

探討氮化硼與氮化矽於燃燒合成含金屬氮化物複合材料之實驗研究

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摘要

本實驗研究係用以自持性傳遞高溫合成法(Self-propagating High-temperature Synthesis, SHS)進行燃燒反應合成，並且在組成中利用氮化硼(Boron Nitride)與氮化矽(Silicon Nitride)為反應物燃燒合成氮化鈦/二硼化鈦(TiN-TiB₂)、氮化鉭/硼化鉭(TaN-TaB)以及氮化鈦/矽化鈦(TiN-Ti₅Si₃)等含金屬氮化物之複合材料，其中BN及Si₃N₄可提升在固態來源中金屬氮化物的形成。在本研究的第一部份中，運用兩種系統的製成方式來反應合成複合材料(TiN-TiB₂)，一為在組成上搭配Ti和BN粉末的比例在氮氣壓力下反應，以燃燒合成TiN所佔比例為75~87.5之莫耳百分比的複合材料，另法則是在實驗中搭配組成Ti/BN/B在氮氣下反應，使其有足夠的硼成份反應合成50~75之莫耳百分比的TiB₂，由於在以往的反應系統中皆是固相與氣相間的反應，並且試片的孔隙度與稀釋劑TiN對於產物氮化率有明顯的影響，反之，組成上的改變在燃燒合成後易影響試片的結構。由實驗結果顯示，組成為(1.5Ti+BN)在氮氣下反應時，可完全轉換至(TiN/TiB₂=67/33)之莫耳比，並且證實BN確實是可完全分解反應生成TiN及TiB₂，另外在1.48MPa的氮氣壓力下包括無添加稀釋劑的組成(2Ti+BN)、60%之試片最大理論密度(Theoretical Maximum Density, TMD)、可直接生成75之莫耳百分比的TiN，以及在相同60%TMD下需添加稀釋劑之組成中能完全轉換高達83或87.5之莫耳百分比的TiN含量。在本研究的第二部份中，運用兩種方式來製成(TiN-Ti₅Si₃)之複合材料，一種是利用氮化矽(Si₃N₄)作為固態燃燒系統裡氮的固態來源，另一種則是運用Ti與Si粉末在氮氣壓力下反應，在Ti與Si₃N₄及Ti-Si₃N₄-Si之兩種固態燃燒反應系統下，能有效地生成(TiN-Ti₅Si₃)之產物比例可由20~80之莫耳百分比。此結果證實了Si₃N₄對於生成(TiN-Ti₅Si₃)之貢獻。不過，在Ti與Si於氮氣下靠固相與氣相的反應中，由實驗證實是個不理想之方法，對生成TiN而言，例如以80之莫耳百分比來說，發現Si與氮氣之間的反應不甚良好，反之，像20或甚至50之莫耳百分比一樣僅有低含量的TiN合成(TiN-Ti₅Si₃)，並且有中間產物TiSi₂及Si殘留。在本研究的第三部份中，嘗試進行(TaN-TaB)之複合材料，發現反應物BN於低氮氣壓力下皆反應不完全，因此，在最後的產物觀察分析中，有Ta₂N的中間產物生成，及一些未反應的Ta、BN殘留。故透過此研究建議，在燃燒反應(TaN-TaB)中，其BN的利用獲益不及(TiN-TiB₂)來的好。

關鍵詞：自持傳遞高溫合成，氮化鈦/二硼化鈦，氮化鉭/硼化鉭，氮化鈦/矽化鈦，二次燃燒，稀釋劑

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參考文獻

- [1] R. Niewa, F.J. DiSalvo, Chem. Mater., "Recent developments in nitride chemistry," Chem. Mater., Vol. 10, pp.2733, 1998.
- [2] A. Calka, "Formation of titanium and zirconium nitrides by mechanical alloying," Appl. Phys. Lett., Vol. 59, pp.1568, 1991.
- [3] Y. M. Shy, L.E. Toth, R. Somasundaram, "Superconducting properties, and structure of NbN thin films," J. Appl. Phys., Vol. 44, pp.5539, 1973.
- [4] T. Yamada, M. Shimada, M. Koizumi, "Fabrication and characterization of titanium nitride by high pressure hot pressing," Ceram. Bull., Vol. 59, pp. 611, 1980.
- [5] N. Pessall, R.E. Gold, H.A. Johansn, "Study of the perovskites Pb(NbFe)_{1/2}O₃ and Sr(TaFe)_{1/2}O₃ with the mossbauer effect," J. Phys. Chem. Solids., Vol. 29, pp. 19, 1968.
- [6] L. Shi, Z. Yang, L. Chen, and Y. Qian, "Synthesis and characterization of nanocrystalline TaN," J. Solid State Commun., Vol. 133, pp. 117, 2005.
- [7] K. Morsi, "Review : reaction synthesis processing of Ni-Al intermetallics materials," Mater. Sci. Eng.A, Vol. 299, pp. 1-15, 2001.

- [8] M. N. Warnes, R. Balasubramaniam, and A. Ghosh, "Oxidation behavior of titanium aluminides of high niobium content," *Intermetallics*, Vol. 8, pp. 717-720, 2000.
- [9] B. M. Warnes, N. S. DuShane, and J. E. Cockerill, "Cyclic oxidation of diffusion aluminide coatings on coal base super alloys" *Surface Coatings Technol.*, Vol. 148, pp. 163-170, 2001.
- [10] D. A. Hoke, D. K. Kim, J. C. LaSalvia, and M. A. Meyers, "Combustion Synthesis/Dynamic Densification of a TiB₂-SiC Composite," *J. Am. Ceram. Soc.*, Vol. 79, No. 1, pp. 177-182, 1996.
- [11] Z. A. Munir, "Synthesis of High Temperature Materials for Self-Propagating Combustion Method," *Am. '86 Ceram. Soc. Bull.*, Vol. 67, No. 2, pp. 342-349, 1988.
- [12] 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.
- [13] 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.
- [14] V. Gauthier, F. Bernard, E. Gaffet, D. Vrel, M. Gailhanou, and J. P. Larpin, "Investigation of the formation mechanism of nanostructured NbAl₃ via MASHS reaction," *Intermetallics*, Vol. 10, pp. 377-389, 2002.
- [15] C. Nishimura, C. T. Liu, "Reaction sintering of Ni₃Al to near full density," *Mater.*, Vol. 26, pp. 381-385, 1992.
- [16] Z. A. Munir, U. Anselmi-Tamburini, "Self-propagating exothermic reaction : the synthesis of high-temperature materials by combustion," *Mater. Sic. Rep.*, Vol. 3, pp. 277-365, 1989.
- [17] A. G. Merzhanov, "History and recent development in SHS," *Ceram. Int.*, Vol. 21, pp. 371-379, 1995.
- [18] J. J. Moore, H. J. Feng, "Combustion synthesis of advanced materials : Part I , " *Mater. Sci.*, Vol. 39, pp. 243-273, 1995.
- [19] P. Mossino, "Some aspects in self-propagating high-temperature synthesis," *Ceram. Int.*, Vol. 30, pp. 311-332, 2004.
- [20] A. G. Merzhanov, "Solid flame : discoveries, concepts, and horizons of cognition," *Comb. Sic. Technol.*, Vol. 98, pp. 307-336, 1994.
- [21] J. J. Moore, H. J. Feng, "Combustion syntheris of advanced materials : Part I. reaction parameters," *Prog. Mater. Sci.*, Vol. 39, pp. 243-273, 1995.
- [22] J. J. Moore, H. J. Feng, "Combustion syntheris of advanced materials : Part . classification, applications and modeling," *Prog. Mater. Sci.*, Vol. 39, pp. 275-316, 1995.
- [23] A. Makino, "Fundamental aspects of the heterogeneous flame in the self-propagating high-temperature synthesis (SHS) process," *Progr. Energy Combust. Sci.*, Vol. 27, pp. 1-74, 2001.
- [24] H. Kudo, O. Odawara, "Characteristics of self-propagating reaction in TiN combustion synthesis," *J. Mater. Sci.*, Vol. 24, pp. 4030-4033, 1989.
- [25] A. Pivkina, P. J. Van der Put, Y. Frolov, and J. Schoonman, "Reaction-Bonded Titanium Nitride Ceramics," *J. Am. Ceram. Soc.*, Vol. 16, pp.35-42, 1996.
- [26] R. Tomoshige, A. Murayama, and T. Matsushita, "Production of TiB₂-TiN Composites by Combustion Synthesis and Their Properties," *J. Am. Cream. Soc.*, Vol. 80, No. 3, pp. 761-764, 1997.
- [27] E. Galvanetto, F.P. Galliano, F. Borgioli, U. Bardi and A. Lavacchi, "XRD and XPS study on reactive plasma sprayed titanium-titanium nitride coatings," *Thin Solid Films*, Vol. 384, pp. 223-229, 2001.
- [28] J. H. Shim, J. S. Byun, Y. W. Cho, "Mechanochemical synthesis of nanocrystalline TiN/TiB₂ composite powder," *Mater. Sci.*, Vol. 47, pp. 493-497, 2002.
- [29] J. Yang, J. Wu, and W. Hua, "Study on mechanical alloying and subsequent heat treatment of the Ti-Si system," *Physica:B*, Vol. 279, pp. 241-254, 1999.
- [30] I. J. Shon, H. C. kim, D. H. Rho, and Z. A. Munir, "Simultaneous synthesis and densification of Ti₅Si₃ and Ti₅Si₃-20%ZrO₂ composites by field-activated and pressure assisted combustion," *Mater. Sci. Eng.A*, Vol. 269, pp. 129-135, 1999.
- [31] H. Inui, M. Moriwaki, N. Okamoto, and M. Yamaguchi, "Plastic deformation of single crystals of TiSi₂ with the C54 structure," *Acta. Materialia.*, Vol. 51, pp. 1409-1420, 2003.
- [32] G. Llauro, F. Gourblieau, F. Sibieude, and R. Hillel, "Oxidation behavior of CVD TiN-Ti₅Si₃ composite coatings," *Thin Solid Films*, Vol. 315, pp. 336-344, 1998.
- [33] I. Gotman, N. A. Travitzky, and E. Y. Gutmanas, "Dense in situ TiB₂/TiN and TiB₂/TiC Ceramic matrix composites : reactive synthesis and properties," *Mater. Sci. Eng.A*, Vol. 244, pp. 127-137, 1998.
- [34] 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.
- [35] C. L. Yeh, H. C. Chuang, "Combustion characteristics of SHS process of titanium nitride with dilution," *Ceram. Int.*, Vol. 30, pp. 705-714, 2004.