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Magnetic Characteristics and Ionic Conductivity

Dr. Dharmendra Kr. Singh

Deptt. of Physics, J. P. University, Chapra

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ABSTRACT

Recently Ishihara et al. [175] fabricated thin films of LaGeOs as a new oxide ionic conductor, on dense polycrystalline Al,0, substrates by a pulsed laser deposition (PLD) method and studied the effect of the film thickness on the oxide ionic conductivity on the nanoscale. The effective deposition parameters were optimized to obtain LaGeos thin films with stoichiometric composition. Annealing was found necessary to get crystalline LaGeo, thin films. It was also found that the annealed LaGeOs film exhibited extraordinarily high oxide ionic conductivity. Due to the nano-size effects, the oxide ion conductivity of Lasi Geo, thin films increased with the decreasing thickness as compared to that in bulk La, sGeOs4. In particular, the improvement in conductivity of the film at low temperature was significant.The electrical conductivity of the La, sGeOsa film with a thickness of 373 nm is as high as 0.05 S.cm' (log (r/S cm") = -1.3) at 573^0K.

1. Introduction

Many experiments suggest that magnetic characteristics depend on material size. Although understanding magnetic structure of nano-structure materials is far away from its complete state, there is a clear imagination from saturated magnetism; es recent contradictory results about chemical and physical structure of nano-crystalline materiels is justifiable. According first studies, nano-crystalline materials show a great deal decrease in saturated magnetism with decrease in grain size. Approximately 40% of decrease in saturation magnetism was obtained in comparison with bulk alpha Fe for nano-crystalline Fe with grain size of 6 nm, developed by simultaneous deposition od nano-particles obtained from consolidation of pure gas. This behavior is due differences in magnetism fine-structure of nano-crystal and common multi-crystalline Fe.

2. Explanation

In a same way, strong effects of particle size on saturation magnetism were obtained during study of super tiny unconsolidated particles produced through g*s evaporation. For super tiny particles (10-50 nm) of Ni, Co, and Fe, an intense decrease was observed in saturated magnetism with grain size reduction, which was accompanied with nonmagnetic oxidized layers on particle. Another study on these super tiny partices has shown magnification is negatively associated with decrease of particles size. Decrease in saturation magnetism is accompanied with surface effects- which are more important than grain size. Also, decrease of saturation magnetism rate in Ni powder, due to evaporation of produced gas resulted from structural disorder in interface, was recorded.

Measured magnetic momentum of interface atoms is about half of that of atoms in coarse grain material. Further, it was found that super tiny Ni particles saturation magnetism considerably reduces with grain size decrease. It was recorded tha accidental magnification of nano-crystalline gallium (Ga) samples produced by ga consolidation and dimensional compaction is about 75% of its multicrystal. It must be added all mentioned samples are created using gas consolidation method resulting production of materials with high internal porosity, which creates a big deal of surface area for oxide development after posing to free air. On the other hand, it was recorded that saturation magnetism is not significantly associated with grain size. Ni grains sia has been declined from 10 to 100 nm; then for Ni samples with tiniest grain sia observed magnetism is just 10% less than that of multi-crystalline Ni. These resut were observed for bulk nanocrystalline Ni created with electro-deposition method and creation mechanism was said to be unavoidable development of porous oxide.

Obtained results are coordinated with recent calculations, implying effect structural disorder. At these studies, grain boundary size is a source for differe disorder states. Measurements show that magnetic momentum is not really sensitive to magnitude of structure disorder from grain boundaries. Once material structure is amorphous, average momentum is only 159% of decrease; hence, for nano-crystalline Ni with grain sizes of 10 nm, where grain boundary atoms occupy 30% space, final effect of structural disorder on medium momentum would be negligible. Other recent records prove these results. For instance, for nano-crystal created by rolling, there is no significant difference in saturation magnetism for material with grain sizes of 1 nm and 50 um. similar results have recorded for Ni nano-crystals. Also, for nano-crystalline Ni created from gas consolidation method, before posing it to free air saturation magnetism is independent from grain size, but as soon as its pose to free air saturation magnetism declines to 80% of its original value.

Recently Ishihara et al. [175] fabricated thin films of LaGeOs as a new oxide ionic conductor, on dense polycrystalline Al,0, substrates by a pulsed laser deposition (PLD) method and studied the effect of the film thickness on the oxide ionic conductivity on the nanoscale. The effective deposition parameters were optimized to obtain LaGeos thin films with stoichiometric composition. Annealing was found necessary to get crystalline LaGeo, thin films. It was also found that the annealed LaGeOs film exhibited extraordinarily high oxide ionic conductivity. Due to the nano-size effects, the oxide ion conductivity of Lasi Geo, thin films increased with the decreasing thickness as compared to that in bulk La, sGeOs4. In particular, the improvement in conductivity of the film at low temperature was significant.The electrical conductivity of the La, sGeOsa film with a thickness of 373 nm is as high as 0.05 S.cm' (log (r/S cm") = -1.3) at 573^0K.

The oxide ion conductor is an important functional material applied in different fields such as fuel cells, oxygen sensors, oxygen pumps, water electrolysis, and oxygen separating ceramic membrane. Among these application areas, the electrolyte of fuel cell is attracting much interest. Several numbers of new oxide ion conductors such as strontium and magnesium doped lanthanum gallate (LSGM) and $La_{10}Si_6O_{27}$ apatite oxide and were reported recentiy. Among the new oxide ion conductors fabricated recently, La- deficient La_2GeO_5, is highly interesting, because of its high oxide ion conductivity over a wide range of oxygen partial pressure and unique structure. In La_2Geo_5 based oxides, La deficiency leads to the formation of oxygen vacancies and oxide ion conductivity in Las GeOs is the highest in La, Geos based oxides. The transport number of the oxide lon is nearly unity in the o, partial pressure range 1-104 atm and the conductivity is comparable to that of well-known fast oxide ion conductors, e.g., Laio1GeO, G3Mg0s and Gd-doped CeO. Recently, nano-size effects on ionic conductivity have Deen attracting much interest because of Improved ion conductivity. Some researchers reported that the fluoride ionic conductivity in CaF and BaF, hetero-layered films, prepared by molecular-beam epitaxy, increases proportionally with increasing interface density, namely, decreasing thíckness, when the interface spacing is larger than 50 nm which is in agreement with the semi-infinite space-charge calculation. In contrast, due to the positive charge at grain boundary, negative nano-size effects were reported for the axide ion conductivity in Ceo, based oxides, On the other hand, it is reported that the exide ion conductivity in the laminated films consisting of Zro, and Gd doped CeO: (GDC) thin film increases with decreasing number ofr lamination. The effects of nano grain size on the ionic conductivity on La,GeO, based oxide film and it was found that the conductivity was improved by decreasing film thickness of La,GeOs. However, in the conventional study, nano-size effects are not studied systematically and so, the nano- şize effects are still not clear.

New oxide ion conductor of $La_{1.61}GeO_{5-\delta}$ film of various thicknesses was fabricated as thin films of varying thickness on dense polycrystalline Al,O, substrates by using pulsed laser deposition. The obtained LaeiGeOs film by Ishihara et al. exhibited almost the pure oxide ionic conductivity and the oxide ion conductivity increased with the decrease of the film thickness. In particular, increase of conductivity at low temperature was more significant. Considering the stable valence number of La and variable valence of Ge (3+ and 4+), the amount of oxygen vacancies can be determined by the composition of the film. Since the composition of the prepared La6 GeOs films is almost the same, it is generally considered that the increased conductivity may not be explained by the change in the amount of oxygen vacancy but by the improved mobility of oxide ion by the local stress caused by the mismatch in lattice parameter between the film and the substrate. Figure 2.10 illustrates arrhenius plots of La6iGeOs thin films that the bulk La1.61GeO5- sample. PO2 dependence of the electrical conductivity in La1. 61GeO5- thin film with various thickness at 8730K.

Thermal Stability

Thermal stability of hand-crystals is ot great importance in high temperature TEM and an indirect method, involving determination of thermal stability using haress measurements as a function of annealing time. For synthetic growth of grains there are some preventing factors for grain boundary movements leading to their thermal stability applications. For electro-deposited nano-crystals thermal stability is examined through There is a slowing dual force in nano-crystals due to triple connections. It can be easil shown that grain growth for fined multi-crystal materials is controlled by inheren movement of triple connections. For thermal stability of nano-structures, extr distributions of triple connections lead to preferred dissolve in these spots. Such dissolve was observed in nano-crystals in triple connections using TEM method. stability with grain sizes of 10 and 20 nm was investigated, using TEM. Degradatie temperature for these materials is 3530K. This lack of stability is due to unusL germination after annealing.

Nanocoatings Applications

Nano-crystalline structures made of electro-deposition have some commer applications, due to these following reasons: 1. Electro-shaping and electroplating are recognized industries with extensive usage. 2. Their low cost: Nano-crystals can be created using a simple modification in electrical parameters applied for electroplating and electro-shaping current. 3. High potential of producing materials, alloV, and composites with metallic matrix in different forms at one stage (.e. coatings, comolicated shapes, and etc) 4. Capability of producing nano-structures with high density and no porosity.

Structural Applications

As it is expected from Hall-Petch assumptions, there are different practical applications for nano-crystals based on existed criteria for development of resistant coatings. Preferential mechanical properties of electro deposited nano structures are among their most important industrial applications, Etectroplating process is applied for in situ maintenance of nuclear steam generator tubes, This process is successfully applied in aqueous reactors in US and Canada and registered as a standard method for repairing pressure tube., Through this application, Ni with grain size of 100 nm, is created on interior walls of steam generator tubes to perform a complete structural maintenance in- places where primary homogeneity of tube structure is mitigated. High strength and convenient malleability of these 100 nm grains result in application of a thin plate (0.5-1 mm) which minimizes fluid current and heat transition in steam generator. Recent geometrical models and empirical achievements have shown that nano-structural materials can have a high resistance against creep and inter-granular cracking. Different applications of nano-structural materials, where their inter-granular properties of resistance against cracking are used, include: positive plates of Acid-Pb batteries and load shaped lines (made of Cu, Pb, and Ni) for industrial applications.

Functional Applications

One of the most successful applications of nano-structural materials is in soft magnetic materials for engines, transformators, and etc. Predicted decrease in anisotropy of magnetic crystal during grain size decrease, compared to its predefined thickness, has been investigated, Electro-deposited nano crystals would have a low coordination without causing any damage to saturation magnetism. Hence, application of these ferromagnetic materials with high efficiency in engines, transformators, anti-attack applications, has been enhanced due to recent advancements in electroplating technology. Through this technology it is possible to economically mass production of plates, thin sheets, and wires. Another Important application of electroplated nano- crystalline materials is for production of thin copper-made sheets for print circuit sheets. Etching rate increases when grain size decines and grain sizes of 50-100 nm provide optimum etching with maintaining convenient electrical conductivity. At it previously mentioned, high density of intra-crystalline defects is present in bulk state and cutting free surface of nano-structure materials offers a good chance for hydrogen and catalyststorage applications. There are many different applications for usage of these materials in both electrodeposited and electro-shaping methods for battery systems and alkaline fuel cell electrodes.

Classification of Applications

Improved hardness, wear and corrosion resistances, as well as decrease of saturation magnetism, acceptable thermal range, elastic properties, and electrical esistance make nano-crystal coatings an ideal candidate for protecting and associated coatings (such as in contact of hard and soft surface, coatings with less abrasive resistance, electronic conductivity, and alternative coatings for Cr and Cd in aerospace applications). Once such thin coatings are used, sediment finestructural changes with coating thickness increase of a great importance. Most previous studies on electrodeposited metals, not necessarily on their nanocrystalline form, have shown that increase of coating thickness causes to increase of grain size. For electrodeposited nano-crystalline Ni, it is found that first the sediment was amorphous with transition to nano-crystalline state and then there is an increase in grain size. In contrary, electrodeposited nano-crystals of Ni suggest that in most cases nano-crystals are exactly settled on interface with matrix and grain size is basically dependent from coating thickness. For distinct electrochemical conditions there is a thin transition layer made of coarser grains. Finally it has been proven that at initial layer with thickness of 200 nm grain sizes is independent from thickness.

3. Key Points for Development

Environment and Stability

In most cases surface engineering leads to economically use of materials and, consequently, profitability in many applications. For instance, increasing service lifetime there will be a decrease in wastes and energy consumption, which caused to retrieve improvement. Many advanced surface engineering processes have negligible environmental effects. One of developing activities in this filed is recoating of high-cost panels. Environmental rules, limiting each one of these panels wear, have a big share in progress of these industries.

Surface Engineering Share in Key Industry Sections

Building planes and vehicles comprehensively depend on surface-engineered panels. About 80% of these industries make use of coating. England has first position in field of steam turbines coating and annually obtains 1 billion pound bonus. Advanced coating of panels has considerably increased during last decades. In 1997, 23% of quick machining components for steel and 67% of monolithic carbide panels are coated by physical and chemical evaporation. Coating with Physical Vaporization Detector (PVD) method involves 5 billion pounds annual revenue world wide. PVD coating in production of multi-layers for high efficiency cutting tools has made dry machining possible, which needs a cooler coating with no decrease in profitability. Surface engineering of dual compounds and light alloy panels are used in special vehicles and advance applications such as coast equipment, medicine, and sports. Continuous manufacturing and performance of packaging industry is widelyassociated with surface engineering. Thanks to surface engineering, 44 billion drink cans are annually produced in Europe. Coating role for improvemnent of productions and then packaging is vital; especially in preventing air and moisture diffushon on potato chips and prepared food, or as a protector against crashing or cracking for thin glasses. Multilayer sputtering magnetron of a coating with low diffusion on construction glasses decreases thermal waste to 60% during winters, which amounts to a significant annual figure of fuel/m of glass. It is expected that 50% of buildings use these glasses till 2005. Plasma improvement of polyethylene surface with high molecular weight causes its durability against slight shakes, which is applied in medicine, For tissue recovery with advanced bio-sensors, all attached plastic bionedical panels to substrates use engineered surfaces to create efficient and compatible performance with human body, All electronic panels and advance sensors, optical coatings, and etc. also are benefited frorn surface engineering technology during building process.

Estimation of Corrosion and Erosion Costs

During last 10 years, due to educations for improvement of awareness from corrosion related issues, there was a 515 million pounds saving in England. Studies show similar values of total gross products for India, China, and United States. For United States decay costs exceeds 100 billion dollars annually. This is 1,300 million pounds for England, which is 3.5% of State gross product, where 3.0 million pounds is saved. This armount is 48-50 billion dollars in United States, which compose 4% of per capita gross production. As it previously remarked, this amounts to 10% of national gross production in developing countries.

Surface Engineering in Automobile Industry

There are nearly 27 million cars and 3.3 commercial vehicles in England roads. Car sale in Europe was about 12 million in 1997, where England share was about 1.7 million. It is estimated that car manufacturing will be 17% of England's surface engineering. Surface ernigineering has a significant role in this industry; since 6% of engine building costs and power transfer is for coating technology Total produced color for this industry exceeds 200 million pounds, Protective steel and body panels, as infrastructures, need to be repaired; so, many of then are galvanized and prepared for painting with another itable coating. While metals mostly are coated by organic painting, plastics should be ritially metalized, Here, application of wet processes competes with advancements in ID and CVD methods, Market is not the only effective factor on technology progress, it there are some environmental and leghalation concerns which are considered as a Bonerful encouragement in this field. Painting just involves about 2 kg of vehiclesweight, while painting process emits about s kg Volatile Organic Compounds (VOC) to the atmosphere. Efforts for reduction ofr this effect led to development of powder technology advancement. Most of coatings changes involve using the CrVI, where some substitute are being made for that. Automobile industry is directed to reaching products with higher compatibility with environment; as in their producing method application of CRVI is avoided. Mentioned cases are only a small part of coating applications.

Surface Engineering in Power Generation Industry

Here, power generation is addressed to high efficiency engines for aerospace industry, marine gas turbines, and electric generating turbines. Gas turbines are considered as a part of combinational cyclic developed machinery. Gas turbines have some advantages compared with equipment of power generating from fossil fuels, such as higher efficiency, lower constructing costs and using different fuels. This equipment work at higher temperatures and combustion and hot gas pass occurs within them. Here, creep, oxidization, and corrosion are regarded among important factors. Achieving ideal conditions, coating is of a great importance. Coating system is widely applied in gas turbines to protect gas pass route and increase system lifetime.

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