探討反應模式與反應物熔點對燃燒合成金屬氮化物/碳化物之研究

劉二瑋、葉俊良

E-mail: 9509791@mail.dyu.edu.tw

摘 要

本實驗研究是以自持傳遞高溫合成法（Self-propagating High temperature Synthesis, SHS）探討在不同之反應模式下，所合成之金屬氮化物與碳化物。由於反應物反應形式之不同，所得之產物與結果則有所差異，因此本實驗中所探討之反應模式，乃以反應物進行反應之形式區分，主要為固相-氣相之燃燒反應、固相-固相之燃燒反應，以及同時進行固相-固相與固相-氣相之燃燒反應，並於此三種反應模式中特別針對其火焰鋒面傳遞模式、火焰鋒面傳遞速度及燃燒溫度變化等燃燒特性加以觀察，並於固相-氣相反應模式中研究試片密度、預熱溫度、稀釋劑含量及氮氣壓力對於火焰傳遞速度與產物轉換率之影響；在固相-固相反應模式中則探討試片密度、預熱溫度、稀釋劑含量對於產物組成之影響；而同時進行固相-固相與固相-氣相反應模式中，則是改變金屬粉末與碳粉末之混合比以合成不同[C]/([C]+[N])函數比之金屬碳氮化物，最後再將實驗所得之產物進行產物顯微結構之觀察與成份分析。在固相-氣相之燃燒反應中，分別以鉭及鋁為反應物，於0.274～4.238MPa之氮氣環境下燃燒合成金屬氮化物，由於鉭之熔點甚高，因此利用低熔點之鋁作為反應物，以探討反應物熔點對於固相-氣相燃燒反應之影響，實驗結果顯示，在固相-氣相燃燒反應過程中，均有出現二次燃燒現象，而由於鋁之熔點較低，因此在反應過程中明顯熔化變形，由於反應需外部氮氣滲透參與反應，因此試片密度與氮氣壓力則為固相-氣相反應中之重要參數，降低試片密度與提高氮氣壓力均可有效提升產物之氮化率，而氮-鋁反應時易因高溫熔化，故需添加稀釋劑來加以改善，當稀釋劑含量為50wt%時，則可有效防止試片熔化而使產物氮化率提升。而固相-固相之反應模式則是將鉭與碳於氬氣中形成碳化鉭，實驗結果顯示可合成出TaC與Ta2C兩種產物，藉由熱電偶所量測之反應溫度約介於1700～1800oC之間，而產物TaC外觀上則明顯膨脹且有明顯裂痕，經成分分析後可知產物中會有少許鉭殘留，而產物Ta2C中則有生成少許TaC，只需提高產物密度即可改善，而藉由火焰鋒面傳遞速度與反應溫度，可計算出碳-鉭反應之活化能分別為TaC：187.42及Ta2C：298.97 kJ/mole。而將鉭與碳置於氮氣中燃燒，即可同時進行固相-固相與固相-氣相反應而生成碳氮化鉭，而碳含量與氮氣壓力則為影響反應之最主要參數，增加氮氣壓力則可使產物氮化率提升，含碳量越高時越不容易發生二次燃燒，而產物分析中發現，所得之產物均有鉭殘留，且含碳量較低之產物易有中間產物Ta2N生成。

關鍵詞 : 自持傳遞高溫合成法 ; 反應模式 ; 固相-氣相之燃燒反應 ; 固相-固相之燃燒反應 ; 同時進行固相-固相與固相-氣相之燃燒反應 ; 反應物熔點

目錄

參考文獻

1. Merzhanov, A. G.,“ Solid Flames: Discoveries, Concepts, and Horizons of Cognition, ” Combustion Science and Technology, Vol. 98, pp. 307-336, 1994. 2. Moore, J. J., and Feng, H. J.,“ Combustion Synthesis of Advanced Materials: Part I. Reaction Parameters, ” Progress in Materials Science, Vol. 39, pp. 243-273, 1995. 3. Moore, J. J., and Feng, H. J.,“ Combustion Synthesis of Advanced Materials: Part II. Classification, Applications and Modeling, ” Progress in Materials Science, Vol. 39, pp. 275-316, 1995. 4. Makino, A.,“ 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. 5. H. Kudo, O. Odawara,“ Characteristics of Self-Propagating Reaction in TiN Combustion Synthesis, ” J. Mater. Sci., 24, pp. 4030-4033, 1989. 6. Yeh, C. L. and Chuang, H. C.,“ Combustion Characteristics of SHS Process of Titanium Nitride with TiN Dilution, ” Ceramics International, Vol. 30, No. 5, pp. 705-714, June, 2004. 7. Merzhannov, A. G. and Borovinskaya, I. P.,“ Self-Propagation High-Temperature Synthesis of Refractory Inorganic Compounds, ” Doklady Akademii Nauk USSK, Vol. 204, No. 2, pp. 366-369, 1972. 8.

Karen Holloway, Peter M. Fryer, Cyril Cabral, Jr., J. M. E. Harper, P. J. Bailey, and K. H. Kelleher, ” Tantalum as a diffusion barrier between copper and silicon: Failure mechanism and effect of nitrogen additions ” Journal of Applied Physics, June 1, Volume 71, Issue 11, pp. 5433-5444, 1992. 9. Kyung-Hoon Min, Kyu-Chang Chun, and Ki-Bum Kim, "Comparative study of tantalum and tantalum nitrides (Ta2N and TaN) as a diffusion barrier for Cu metallization" Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures, Volume 14, Issue 5, pp. 3263-3269, September 1996. 10. Leng, Y. X., Sun, H., Yang, P., Chen, J. Y., Wang, J., Wan, G. J., Huang, N., Tian, X. B., Wang, L. P., and Chu, P. K., Biomedical properties of tantalum nitride films synthesized by reactive magnetron sputtering, Thin Solid Films,398,471-475, 2001. 11. Agrafiotis, C. C., Puszynski, J. A., and Hlavacek, V., “ Experimental Study on the Synthesis of Titanium and Tantalum Nitrides in the Self-Propagating Regime, ” Combust. Sci. Technol., 76, pp. 187-218, 1991. 12. Khyzhun Yu., Kolyagin V.A., Electronic structure of cubic and rhombohedral tantalum carbonitrides studied by XPS, XES, and XAS methods, J. Electron Spectrosc. Relat. Phenom. 137 – 140, pp. 463 – 467, 2004. 13. P. Huber, D. Manova, S. B. Mandl, ” Rauschenbach, Formation of TiN, TiC and TiCN by metal plasma immersion ion implantation and deposition, ” Surf. Coatings Technol., 174-175, pp. 1243-1247, 2003. 14. J. B. Holt, Z. A. Munir, “ Combustion synthesis of titanium carbide : theory and experiment, ” J. Mater. Sci., 21, pp. 251-259, 1986. 15. M. Eslamloo-Grami, Z. Munir, “ Effect of Porosity on the Combustion Synthesis of Titanium Nitride, ” J. Am. Ceram. Soc., 73(5), pp. 1235-1239, 1990. 16. M. Eslamloo-Grami, Z.A. Munir, “ Effect of Nitrogen Pressure and Diluent Content on the Combustion Synthesis of Titanium Nitride, ” J. Am. Ceram. Soc., 73, No. 5 , pp. 2222-2227, 1990. 17. C. C. Agrafiotis, J. A. Puszynski and V. Hlavacek, “ Experimental Study on the Synthesis of Titanium and Tantalum Nitrides in the Self-Propagation Regime ” Comb. Sci. Technol., Vol. 76, pp. 187-218, 1991. 18. M. Eslamloo-Grami, Z.A. Munir, “ The mechanism of combustion synthesis of titanium carbonitride, ” J. Mater. Res., 9(2), pp. 431-435, 1994. 19. A.B. Avakyan, A.R. Bagramyan, I.P. Borovinskaya, S.L. Grigoryan, A.G. Merzhanov, in: A.G. Merzhanov (Ed.), “ Processes of Burning in Chemical Technology and Metallurgy ” , Institute of Chemical Physics of the USSR, Chernogolovka, pp. 98, in Russian, 1975. 20. E.M. Gololobov, V.B. Shipilo, N.I. Sedrenok, A.I. Dudyak, Patent USSR No. 722341, dated 21 November 1979. 21. E.M. Gololobov, N.I. Sedrenok, in: Nitrides: Manufacturing, Properties and Applications, Vol. Vol. 1, Zinatne, Riga, pp. 87, 1984., 22. E.M. Gololobov, N.I. Sedrenok, N.A. Prytkova, Cryogenic Materials and their Welding, Naukova Dumka, Kiev, 1989. 23. O.Yu. Khyzhun, V.A. Kolyagin, X-Ray photoelectron and emission spectra of cubic and rhombohedral tantalum carbonitrides, Journal of Alloys and Compounds 363, pp. 32 – 39, 2004. 24. Chen, Y.-J., Li, J.-B., Wei, Q.-M., Zhai, H.-Z., "Preparation of different morphology of TaCx whiskers" Materials Letters 56 (3), pp. 279-283, 2002. 25. A. L. Giorgi, E. G. Szklarz, E. K. Storms, Allen L. Bowman, and B. T. Matthias, ” Effect of Composition on Superconducting Transition Temperature of Tantalum Carbide and Niobium Carbide ” Physical Review, Vol.125 Num.3, 1962. 26. Pedro Miguel Amaral, Jorge Cruz Fernandes, Luis Guerra Rosa, Diego Martinez, Jose Rodriguez, Nobumitsu Shohoji, “ Carbide formation of Va-group metals (V, Nb and Ta) in a solar furnace ” International Journal of Refractory Metals & Hard Materials, 18 pp. 47-53, 2000. 27. Cruz Fernandes J, Amaral PM, Guerra Rosa L, Martinez D, Rodriguez J, Shohoji N., “ X-ray diffraction characterisation of carbide and carbonitride of Ti and Zr prepared through reaction between metal powders and carbon powders (graphitic or amorphous) in a solar furnace ” International Journal of Refractory Metals and Hard Materials, Vol: 17, Issue: 6, November, pp. 437-443, 1999. 28. V. M. Shkiro, G. A. Nersisyan and I. P. Borovinskaya, "Principles of combustion of tantalum-carbon mixtures" Combust Explos Shock Waves 14 (4), pp. 455-460, 1978. 29. VA Knyazik, AS Shteinberg, High-temperature interaction in the Ta – C system under electrothermal explosion conditions, J. Mater. Synth. Process 1, pp. 85 – 91, 1993. 30. G. A. Slack, R. A. Tanzilli, R. O. Pohl, and J. W. Vandersande, "The Intrisic Thermal Conductivity of AlN," J. Phy. Chem. Solids, 48(7), 641, 1978. 31. T. J. Mroz, Jr., "Aluminum Nitride," Ceram. Bull., 71(5), 782, 1992. 32. A. W. Weimer, G. A. Cochran, G. A. Eisman, J. P. Henley, B. D. Hook, L. K. Mills, T. A. Guiton, A. K. Knudsen, N. R. Nicholas, J. E. Volmering, and W. G. Moore, "Rapid Process for Manufacturing Aluminum Nitride Powder," J. Am. Ceram. Soc., 77, [1] 3-18, 1994. 33. F. J.-M. Haussonne, "Review of Synthesis Method for AlN, "Mater. Manuf. Processes, 10(4), 717, 1995. 34. V. Rosenband, A. Gany "Activation of combustion synthesis of aluminum nitride powder "Journal of Materials Processing Technology 147 197 – 203, 2004. 35. R.-C. Juang, C.-J. Lee, C.-C. Chen "Combustion synthesis of hexagonal aluminum nitride powders under low nitrogen pressure" Materials Science and Engineering A 357 219 / 227, 2003. 36. M. Bo?kowski, M. Wroblewski, B. ?ucznik, I. Grzegory "Crystal growth of aluminum nitride under high pressure of nitrogen" Materials Science in Semiconductor Processing 4 543-548, 2001. 37. Steven M. Bradshaw and John L. Spicer, ” Combustion Synthesis of Aluminum Nitride Particles and Whiskers ” J. Am. Ceram. Soc., 82 [9] 2293 – 300, 1999. 38. Woo-Sik Jung, Hyeong Uk Joo, ” Catalytic growth of aluminum nitride whiskers by a modified carbothermal reduction and nitridation method ” , Journal of Crystal Growth, 285 566 – 571, 2005. 39. Alexander Gromov, Vladimir Vereshchagin “ Study of aluminum nitride formation by superfine aluminum powder combustion in air ” Journal of the European Ceramic Society 24 2879-2884, 2004. 40. Marin-Ayral, R. M., Pascal, C., Martinez, F., and Tedenac, J. C., “ Simultaneous Synthesis and Densification of Titanium Nitride by High Pressure Combustion Synthesis, ” Journal of the European Ceramic Society, Vol. 20, pp. 2679-2684, 2000. 41. Shibuya, M., Despres, J. F., and Odawara, O., “ Characteristic Sample Temperature and Pressure during Processing of Titanium Nitride Combustion Synthesis with Liquid Nitrogen, ” Journal of Materials Science, Vol. 33, pp. 2573-2576, 1998. 42. A. Makino, Fundamental aspects of the heterogeneous flame in the self-propagating high-temperature synthesis (SHS) process, Progress in Energy and Combustion Science, 27, pp. 1 – 74, 2001. 43. Zhang, S. and Munir, Z. A., “ The Combustion Synthesis of Refractory Nitrides, Part II The Synthesis of Niobium Nitride, ” J. Mater. Sci., 6, pp. 3380-3385, 1991.