Electrodeposition of Alloys of Iron Group Elements with Tungsten & Phosphorus and their Structural and Magnetic Properties(タングステントとリンを含む鉄族元素合金の電着とその構造および磁気的性質)

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論文内容要旨

Chapter 1 Introduction

Alloys of tungsten and phosphorus with iron group elements (Fe, Co, Ni) are very important because of excellent mechanical, wear resistant and high temperature erosion resistant properties of tungsten alloys and good corrosion resistant, magnetic, electro-catalytic and surface hardness properties of phosphorus alloys. However, generally thermal techniques such as solidification and thermal evaporation cannot be used for the preparation of these alloys. The main reason is the large disparity in the melting points and vapor pressures of these elements.

Electrodeposition is an easy route for the preparation of these alloys. Although electroless deposition may also be an alternate, but it is very laborious and difficult to control process. The electrodeposition of tungsten and phosphorus is very interesting because these elements cannot be deposited in their pure form, but can only form alloys with iron group elements. Such an electrodeposition behavior was given the name "induced electrodeposition" by Brenner. Most of the studies on electrodeposition of tungsten alloys have been limited to binary alloys. Somewhat similar case has been with phosphorus alloys, although ternary Co-Ni-P alloys have also been investigated for use in magnetic memory devices. So far there has been a little study on the electrodeposition of ternary alloys and approximately no study on the electrodeposition of tertiary alloys of tungsten and phosphorus alloys.

The purpose of the present study is to develop ternary and tertiary alloys of tungsten and phosphorus with iron group elements to study their electrodeposition behavior and structural, wear resistant and magnetic properties. For this purpose, Ni-W-P, Ni-Fe-W-P, Ni-Fe-W, Co-Ni-P, Fe-Co-P and Fe-Co-Ni-P alloy systems have been investigated.

Chapter 2 Experimental Methods

The alloys were electrodeposited on copper substrates from proper aqueous solutions under proper operating conditions using direct current provided by Electrochemical Measurement System HZ-3000. The substrates were pretreated before electroplating either by mechanical polishing or electrochemical polishing depending on the surface finish requirements. The potential was measured against standard calomel electrode, while inert Pt electrode was used as counter electrode except for Co-Ni-P alloys, for which cobalt plate was employed. Compositional analysis of the electrodeposited alloys was done by energy dispersive spectroscopy (EDS) and electron probe microanalyser (EPMA). For structural analysis, X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques were employed. Hardness was measured by nanoindentor hardness tester or microhardness tester. Magnetic properties were determined by vibrating sample magnetometer and thermal analysis was performed by differential scanning calorimetry (DSC).

Chapter 3 Ni-W-P and Ni-Fe-W-P Alloys

In the last decade, electrodeposited Ni-W binary alloys have attracted a lot of interest because of their high hardness and high heat resistance properties. On the other hand, electrodeposited Ni-P alloys show high corrosion resistance. Advantages of the two systems can be merged together, if ternary Ni-W-P alloys are electrodeposited. Such ternary alloys have been produced by electroless deposition and show very good combination of properties. However, electroless deposition has many drawbacks such as laborious nature of the process and high amounts of waste etc. Therefore, electrodeposition behavior of Ni-W-P alloys must be clarified and proper conditions for their electrodeposition must be investigated. For this purpose, sodium hypophosphite was introduced in a conventional electroplating bath used for the electrodeposition of Ni-W binary alloys. It was observed that the tungsten content of the electrodeposited alloys was very sensitive to the hypophosphite content of the plating bath and even very small amounts of hypophosphite decreased the tungsten content drastically. Addition of Fe to the electroplating bath was found useful to remove this sensitivity. One interesting feature of these alloys was that the total W+P content of these alloys was constant. It was observed that increase in phosphorus content of the alloys makes their structure finer and finer and alloys more that 15 at% P had amorphous phase. Tungsten was found to increase the thermal stability of the amorphous phase of the alloys. All Ni-Fe-W-P alloys were amorphous in structure. Considering the electrodeposition behaviors of Ni-P and Ni-W alloys studied already as well as the variation in the chemical composition along the cross sections of the alloys and sensitivity of the tungsten content to the hypophosphite content in the present work, a mechanism was suggested that strong interaction between Ni and P during electrodeposition results in preferential reduction of these elements and inhibits the reduction of tungstate ions. This also results in decrease in cathode current efficiencies of the alloys.

Chapter 4 Ni-Fe-W Alloys

It is known from previous studies that higher amounts of tungsten are induced by iron than by nickel during electrodeposition. On the other hand, it is much easier to get compact electrodeposits from nickel baths at much higher cathode current efficiencies, while Fe-W electrodeposits are generally poor in quality and are deposited at very low cathode current efficiencies as well as at lower current densities. As a result deposition rates for Fe-W alloys are very low. Recently, Ni-W alloys have shown much higher hardness values (770 VHN) in as-deposited state. Addition of iron to Ni-W alloys to form Ni-Fe-W ternary alloys can be useful to get alloys with hardness even better than Ni-W alloys at deposition rates higher than those for Fe-W alloys. In the present study, electrodeposition conditions, such as current density and solution chemistry were optimized to produce Ni-Fe-W alloys with much better qualities. An alloy with composition of 60Ni-12Fe-28W showed a surface hardness of 966 VHN in as-deposited state, which is much higher than Ni-W alloys in as-deposited state. Previously Donten has reported the electrodeposition of ternary Ni-Fe-W alloys. Those alloys were deposited at rates of 4 μm / hr, while the above-mentioned alloy was deposited at a rate of 64 μm / hr, which is about 16 times higher than alloys of Donten. The structure of this alloy was found to be a composite having an amorphous matrix phase with FCC $Ni_{17}W_3$ crystals of 5 nm size embedded into it.

Chapter 5 Co-Ni-P, Fe-Co-P and Fe-Co-Ni-P Alloys

Binary Co-P and Fe-P alloys show soft magnetic properties in amorphous state. Since much higher amounts of phosphorus (> 20 at%) are needed to make them amorphous, therefore, they cannot show very high saturation magnetization values. Recently, ternary Co-Ni-P crystalline alloy films have been reported, which show saturation magnetization values of the order of 1.4 T, which is much higher value for alloys of this system. The main reason seems to be very low phosphorus content and very high cobalt content of the alloys. In the present work, successful attempt was made to prepare Co-Ni-P alloys in amorphous state while keeping the cobalt content high and phosphorus content low through manipulation of the operating conditions. An amorphous alloy having a composition of 75Co-19Ni-6P has shown a saturation magnetization of 1.06T. Such alloys were, however, found to show relatively high coercivity even in amorphous state.

It was also tried to produce Fe-Co-P alloys from similar baths as used for the electrodeposition of the above-mentioned Co-Ni-P alloys. These alloys were nanocrystalline and showed very high saturation magnetization values approaching up to 2.0T. The coercivity values of these alloys were much lower than those of amorphous Co-Ni-P alloys. Addition of nickel to these alloys was found to be useful to decrease coercivity further, but it also resulted in decrease in saturation magnetization.

Chapter 6 Conclusions

Alloys of iron group elements (Fe, Co, Ni) with tungsten and phosphorus comprising the systems, Ni-W-P, Ni-Fe-W-P, Ni-Fe-W, Co-Ni-P, Fe-Co-P and Fe-Co-Ni-P have been prepared by electrodeposition from aqueous solutions. The aim was to study their deposition characteristics and to find out new compositions with useful mechanical and / or magnetic properties and to investigate the conditions under which such alloy compositions could be produced.

It was found to be difficult to produce Ni-W-P alloys with high contents of both W and P. Additions of even very small amounts of hypophosphite, as a source of phosphorus, were sufficient to drop the tungsten content of the alloys drastically. Addition of Fe was found to be useful to overcome this problem. From the variation of composition along the cross section of Ni-W-P alloys and considering the theories explaining the deposition phenomenon of electrodeposition of Ni-W and Ni-P alloys, it was suggested that strong interaction between Ni and P is responsible for inhibiting the reduction of tungstate.

By controlling the electrodeposition conditions, Ni-Fe-W alloys with much better hardness properties and relatively higher ductility were produced. An alloy with composition of 60Ni-12Fe-28W showed a surface hardness of 966 VHN in as-deposited state. It was deposited at a rate of 64 μm / hr and has a structure consisting of an amorphous matrix with FCC $Ni_{17}W_3$ crystals of 5 nm size embedded into it.

By controlling the electrodeposition conditions, amorphous Co-Ni-P alloys showing saturation magnetization values higher than 1T were produced. However, such alloys showed relatively higher coercivity values. Nanocrystalline Fe-Co-P alloys electrodeposited from similar solutions as used for electrodeposition of Co-Ni-P alloys showed saturation magnetization values approaching up to 2 T with much lower coercivity values. Addition of nickel was useful to further decrease the coercivity, but at the cost of saturation magnetization.

論文審査結果の要旨

鉄、コバルト、ニッケルの鉄族元素とタングステンおよびリンから成る合金は、力学特性、磁気的性質および耐食性において優れた性質を有することが期待できる。これらの合金では大きな融点差と蒸気圧差のために、凝固法などを用いた材料作製は困難であるが、電着法を利用することによりアモルファス相などの非平衡合金膜を作製することが可能であると考えられる。

タングステンやリンを含む非平衡合金の電着法による創製研究はこれまで二元合金に限られており、タングステンおよびリンを含む多元系合金の電着法を用いた創製研究は行われていなかった。本研究は、電着法によりタングステンおよびリンと鉄族元素の３元および４元の多元系合金（Ni-W-P、Ni-Fe-W-P、Ni-Fe-W、Co-Ni-P、Fe-Co-P、Fe-Co-Ni-P 系）の創製を試み、それらの電着挙動、構造、組織、硬さおよび磁気特性を調査することを目的としている。本論文はこれらの研究結果を纏めたものであり、全体６章からなる。

第１章は序論であり、本研究の背景と目的について述べた。

第２章は本研究に用いた実験方法について述べた。

第３章では、 Ni-W-P および Ni-Fe-W-P 合金の電着挙動について調査した。次亜リン酸ナトリウムを添加した Ni-W 浴を用いることにより Ni-W-P 三元合金膜の作製を試みた。次亜リン酸ナトリウムの添加は合金膜中のタングステン濃度を減少させるが、浴に Fe を添加することでこの問題を克服した。次亜リン酸ナトリウム添加によるタングステン濃度の減少は Ni と P の強い相互作用に起因していることを明らかにした。Ni-W-P 三元系ではリン濃度が 15%以上でアモルファス相が、Ni-Fe-W-P 四元系では 25～40 at% Fe、6～22 at% W、2～13 at% P の組成範囲においてアモルファス相が生成することを見出した。また、タングステン濃度が高いほどアモルファス相の熱的安定性が増大することを明らかにした。

第４章では、Ni-Fe-W 合金の電着挙動について調査した。電着条件を適切に制御することで高硬度を有する Ni-12Fe-28W 膜を毎時 64μm の電着速度で作製できることを示した。この製膜速度は Ni-W 合金での従来の値に比べて約 16 倍も高い値である。また、その膜はアモルファス母相中に 5nm 径の立方構造の $Ni_{17}W_3$ が均一に分散したナノ複相組織を有することを明らかにした。

第５章では、Co-Ni-P、Fe-Co-P および Fe-Co-Ni-P 合金の電着挙動と磁気特性について調査した。適切な電着条件を選択することにより、従来よりも低い 6 at%のリン濃度でもアモルファス相膜が生成でき、それらの膜は強磁性を示した。飽和磁束密度はアモルファス構造を有する Co-19Ni-6P 合金膜では 1.06T、ナノ結晶構造を有する Fe-Co-P 合金膜では 2.0T の高い値を有しており、Fe-Co-P 膜は著しく低い保磁力を具備していた。また、Fe-Co-P に Ni を添加することにより電着膜の軟磁気特性が改善されることを明らかにした。

第６章は結論である。

以上、要するに本論文は、鉄族元素とタングステンおよびリンからなる多元系合金膜を電着法により作製し、Ni-W-P、Ni-Fe-W-P、Ni-Fe-W、Co-Ni-P、Fe-Co-P および Fe-Co-Ni-P 合金膜の作製条件、構造、組織、機械的性質および磁気特性を明らかにしたものであり、金属工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。