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Titanium Evolution Under Neutron Irradiation in Ni_xC_{1-x}/Ti Multilayers

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Abstract : Supermirrors, which are Ni_xC_{1-x}/Ti aperiodic multilayers, have become more and more important for use in neutron guides. The effects of neutron radiation on the structural and optical properties of such stacks have been studied to estimate the lifetime of the neutron guides. The results presented here have been obtained by neutron reflectivity, X-ray diffraction, Conversion-Electron Extended X-ray Absorption Fine Structure and High Resolution Transmission Electron Microscopy. It has been observed that the reflecting performances of the supermirrors were not altered by irradiation, but that a structural change did occur in the Ti layers.

1. INTRODUCTION

Neutron scattering is an important tool for the investigation of condensed matter. The new generation of neutron guides made from supermirrors will markedly increase the intensity of the incident beams, which is of great benefit for condensed matter studies. Supermirror neutron guides are aperiodic multilayers of spacer (in our case Ti) and reflecting (in our case Ni_xC_{1-x}) materials alternately deposited on a flat surface (a glass substrate for instance) [1, 2]. The thicknesses of the layers are calculated so that a succession of first order Bragg peaks lengthens the natural total reflection "plateau". Such optimized stacks thus present a high contrast index [3, 4] and the critical value of its apparent total reflection angle is considerably increased compared to that of standard neutron guides coated with pure Ni. These guides being submitted to neutron beams (that is to say neutron irradiation), we have been interested in determining the effects of the radiation on the supermirror performance. With this aim, irradiated and non-irradiated Ni_xC_{1-x}/Ti multilayers have been studied by neutron reflectivity, X-ray diffraction, Conversion-Electron Extended X-ray Absorption Fine Structure (CE-EXAFS) and High Resolution Transmission Electron Microscopy (HRTEM). The unexplained structural modification of the titanium layers presented previously [5, 6] is now well understood and described below.

2. SAMPLES

Periodic stacks, also called monochromators, are easier to characterize than supermirrors due to a lower number of defining parameters. For this reason 10 bilayers of Ni_xC_{1-x}/Ti deposited on a 3mm-thick Silicon wafer were submitted to thermal neutron irradiation under a dose of 3.10^{19}n.cm^{-2} at the Orphée reactor (Saclay, France). The flux being 4.10^{13}n.cm^{-2}.s^{-1}, the irradiation lasted approximately ten days under neutrons whose energy ranges from 5 to 80meV. In neutron guides (where the flux is 10^{10}n. cm^{-2}.s^{-1}), the same dose corresponds to an irradiation of about 100 years. The thickness d of a bilayer is 100Å (42Å of Ni_xC_{1-x} plus 58Å of Ti).
These samples and real neutron guides also differ in their substrate. Effectively, the glass substrate used in neutron guides is likely to be much more damaged by irradiation than the Si substrate used here : this study

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thus only concerns the effects of neutron radiation on the multilayers and does not take the influence of the substrate on the layers into account.
The stack begins with a Ti layer on the substrate and finishes with a Ni_xC_{1-x} layer (which we shorten to NiC) in contact with air. Another monochromator was prepared simultaneously, kept as grown and taken as control.

3. EXPERIMENTAL RESULTS

3.1 Neutron reflectivity measurements

Both control and irradiated samples were characterized by neutron reflectivity on the reflectometer EROS at the Laboratoire Léon Brillouin (Saclay, France). The time of flight technique was used, in which the incident angle is fixed while the neutron wavelength varies from 2 to 23Å [7]. The experimental data processing is done by a numerical simulation [8] in which the fitting parameters are : the bilayer period (d), the ratio (γ) of Ni thickness to bilayer thickness, the neutron coherent scattering length density Nb of each material (N being the atomic density and b the neutron coherent scattering length), the roughness (σ_s) at the substrate/first layer interface, the roughness (σ_{air}) at the last layer/air interface and the roughness ($\sigma_{NiC/Ti}$) at the NiC/Ti or Ti/NiC interfaces which is considered as constant for the whole stack (this approximation reduces the number of parameters but is not physically verified).
The experimental and simulated curves of both control and irradiated samples are presented in Figure 1. One can observe on these curves that the intensities of the Bragg peaks do not decrease after irradiation, which means the optical performances of the multilayers are not altered by the irradiation. Nonetheless, it is observed that the positions of the Bragg peaks do not coincide on these curves : on the irradiated sample, the Bragg positions are slightly smaller than on the control. This corresponds to an increase in the period of the stack of about 10% due to a structural irradiation effect. The total reflection edge is also weaker, which shows that the mean neutron coherent scattering length density has decreased (control sample : 2.41×10^{-6}Å^{-2}; irradiated one : 0.798×10^{-6}Å^{-2}).

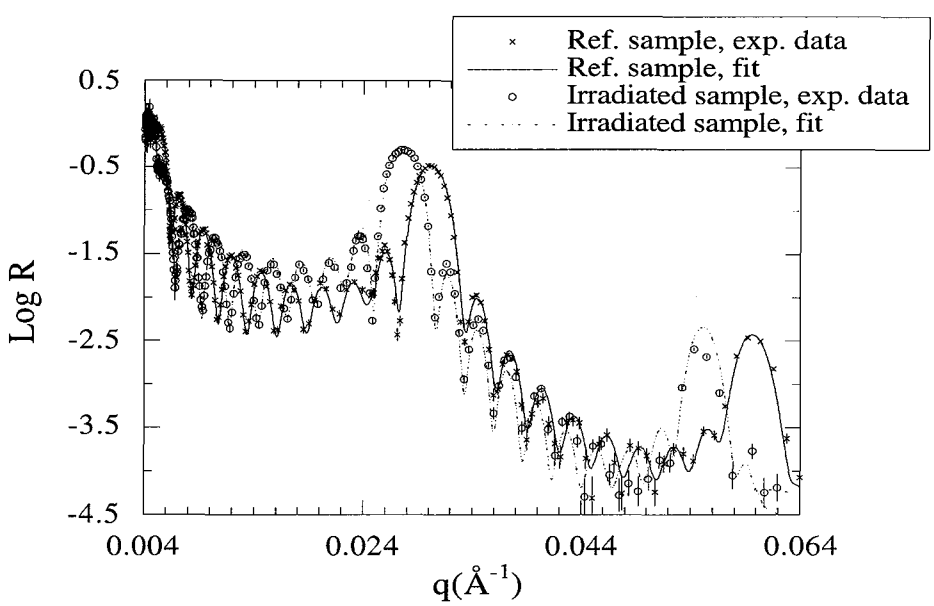

Figure 1 : Neutron reflectivity versus component of momentum $q=2\pi \sin\theta \lambda^{-1}$ (where θ is the incident angle) for the control and irradiated samples. The simulation parameters are : control sample : d=105.5Å, Nb(Ni)=8.5×10^{-6}Å^{-2} and Nb(Ti)=-2×10^{-6}Å^{-2}; irradiated sample : d=114Å, Nb(Ni)=7.7×10^{-6}Å^{-2} and Nb(Ti)=-4.2×10^{-6}Å^{-2}.

3.2 X-ray diffraction measurements

These measurements were carried out on the CILAS (Orléans, France) company's diffractometer with an incident wavelength of K_α(Cu)=1.542Å. The purpose of this investigation was to find more details about the structural change which occurred in the layers after irradiation. In the control sample, the X-ray diffraction spectrum (Figure 2a) shows a strongly-textured Ti in the (002) direction of the hexagonal structure, and a strongly-textured Ni in the (111) direction of the face-centered cubic (fcc) structure. After irradiation (Figure 2b), the Ni texture remains unchanged, but that of Ti disappears and a new diffraction peak is observed in a position (θ=17.25°, d_{hkl}=2.6Å) which does not tally with the hexagonal close packed (hcp) structure. Other results have attributed this peak to the (111) peak of a face-centered cubic structure with a lattice parameter of 4.38Å : this point is discussed further below.

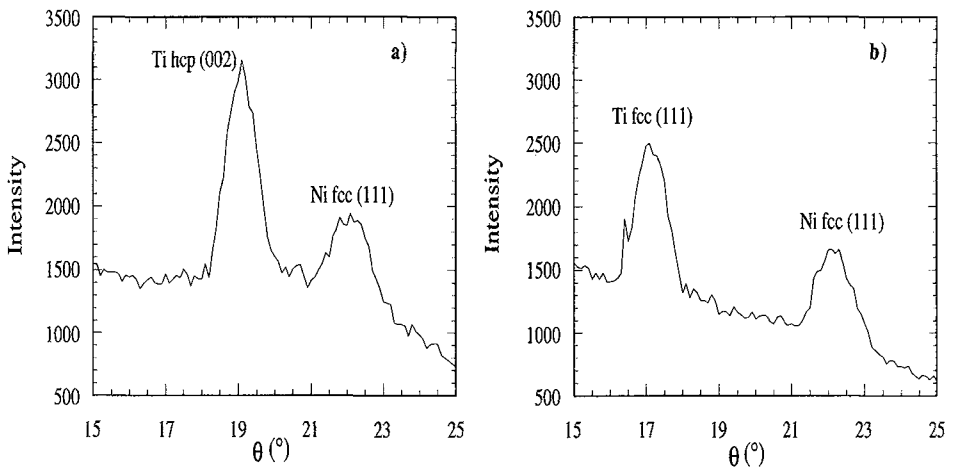

Figure 2 : X-ray diffraction spectra of **a)** the reference sample and **b)** the irradiated one.

3.3 Conversion-Electron Extended X-ray Absorption Fine Structure (CE-EXAFS)

In order to obtain more information on the crystallographic structure observed by X-ray diffraction, both samples have been investigated by CE-EXAFS at low temperature (80K) under synchrotron radiation at the LURE (Orsay, France). Measurements have been done at the Ni as well as at the Ti K-edge threshold energy.

No evolution of the signal is observed at the Ni threshold but a new Ti-Ti distance of 3.08Å must be introduced to simulate the irradiated sample signal at the Ti threshold (Figure 3). This value corresponds to no Ti-Ti distance in any of pure Ti structure, nor to any known Ti-Ni distance. But, as for X-ray diffraction experiments, it corresponds to a Ti-Ti distance in a face-centered cubic structure with a lattice parameter of 4.38Å.

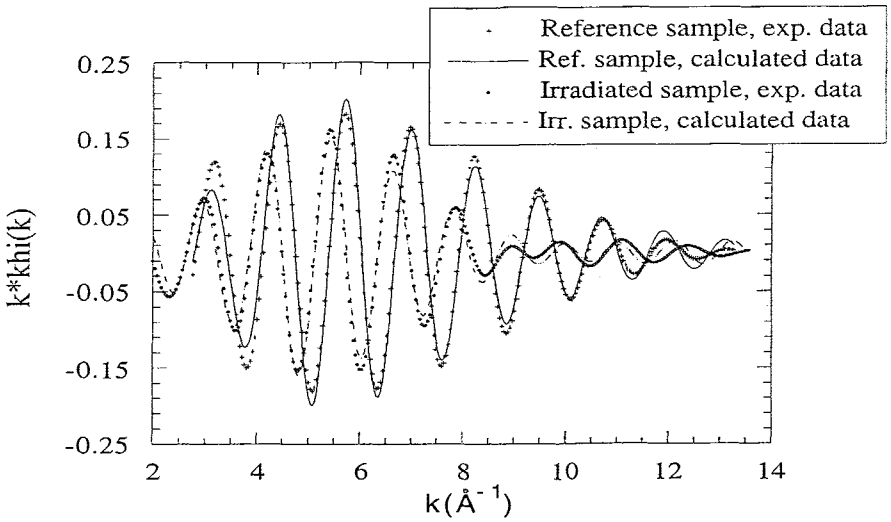

Figure 3 : Comparison of the control and irradiated first neighbors EXAFS signals at the Ti threshold energy. The simulation parameters of the irradiated sample are as followed : N_{Ti1}=2, R_{Ti1}=2.89Å ; σ_{Ti1}=0.051Å, N_{Ti2}=5.8, R_{Ti2}=3.05Å, σ_{Ti2}=0.077Å where N_{Tij} is the number of jth nearest neighbors, R_{Tij} the distance between these neighbors and σ_{Tij} the standard deviation of their position.

3.4 High Resolution Transmission Electron Microscopy

HRTEM experiments [9, 10] were carried out to identify the new phase in the Ti layers. The samples have been studied in the JEOL 4000EX microscope at the SP2M laboratory (CENG, France). The resolution is of 1.7Å at a 400kV energy. Figure 4 shows an image of the irradiated layers. One can notice three directions of orientation of the grains in the Ti layers (in bright) : some grains are parallel to the growth axis of the layers ; for some others, angles of 55° or 70° between the growth axis and their direction of orientation are measured. According to electron diffraction results (Table I), these orientations coincide once again with those of a face-centered cubic structure with a lattice parameter of 4.38Å.

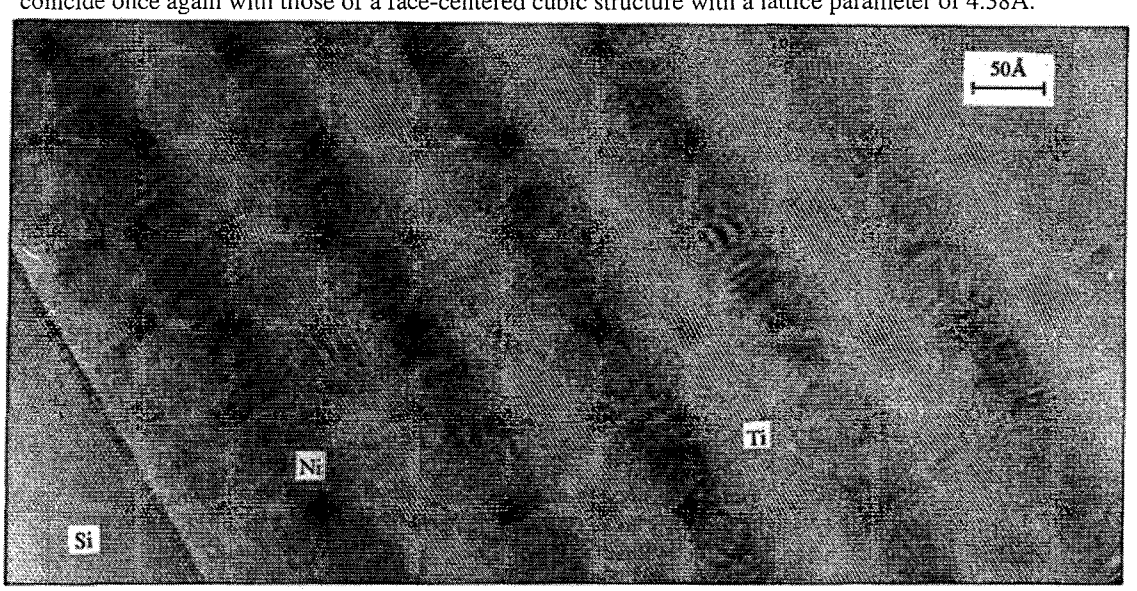

Figure 4 : High Resolution Transmission Electron Microscopy image of the irradiated sample.

fcc Nickel : theoretical d_{hkl}(Å) ; hkl	**hcp Titanium : theoretical d_{hkl}(Å) ; hkl**	Control sample : experimental d_{hkl}(Å)	Irradiated sample : experimental d_{hkl}(Å)	fcc structure with a lattice parameter of 4,38Å : calculated d_{hkl}(Å) ; hkl
	2,55 ; 100	**2,55**	2,53	2,53 ; 111
	2,34 ; 002	**2,35**		
	2,24 ; 101	**2,25**		
			2,19	2,19 ; 200
2,03 ; 111		*2,05*	*2,05*	
1,76 ; 200		*1,77*	*1,80*	
	1,73 ; 102			
			1,56	1,55 ; 220
	1,475 ; 110	**1,46**		
	1,33 ; 103	**1,33**		1,32 ; 311
	1,28 ; 200		1,29	
1,25 ; 220	**1,25 ; 112**	**1,25**		1,26 ; 222
	1,23 ; 201			
	1,17 ; 004	**1,18**		
	1,12 ; 202			1,09 ; 400
1,06 ; 311	**1,06; 104**	**1,07**		
1,02 ; 222		*1,02*	*1,03*	

Table I : Electron diffraction results : comparison of the calculated and experimental interreticular distances of fcc Ni, hcp Ti and the fcc structure. The interreticular distances and hkl values are written in italic for fcc Ni, in bold for hcp Ti and underlined for the fcc structure.

4. DISCUSSION

The non-variation of the Bragg peaks under thermal neutron irradiation shows that supermirror performance remains constant after irradiation.

Further information were obtained from X-ray diffraction, CE-EXAFS and HRTEM experiments. According to the X-ray diffraction spectra, the Ni layers remain unchanged after irradiation, while the Ti layers change texture. Furthermore, the Ti EXAFS signal shows the existence of an additional Ti-Ti distance of 3.08Å. One can thus deduce that a new phase containing Ti has appeared. HRTEM has attributed this phase to an fcc structure textured in the (111) direction and whose lattice parameter is of 4.38Å, which corresponds to the interreticular distance of 2.60Å and the interatomic Ti-Ti distance of 3.08Å found by the other techniques. There is no known corresponding phase of pure Ti (βTi and ωTi) [11, 12, 13] but one can be found in combinations of Ti with small atoms such as C, H, N, O [14, 15].

Elastic Recoil Detection Analysis (ERDA) experiments have recently confirmed the presence of hydrogen in the Ti layers in the irradiated sample, but no hydrogen was found in the control sample. We thus propose the following explanation : during the irradiation treatment, the samples were sealed under "normal" atmosphere in an aluminum container before being submerged in the reactor core. The fcc phase that appeared in the Ti layers is a consequence of a reaction between the γ-rays of the incident radiation and the water moistening the air in the container. This reaction produces hydrogen which is then absorbed by Ti to form a TiH_x compound. The quantity of hydrogen produced has been calculated and found sufficient to form an fcc TiH_x compound. This hypothesis is in good agreement with the decrease of the scattering length density shown by neutron reflectivity (calculated values : Nb_{Ti}=-1.95x10^{-6}Å^{-2}, Nb_{fccTiH}=-3.3x10^{-6}Å^{-2} ; experimental values : Nb_{Ti}=-2.0x10^{-6}Å^{-2}, Nb_{fccTiH}=-4.2x10^{-6}Å^{-2}). Since the interreticular distance in the (111) texture direction of fcc TiH_x is about 10% smaller than that of the hcp Ti in the (001) texture direction, the increase in the period of the stack is also consistent with this hypothesis.

5. CONCLUSION

NiC/Ti multilayers have been submitted to thermal neutron irradiation in order to determine the effects of such radiation on the neutron optical properties of the stack when used as supermirrors. The experiments show that performances of the supermirrors are not altered under thermal neutron irradiation. Nevertheless, a structural change did occur in the Ti layers, and is attributed to the formation of a fcc TiH_x compound whose crystalline parameter is 4.38Å.

References

[1] V.F. Turchin, Soviet At. Energy (trans. from Atomnaya Energiya), **22**, (2), p119, 1967

[2] F. Mezei, Commun. on Phys. **1**, 81-85, 1976

[3] F. Samuel, B. Farnoux, B. Ballot, B. Vidal, SPIE Proc., **1738**, p54-66, 1992

[4] B. Ballot, F. Samuel, B. Farnoux, SPIE Proc. , **1738**, 159-165, 1992

[5] B. Ballot, A. Menelle, J. Mimault, T. Girardeau, F. Samuel, K. Al Usta, 37th Colloque de Métallurgie de l'INSTN "Microstructures et Recristallisation", June21st-23rd 1994, Journal de Physique IV, C3, **5**, p305-310, April 1995

[6] B. Ballot, thesis, University of Paris XI, February 16th, 1995

[7] B. Farnoux, Neutron Scattering in the Nineties, Conf. Proc. IAEA, p205-209, Vienna, 1985

[8] O. Guiselin, L. T. Lee, B. Farnoux, A. Lapp, J. Chem. Phys., **95**, (6), 4632-4640, 1991

[9] B. Ballot, A. Menelle, K. N'guy, J. Mimault, T. Girardeau, J.L. Rouvière, F. Samuel, K. Al Usta, Société Française de Neutronique, 4e Journées de la Diffusion Neutronique, Port d'Albret, May 17th-19th, 1995

[10] B. Ballot, K. N'guy, A. Menelle, J. Mimault, T. Girardeau, J.L. Rouvière, F. Samuel, K. Al Usta, 15th European Conference on Surface Science, Lille, Sept. 4th-8th, 1995

[11] D. A. Young, *Phase Diagrams of the Elements,* University of California Press, p170, 1991

[12] P. Villars, L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases,* **3**, Ed. American Society for Metals, p3238, 1985

[13] S.K. Sikka, Y.K. Vohra and R. Chidambaram, Prog. in Mat. Sc., **27**, p245-310, 1982

[14] P. Pascal, Nouveau Traité de Chimie Minérale, **9**, Masson et Cie Editeurs, Paris, 1963

[15] M. Hansen, Constitution of Binary alloys, Mc Graw-Hill Book Company, New York, 1958