

上海大学出版社

2006年上海大学博士学位论文 10



机械合金化纳米晶 Fe-C 过饱和固溶体系的结构和 磁性能的研究

- 作者：许士跃
- 专业：无线电物理
- 导师：张金仓



001289188

上海大学出版社

2006年上海大学博士学位论文 10



机械合金化纳米晶 Fe-C 过饱和固溶体系的结构和 磁性能的研究

- 作者：许士跃
- 专业：无线电物理
- 导师：张金仓

贵阳学院图书馆



GYXY1289188

881285100

图书在版编目(CIP)数据

2006 年上海大学博士学位论文. 第 1 辑/博士学位论文编辑部编. —上海:上海大学出版社,2009.12

ISBN 978-7-81118-511-9

I. 2... II. 博... III. 博士—学位论文—汇编—上海市—2006 IV. G643.8

中国版本图书馆 CIP 数据核字(2009)第 162521 号

2006 年上海大学博士学位论文
——第 1 辑

上海大学出版社出版发行

(上海市上大路 99 号 邮政编码 200444)

(<http://www.shangdapress.com> 发行热线 66135110)

出版人:姚铁军

*

南京展望文化发展有限公司排版

上海华业装潢印刷厂印刷 各地新华书店经销

开本 890×1240 1/32 印张 264.75 字数 7 376 千

2009 年 12 月第 1 版 2009 年 12 月第 1 次印刷

印数:1—400

ISBN 978-7-81118-511-9/G·513 定价:1000.00 元(50 册)

Shanghai University Doctoral Dissertation (2006)

Structural and Magnetic Properties of nanocrystalline Fe – C Systems by Mechanical Alloying

答辩委员会名单:

主任: 杨宝龙 Candidate: XU Shiyue 200062

委员: 周仕明 Major: Radio Physics 200433

赵秉康 Supervisor: Zhang Jincang 200050

任应鸣 教授, 中国科学院金属所 200444

李春芳 教授, 上海大学材料系 200444

导师: 韩金全 教授, 上海大学 200444

Shanghai University Press

• Shanghai •

答辩委员会评语 上海大学

本论文经答辩委员会全体委员审查,确认符合上海大学博士学位论文质量要求。

答辩委员会名单:

主任: 杨燮龙	教授, 华东师范大学物理系	200062
委员: 周仕明	教授, 上海复旦大学物理系	200433
赵景泰	教授, 中科院硅酸盐所	200050
任忠鸣	教授, 上海大学材料系	200444
李春芳	教授, 上海大学物理系	200444
导师: 张金仓	教授, 上海大学	200444

三、在过饱和 Fe-C 和 $\text{Fe}_3\text{Ni}_3\text{-C}$ 的纳米晶体系中,发现金属原子磁矩与合金的混合热 ΔH 呈线性关系,这一结果有助于认识机械合金化生成难互溶合金体系的机理。

许士跃同学的论文写作条理清楚,实验数据可靠,分析合理。在答辩过程中能够回答专家提出的问题,思路清晰,体现了许士跃同学有较深的基础知识的积累,已具备较强的独立科研能力。

学大商工

合并人商,查审员委科全会员委辑答登文创本

。朱要量则文创位学士制学大商工

评阅人名单:

周仕明	教授, 上海复旦大学物理系	200433
马学鸣	教授, 华东师范大学物理系	200062
徐政	教授, 同济大学材料系	200092

评议人名单:

赵景泰	教授, 中科院硅酸盐所	200050
周世平	教授, 上海大学物理系	200444

答辩委员会对论文的评语

许士跃同学的博士学位论文“机械合金化纳米晶 Fe-C 过饱和固溶体系的结构和磁性能研究”，对利用机械合金化技术制备纳米晶 Fe-C 和 Fe-Ni-C 过饱和固溶体体系的结构和磁性能进行了系统研究，论文主要结果为：

一、利用机械合金化方法成功地制备了过饱和 Fe-C、Fe₅₅Ni₄₅-C 纳米晶体系，对其结构和磁性能作了研究，讨论了纳米晶 Fe-C 和 Fe-Ni-C 体系中矫顽力与晶粒尺寸之间的关系；

二、发现了合金磁矩对 C 含量的变化率 $\frac{d\mu}{dx}$ 在纳米晶 Fe-C 和 Fe-Ni-C 两个体系中基本相同，结合理论研究，发现并指出了过渡族金属—类金属的合金磁性理论所存在的局限性；

三、在过饱和 Fe-C 和 Fe₅₅Ni₄₅-C 纳米晶体系中，发现金属原子磁矩与合金的混合热 ΔH 呈线性关系，这一结果有助于认识机械合金化生成难互溶合金体系的机理。

许士跃同学的论文写作条理清楚，实验数据可靠，分析合理。在答辩过程中能够回答专家提出的问题，思路清晰，体现了许士跃同学有较深的基础知识的积累，已具备较强的独立科研能力。

答辩委员会表决结果

经答辩委员会表决,全票同意通过许士跃同学的博士学位论文答辩,建议授予理学博士学位。

答辩委员会主席: **杨宝龙**

2006年3月

摘 要

机械合金化作为一种制备合金的非平衡技术,自 20 世纪 70 年代初首先被应用于制备镍基氧化物弥散强化超合金以来,引起了物理学家和冶金学家的广泛重视并取得了令人瞩目的成就。它的重要特点在于将材料粉末经磨球的不断碰撞、挤压,反复变形、断裂、冷焊,原子之间相互扩散最终形成合金状态。机械合金化属于一种强制反应,当外界给予高能量的机械力时,粉末内部引入了大量的应变、缺陷,使得合金过程中的热力学和动力学不同于普通的固态反应,其制备非晶、纳米合金和金属间化合物、过饱和固溶体、复合材料等,使得该技术现已成为研制新型材料的一种重要手段。基于该方法的显著优点以及在所制备材料的特性和物理机制方面诸多问题需要澄清,本文成功将机械合金化方法成功应用于纳米晶 Fe-C 体系合金的制备,实现了过饱和固溶体纳米结构 Fe-C 和 Fe-Ni-C 系列体系合金,并系统研究了它们的结构和磁性能,该研究一方面可以系统了解 C 在 bcc 和 fcc 相中固溶度的扩展程度;另一方面可以对过渡族金属—类金属的合金的磁性物理问题进行深入的探讨,为机械合金化制备纳米晶过饱和固溶体提供了重要的基础研究资料,也为该类材料的实用化发展奠定了基础。

本文工作可概括为以下几个方面:

1. 用机械合金化方法合成了过饱和纳米晶固溶体 $\text{Fe}_{1-x}\text{C}_x$ 和 $(\text{Fe}_{55}\text{Ni}_{45})_{1-x}\text{C}_x$ ($0 \leq x \leq 0.9$)。通过 x 射线衍射技术、电子扫描、差热以及穆斯堡尔谱等方法对粉末的结构、磁

性、热性作了分析和研究。 $\text{Fe}-\text{C}(\text{bcc})$ 是用纯铁和石墨经球磨合成的。分析表明 $\text{Fe}_{1-x}\text{C}_x$ 的晶粒尺寸是随 x 的上升而增加的。在 $0 \leq x \leq 0.67$ 的范围内形成了纳米晶;在 $0.75 \leq x \leq 0.9$ 范围只是大晶粒体系。 $\text{Fe}_{55}\text{Ni}_{45}-\text{C}(\text{fcc})$ 是由纳米晶 $\text{Fe}_{55}\text{Ni}_{45}$ 和石墨通过研磨合成的。与 $\text{Fe}-\text{C}$ 体系相似,在 $\text{Fe}_{55}\text{Ni}_{45}$ 体系里的高碳含量 ($0.8 \leq x \leq 0.9$) 的样品内的碳原子的溶解度很小。在 $\text{Fe}-\text{C}$ 和 $\text{Fe}_{55}\text{Ni}_{45}-\text{C}$ 体系里碳的固溶度通过球磨都得到明显的提高。在 $\text{bcc Fe}-\text{C}$ 体系里 $0 \leq x \leq 0.5$ 范围合金原子磁矩要小于单纯稀释,铁原子的磁矩随 x 的上升而下降。在 $\text{fcc Fe}_{55}\text{Ni}_{45}-\text{C}$ 体系里晶格常数在 $0 \leq x \leq 0.25$ 范围随 x 上升而线性增长,同时它的金属原子磁矩也随 x 的上升而线性地下降。 $\text{Fe}-\text{C}$ 和 $\text{Fe}_{55}\text{Ni}_{45}-\text{C}$ 体系的高碳含量的样品的合金磁矩与磁单纯稀释一致,表明在高碳含量的样品中,金属粉末与石墨仅仅是单纯混合状态。

2. 根据 Miedema 半经验公式对纳米晶 $\text{Fe}-\text{C}$ 和 $\text{Fe}_{55}\text{Ni}_{45}-\text{C}$ 合金体系分别作了生成焓的计算。结果表明由于石墨结构转换能量很大使得这两个体系的生成焓随碳含量 x 的上升而上升。实验中发现在 $\text{Fe}-\text{C}$ 体系里晶粒尺寸随 x 而上升,与 $\text{Fe}-\text{C}$ 的生成焓的趋势大致相同。由于高碳含量样品的生成焓的值很高,合金形成的困难程度也随之上升。

3. 在纳米晶 $\text{Fe}-\text{C}$ 和 $\text{Fe}_{55}\text{Ni}_{45}-\text{C}$ 合金体系中呈现出矫顽力与晶粒尺寸有关的现象。当晶粒尺寸小于某一临界尺寸时,矫顽力随晶粒尺寸的上升而增加;当晶粒尺寸大于临界尺寸时,矫顽力又随晶粒尺寸的上升而下降。在这两个体系里矫顽力都与晶粒尺寸 D 成 D^6 关系。纯金属纳米晶 $\alpha-\text{Fe}$ 和 $\text{Fe}_{55}\text{Ni}_{45}$ 的矫顽力与 D^6 不成线性关系。那些碳原子实际溶解度很小的样品也不满足 D^6 的关系。这表示 D^6 的关系需要在

纳米晶金属内的碳含量要达到一定数量级。

4. 合金磁矩对类金属含量的变化率 $\frac{d\mu}{dx}$ 在纳米晶 Fe-C 和 Fe₅₅Ni₄₅-C 这两个合金体系里都是大致相同的。这表示 $\frac{d\mu}{dx}$ 与合金中的金属原子 Fe、Ni 无关。实验结果与过渡族金属和类金属合金的有关磁性理论作了比较。Band-gap (magnetic valence model) 与实验数据有明显差距, 而 coordination 模型不能对 Fe-C 体系进行推算。这两个理论都无法解释在 Fe、Co、Ni 与类金属 B、C、P 等的合金体系里, $\frac{d\mu}{dx}$ 都基本相同的现象。

5. 金属原子磁矩较好地反映了粉末的合金化程度。在纳米晶 Fe-C 和 Fe₅₅Ni₄₅-C 合金体系里金属原子磁矩的最小值分别出现在 $x=0.5$ 和 $x=0.67$ 。金属原子磁矩的下降可认为是金属原子和类金属原子之间的 p-d 键导致的。分析结果显示在这两个体系里金属原子磁矩与体系的混合热呈线性关系, 其中的混合热是根据 Miedema 对固溶体的混合热公式来计算的。这表示体系的混合热(生成焓的化学项)可用来衡量 p-d 键的强弱。

本文的基本结构分为六章: 第一章综述了机械合金化技术的发展概况与 Miedema 理论以及本文的研究目的; 第二章介绍了样品的制备和实验方法和纳米晶体系的晶粒尺寸的计算方法; 第三、第四章叙述了 Fe-C 和 Fe₅₅Ni₄₅-C 的实验结果; 第五章对实验结果和现有的磁性理论作了对比, 从中显示出传统的过渡族金属和类金属合金的磁性理论和实验数据存在不小偏差, 指出了该理论的局限性; 最后一章对本文的实验和理论方面的工作进行了总结, 提出了目前在过渡族金属—类金属的合

金体系的磁性理论方面存在的缺陷和局限性,为过渡族金属—类金属合金体系磁性理论的进一步发展提出了自己的看法。

关键词 Fe-C 合金体系,机械合金化,纳米晶合金,过饱和固溶体,磁性

Abstract

As a non-equilibrium technique, mechanical alloying was first used to prepare oxide dispersion strengthened in Ni-based superalloys in the year 70' of the 20th century. It has received a considerable attention from physicists and metallurgists. Its specific feature is the repeating deformation, fracture and cold welding during the collision between the balls and powder particles, leading to the final steady state of alloys. At the same time the high intensity of stain and defects are introduced in the materials by high energy of ball milling. Thus its thermodynamic and kinetic condition are different from the other solid state reaction. It is characterized by a competition between the thermodynamic driven decomposition and the mechanical driven alloying process. Over the past few years, mechanical alloying has shown to be a powerful technique to synthesize a great variety of nanocrystalline, amorphous, intermetallics, supersaturated solid solution and composite materials. However the properties of such materials and the mechanism of mechanical alloying are not yet clear. Therefore author has prepared and investigated the supersaturated solid solution of Fe - C and Fe - Ni - C. It was hoped to extend the solubility of carbon in bcc and fcc structures by mechanical alloying process. On the

other hand the studies on the structural and magnetic properties of Fe - C and Fe - Ni - C would be helpful to develop the theory concerning the magnetic properties of transition-metal-metalloid alloys. It is of prime interest in materials research because of their impact on both theoretical studies and industrial application.

The remarkable points of this paper could be summarized as follows:

I. Supersaturated solid solution $\text{Fe}_{1-x}\text{C}_x$ and $(\text{Fe}_{55}\text{Ni}_{45})_{1-x}\text{C}_x$ were prepared in a wide concentration range ($0 \leq x \leq 0.9$). The microstructure, magnetic and thermal properties of the milled powders were followed by x-ray diffraction, scanning electron microscopy, differential scanning calorimetry and Mössbauer spectroscopy. Fe - C (bcc) powders were synthesized by mechanical alloying of elemental Fe and graphite. It is found that the crystallite size of $\text{Fe}_{1-x}\text{C}_x$ increases with increasing x . The nanocrystalline phase of Fe - C was formed for $0 \leq x \leq 0.67$ and large grain phase for $0.75 \leq x \leq 0.9$. $\text{Fe}_{55}\text{Ni}_{45}$ - C (fcc) were prepared from nanocrystalline $\text{Fe}_{55}\text{Ni}_{45}$ and graphite. It is similar to Fe - C that the dissolution of carbon is low in the samples of high carbon content ($0.75 \leq x \leq 0.9$) because of the presence of huge volume of graphite. In both bcc Fe - C and fcc $\text{Fe}_{55}\text{Ni}_{45}$ - C, the solubility of carbon is obviously extended by mechanical alloying process. For bcc Fe - C, the magnetization is reduced well below the simple magnetic dilution and Fe moment decreases with increasing carbon

content for $0 \leq x \leq 0.5$. For fcc $\text{Fe}_{55}\text{Ni}_{45}-\text{C}$, the lattice constant increases linearly with increasing C content in the concentration range of $0 \leq x \leq 0.25$. It shows that metal and graphite powders were merely mixed for the samples of high content in both Fe-C and $\text{Fe}_{55}\text{Ni}_{45}-\text{C}$. Their magnetic moments per alloy atom coincide with the simple magnetic dilution.

II. The formation enthalpy of both Fe-C and $\text{Fe}_{55}\text{Ni}_{45}-\text{C}$ were calculated from Miedema's semi-empirical model. It shows that the formation enthalpy of both system increases with increasing C content, which is due to high energy of structural transformation of carbon from graphite to hypothetical close-packed metallic structure. The crystallite size of Fe-C increases with increasing C content, coinciding with the formation enthalpy of Fe-C. For both systems the alloying reaction does not take place for those samples of high C content. For high C content, the high value of the formation enthalpy predicts the difficulty of alloy formation in both systems.

III. The correlation between crystallite size D and coercivity force H_c is found in both mechanically alloyed powders mixture. For grain size D below a critical value coercivity H_c increases with increasing grain size D . For large grain size D exceeds the critical value, H_c decreases with increasing D . The linearity between D^6 and H_c is observed in both Fe-C and $\text{Fe}_{55}\text{Ni}_{45}-\text{C}$. Pure metal α -Fe and $\text{Fe}_{55}\text{Ni}_{45}$ of nanocrystalline phase do not fit the D^6 relation, neither do

the samples of low dissolution of carbon inside metal. It suggests the requirement of a minimum carbon content for D^6 relation.

IV. It is observed that the moment variation with metalloid content $\frac{d\mu}{dx}$ is independent of transition-metal atom Fe and Ni. The reduction of moment per alloy atom $\frac{d\mu}{dx}$ is the approximately same in both Fe - C and $\text{Fe}_{55}\text{Ni}_{45}$ - C ($0 \leq x \leq 0.5$). In this paper, the experimental data were compared with the theories of magnetic properties in TM-M (transition-metal-metalloid) alloys: band-gap theory and coordination model. The obvious difference was shown between the experimental data and the band-gap theory. By the definition of the coordination model, the results of Fe - C cannot be described by the coordination model. Both theories do not predict the $\frac{d\mu}{dx}$ is similar for transition metal Fe, Co and Ni alloys with metalloids such as B, C and P.

V. The alloying effect of C can be better described by the moment per metal atom. The minimum of moment of metal atom occurs at $x = 0.5$ and $x = 0.67$ in Fe - C and $\text{Fe}_{55}\text{Ni}_{45}$ - C, respectively. The reduction of moment can be attributed to p - d hybrid bonding between TM and M atoms in TM-M alloys. The degree of p - d hybridization might be measured by the heat formation ΔH of alloys (chemical part of formation enthalpy). It has shown a perfect linearity

between ΔH and moment per metal atom in both Fe - C and $\text{Fe}_{55}\text{Ni}_{45}$ - C. The heat formation of alloys ΔH is calculated from Miedema formula for solid solution.

The first chapter of this paper mentions the current development of mechanical alloying technique, the extended solubility in the immiscible system and objective of this work as well as Miedema's semi-empirical model. The second chapter gives the experimental method, preparation of samples and the estimation method on the crystallite size of nanocrystalline system. The third and fourth chapters present the experimental results of Fe - C and $\text{Fe}_{55}\text{Ni}_{45}$ - C. Chapter five describes the comparison of experimental data with the theories of magnetism in TM-M alloys. It shows an obvious disagreement between the experimental data and theoretical prediction. The last chapter summarizes the experimental and theoretical analysis work in this paper. The problems of theories on the magnetism of TM-M alloys are discussed. It requires more experimental data of TM-M alloys for the improvement of the theory of magnetism.

Key words Mechanical alloying, supersaturated solid solution, Fe - C series alloys, nanocrystalline materials, magnetic characteristics