

自持性燃燒合成金屬碳氮化物之實驗研究

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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) 於 0.274 ~ 1.653 MPa 之氮氣環境下燃燒合成碳氮化鈦 (Titanium Carbonitrides, Ti(CN))、碳氮化鈮 (Niobium Carbonitrides, Nb(CN)) 及碳氮化鈮 (Vanadium Carbonitrides, V(CN)) 等過渡金屬碳氮化物, 並改變過渡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, 且特別針對其火焰鋒面傳遞模式、火焰鋒面傳遞速度 (Flame-Front Velocity) 及燃燒溫度變化等燃燒特性詳細地觀察; 並研究試片密度、稀釋劑含量及氮氣壓力對於火焰傳遞速度與產物轉換率 (Conversion) 之影響, 以及產物顯微結構之觀察與成份分析。實驗結果顯示此三種燃燒反應皆具有二次燃燒 (Afterburning) 之特性, 且燃燒合成碳氮化鈦之產物試片具有熔化 (Melting) 之現象, 而碳氮化鈮燃燒反應具有脈衝波 (Pulsating) 燃燒傳遞之特性。藉由熱電偶量測得知碳氮化鈮之反應溫度約 1250°C ~ 1750°C 之間, 而碳氮化鈮之反應溫度約 1350°C ~ 1570°C。且 Nb(CN) 與 V(CN) 燃燒反應之後試片皆無熔化之現象, 故氮氣壓力與稀釋劑含量對產物轉換率並未造成顯著之影響, 因此其產物氮化率約 53% ~ 80% 左右; 但燃燒合成 Ti(CN) 之產物試片具有熔化現象, 因此藉由添加稀釋劑可吸收部份反應所釋放之熱量, 而減少鈦因受高溫而熔化之現象, 進而有效地抑制反應過程中試片之熔化變形維持其多孔性, 使得外界之氮氣依舊持續地供應反應所需, 故而有效地提高產物氮化率, 其最高幾乎可完全轉換達到所預期之各種不同組態碳氮化鈦產物, 因此其產物氮化率主要是受到稀釋劑含量之影響較氮氣壓力與試片密度為明顯。而燃燒合成 Ti(CN)、Nb(CN) 與 V(CN) 三種產物之 X 光粉末繞射分析 (X-Ray Diffraction, XRD) 結果顯示, 未添加稀釋劑之試片仍皆有許多未參與反應之金屬, 且其分別都有中間產物 Ti₂N、Nb₂N 以及 V₂N 之生成; 但若於反應物中添加稀釋劑則可有效地減少中間產物之生成近乎沒有。其掃描式電子顯微鏡 (Scanning Electron Microscope, SEM) 所攝得之顯微結構照片則顯示出未添加稀釋劑之碳氮化鈦試片與氮氣反應後其產物具嚴重之熔化現象; 而其添加高稀釋劑之試片與氮氣反應後其外觀上雖並無明顯之收縮、變形, 但於顯微結構下仍具有些微熔化之情形。

關鍵詞: 碳氮化鈦, 碳氮化鈮, 碳氮化鈮, 自持傳遞高溫合成, 二次燃燒, 脈衝波, 火焰鋒面, 稀釋劑

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參考文獻

- [1] W. Lengauer, "Transition metal carbides, nitrides and carbonitrides, in: R. Riedel (Ed.), " Handbook of Ceramic Hard Materials, 1, Wiley-VCH, Weinheim, pp. 202-252 (2000).
- [2] S. Zhang, "Material development of titanium carbonitride-based cermets for machining application," Key Eng. Mater, 138-140, pp. 521-543 (1998).
- [3] S. Bolognini, G. Feusier, D. Mari, T. Viatte, W. Benoit, "High temperature mechanical behavior of Ti(C,N)-Mo-Co cermets," Int. J. Refract. Metals Hard Mater, 16, pp. 257-268 (1998).
- [4] P. Ettmayer, H. Kolaska, W. Lengauer, K. Dreyer, "Ti(C,N) cermets-metallurgy and properties," Int. J. Refract. Metals Hard Mater., 13, pp. 343-351 (1995).
- [5] T. Francavilla, S. Wolf, E. Skelton, "Superconducting properties of reactively sputtered NbCN thin films," IEEE Transactions on Magnetics, 17(1), pp. 569-572 (2000).
- [6] M. Ohmer, J. Wollan, J. Ho, "Improved superconducting properties of multifilamentary niobium carbonitride wire," IEEE Transactions on Magnetics, 11(2), pp. 159-162 (1975).
- [7] W. Smith, R. Lin, J. Coppola, J. Economy, "Preparation and properties of multifilament niobium carbonitride superconductor," IEEE Transactions on Magnetics, 11(2), pp. 182-184 (1975).
- [8] J. R. Gavaler, M. A. Janocko, C. K. Jones, "Superconducting Properties of Niobium Carbonitride Thin Films," J. App. Phys., 19(8), pp. 305-307 (1971).
- [9] A. G. Merzhanov, "Solid Flames: Discoveries, Concepts, and Horizons of Cognition," Comb. Sci. Technol., 98, pp. 307-336 (1994).
- [10] J. J. Moore, H. J. Feng, "Combustion Synthesis of Advanced Materials: Part I. Reaction Parameters," Prog. Mater. Sci., 39, pp. 243-273 (1995).
- [11] J. J. Moore, H. J. Feng, "Combustion Synthesis of Advanced Materials: Part II. Classification, Applications and Modeling," Prog. Mater. Sci., 39, pp. 275-316 (1995).
- [12] A. Makino, "Fundamental Aspects of the Heterogeneous Flame in the Self-propagating High-temperature Synthesis (SHS) Process," Progr. Energy Combust. Sci., 27, pp. 1-74 (2001).
- [13] H. Kudo, O. Odawara, "Characteristics of Self-Propagating Reaction in TiN Combustion Synthesis," J. Mater. Sci., 24, pp. 4030-4033 (1989).
- [14] S. Kang, "Some issues in Ti(CN)-WC-TaC cermets," Mater. Sci. Eng., A209, pp. 306-312 (1996).
- [15] A. Bellosi, V. Medri, F. Monteverde, "Processing and properties of Ti(C,N)-WC-based materials," J. Am. Ceram. Soc., 84(11), pp. 2669-2676 (2001).
- [16] F. Monteverde, V. Medri, A. Bellosi, "Microstructure of hot-pressed Ti(C,N)-based cermets," J. Am. Ceram. Soc., 22, pp. 2587-2593 (2002).
- [17] A. Jha, S.J. Yoon, "Formation of titanium carbonitride phases via the reduction of TiO₂ with carbon in the presence of nitrogen," J. Mater. Sci., 34(2), pp. 307-322 (1999).
- [18] J. Xiang, Z. Xie, Y. Huang, H. Xiao, "Synthesis of Ti(C,N) ultrafine powders by carbothermal reduction of TiO₂ derived from sol-gel process," J. Eur. Ceram. Soc., 20, pp. 933-938 (2000).
- [19] L. M. Berger, W. Gruner, E. Langholf, S. Stolle, "On the mechanism of carbothermal reduction process of TiO₂ and ZrO₂," Int. J. Refract. Metals Hard Mater., 17, pp. 235-243 (1999).
- [20] H. Pastor, "Titanium carbonitride-based hard alloys for cutting tools," Mater. Sci. Eng., A105/106, pp. 401-409 (1988).
- [21] L. Ma, H. Bian, G. Liu, "Influence of CH₄/N₂ ratio on microstructure and mechanical properties of PCVD-Ti(C_xN_{1-x}) coating," Int. J. Refract. Metals Hard Mater, 13, pp. 369-374 (1995).
- [22] 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).
- [23] J. B. Holt, Z. A. Munir, "Combustion synthesis of titanium carbide: theory and experiment," J. Mater. Sci., 21, pp. 251-259 (1986).
- [24] 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).
- [25] 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).
- [26] 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).
- [27] M. Eslamloo-Grami, Z.A. Munir, "The mechanism of combustion synthesis of titanium carbonitride," J. Mater. Res., 9(2), pp. 431-435 (1994).
- [28] Ranjan, G.S. Upadhyaya, "Effect of copper and VCN additions on sintering of low alloy steel," Mater. Design, 22, pp. 359-367 (2001).
- [29] S. Abisset, F. Maury, L. Pelletier, J. M. Carretas, A. Pires De Matos, "Depot Chimique En Phase Vapeur A Basse Temperature De Revetements Dans Le Systeme [30] V-C-N A Partir De Bis(Arene) Vanadium." Ann. Chim. Sci. Mat, 23, pp. 695-706 (1998).