物，藉由置換反應形式進行試驗，並針對不同硼含量的變化作探討。並且在實驗結果分別對於火焰鋒面傳遞模式及速度、燃燒溫度以及生成產物之影響作為探討。

實驗第一部份則是觀察不同莫爾比之鉭硼(Ta-B)化物及釩硼(V-B)化物，鉭硼化物部份其固相火焰觀察則觀察到其火焰鋒面皆是以螺旋火焰鋒面向下傳遞，並且火焰鋒面傳遞速度及燃燒溫度得知整體速度為4~11.7 mm/s、燃燒溫度則約1200~1750。組態為Ta : B = 1 : 1時速度為最高約10.3~11.7 mm/s、燃燒溫度為1750，而組態2 : 1則最慢速度約4 mm/s、燃燒溫度約為1200。產物組成方面，組態Ta : B = 1 : 1及1 : 2皆生成單相產物TaB及TaB₂，並計算出活化能約187.7 kJ/mol及96.7 kJ/mol，而其他組態則生成多相產物Ta₂B、TaB、TaB₂、Ta₃B₄以及些許鉭元素殘留。釩硼化物部份其固相火焰反應模式則會隨著初始溫度的變化而改變，在初始溫度為100 時火焰鋒面皆是以螺旋方式傳遞，而當初始溫度為200以上時所有組態皆以平整穩態火焰傳遞。組態為V : B = 5 : 6時火焰鋒面傳遞速度為最高約26 mm/s，而組態1 : 2則為最低約2 mm/s，整體燃燒溫度則約介於1470~1600 之間。產物組成部分，組態V : B = 3 : 2、1 : 1、5 : 6及3 : 4皆生成單相產物VB，而組態2 : 3、1 : 2則生成多相產物VB、V₃B₄、VB₂。

第二部份為藉由金屬氧化物進行置換反應生成鈮硼(Nb-B)化物、鎢硼(Cr-B)化物、鎔硼(W-B)化物。鈮硼化物其反應範圍在Nb₂O₅ : B = 1 : 5 ~ 1 : 10之間，火焰鋒面則是以平整穩態傳遞，而火焰鋒面傳遞速度則是在比例為1 : 8.5時最高約3.9 mm/s，而1 : 5則為最慢約1.75 mm/s；燃燒溫度則是在比例1 : 8.5及1 : 9時為最高，約介於1300~1380 之間，而比例1 : 5則為最低約1050。產物生成則在比例為Nb₂O₅ : B = 1 : 9及1 : 10生成單相產物NbB₂，而其他比例則生成多相產物NbB、Nb₃B₄以及些許金屬氧化物殘留。鎢硼化物反應範圍在Cr₂O₃ : B = 1 : 4 ~ 1 : 9，火焰鋒面以穩態傳遞，火焰鋒面傳遞速度則在比例為1 : 6時為最高約2.7 mm/s而最慢則在比例為1 : 4約0.9 mm/s，整體燃燒溫度約在705~828 之間。產物組成則無法生成單相產物，僅有在1 : 9時能生成較接近單相產物CrB₂，其他比例下則生成多相產物CrB、CrB₂、Cr₅B₃。鎔硼化物在不同硼含量下添加鎢參與反應，其反應範圍在WO₃ : B : W = 1 : 6、7、7.5 : 0.5 ~ 2.3，火焰鋒面則是以螺旋火焰傳遞，傳遞速度及燃燒溫度則可以明顯看出隨著鎢的添加而降低，約介於1.5~3.2 mm/s及1300~1550 之間。產物組成則生成多相產物W₂B、WB、WB₂、WB₄及些許鎢。

綜合以上結果，在燃燒合成金屬硼化物的探討中，得到藉由元素間的反應或者搭配金屬氧化物來參與反應合成的結果。而在產物的生成方面，則歸納出單硼化物(MB)及二硼化物(MB₂)的相最容易生成。

關鍵詞：燃燒合成、金屬硼化物、置換反應

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- [1]R. Ramberg, C. F. Wolfe, W. S. Williams, " Engineering Property Limitations of Structural Ceramics and Ceramic Composites above 1600 °C, " Ceramic Engineering and Science Proceedings, Vol. 68, (1985) pp. 78-79.
- [2]W. S. Williams, " Scattering of Electrons by Vacancies in Nonstoichiometric Crystals of Titanium Carbide, " Journal of Applied Physics, Vol. 135, (1964) pp.505-510.
- [3]R.A. Varin, Ch. Chiu, S. Li, A. Calka, D. Wexler, " Application of controlled and electrical discharge assisted mechanical alloying for the synthesis of nanocrystalline MgB₂ superconducting compound, " Journal of Alloys and Compounds, Vol. 370, (2004) pp. 230-243.
- [4]S. Sugiyama, H. Taimatsu, " Mechanical properties of WC – WB – W₂B composites prepared by reaction sintering of B₄C – W – WC powders, " Journal of the European Ceramic Society, Vol. 24, (2004) pp. 871-876.
- [5]N. Gidikova, " Vanadium boride coating on steel, " Materials Science and Engineering, Vol. 278, (2000) pp. 181-186.
- [6]L.G. Yu, K.A. Khor, G. Sundararajan, " Boride layer growth kinetics during boriding of molybdenum by the Spark Plasma Sintering (SPS) technology, " Surface and Coatings Technology, Vol. 201, (2006) pp. 2849-2853.
- [7]A.G. Merzhanov, I.P. Borovinskaya, Dokl Akad Nauk SSSR, Vol. 204, (1972) pp. 366. (in Russian)[8]A.G. Merzhanov, A.K. Filonenko, I.P. Borovinskaya, Dokl Akad Nauk SSSR, Vol. 208(1973) pp. 892 (in Russian).
- [9]A.G. Merzhanov, I.P. Borovinskaya, " A New Class of Combustion Processes, " Combustion Science and Technology, Vol. 10, (1975) pp. 195-201.
- [10]Y. Kopit, " High-temperature synthesis gears up for continuous powder production ", Metal Powder Report, Vol. 58, PP.16-19, 2003.
- [11]A. Makino, C. K. Law, " Heterogeneous flame propagation in the self-propagating high-temperature synthesis (SHS) process: theory and experimental comparisons, " The Combustion Institute, Pittsburgh, (1992) pp. 1883 – 1891.
- [12]A.P. Hardt, R.W. Holsinger, " Propagation of gasless reactions in solids-II. Experimental study of exothermic intermetallic reaction rates, " Combustion and Flame, Vol. 21, (1973) pp. 91-97.

- [13]A.I. Kirdyashkin, Yu.M. Maksimov and A.G. Merzhanov, " Effects of capillary flow on combustion in a gas-free system, " Combustion, Explosion, and Shock Waves, Vol. 17 (1981) pp. 591-595.
- [14]A.A. Zenin, A.G. Merzhanov, G.A. Nersisyan, " Thermal Wave Structure in SHS Processes, " Combustion, Explosion, and Shock Waves, Vol. 17, (1981) pp. 63-71.
- [15]V.I. Itin, A.D. Bratchikov, A.G. Merzhanov, V.M. Maslov, " Principles of self-propagating high-temperature synthesis of titanium compounds with elements of the iron group, " Combustion, Explosion, and Shock Waves, Vol. 17, (1981) pp.293-298.
- [16]I.P. Borovinskaya, A.G. Merzhanov, N.P. Novikov, A.K. Filonenko. " Gasless combustion of mixtures of powdered transition metals with boron, " Combustion, Explosion, and Shock Waves, Vol. 10, (1974) pp.2-10.
- [17]N.P. Novikov, I.P. Borovinskaya, A.G. Merzhanov, " Dependence of the composition of the products and the combustion rate in metal-boron systems on the ratio of the reagents, " Combustion, Explosion, and Shock Waves, Vol. 10, (1974) pp.175-178.
- [18]V.M. Maslov, I.P. Borovinskaya, A.G. Merzhanov, " Problem of the Mechanism gasless Combustion, " Combustion, Explosion, and Shock Waves, Vol. 12, (1976) PP. 631-636.
- [19]Yu.M Maksimov, A.G. Merzhanov, Raskolenko LG, A.T. Pak, O.K. Lepakova, Dokl Akad Nauk SSSR Vol. 286, (1986) pp. 911.(in Russian)
- [20]Yu.S. Naiborodenco, V.I. Itin, " Gasless Combustion of Metal Powder mixtures, " Combustion, Explosion, and Shock Waves, Vol. 11, (1975) pp. 293-300.
- [21]Yu.S. Naiborodenco, V.I. Itin, " Gasless Combustion of mixtures of Metal Powder, " Combustion, Explosion, and Shock Waves, Vol. 11, (1975) pp. 626-629.
- [22]V.N. Bloshenko, V.A. Bokii, I.P. Borovinskaya, A.G. Merzhanov, " Self-cleaning of SHS titanium carbide from impurity oxygen, " Combustion, Explosion, and Shock Waves, Vol. 20, (1984) PP. 676-679.
- [23]V.M. Shkiro, I.P. Borovinskaya, " Study of combustion mechanism for mixtures of titanium with carbon, " Akad. Nauk SSSR, (1975) pp. 253 – 258 (in Russian).
- [24]A. G. Merzhanov, Z. A. Munir and J. B. Holt (Eds), " Combustion and Plasma Synthesis of High-Temperature Materials, " VCH, New York, (1990) pp. 1-53.
- [25]L.L. Wang, Z. A. Munir and J.B. Holt (Eds), " Combustion and Plasma Synthesis of High-Temperature Materials, " VCH, New York, (1990) pp. 204-210.
- [26]R.A. Cutler, A.V. Virkar and J.B. Holt, " Synthesis and Densification of Oxide-Carbide Composites, " Ceramic Engineering and Science, Vol. 6, (1985) pp.715.
- [27]J.B. Hol, G. L. Messing (Ed), " Advances in Ceramics, " Vol. 21, Ceramic Powder Science, The American Ceramic Society, Westerville, OH, (1987) pp. 301-10.
- [28]L.L. Wang, Z.A. Munir, Y.M. Maximov, " Review Thermite reactions: their utilization in the synthesis and processing of materials, " Journal of Materials Science, Vol. 28, (1993) pp. 3693-3708.
- [29]N. Gidikova, " Vanadium boride coatings on steel, " Materials Science and Engineering A, Vol. 278, (2000) pp. 181-186.
- [30]I.P. Borovinskaya, A.G. Merzhanov, N.P. Novikov, A.K. Filonenko, " Gasless combustion of powder mixtures of the Transition metals with boron, " Combustion, Explosion, and Shock Waves, Vol. 10, (1974) pp. 2-10.
- [31]D.D. Radev, M. Marinov, " Properties of titanium and zirconium diborides obtained by self-propagated high-temperature synthesis, " Journal of Alloys and Compounds. Vol. 244, (1996) pp. 48-51.
- [32]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, (1980) pp. 83-87.
- [33]S. Otani, M.M. Korsukova, T. Mitsuhashi, " Floating zone growth and high-temperature hardness of NbB₂ and TaB₂ single crystals, " Journal of. Crystal Growth Vol. 194, (1988) pp.430-433.
- [34]T. Tsuchida, T. Kakuta, " Synthesis of NbC and NbB₂ by MA-SHS in air process, " Journal of Alloys and Compounds. Vol. 398, (2005) pp. 67-73.
- [35]J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, " Superconductivity at 39K in Magnesium Diboride, " Nature, Vol.410, (2001) pp.63-64.
- [36]S. Okada, K. Kudou, K.Iizumi, K. Kudaka, I. Higashi, T. Lundstrom. " Single-crystal growth and properties of CrB, Cr₃B₄, Cr₂B₃ and CrB₂ from high-temperature aluminum solutions, " Journal of Crystal Growth, Vol. 166 (1996) 429-435.