Microsc. Microanal. Microstruct. **8** (1997) 239–249 AUGUST/OCTOBER **1997**, PAGE 239

Stress evolution under neutron irradiation of NiC/Ti supermirrors

Kalyana N'Guy-Maréchal ([1]), Alain Menelle ([1]), Patrice Gergaud ([2]) and Klaus Al Usta ([3])

([1]) Laboratoire Léon Brillouin (CEA-CNRS), CE Saclay, 91191 Gif-sur-Yvette, France
([2]) MATOP, Faculté des Sciences de Saint Jérôme, 13397 Marseille Cedex, France
([3]) Compagnie Industrielle des Lasers, BP 27, Route de Nozay, 91460 Marcoussis, France

(Received 19 June 1997, Accepted 5 January 1998)

PACS.68.60.Bs – Mechanical and acoustical properties
PACS.61.80.Hg – Neutron radiation effects
PACS.89.20.+a – Industrial and technological research and development

Abstract. — We present here the stress evolution under thermal neutrons irradiation of NiC/Ti multilayers used in supermirror neutron guides. After irradiation, titanium undergoes a change of structure. Stresses in nickel layers have been determined: it is shown that the evolution under irradiation depends on the deposition process.

Introduction

The development of the use of neutron in the study of condensed matter leads to the need of high quality neutron optic devices, and especially very efficient neutron guides. The use of supermirrors coatings enables to reach that goal. Supermirrors are aperiodic multilayers of spacer (in our case Ti) and reflecting (in our case Ni_xC_{1-x}, where $x = 90\%$) materials alternately deposited on a flat surface (glass substrate for instance). These guides being submitted to neutron irradiation, we are interested in determining the effects of the radiation on the structural and mechanical properties of these guides in order to estimate their lifetime. In this aim, Ni_xC_{1-x}/Ti multilayers have been characterized before and after neutron irradiation by neutron reflectivity and X-ray diffraction. Stress evolution under irradiation have been determined in the layers to ensure that the layers will not peel off from the glass substrate.

Samples

This subject has been studied at the Léon Brillouin Laboratory (CEA Saclay, France) in collaboration with the CILAS company for many years already. One of the reason is that it takes two to twelve months (depending on the irradiation dose) to carry out neutron irradiation and let the samples deactivate before characterizing them.

A first set of samples has been elaborated by RF magnetron sputtering at the Laboratoire d'Optique Électromagnétique (LOE), University of Saint Jérôme (Marseille, France) by Vidal

Article available at http://mmm.edpsciences.org or http://dx.doi.org/10.1051/mmm:1997100

and Jiang [1] with a sputtering power of 0.3 kW. These samples were made of stacks of ten Ni_xC_{1-x}/Ti bilayers of 10 nm thick each deposited on a silicon substrate (Ni_xC_{1-x} will be shortened as NiC in the rest of the text). More recently, a second set of samples has been prepared, also by RF magnetron sputtering, at the CILAS laboratory. These samples were thus deposited in exactly the same conditions as for the real supermirror neutron guides with a sputtering power of 1.2 kW. The coatings are identical to the ones made in Marseille, but the substrate here is either silicon single crystal or glass. Characterizing both sets of samples before and after irradiation enabled us to determine the aging of each sample after irradiation, but also to compare the behavior of the samples according to the substrate nature and sputtering conditions [2].

The glass substrate we have chosen, called A8866, presents the same mechanical properties and behavior under neutron radiation as the BORKRON glass which is actually used to make supermirrors neutron guides, but does not contain zinc. For this reason, A8866 glass is less active after irradiation than BORKRON. This enables an easier handling of the activated samples. In addition, it allows one to study a system which is closer to real neutron guides, but also to understand the influence of the substrate on the behavior of the multilayers. In particular it is well known that neutron irradiation of the boron contained in glass induces the formation of helium bubbles in the glass, and possibly in the coating. These bubbles may modify the residual stresses in the substrate, and even in the coating, which could generate the decohesion of the coating.

The samples have been submitted to thermal neutron irradiation which energy ranges from 5 to 80 meV under fluences of 3×10^{19} n cm^{-2}, 6×10^{19} n cm^{-2} and 1.2×10^{20} n cm^{-2} for irradiation time of one two or four weeks and respectively named OR1/4, OR1/2 and OR1. The fluence rate was of 4×10^{13} n cm^{-2} s^{-1}. LOE samples have been irradiated in a container sealed in air whereas the CILAS samples were sealed under a helium atmosphere in a watertight container to avoid the problem of hydrogen formation encountered with irradiation in air [3]. Moreover, CILAS samples have also been annealed at a temperature of 150 °C, which is the estimated heating of the samples during irradiation, for periods of one, two and four weeks, corresponding to the OR1/4, OR1/2 and OR1 irradiation times respectively.

X-Ray Diffraction

All the XRD experiments have been carried out on a four circles diffractometer with a copper radiation ($\lambda = 0.154059$ nm) at the École Nationale Supérieure d'Arts et Métiers (Paris, France). The diffraction peaks are recorded with a ponctual germanium detector cooled with liquid nitrogen.

The non-irradiated layers are polycrystalline and exhibit a fibber texture with a $\langle 111 \rangle$ axis for the nickel and a $\langle 002 \rangle$ axis for the titanium. The spectra obtained after irradiation of the samples deposited on glass and Si present the same characteristics. They all show a change of structure in Ti layers: the initial (002) peak has disappeared and is replaced by a (111) and/or a (200) peak attributed to a face-centered cubic structure (Fig. 1). This fcc Ti phase has been previously observed by Jankowsky and Wall [4] on Ti deposited on a Ni single crystal and in Ni/Ti multilayers. This change of structure has not been observed in the annealed samples. We can thus assume that this structural modification is a consequence of neutron irradiation itself, but not of the heating during irradiation, but this will be discussed further. Furthermore, nickel structure remains unchanged after irradiation as well as after annealing.

Table I. — *Sample parameters.*

Reference	Coating	NiC thickness (nm)	Ti thickness (nm)	Substrate	Treatment
LOE_1	10 bilayers	5	5	Si	none
LOE_2	〃	〃	〃	〃	OR1
LOE_3	〃	〃	〃	〃	OR1/2
CILAS_G1	10 bilayers	5	5	A8866	none
CILAS_G2	〃	〃	〃	〃	OR1
CILAS_G3	〃	〃	〃	〃	OR1/2
CILAS_G4	〃	〃	〃	〃	OR1/4
CILAS_G5	〃	〃	〃	〃	annealing at 150°
CILAS_S1	10 bilayers	5	5	Si	none
CILAS_S2	〃	〃	〃	〃	OR1
CILAS_S3	〃	〃	〃	〃	OR1/2
CILAS_S4	〃	〃	〃	〃	OR1/4
CILAS_S5	〃	〃	〃	〃	annealing at 150°

Stress Determination Using X-Ray Diffraction

Stress determination using X-ray diffraction is based on the use of the lattice plane spacing d_{hkl} of an $\{hkl\}$ family plane as an internal strain gauge. Bragg's law links the strain ε to the diffraction angle θ measured in the analyzed sample:

$$\varepsilon = \frac{d - d_0}{d_0} = \frac{\Delta d}{d_0} = -\cot g\theta \Delta\theta \tag{1}$$

where $\Delta\theta = \theta - \theta_0$, d_0 and θ_0 respectively being the lattice spacing and the Bragg angle of the stress-free state.

Knowing the strain, it is then possible to determine the corresponding macroscopic stress thanks to Hooke's law:

$$\sigma = C\varepsilon \tag{2}$$

where C is the X-ray elastic constants tensor of the material.

In case of textured material, a specific analysis must be improved. It has been fully explained for cubic materials elsewhere [5]. The main assumptions are:

- the material is fibber textured,
- the in-plane stress is isotropic and biaxial: $\sigma_1 = \sigma_2 = \sigma_\phi = \sigma$,
- the stress is constant in each grain (Reuss hypothesis).

With these assumptions, the d_{hkl} measurements can be performed on different (hkl) planes corresponding to appropriate ψ angles (with respect to the texture axis) but for only one ϕ (see Fig. 2) angle (Tab. II). According to mechanics laws, we can then rely the measured strain ε as a function of the single crystal elastic constants S_{ij} and the in-plane stress σ.

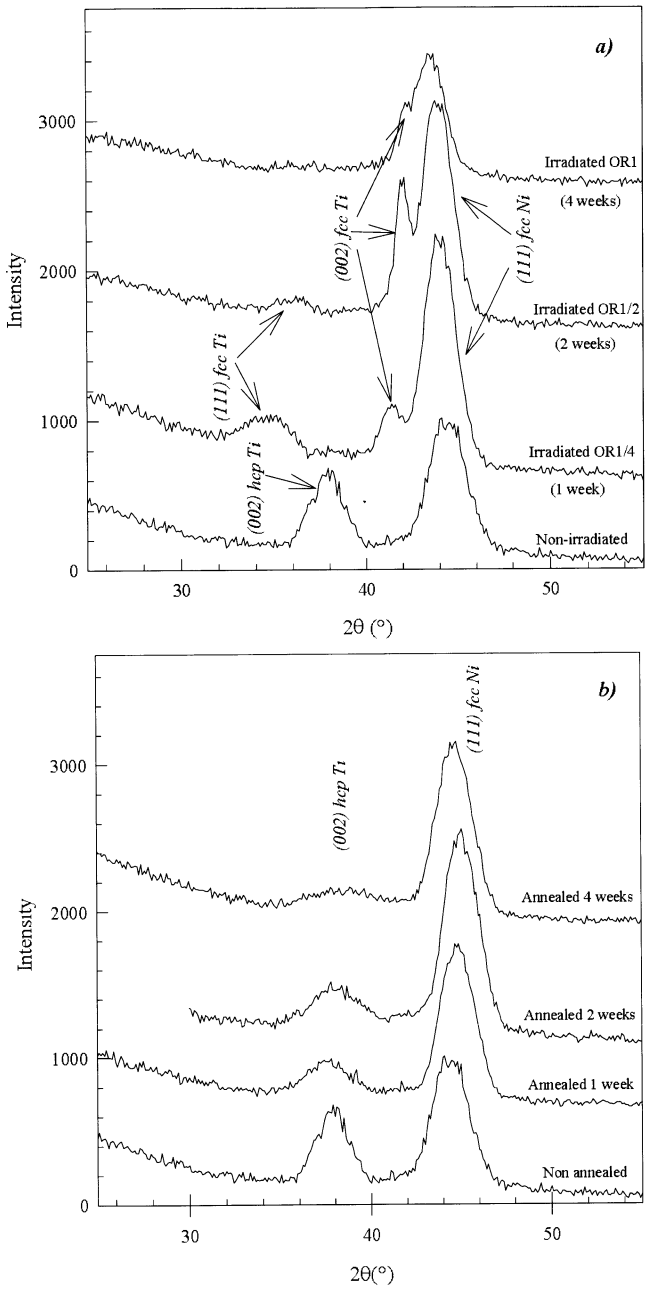


Fig. 1. — X-ray diffraction spectra of the a) irradiated and b) annealed CILAS samples deposited on a glass substrate (curves have been shifted vertically for clarity).

In the case of a cubic material with a $\{111\}\langle uvw\rangle$ fibber texture, the relationship is written as:

$$\varepsilon_\psi \left(2S_{12} + \frac{1}{2}S_{44}\sin^2\psi + \frac{2}{3}S_0\right)\sigma \quad \text{with} \quad S_0 = S_{11} - S_{12} - \frac{1}{2}S_{44}. \tag{3}$$

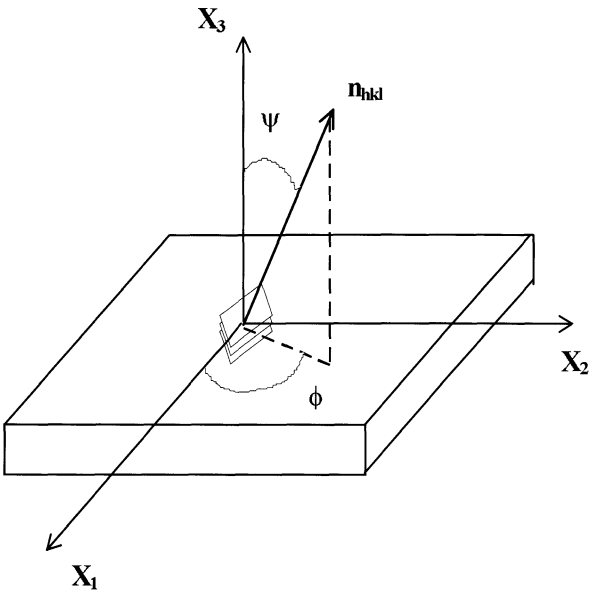


Fig. 2. — Definition of ϕ and ψ angles in the sample's basis.

From the slope p of the $\varepsilon = f(\sin^2 \psi)$ curve (Fig. 3) one can deduce the residual stress σ:

$$\sigma = \frac{2p}{S_{44}} \quad \text{where} \quad S_{44} = 8.36 \times 10^{-6} \text{ MPa}^{-1} \quad \text{for nickel.} \tag{4}$$

Of course, it is now well-known that for such thin films the stress free lattice parameter is in general rather different from the bulk value. Using a bad lattice parameter will lead to wrong stress result. The determination of this parameter is therefore fundamental, especially for our NiC films. As a consequence, the lattice parameter of the nickel films has been deduced from the value of a_ψ for a ψ value defined by $\varepsilon_\psi = 0$, leading to $\sin^2 \psi = (2S_{12} + 2/3S_0)/(1/2\ S_{44})$, and introduced in the strain and thus stress calculus. This calculus is correct assuming the stress component σ_{33} normal to the surface null, which is in accordance with mechanical equilibrium of the system.

In the case of the hcp Ti, the same calculus can be written. In the specific case of $\{001\}\ \langle uvw \rangle$ fibber texture, we obtain the following expression between the measured strain ε_ϕ and the stress σ:

$$\varepsilon_\psi = ((S_{11} + S_{12} - 2S_{13}) \sin^2 \psi + 2S_{13})\sigma \tag{5}$$

leading to the stress through:

$$\sigma = \frac{p}{S_{11} + S_{12} - 2S_{13}} \quad \text{where} \quad \begin{vmatrix} S_{11} &= & 9.625 \times 10^{-6} \text{ MPa} \\ S_{12} &= & -466 \times 10^{-6} \text{ MPa} \\ S_{13} &= & -1.893 \times 10^{-6} \text{ MPa} \end{vmatrix} \cdot \tag{6}$$

In the case of hexagonal structure, it is no more possible to extract the two stress free lattice parameters from the stress analysis. One more hypothesis is necessary. In this work, we assumed a constant c/a ratio equal to the bulk one, whatever the irradiation or thermal treatment of the samples. This implies an isotropic deformation of the unit cell with a possible

Table II. — *Bragg angles measured in each material as a function of ϕ angles.*

fcc Ni; texture $\{111\}\langle uvw\rangle$		
$h\ k\ l$	2θ (°)	ψ (°)
1 1 1	44.50	0; 70.53
2 0 0	51.85	54.74
2 2 0	76.39	35.26
3 1 1	92.95	29.50; 58.50; 79.98
2 2 2	98.45	0; 70.53

		fcc Ti; texture $\{1\ 1\ 1\}\langle uvw\rangle$	fcc Ti; texture $\{0\ 0\ 1\}\langle uvw\rangle$
$h\ k\ l$	2θ (°)	ψ (°)	ψ (°)
1 1 1	33.84	0; 70.53	54.74
2 0 0	39.28	54.74	0; 90
2 2 0	56.76	35.26	45; 90
3 1 1	67.75	29.50; 58.50; 79.98	25.24; 72.45
2 2 2	71.20	39.23; 75.04	35.26

hcp Ti; texture $\{002\}\langle uvw\rangle$		
$h\ k\ l$	2θ (°)	ψ (°)
1 0 0	35.09	90
0 0 2	38.39	0
1 0 1	40.17	61.37
1 0 2	52.96	42.49
1 1 0	62.96	90
1 0 3	70.62	31.41
2 0 0	74.17	90
1 1 2	76.21	57.77
2 0 1	77.37	74.73
0 0 4	82.22	0
2 0 2	86.76	61.37
1 0 4	92.67	24.61

microstructure evolution. The stress result depends strongly on this hypothesis and further work should be done to validate that item.

All the strain measurements have been performed using the ψ geometry and with the copper K_α radiation. In order to increase the accuracy of the measurements, peaks should be chosen at high Bragg angles. Unfortunately, in our materials the microstructure seems to be so distorted that the intensities of the peaks are very weak for 2θ angles greater than 100°. As a consequence, the measurements were performed in rather bad conditions and the strong standard deviation in stress analysis (Tabs. III and IV) is the outcome of that. In order to

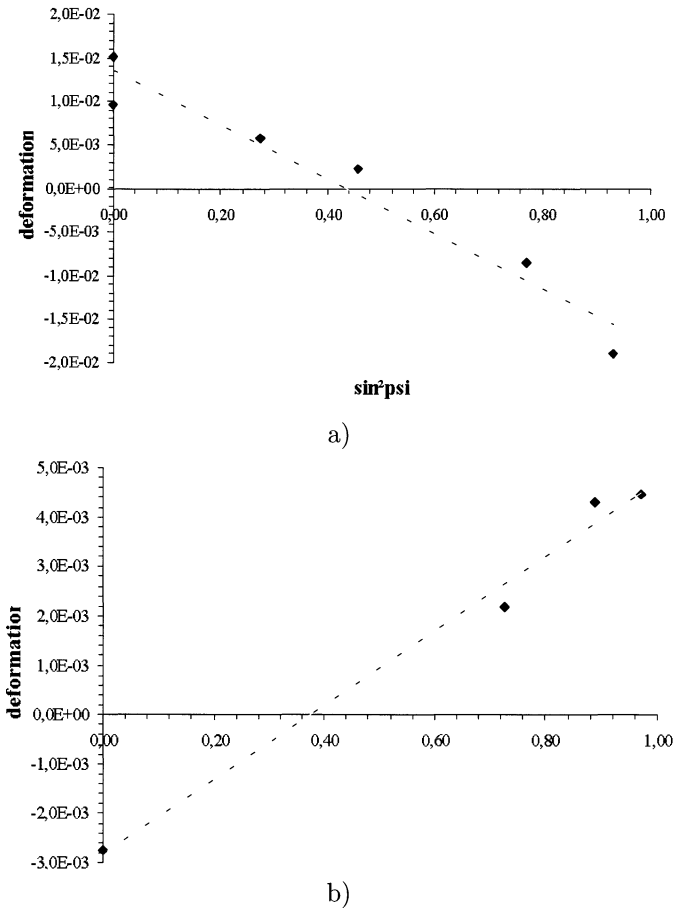


Fig. 3. — Variation of the strain ε as a function of $\sin^2 \psi$ in the case of a) titanium layer analysis and b) nickel layer after irradiation.

take into account an eventual misalignment of the diffractometer, powder corrections have been performed. It consists in measuring the Bragg peaks measured on the samples on a stress free nickel and titanium powders. The mismatch between the obtained value and the theoretical one is then subtracted from the peaks positions measured on the thin films. The peaks used for the analysis are detailed in the Table II. All the spectra are treated with an adjustment program in order to determine the 2θ position. Examples of strain analysis are plotted in Figure 3.

Experimental Results

The results obtained in the nickel and titanium layers are reported in Figure 4 and Table III respectively. It is quite difficult to extract some coherent interpretation from the stress analysis in titanium layers. These results depend on the assumptions we did for the stress calculus and moreover, when we have the structure modification from hexagonal to cubic, it is no more possible to calculate the stress because of the unknown elastic constants. Figure 4 shows the

Table III. — *Stresses in titanium layers.*

Reference	Treatment	Stress in Ti (MPa)
LOE1 (Si)	none	-2150 ± 150
LOE3 (Si)	OR1/2	p = −0.042
LOE2 (Si)	OR1	-2000 ± 250
CILAS_G1	none	-2400 ± 650
CILAS_G4	OR1/4	–
CILAS_G3	OR1/2	p = −0.0126
CILAS_G2	OR1	–
CILAS_G5	1 week-annealing	–
CILAS_G5	2 weeks-annealing	–
CILAS_G5	4 weeks-annealing	–
CILAS_S1	none	-3600 ± 450
CILAS_S4	OR1/4	p = −0.3427
CILAS_S3	OR1/2	1600±?
CILAS_S2	OR1	p = 0.0242
CILAS_S5	1 week-annealing	–
CILAS_S5	2 weeks-annealing	−3150±?
CILAS_S5	4 weeks-annealing	-900 ± 2050

evolution as a function of time of stresses in the NiC layers for the irradiated (Fig. 4a) and annealed (Fig. 4b) samples. We can see that stresses decrease in the CILAS samples after irradiation whereas they increase in the LOE samples. We can also notice that stresses remain almost constant in the CILAS samples whatever the annealing time. Figure 5 shows clearly, despite of the strong standard deviation, that the stress free lattice parameter of the nickel is nearly constant whatever the irradiation or annealing time except for the samples deposited on glass and irradiated. For these ones, the lattice parameter increases strongly with the irradiation time. From these observations, different conclusions concerning the behavior of the NiC layers can be extracted.

- The coatings deposited at CILAS and at LOE have the same characteristics (same substrate, same layers...). The main difference between them is the deposition technique. The deposition conditions, through may be the deposition rate, have a strong influence on the layers behavior.
- Stress relaxation after irradiation should be attributed to radiation damages rather than to temperature effects.
- Glass substrate strongly influenced the layers in term of microstructure (lattice parameter evolution).

Discussion

The cubic titanium structure we found has been already observed [4, 6]. It is sometimes explained by the formation of TiH_x structure. For our materials, this implies hydrogen contamination which is in fact observed using RBS analysis. The hydrogen contamination seems

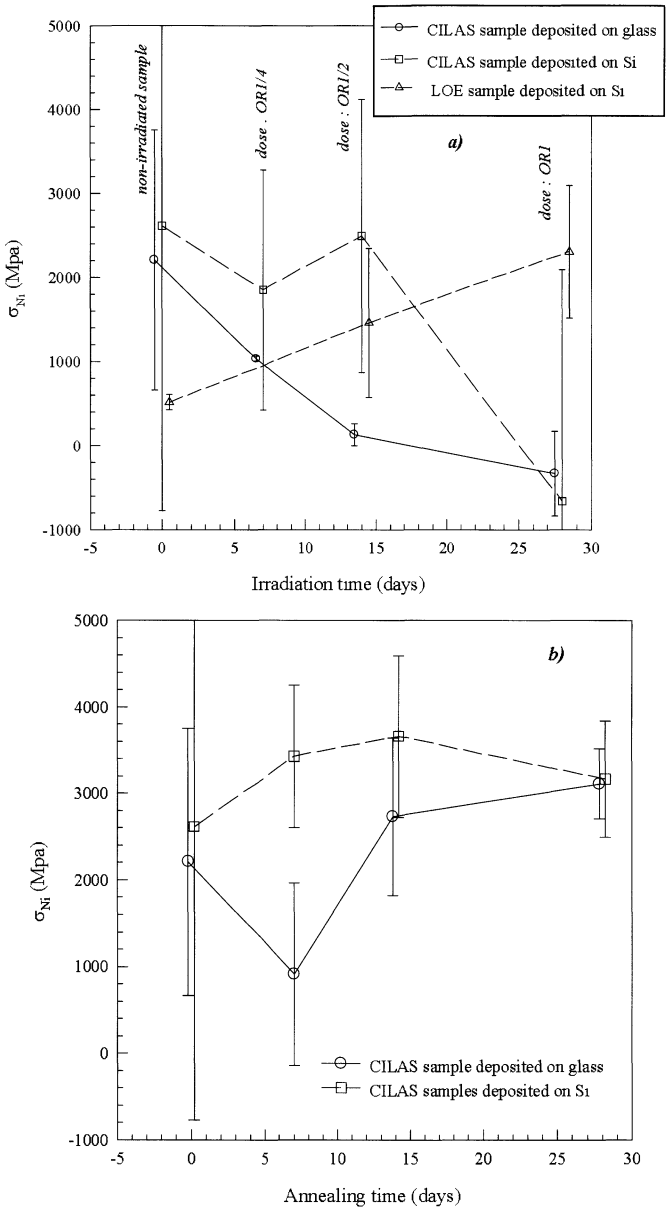
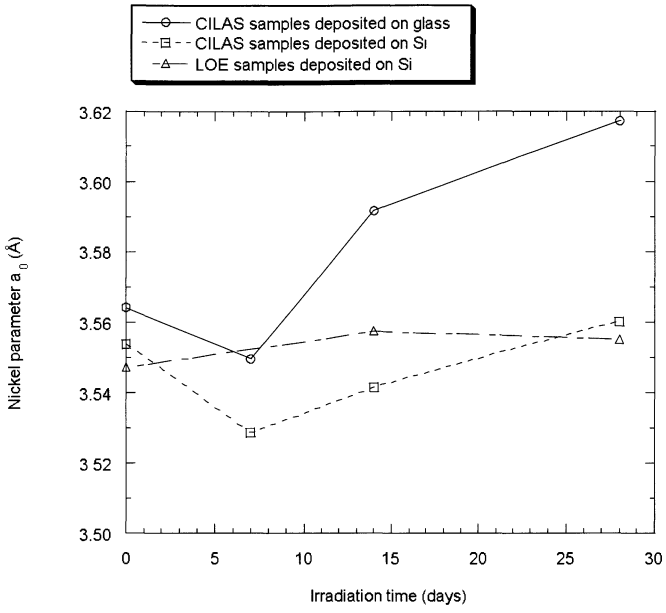


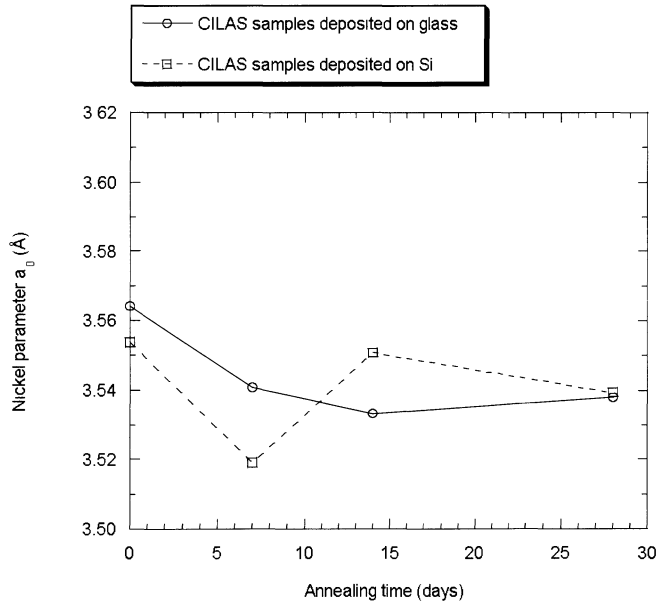
Fig. 4. — Evolution of stresses in the NiC layers in a) the irradiated LOE and CILAS samples and b) the annealed CILAS samples (data have been shifted horizontally of 0.5 day between sets of data for clarity).

to be due to the glass substrate which contains many OH bonds. As a matter of fact, all the samples have been irradiated in the same box. As a consequence the samples deposited on silicon can be contaminated by the glass substrate explaining by the way the cubic titanium structure observed on few of these films.

The stress-free lattice parameter results obtained for nickel layers are in accordance with other experiments [7] (RBS and reflectivity measurements...). It has been shown in these



a)



b)

Fig. 5. — Evolution of stress-free lattice parameter in the Ni layers in a) the irradiated LOE and CILAS samples and b) the annealed CILAS samples.

experiments that hydrogen contamination from the glass substrate is possible. Such contamination could explain the lattice parameter increase. Moreover, the reflectivity measurements show that a strong mixing (Ni, H, Ti?) appears at the substrate interface and between interfaces. This evolution is nevertheless only sensitive with the glass substrate and is surely linked to the glass behavior under irradiation.

In terms of stress evolution, the relaxation observed in the CILAS samples is in accordance with ion irradiation phenomenon [8]. The stress decrease is stronger for films on glass substrates which is may be linked to the former discussed contamination. Whatever, the stress increase in LOE samples is not explained. This result is not clearly correlated to other experiments. This different behavior may be linked to the difference of deposition rate used in the LOE and CILAS laboratories. Further studies are necessary to conclude on that point.

Conclusion

We have studied the evolution under irradiation of the microstructure and stresses in NiC/Ti multilayers used in the fabrication of neutron supermirrors. We have evidenced a cubic titanium structure. Its origin could be due to hydrogen contamination leading to a fcc TiH_x structure. Moreover, for the CILAS samples, we observed a relaxation in accord with ion irradiation. Whatever, a stress increase has been observed in LOE samples. This should be related to deposition parameters and kind of substrate.

Acknowledgments

The authors would like to thank Mr Vidal and Mr Jiang of the LOE (Marseille) for the elaboration of the first set of samples. We are grateful to Mr Lebrun and his diffraction team at the École Nationale Supérieure d'Arts et Métiers (Paris) without whom no stress determination could have ben carried out.

References

[1] Vidal B., Jiang J. and Samuel F., Neutrons Optical Devices and Applications, *SPIE Proc.* **1738** (1992) 30-41.

[2] N'Guy-Maréchal K., Menelle A. and Al Usta K., Tenue sous irradiation de multicouches Ni_xC_{1-x}/Ti, *J. Phys. IV* **C7** (1996) 183-188.

[3] N'Guy K., Menelle A., Gergaud P. and Al Usta K., Advanced Materials for Optics and Precision Structures, *SPIE Proc.* **2857** (1996) 113-120.

[4] Jankowski A.F. and Wall M.A., Formation of face-centered cubic titanium on a Ni single crystal and in Ni/Ti multilayers, *J. Mater. Res.* **9** (1994) 31-38.

[5] Zaouali M., Lebrun J.L. and Gergaud P., X-ray diffraction determination of texture and internal stresses in magnetron PVD Molybdenum thin films, *Surf. Coat. Technol.* **50** (1991) 5-10.

[6] Elsehans O., Böni P., Friedli H.P., Grimmer H., Buffat P., Leifer K., Söchtig J. and Anderson I.S., *Thin Solid Films* **246** (1994) 110-119.

[7] N'Guy-Maréchal K., Tenue sous irradiation de supermiroirs pour gyides de neutrons, Ph.D. Thesis, 1997.

[8] Tamisier F., Étude de la structure et de l'évolution sous irradiation aux ions de multicouches Au/Ni et Ni/Mo, Ph.D. Thesis, 1998.