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水性溶胶-凝胶法制备  $\text{Al}_2\text{O}_3\text{-SiO}_2$  纤维的研究

Preparation and characterization of alumina-silica fibers via  
the water soluble sol-gel method

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水生容校一凝校去制备 $\text{Al}_2\text{O}_3\text{-SiO}_2$ 纤维的研究

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厦门大学

**Preparation and characterization of alumina-silica fibers via  
the water soluble sol-gel method**



A Dissertation Submitted to  
Xiamen University in Fulfillment of the Requirements for the  
Degree of Doctor of Philosophy in Materials

By Li Zhang

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College of Materials

Xiamen University

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## 摘 要

本论文采用水性溶胶法制备氧化铝基纤维。首先通过氯化铝和金属铝粉反应合成水性的氧化铝溶胶，正硅酸乙酯碱性（氨水）催化水解合成二氧化硅溶胶，然后把两种胶体混合后制备双相溶胶纺丝液，连续干法纺丝得到凝胶纤维，最后热处理转变成  $\text{Al}_2\text{O}_3\text{-SiO}_2$  陶瓷纤维。本工作对纤维制备过程中的基础科学问题进行了系统的研究。

系统地研究了铝粉和氯化铝比例、铝盐浓度、反应时间、氧含量等因素对氧化铝溶胶组成和结构的影响。首次提出铝粉和氯化铝的反应机理，指出决定铝溶胶性能的关键因素是溶液的 pH 值。在铝粉溶解过程中，溶液中铝离子不断发生水解、缩合并长大成团簇，无规团聚和有序堆积同时存在。通过改变实验条件可影响反应过程的 pH，从而控制溶胶中低聚铝离子（如  $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_4]^{4+}$ 、 $[\text{Al}_3(\text{OH})_4(\text{H}_2\text{O})_{10}]^{5+}$ ）、多聚铝离子（如  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ ）、非晶胶团、片层结构以及氢氧化物结晶（如水铝石）等成分的比例，优化溶胶的纺丝性能。

制备二氧化硅溶胶时，提高反应物、催化剂（氨水）浓度和水解温度都会促进正硅酸乙酯的水解和缩聚反应，产生大粒径的硅胶粒。水解程度不足，硅溶胶陈化时易凝胶化。在适当的条件下进行水解（如氨水浓度为  $0.30\text{mol}\cdot\text{L}^{-1}$ ，正硅酸乙酯浓度为  $0.77\text{mol}\cdot\text{L}^{-1}$ ，乙醇和水的体积比为 4/1，反应温度  $20^\circ\text{C}$ ），可得到稳定的纳米硅溶胶。碱性（pH~10）硅溶胶和氧化铝溶胶混合前，需要先酸化处理（pH~2），使硅溶胶的 zeta 电位由负值变为正值。在 zeta 电位为 0 附近（相应的 pH 值为 3~8），硅溶胶的稳定性差，容易发生凝胶化，应尽量避免。

氧化铝溶胶的溶胶-凝胶转变主要是靠胶粒之间的物理作用，而非化学交联，因此取决于氧化铝浓度，并具有可逆性。碱性水解得到二氧化硅溶胶呈球状，会降低氧化铝溶胶可纺性，需要添加纺丝助剂 PVA 来保证连续干法纺丝。

凝胶纤维在热解过程中依次经历了脱除溶剂水（ $<200^\circ\text{C}$ ）、结构羟基脱水（ $200^\circ\text{C}\sim 500^\circ\text{C}$ ）以及  $[\text{AlO}_5]$  的羟基脱水（ $>500^\circ\text{C}$ ）三个阶段。高温段集中脱水对纤维组织和性能影响最大，产生的气体会破坏纤维结构，甚至造成粉化。

纯氧化铝凝胶纤维热处理过程中，由于不同氧化铝晶相之间密度和晶体尺寸

的差异，低温过渡相氧化铝向高温相  $\alpha\text{-Al}_2\text{O}_3$  转变时，形成“蠕虫状”结构，同时晶粒迅速长大，纤维呈现疏松多孔显微组织，失去强度。加入二氧化硅，高温下二氧化硅粘滞流动包覆在氧化铝粒子表面，抑制氧化铝晶型转变，并与氧化铝发生反应生成莫来石。硅溶胶添加量越大，颗粒越小，固相反应越容易发生，所得纤维结构越致密。若二氧化硅溶胶的粒径过大（亚微米），对氧化铝相变的影响较小，自身容易结晶形成方石英，不利于莫来石形成。同时，二氧化硅粘滞流扩散后，物质迁移造成原来的颗粒中心出现大尺度气孔，导致纤维粉化。因此，采用双相溶胶法制备  $\text{Al}_2\text{O}_3\text{-SiO}_2$  纤维时，以小粒径二氧化硅溶胶作为硅源是制备高品质纤维的关键。

关键词： $\text{Al}_2\text{O}_3\text{-SiO}_2$  纤维； $\text{Al}_2\text{O}_3$  纤维；莫来石；氧化铝溶胶；二氧化硅溶胶

## Abstract

In this work, water soluble sol-gel method was used to prepare alumina-based fibers. Water soluble alumina sol was synthesized by the reaction of aluminum metal powder (Al) and crystalline aluminum chloride hydrated ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) solution. Silica sol was synthesized through hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol/water solution and with ammonium hydroxide as the catalyst. The two sols were combined and polyvinyl alcohol (PVA) was added as the spinning aid. The mixture was concentrated under vacuum to obtain a fluid suitable for dry spinning. Continuous gel fibers were dry-spun. After pyrolysis, the gel fibers were converted into  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  ceramic fibers. The fundamental scientific problems involved in the continuous ceramic fiber preparation were thoroughly investigated in this work.

The factors affecting the chemical compositions and chemical structure of alumina sol, such as Al/ $\text{AlCl}_3$ ,  $\text{AlCl}_3$  concentration, reaction time and oxygen content of Al powder, were studied, and the reaction mechanism has been proposed for the first time. As Al powder dissolved, the pH of the solution increased slowly. The aluminum ions were hydrolyzed and condensed to form various kinds of polynuclear Al species, including randomly packed, ordered and crystallized clusters. The pH value in the reaction system controls the content of polynuclear Al species such as  $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$ ,  $[\text{Al}_3(\text{OH})_4(\text{H}_2\text{O})_{10}]^{5+}$ ,  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$  etc, layered structure component, noncrystalline colloidal and crystalline precipitate. Spinnable alumina sol was obtainable by dissolving 5mol metal Al in 1000ml  $\text{AlCl}_3$  solution ( $1\text{mol}\cdot\text{L}^{-1}$ ) for 6~12 hours.

For the preparation of silica sol by the hydrolysis of TEOS, higher reactant (TEOS) and catalyst ( $\text{NH}_3\cdot\text{H}_2\text{O}$ ) concentration, and temperature will accelerate the hydrolysis and condition, promoting the growth of silica particles from nanometer scale to submicron. During aging, sol-to-gel transformation took place easily in partially-hydrolyzed silica sol. Highly stable nano-size silica sol was obtainable at  $[\text{NH}_3\cdot\text{H}_2\text{O}]=0.30\text{mol}\cdot\text{L}^{-1}$ ,  $[\text{TEOS}]=0.77\text{mol}\cdot\text{L}^{-1}$ , ethanol/water=4/1(volume ratio) and

20°C. The as-prepared silica sol was basic (pH~10). It must be adjusted to be acidic (pH~2) before mixing with alumina sol. Otherwise, alumina will be precipitated out. The silica sol was readily gelled at pH 3~8 where its zeta potential was near 0. By adding HCl the zeta potential changed from negative to positive, the precipitation or gelation can be avoided.

The sol-to-gel transition in alumina sol was reversible. That is to say, the gel can be redissolved into water to become sol repeatedly. During concentration, the colloidal particles approach towards each other, resulting in the rapid increase in viscosity. However, there are no chemical bonds formed between alumina colloidal particles. The silica sols prepared in basic condition were spherical, and hence they tended to decrease the spinnability of the alumina sol. To obtain a sol suitable for continuous spinning, fiber-forming additive PVA was necessary.

During pyrolysis, the gel fiber lost its absorbed free water below 200°C, while the structural water from Al-OH groups was removed between 200 and 500°C. The hydroxyl groups on aluminum pentahedron were released above 500°C, which has important effect on the structure and property of the pyrolyzed fiber. If not controlled properly, its removal can cause fiber cracking and disintegration.

Without any additives, alumina gel will crystallize into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> above 1100°C with vermicular microstructure, large pores are formed between the dendritic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites. As the consequence, the fiber lost its mechanical property and integrity. The addition of silica promotes sintering and suppressing the grain growth. The silica formed a thin film surrounding the alumina particles by viscous flow, retarding the phase transformation of transition alumina into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Silica reacts with alumina above 1200°C. The smaller the particle size, the easier the reaction takes place. However, when the silica particles are too large, for example, in submicron size, its effects on alumina phase transformation are markedly reduced. Such large silica particles tend to crystallize into cristobalite first before reacting with alumina to form mullite. After the mullitization, pores are left in the places originally occupied by the silica particles, the resultant ceramic fibers have very low strength and transparency. In all words, small size of silica colloidal particle was essential to make high

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