

论文摘要

中国有色金属学报

ZHONGGUO YOUSEJINSHUXUEBAO XUEBAO

第6卷 第3期 (总第20期) 1996年9月

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文章编号: (1996)03-74-5

超硬无机材料纳米粉末CVD合成热力学分析^①

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摘要: 通过热力学分析研究了超硬无机材料, 如SiC、Si₃N₄、TiC、TiN等纳米粉末的化学气相沉积(CVD)合成反应过程和核化过程的有关热力学规律。结果表明: 合成物以共价键和以金属键为主的合成反应和化学反应过程对温度、压力均比较敏感, 热力学驱动力随温度变化增加比较明显, 对外压的敏感表现为增大压力对合成反应不利。合成物以离子键为主时, 反应的热力学驱动力随温度变化不明显, 外压的影响也不显著。对于核化过程, 合成物以金属键和离子键为主的体系, 核化所需临界过饱和度较低, lg(p / p₀)在1-10之间, 而对合成物以共价键为主的体系, 核化所需过饱和度较高, lg(p / p₀)约在15-20之间, 因实验过程很难达到这样高的过饱和度, 因此合成粉体常以非晶态形式存在, 以降低核化阻力。

关键字: 超硬无机材料 纳米粉末 化学气相沉积(CVD) 热力学

THERMODYNAMIC ANALYSES FOR SUPERHARD INORGANIC MATERIAL NANOSIZED POWDER CVD SYNTHESIS PROCESSES

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Abstract: Thermodynamic analyses for the superhard inorganic material, such as SiC, Si₃N₄, TiC, TiN and so on, nanosized powder CVD synthesis processes were made systematically. For the metallic and the covalent bonding compounds, the synthesis reaction thermodynamic driving forces increased with the synthesis temperature considerably, compared with the ionic bonding compound synthesis reaction. The system pressure increase was of noticeable negative influence on the metallic and covalent bonding compound synthesis, but for the ionic compounds, its effect could be neglected. During the nucleation processes, the critical supersaturation for the metallic and the ionic bonding compound synthesis reaction was about 1~10,

much lower than that for the covalent bonding compound synthesis, which was in the range of 15~20. In practice, it was impossible for the covalent bonding compound synthesis reaction to meet the above requirement. Therefore, in most cases the as-synthesized powder exists in amorphous state to reduce the nucleation activation energy.

Key words: inorganic compounds nanosized powder CVD synthesis thermodynamic analyses

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