上海大学出版社
2005年上海大学博士学位论文 36

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● 专 业： 材 料 学
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Shanghai University Doctoral
Dissertation (2005)

Fabrication of a Newly Developed AgC Electrical Contact Material and Research of Its Properties

Candidate: Yu Haifeng
Major: Materials Science
Supervisor: Ma xueming

Shanghai University Press
· Shanghai ·

上 海 大 学

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答辩委员会对论文的评语

余海峰同学在其博士学位论文"新型 AgC 电接触材料制备及其性能研究"中，利用高能球磨技术获得纳米石墨粉，结合还原剂液相喷雾化学包覆技术制备出纳米晶银石墨包覆粉，利用该粉体良好的烧结致密性能，成功实现了块体高性能 AgC 触头的制备；在制备工艺、性能及失效机制之间的关系等方面，得到了一系列重要成果. 论文目标明确，选题合理，研究结果具有重要的学术意义和应用价值. 取得主要创新性结果如下：

(1) 开发了高能球磨与还原剂液相喷雾化学包覆相结合的新技术制备出特殊烧结粉体，使烧结 AgC 触头性能全面改善，特别是耐电弧腐蚀性能得到明显提高. 提供了一种新的触头生产制备工艺，成功进行了小规模产业化并批量供应市场.

(2) 在 ASTM 触头材料试验机上测试并研究了球磨-包覆工艺 AgC 新型触头材料的耐电弧磨损性能和特性及其电弧腐蚀特征，并对其耐电弧磨损性能提高的机理进行了分析与探讨.

(3) 以适量碳纳米管作为纤维增强体，制备出一种新型的碳纳米管增强 AgC 电接触材料，具有更加突出的机械物理性能和电弧磨损性能，就此材料及其制备方法申请了国家发明专利.

论文结构合理，条理清楚，写作文笔流畅. 试验方法选择

恰当，数据翔实可信，理论分析合理，结论正确. 工作的系统性和理论与实践的有机结合是该文的一个重要特点，这是一篇优秀的博士论文. 在答辩过程中该同学表达清楚，思路清晰，逻辑性强，回答问题正确. 表明该同学较好地掌握了本学科坚实宽广的基础理论和专门知识，具备独立从事科研工作的能力.

答辩委员会表决结果

经答辩委员会全体成员讨论和无记名投票，一致认为余海峰同学的博士论文已经达到博士学位论文要求，同意通过该同学的博士论文答辩，建议授予博士学位.

答辩委员会主席：李　劲

2005 年 1 月 7 日

摘　要

基于纳米材料诱人的特性和应用前景，本论文首次将纳米技术应用在AgC触头材料的制备中，研制出性能优异的新型AgC触头，并对其机械物理性能和耐电弧磨损性能进行了系统研究.

为整体改善传统机械混粉AgC触头的机械物理性能和耐电弧磨损性能，首先从粉体制备上入手，引入化学包覆工艺改善其成分偏聚和组织不均匀性，采用高能球磨获得纳米级石墨，作为后续银原子非均质形核核心，结合还原剂液相喷雾技术制备出纳米晶AgC包覆粉，利用该粉体良好的烧结致密性能实现了块体触头性能的全面改善.

以纯度为C%>99.5%、粒度为200目的石墨粉为原料，通过QM-1SP型行星式球磨机，经过最佳球磨时间10 h高能球磨后，制备出一维纳米级石墨，平均厚度50～60 nm.对球磨包覆Ag-5%C粉的X衍射测试表明，制备的包覆粉中Ag的平均晶粒尺寸约为50 nm.

论文研究了制备出的纳米晶AgC包覆粉体的烧结性能及其块体触头材料的机械物理性能，研究了球磨时间对触头性能及组织的影响以及烧结温度对其性能的影响，对AgC体系三种不同的粉体制备工艺触头材料进行了组织和机械物理性能对比分析并建立了简要的机理模型分析，研究了纳米晶包覆粉的配比添加对常规机械混粉触头性能的影响.

研究结果表明，随着球磨时间的增加，AgC块体触头出现

了石墨定向组织.电导率均匀组织时最高,出现石墨定向组织时降低,又随定向组织的增多而回升,但材料的硬度和致密性下降.随着烧结温度的升高,触头的致密度增加,硬度上升,电导率明显提高.在840℃左右,材料性能最佳.与机械混粉和滴加-包覆工艺相比,球磨石墨喷雾-包覆工艺制备的Ag-5%C材料具有极好的机械物理性能和更加均匀的组织.新工艺中采用还原剂液相喷雾技术,大大增加了还原剂与反应溶液单位时间接触面积,提高了分散在反应溶液中的C粉充当Ag原子非均质形核核心的几率;同时大大降低了还原剂在反应溶液中的局域浓度,有效抑制了Ag原子长大速率.两方面作用下该技术实现了细化包覆粉体及其晶粒度的作用并改善了其包覆效果,更好地消除了C在Ag基体中的成分偏聚.利用球磨-包覆工艺制备的纳米晶Ag-5%C包覆粉,混合在传统的Ag-5%C机械混粉中,实现了通过利用纳米晶粉的晶粒长大填补机械混粉材料中的微小孔隙,从而达到了改善机械物理性能的目的.

将制备出的新型AgC触头与传统粗石墨机械混粉工艺触头安装在ASTM机械式低频断开触头材料寿命试验机上进行了不间断电弧磨损对比分断试验,同时结合4组混合配粉触头进行了分阶段电弧磨损对比分断试验,测试并研究了该新型触头材料的耐电弧磨损性能和特性及其电弧腐蚀特征,并对其耐电弧磨损性能提高的机理进行了分析与探讨.

研究结果表明,不间断电弧磨损试验中球磨包覆工艺制备的新型AgC触头平均分断电弧质量损失远低于粗石墨机械混粉触头,抗电弧腐蚀性能提高了40%以上并具有更好的抗熔焊性能.分阶段电弧磨损试验中各组样品在最初阶段损耗量相差不大,随着分断次数的增加,相较于常规机械混粉工艺触头,球磨-包覆Ag-5%C触头每一阶段均表现出少得多的电弧损耗

量. Ag－5%C机械混粉触头随分断次数电弧磨损量呈指数大于1的指数函数规律上升,即到分断后期,由于表面坑洼程度加剧导致电涡流磨损现象的存在,电弧对触头的腐蚀加重,触头性能急剧劣化甚至失效. 而球磨-包覆Ag－5%C触头随分断次数电弧磨损量呈近线性规律变化,在分断各阶段电弧腐蚀对材料的损耗比较稳定,不会出现分断后期性能和损耗急剧劣化的情况. AgC体系触头材料经电弧侵蚀后其工作面上形成的形貌特征包括结构松散区、富银区、C沉积区、电弧冲击坑、气孔和孔洞以及裂纹,在电弧冲击作用下新工艺触头表现出了比传统粗石墨机械混粉触头更好的阻止熔融Ag珠喷溅损失脱离基体和阻碍表面裂纹生成扩展的能力.

将研制的新型AgC触头材料应用在上海施耐德低压终端电器有限公司及北京ABB低压电器有限公司生产的小型断路器上,分别通过了国家低压电器质量监督检验中心的运行短路能力试验测试. 该新型材料已经小批量供应上海施奈德和北京ABB等生产企业,并取得了良好的经济收益.

采用将高能球磨、化学包覆和粉末冶金工艺相结合配以适量碳纳米管作为纤维增强体的思路,制备出一种新型的碳纳米管增强AgC电接触材料并申请了国家发明专利. 试验采用的碳纳米管直观团聚体尺寸数十微米,由网状碳纳米管纠结构成,构成的碳纳米管丝平均尺寸30～60 nm,制备出的碳纳米管增强Ag－5%C包覆粉中银的平均晶粒尺寸约为50 nm. 包覆粉中微米尺寸的Ag颗粒呈絮凝状结构包覆在石墨片及碳纳米管的外面,这种絮凝体内部孔洞尺寸细小且分布均匀,有助于后续烧结过程的进一步致密化. 相较于传统机械混粉Ag－5%C触头,球磨-包覆工艺和碳纳米管增强球磨-包覆工艺Ag－5%C触头均表现出了极佳的机械物理性能,主要性能指标大幅提

高；同为球磨-包覆工艺，碳纳米管增强 Ag-5%C 触头硬度进一步提升.

尽管在电弧磨损最初阶段材料损耗量相差不大，随着分断次数的增加，相较于传统机械混粉触头，球磨-包覆工艺和碳纳米管增强球磨-包覆工艺 Ag-5%C 触头每一阶段的材料损耗量都少得多，表现出了优异的耐电弧磨损性能. 同为球磨-包覆工艺，碳纳米管增强 Ag-5%C 触头耐电弧磨损性能各分断阶段均显示了轻微程度的劣化. 尽管如此，碳纳米管增强球磨-包覆 Ag-5%C 触头随分断次数电弧磨损量呈指数小于 1 的指数函数规律变化，即到分断后期其材料损耗量趋于稳定，材料损耗速率下降，有效地抑制了电涡流磨损现象，这种优异的电弧磨损特性对于提高其工作寿命具有重要意义. 在触头分断后期，碳纳米管的存在及其强化基体骨架作用，有效地阻止了触头工作面的大量剥离，减轻了工作面坑洼度，抑制了电涡流磨损现象，是碳纳米管增强 Ag-5%C 触头具有优异的电弧磨损特性的机理之所在.

关键词　触头，AgC，纳米技术，球磨，还原剂液相喷雾化学包覆，电弧磨损，碳纳米管

Abstract

In view of the distinguished feature and application prospect of nanomaterials, the nanotechnology was first applied in the fabrication of silver/graphite electrical contact materials, and newly developed AgC electrical contacts were prepared in the thesis. And also, their physical and mechanical properties and arc erosion resistance were systematically researched.

To improve the properties of traditional blending AgC electrical contact material, electroless plating technique was employed in powder preparation to improve their component segregation and microstructure nonuniformity. Nanocrystalline AgC coating powders were then prepared under the combination of the reducer liquid spraying-electroless plating method and nanosized graphite, which came from the high-energy milling and worked as the heterogeneous cores of Ag atoms nucleating. Because of its well sintering densification, the properties of block contacts were totally improved.

The graphite powders with over 99.5% content of C and 200 mesh granularity were used as raw material and milled for the best ten hours on the QM-1SP planetary mill and one-dimension nanosized graphite was then fabricated, with the average thickness of 50～60 nm. The X-ray diffraction test

showed that the average grain size of Ag in the as-prepared electroless plating Ag－5% C powders was about 50 nm.

In the thesis, the sintering properties of fabricated nanocrystalline AgC electroless plating powders and the physical and mechanical properties of their block contacts were researched, along with the influence of milling time on their properties and microstructure and the sintering time on the properties. At the same time, the AgC contacts fabricated by three different techniques were compared on their microstructure and properties and accordingly a brief mechanism model was established. At last, the influence of nanocrystalline electroless plating powders on the properties of conventional blending AgC contacts was researched.

The research showed that with milling time going, graphite orientation structure appeared in the AgC block contacts. At that time, the electrical conductivity went lower, which was highest when uniformly microstructured, but it rose again as the orientation structure growing, with the decline of its hardness and density ratio at the same time. While with the sintering temperature growing, the density ratio, hardness and electrical conductivity of the contacts increased and arrived their highlight at about 840℃. The Ag－5% C material fabricated by milled graphite spraying-electroless plating technique had superior physical and mechanical properties and uniform microstructure to those made by blending and dropping-electroless plating techniques. With the reducer liquid spraying-electroless plating method, the contact area between reaction solution and reducer in unit time and the ratio of graphite powders separated in the reaction solution working as heterogeneous cores of Ag atoms nucleating were greatly increased. At the same time, the local concentration of reducer in reaction solution was largely reduced, and then the growth of Ag atoms was suppressed. Because of the factors mentioned above, the refinement of electroless plating powders and their grains and the improvement of electroless plating effect were achieved, and the component segregation of graphite in the Ag matrix was well eliminated. Mixed with various content of the as-prepared nanocrystalline electroless plating powders, the micropores in blending AgC material were filled by the growth of nanocrystalline grains. As a result, the mechanical and physical properties of the fabricated contacts were improved.

The uninterrupted experiment for erosion behavior of the prepared new type AgC contact and its traditional blending counterpart by breaking arcs were done by using an ASTM Contact Material Automatic Measuring Device. In the meantime, the experiment for erosion behavior of 6 group contacts, the two contacts mentioned and four blending contacts mixed with nanocrystalline electroless plating powders, by breaking arcs were done. The arc erosion resistance properties and characteristics of the as-prepared new type AgC contact material were tested and studied, and also the improvement mechanism of the former was analyzed and discussed.

As was shown in the uninterrupted experiment for erosion behavior, compared with coarse graphite blending material, the new type AgC electrical contact had less average weight loss of breaking arcs and 40% higher arc erosion resistance and better resistance against welding. In the experiment for erosion behavior by stages, the samples had similar weight loss at the beginning, but with breaking time growing, the fabricated new type AgC contact showed better arc erosion resistance at every stage than blending contacts. For blending materials, the relationship between their loss and breaking times took the shape of an exponent function curve, whose exponent was larger than 1. That meant in the anaphase of breaking, the arc erosion got aggravated and the properties of contacts got worse and even noneffective because of the existence of electric vortex erosion, which was caused by the aggravation of the potholes of contact surface. And for milling-electroless plating Ag - 5% C contact, the relationship between its loss and breaking times presented the shape like a linearity function curve, which meant the weight loss tended to be stable at every stage and the situation mentioned above won't happen. After arc erosion, such morphology characteristics were formed on the contact surface of AgC materials as loose structure, Ag enrichment structure, graphite sediment structure, arc impact crater structure, gas pore and hole structure and crack structure. Under the impact of arcs, the new type electrical contact were superior to its traditional blending counterpart to prevent the melted Ag beads to spray and get away from the matrix and keep up the formation and development of surface cracks.

The new type AgC contact material, employed on the miniature circuit breakers from Schneider Shanghai low voltage terminal Apparatus Co., Ltd. and ABB Beijing low voltage Apparatus Co., Ltd., had respectively passed the short circuit circulation test by China National Centre for Quality Supervision and Test of Low Voltage Apparatus. It had been supplied to several manufacturing corporations like SSLVTA and ABB Beijing by small batch and good economic income had been achieved.

Prepared by the combination of high-energy milling, electroless plating and powder metallurgy technique, with carbon nanotubes as the fiber reinforcer, the new type carbon nanotubes-reinforced AgC electrical contact material was fabricated and its National Invention Patent was applied. The carbon nanotubes aggregate employed had the size of tens of microns, which was comprised of carbon nanotubes sized 30～60 nm. And the average grain size of Ag in the as-prepared carbon nanotubes-reinforced Ag - 5% C electroless plat-ing powders was about 50 nm. In electroless plating powders, graphite and carbon nanotubes were coated by microsized Ag granules with flocculent structure and the floccules had small and uniform internal micropores, which was helpful to the further densification in sintering. Thus, the prepared carbon nanotubes-reinforced Ag - 5% C contact showed better physical and mechanical properties compared with blending contacts and better hardness even with other milling-electroless plating contact.

Although they had similar weight loss at the original stages, the new Ag - 5% C electrical contact prepared by milling-electroless plating technique and nanotubes-reinforced milling-electroless plating technique showed better arc erosion resistance than traditional blending contact at the after stages. Even all prepared by milling-electroless plating technique, the arc erosion resistance of nanotubes-reinforced Ag - 5% C contact displayed slight worsening at every stage, and the relationship between its loss and breaking times of the former took the shape of an exponent function curve, with exponent less than 1. That meant in the anaphase of breaking, the arc erosion tended to be stable, the material wastage was decreased and the electric vortex erosion was effectively controlled, which was important to prolong its working life-span. In the anaphase of breaking, because of the existence of carbon nanotubes and its role to reinforce the matrix, the peel-off of the contact surface material was efficiently prevented, the potholes of contact surface were lightened and the arc erosion of current vortex was effectively controlled, which were the mechanism why the carbon nanotubes-reinforced Ag - 5% C electrical contact had excellent arc erosion characteristic.

Keywords electrical contact, silver/graphite, nanotechnology, milling, reducer liquid spraying-electroless plating, arc erosion, carbon nanotubes