Effect of swift heavy ion irradiation on Fe-containing vapor deposited multilayers, electrochemically deposited coatings, and Bi-2223 type high temperature superconductors

Sándor Stichleutner

PhD theses

Physics Doctoral School, Eötvös University

Head of School: Prof. Dr. Zalán Horváth, member of HAS

Materials Science and Solid State Physics Programme

Head: Prof. Dr. János Lendvai, DSc HAS

Supervisors:
Prof. Dr. Ernő Kuzmann, DSc HAS
Prof. Károly Havancsák, PhD

Insititute of Chemistry, Faculty of Science,
Eötvös University

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1 Introduction

Recently, materials having special electronic, magnetic and mechanical properties are in the focus of interest from both scientific and technological points of view. The majority of these materials are in non-equilibrium state thermodynamically, the occurrence of metastable phases is characteristic of these materials. A number of "non-equilibrium" techniques (physical vapor deposition, rapid quenching, electrochemical deposition, etc.) as well as the ion implantation, too, are applied for their preparation. The low energy (10-100 keV) ion implantation is a widely used method also in the electronic industry in order to produce amorphous surfaces with desired properties and to improve the technological properties of the surfaces. On the other hand, we have much less knowledge about the changes caused by swift (100-1000 MeV) heavy ion irradiation.

In order to have a deeper insight into the processes and effects related to the swift heavy ion irradiation, I have studied the effect of swift heavy ion irradiation on Fe-containing vapor deposited multilayers, electrochemically deposited coatings, and Bi-2223 type high temperature superconductors.

Among the analytical investigations the Mössbauer spectroscopy has played a key role. By the help of this method – by measuring the hyperfine interactions between the electrons and the nucleus – it is possible to detect the changes in the microenvironments of the Mössbauer active elements due to swift heavy ion irradiation very sensitively.

2 Background

The characterization and identification of the non-equilibrium phases occurring in alloys of transition metals, or of transition metals with non-transition metals have high importance. Not only the knowledge of the phase composition is important, but also how the particular metastable phases occurring at special circumstances of the preparation are characteristic for the alloys or the alloy systems. The phases in which the long range order totally or partly is absent, e.g. microcrystalline or amorphous alloys, are of special importance. First Watson et al. (Trans. IMF. **64** (1986) 149) have succeeded in preparing, in electrochemical way, homogeneous and thick Fe-Ni-Cr alloy with better mechanical and corrosion resistance than those of stainless steel. XRD investigations carried out on these electrodeposits by Kuzmann et al. (Hyperfine Interact. **45** (1989) 397) showed, in contrast to the expectations, that the structure of these coatings has amorphous or microcrystalline character.

By applying Mössbauer spectroscopy, information on the phase composition and chemical short range order of these novel Fe-Ni-Cr deposits was obtained. The main phase of the deposits was ferromagnetic in contrast to the thermally prepared alloys, which are in paramagnetic state. For comparison, Perin et al. (Surf. Coat. Tech. **103-104** (1998) 93) have found that the main phase of Fe-Ni-Cr samples prepared by ion implantation of multilayers containing a few layers of Cr, Ni and Fe was also a metastable ferromagnetic phase of amorphous character. This means that the formation of the metastable ferromagnetic Fe-Ni-Cr phase found in electrodeposits is not restricted only for electrodeposits but it is valid more generally. On the other hand, it was established that the samples prepared by laser irradiation of Fe-Ni-Cr multilayers contain both metastable and stable phases, the stable phase being identical with that occurring in the thermally prepared alloy. In connection with this, I wanted to find the answer to the question: What kind of phases can be formed in vapor deposited Fe-Ni-Cr films due to swift heavy ion irradiation, and how can the irradiation modify the chemical short range order in electrodeposits containing metastable phases?

I have also investigated the effect of swift heavy ion irradiation in other electrodeposits containing metastable phases. Here I participated in the preparation of these alloys, e.g. in the case of Sn-Co-Fe ternary alloys, where we have found a novel ferromagnetic amorphous Sn-Co-Fe phase in the electrodeposits (Kuzmann et al., AIP Conf. Proc. **765** (2005) 99).

The amorphous alloys are mostly prepared by rapid quenching. However, amorphous iron can not be prepared by rapid quenching because it is not possible to achieve the critical quenching rate. Therefore it was not possible to prepare amorphous iron for a long time. However, in the beginning of the 90es, Suslick et al. (Nature **353** (1991) 414) were able to prepare pure amorphous iron by ultrasonic irradiation of iron pentacarbonyl, $Fe(CO)_5$. Kuzmann et al. (Radiat. Eff. Defect. S. **147** (1999) 255) have succeeded in obtaining partial amorphisation in 70 nm thick ^{57}Fe films vapor deposited onto SiO_2 by the help of swift heavy ion irradiation. Based on these results, our goal was to perform swift heavy ion irradiation on electrochemically prepared Fe thin films.

Another topic attracting very high scientific interest is the investigation of high temperature superconductors (Bednorz and Müller, Z. Phys. B **64** (1986) 189), the mechanism of which has not been clarified yet. Although these materials are crystalline and their atomic arrangements are known according to the diffraction methods, unique information about the microenvironments of Mössbauer nuclides could be obtained (Kuzmann et al., Physica C **312** (1999) 45) from the Mössbauer measurements. It is known that the swift heavy ion irradiation considerably increases the critical current density (e.g. Terai and Kusagaya, Physica C **235-**

240 (1994) 2973), which is a very important parameter from the point of view of applications. It looked to me obvious to perform Mössbauer study on the change of ^{57}Fe substituted Cu microenvironments in the conducting layers of Bi-2223 type high temperature superconductors due to swift heavy ion irradiation.

3 Aim

The effect of swift heavy ion irradiation was studied on vapor deposited 50%Fe-25%Ni-25%Cr multilayers, on electrochemically deposited 8%Fe-3%Ni-89%Cr alloy coatings, on crystalline α-Fe and on 48%Sn-23%Co-29%Fe thin layers, as well as on Bi-2223 type high temperature superconductors of composition $(Bi_{0.93}Pb_{0.17})_2Sr_{1.9}Ca_{2.05}(Cu_{1.02}Fe_{0.01})_3O_y$. The main objective of the work was to find the answers to the following questions:

1. Is it possible to prepare metastable amorphous Fe-Ni-Cr alloys consisting of ferromagnetic and paramagnetic phases from vapor deposited multilayers of corresponding composition by the help of swift heavy ion irradiation?
2. How can the swift heavy ion irradiation affect the phase composition and the chemical short range order of paramagnetic amorphous Fe-Ni-Cr electrodeposits?
3. Is it possible to prepare ferromagnetic amorphous Fe from electrochemically prepared crystalline α-Fe coatings by the help of swift heavy ion irradiation? If yes, what is the relationship between the rate of amorphisation of iron and the dose of the irradiation as well as the energy and mass of the ions used for the irradiation?
4. How can the swift heavy ion irradiation performed with different energy and mass ions affect the phase composition and the chemical short range order of the electrochemically deposited novel ferromagnetic amorphous Sn-Co-Fe alloy coatings?
5. How can the swift heavy ion irradiation affect the five and four oxygen coordinated microenvironments of Cu in the conducting layers between Ca and Sr-O layers in Bi-2223 type high temperature superconductors? Is there any difference, revealable by the help of Mössbauer spectroscopy, between the character of the chemical bonds of Cu (substituted with ^{57}Fe) with apical oxygen and with planar oxygen?

4 Sample preparation and investigation methods

We applied preparation procedures which resulted in new, earlier not known materials with metastable phases. Fe-Ni-Cr and Sn-Co-Fe electrodeposits were prepared at Glasgow

Caledonian University. The vapor deposited multilayers were fabricated at Trento University. The Bi-2223 type superconducting ceramics were prepared at Kepler University in Linz.

The swift heavy ion irradiations were performed with 246 MeV Kr and 710 MeV Bi ions in the range of fluences 10^{11}–10^{14} ion×cm^{-2} at the Laboratory of Nuclear Reactions at the JINR in Dubna, Russia.

The XRD measurements were carried out partly by a computer controlled DRON-2 X-ray diffractometer and partly by a Philips X'Pert diffractometer.

The SEM and AFM measurements were performed at Kepler University in Linz and in the MTA KFKI Research Institute for Technical Physics and Material Sciences as well as at the Department of Materials Physics, Eötvös University.

^{57}Fe és ^{119}Sn conversion electron Mössbauer measurements of non-irradiated and irradiated multilayers, and coatings were carried out at room temperature, while the Mössbauer measurements of superconductors were performed in transmission geometry, using conventional constant acceleration WISSEL, RANGER and KFKI type Mössbauer spectrometers. The Mössbauer spectra were evaluated by the MOSSWINN program.

5 Summary of results, theses

1. I have shown that, upon swift heavy ion irradiation (246 MeV Kr) in vapor deposited multilayers of composition 50%Fe-25%Ni-25%Cr:

a. highly disordered ferromagnetic and paramagnetic phases arise. These phases can be identified as the phases of non-equilibrium Fe-Ni-Cr ternary alloys;

b. the relative amount of both disordered ferromagnetic phase and disordered paramagnetic phase increases with the dose of the irradiation;

c. the arising paramagnetic and ferromagnetic phases are metastable, they transform to the equilibrium Fe-Ni-Cr ternary alloy upon isothermal heat treatment.

2. I have shown that, upon swift heavy ion irradiation (246 MeV Kr) in electrochemically deposited amorphous ferromagnetic 8%Fe-3%Ni-89%Cr alloy coatings:

a. a novel highly disordered amorphous paramagnetic phase arises. This reflects the radiation induced changes in the chemical short range order of the amorphous state;

b. the relative amount of the disordered paramagnetic phase increases with the dose of the irradiation.

3. I have shown that, upon swift heavy ion irradiation (246 MeV Kr, 710 MeV Bi) in electrochemically deposited crystalline ferromagnetic α-Fe coatings:

a. the partial amorphisation of Fe occurs;

b. the relative amount of the ferromagnetic amorphous Fe phase increases with both the energy and the mass of the ions;

c. the relative amount of the ferromagnetic amorphous Fe phase increases with the dose of the irradiation.

4. I have shown that, a paramagnetic phase also arises due to swift heavy ion irradiation (246 MeV Kr, 710 MeV Bi) in electrochemically deposited crystalline ferromagnetic α-Fe coatings. This paramagnetic phase can be assigned to superparamagnetic iron.

5. I have shown that, the transformation of the amorphous state, involving changes in the chemical short range order, occurs upon swift heavy ion irradiation (246 MeV Kr, 710 MeV Bi) in electrochemically deposited novel ferromagnetic amorphous 48%Sn-23%Co-29%Fe alloy coatings. The rate of the transformation depends on the energy and mass of the ions used for the irradiation.

6. I have found that the relative areas of subspectra belonging to Cu sites with two different oxygen coordination environments change in the ^{57}Fe Mössbauer spectra of Bi-2223 type high temperature superconductors upon the effect of swift heavy ion irradiation (246 MeV Kr). The number of sites with square-planar oxygen coordination increases at the expense of the number of sites with fivefold pyramidal oxygen coordination. This can be explained by easy break-up of the bond of apical oxygen with Cu due to the irradiation. This indicates that the metallic character bond of the planar oxygen with Cu is essentially different from the ionic character bond of the apical oxygen with Cu.

6 Utilization of the results

Our new scientific results on one hand expand the knowledge in the related areas, on the other hand broaden the theoretical basis of the practical applications. The results help prepare alloy coatings, amorphous alloys and high temperature superconductors with improved properties. Since we have succeeded in preparing new alloy coatings the corrosion resistance of which is much higher than that of the crystalline ones, these alloys can be applied for preparation of high-tech materials in a wide range.

7 Publications of the author, related to the topic of the dissertation

Journal papers

1. E. Kuzmann, G. Principi, C. Tosello, K. Havancsák, S. Stichleutner, I. Gerőcs, Z. Homonnay, A. Vértes: Mössbauer study of metastable phase formation in vacuum

deposited FeNiCr multilayers due to swift heavy ion irradiation, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 183 (2001) 425-431

2. E. Kuzmann, S. Stichleutner, M. El-Sharif, C. U. Chisholm, L. Sziráki, A. Vértes: Mössbauer investigation of electrodeposited Sn-Zn, Sn-Cr, Sn-Cr-Zn and Fe-Ni-Cr coatings, *Hyperfine Interactions* 141/142 (2002) 425-433
3. E. Kuzmann, S. Stichleutner, M. El-Sharif, C. U. Chisholm, G. Principi, C. Tosello, K. Havancsák, I. Gerőcs, A. Vértes: Mössbauer studies of radiation effects in swift heavy ion irradiated Fe-Ni-Cr multilayers and electrodeposited alloys, *Hyperfine Interactions* C 5 (2002) 591-594
4. S. Stichleutner, E. Kuzmann, Z. Homonnay, Z. Klencsár, A. Vértes, K. Havancsák, W. T. König, O. Heiml, G. Gritzner: Mössbauer study of (Bi,Pb)-2223 superconductors irradiated with 86Kr ions, *Journal of Radioanalytical and Nuclear Chemistry* 261 (2004) 133-135
5. E. Kuzmann, S. Stichleutner, O. Doyle, C. U. Chisholm, M. El-Sharif, Z. Homonnay, A. Vértes: Mössbauer and X-ray diffraction investigations of Sn-containing binary and ternary electrodeposited alloys from a gluconate bath, *Proceedings of American Institute of Physics* 765 (2005) 99-107
6. C. U. Chisholm, E. Kuzmann, O. Doyle, M. El-Sharif, S. Stichleutner, Z. Homonnay, K. Sólymos, A. Vértes: Mössbauer and XRD investigation of electrodeposited Fe, Co and Fe-Co alloys using a gluconate plating process, *Journal of Radioanalytical and Nuclear Chemistry* 266 (2005) 533-542
7. E. Kuzmann, S. Stichleutner, K. Havancsák, M. El-Sharif, C. U. Chisholm, O. Doyle, V. Skuratov, K. Kellner, Gy. Dóra, Z. Homonnay, A. Vértes: Amorphous iron phase formation in swift heavy ion irradiated electrodeposited iron thin films, *Radiation Physics and Chemistry* 75 (2006) 741-746
8. L. Sziráki, E. Kuzmann, C. U. Chisholm, M. El-Sharif, L. Bóbics, S. Stichleutner: Characterization of the passive films on electrodeposited Fe-Ni-Cr alloys in borate solution at pH 8.4, *Central European Journal of Chemistry* 5 (2007) 931-950
9. C. U. Chisholm, E. Kuzmann, M. El-Sharif, O. Doyle, S. Stichleutner, K. Solymos, Z. Homonnay, A. Vértes: Preparation and characterisation of electrodeposited amorphous Sn-Co-Fe ternary alloys, *Applied Surface Science* 253 (2007) 4348-4355
10. A. Paszternák, S. Stichleutner, I. Felhősi, Z. Keresztes, F. Nagy, E. Kuzmann, A. Vértes, Z. Homonnay, G. Pető, E. Kálmán: Surface modification of passive iron by alkyl-phosphonic acid layers, *Electrochimica Acta* 53 (2007) 337-345
11. E. Kuzmann, S. Stichleutner, Z. Homonnay, A. Vértes, A. Paszternák, F. Nagy, I. Felhősi, G. Pető, J. Telegdi, E. Kálmán: Amorphous iron formation due to low energy heavy ion implantation in evaporated 57Fe thin films, *Journal of Radioanalytical and Nuclear Chemistry* 277 (2007) 699-702
12. M. El-Sharif, C. U. Chisholm, E. Kuzmann, L. Sziráki, S. Stichleutner, Z. Homonnay, K. Süvegh, A. Vértes: The structure and composition of novel electrodeposited Sn–Fe and Sn–Co–Fe alloys from a flow circulation cell system, *Hyperfine Interactions* 192 (2009) 1-12

13. S. Stichleutner, E. Kuzmann, K. Havancsák, Z. Homonnay, A. Vértes, O. Doyle, M. El-Sharif, C. U. Chisholm: Mössbauer studies of the effect of swift heavy ion irradiation on electrodeposited Sn-Co-Fe coatings, *Journal of Physics: Conference Series* (2009) accepted for publication

14. C. U. Chisholm, M. El-Sharif, E. Kuzmann, S. Stichleutner, Z. Homonnay, A. Vértes: Electrodeposition of Sn-Fe alloys using gluconate electrolytes and XRD and Mössbauer studies of the deposits, *Materials Chemistry and Physics* (2009) accepted for publication

Recent conference publications

15. S. Stichleutner, Amorphous iron formation in swift heavy ion irradiated electrodeposited iron coatings, *Proceedings of JINR Days in Hungary*, Budapest, 3-7 December 2008 (invited talk), video:

    http://vod.niif.hu/index.php?lg=en&mn=archive&eid=88&sm=listevent

16. S. Stichleutner, E. Kuzmann, K. Havancsák, Z. Homonnay A. Vértes, O. Doyle, M. El-Sharif, C.U. Chisholm, Mössbauer Study of the Effect of Swift Heavy Ion Irradiation on Electrodeposited Sn-Co-Fe Coatings, *Proceedings of International Conference on the Applications of the Mössbauer Effect*, *ICAME 2009*, Vienna, 19-24 July 2009

17. E. Kuzmann, S. Stichleutner, K. Havancsák, V. Skuratov, A. Vértes, Z. Homonnay, O. Doyle, C. U. Chisholm, M. El-Sharif, Mössbauer Study of Amorphous Iron Formation due to Heavy Ion Irradiation, *Abstract Book of International Conference on Mössbauer Spectroscopy and its Applications*, *ICMSA XI*, Ekaterinburg, 1-5 June 2009 (invited talk)

18. E. Kuzmann, S. Stichleutner, K. Havancsák, V. Skuratov, A. Vértes, Z. Homonnay, O. Doyle, C. U. Chisholm, M. El-Sharif, Mössbauer Study of Amorphous Iron Formation due to Swift Heavy Ion Irradiation, *Abstract Book of Colloquium Spectroscopicum Internationale XXXVI*, *CSI XXXVI*, Budapest, 30 August - 3 September 2009 (meghívott előadás)

8 Other publications of the author

1. Z. Homonnay, E. Kuzmann, S. Stichleutner, É. Makó, K. Varga, Z. Németh, A. Szabó, P.Tilky, J. Schunk, G. Patek, Gõzfejlesztõ hõátadó csövek állapotának tematikus vizsgálata, *Magyar Kémiai Folyóirat* 108 (2002) 449-454

2. Z. Homonnay, E. Kuzmann, S. Stichleutner, É. Makó, K. Varga, Z. Németh, A. Szabó, K. Radó, P.Tilky, J. Schunk, G. Patek, Gőzfejlesztő hőátadó csövek korróziós állapotfelmérése, *Korróziós Figyelő* 43 (3) (2003) 77-84

3. K. Varga, Z. Németh, A. Szabó, K. Radó, D. Oravetz, É. Makó, Z. Homonnay, E. Kuzmann, S. Stichleutner, P. Tilky, J. Schunk, G. Patek, Comprehensive investigation of the corrosion state of the heat exchanger tubes of steam generators, In: *Corrosion issues in light water reactors: Stress corrosion cracking (EFC 51)*, Eds. D Féron and J-M Olive, Woodhead Publishing Limited, Abington Hall, 2007

4. K. Nomura, E. Kuzmann, C. A. Barrero, S. Stichleutner, Z. Homonnay: 119Sn Mössbauer study of sol–gel synthetized $Fe_xSb_ySn_{1-x-y}O_{2-\delta}$ powders, *Hyperfine Interactions* 184 (2008) 57-62

5. F. Somodi, I. Borbáth, J. L. Margitfalvi, S. Stichleutner, K. Lázár: Study of Au/SnO_x–Al_2O_3 catalysts used in CO oxidation by in situ Mössbauer spectroscopy, *Hyperfine Interactions* 192 (2009) 13-21