

Total reflection EXAFS data were collected on the dedicated chamber operative at the GILDA beamline. The monochromator was equipped with a Si(111) crystal pair and was run in dynamically focusing mode. The rejection of higher order harmonics was achieved by using a pair of Pt mirrors with an energy cutoff of 10 keV. The beam was sized in the vertical direction by a pair of 40  $\mu\text{m}$  tungsten slits placed 2m apart; the intensity of the incoming beam was monitored by reading the fluorescence from a thin (0.5  $\mu\text{m}$ ) Rh foil, the reflectivity of the sample was measured directly by a large area Si PIN diode.

The sample was obtained in three steps:

i) Evaporation at low vacuum ( $10^{-5}$  mbar) of Ni onto an  $\text{Al}_2\text{O}_3$  (1-211) surface at Room Temperature (RT). The layer thickness was checked by X-ray reflectivity and resulted to be 150  $\text{\AA}$ . The chemical state of the layer was checked by a reflEXAFS spectrum and resulted to be metallic Ni.

ii) Oxidation of the Ni layer. The process was done by annealing the sample at 700  $^\circ\text{C}$  for 30 min. in a 400 mbar  $\text{O}_2$  atmosphere. Also this layer was checked by EXAFS and resulted to be NiO oxide.

iii) Reaction of the NiO layer with the substrate. The reaction was carried out in sequential annealing + EXAFS measurement cycles; each treatment was done at either 930 or 1000  $^\circ\text{C}$  for 120 min in a 60 mbar  $\text{O}_2$  atmosphere. Several treatments resulted to be necessary to complete the reaction.

For comparison purposes the EXAFS spectra in conventional transmission mode of a metallic Ni foil, NiO and  $\text{NiAl}_2\text{O}_4$  powders were also collected.

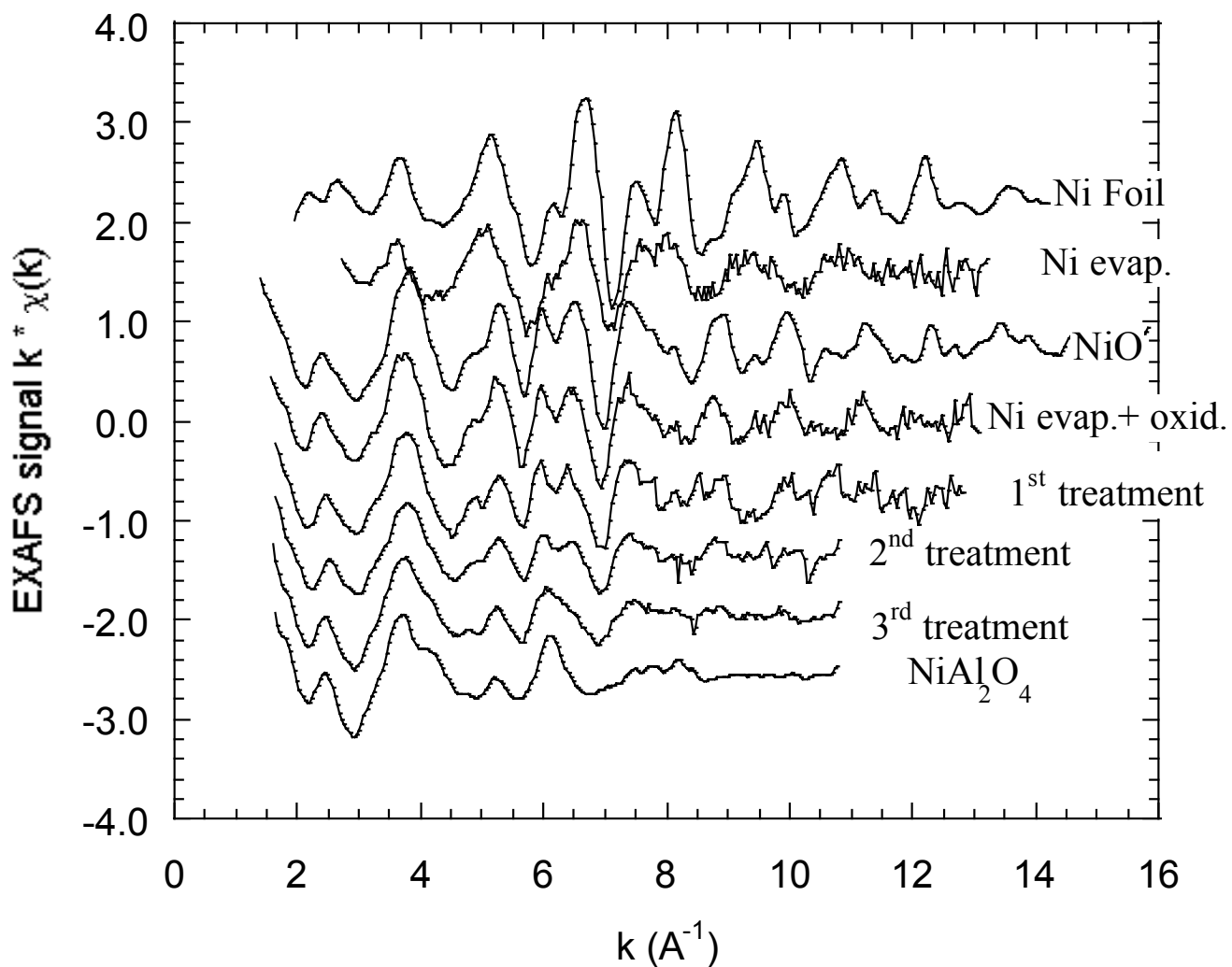
ReflEXAFS spectra were collected at an angle corresponding to 0.8 times the critical value ( $\phi_c = 0.3$  deg): in this condition the extinction length of the evanescent wave  $z_{1/e}$  is  $z_{1/e} = \frac{\lambda}{4\pi\phi_c}$  ( $\lambda$  is the

beam wavelength) and corresponds to roughly 20  $\text{\AA}$  in our case. Reflectivity data were converted in an absorption coefficient using equation (1) and EXAFS signals  $\chi(k)$  were finally extracted by conventional methods and are shown in Fig (1). To obtain normalized XANES spectra, the spectra have been processed by subtracting the smooth pre-edge background fitted with a straight line, and normalized to unit absorption at 1000 eV above the edge, where the EXAFS oscillations are not visible any more.

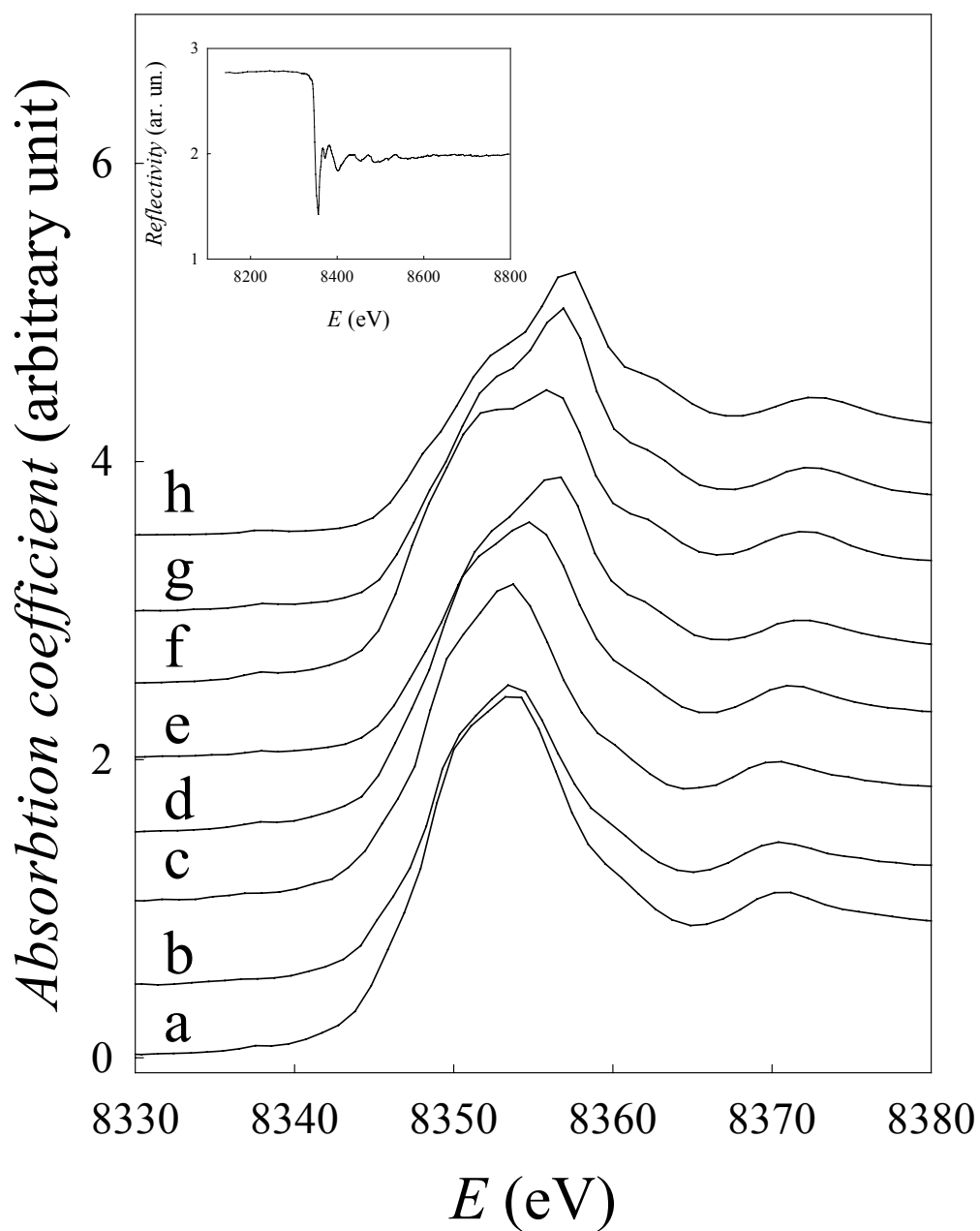
From a qualitative point of view the Figure 1 shows clearly the products of each process. The first step is a formation of a Ni film as shown by the strong resemblance between the sample spectrum and the Ni foil. The reduced amplitude is due to the fact that small particles are formed on the surface instead of a uniform film. After the annealing in  $\text{O}_2$  atmosphere the film is transformed in NiO as evident from the comparison with the spectrum of the NiO powder spectrum. The spectra taken after the treatments at 1000  $^\circ\text{C}$  show a progressive transformation from the NiO-like shape to a spinel-like shape as evident from the comparison with the final  $\text{NiAl}_2\text{O}_4$  spectrum. In addition it is clearly apparent that increasing the reaction time at 1000  $^\circ\text{C}$  increases the reaction advancement degree. A quantitative evaluation is still in progress. Further insights into the reaction dynamics can be obtained by looking at Fig. 2, which shows the normalized XANES spectra after different thermal treatments, both at 930  $^\circ\text{C}$  and at 1000  $^\circ\text{C}$ . While the spectra taken after the treatment at 1000  $^\circ\text{C}$  nicely confirm the trend already shown by the EXAFS spectra of Fig. 1, the XANES of the film being more and more reminiscent of that of  $\text{NiAl}_2\text{O}_4$  with increasing reaction time, the spectra at 930  $^\circ\text{C}$  show something somewhat different: the XANES manifold is quite independent of the reaction time and strongly resembles that of the as grown NiO film but for a remarkable decrease in the white-line amplitude. This is in turn suggestive of a decrease in the atomic correlations in NiO, with the formation of a “disordered” NiO phase, probably with some amount of Al dissolved. This is seemingly confirmed by a preliminary EXAFS analysis and could be related to the processes by which local chemical equilibrium is attained at the NiO- $\text{Al}_2\text{O}_3$  interface.

In summary, in this work the feasibility of a reflEXAFS investigation on the very initial stages of solid state reactions has been demonstrated. In particular, the reaction of a 150  $\text{\AA}$  thick film of NiO

deposited onto  $\text{Al}_2\text{O}_3$  single crystal has been investigated. It has been shown that the reaction to give the spinel phase requires temperatures of the order of  $1000\text{ }^\circ\text{C}$  to take place. In addition increasing reaction advancement degrees could be obtained by increasing the firing time at high temperature. At lower temperatures ( $\cong 930\text{ }^\circ\text{C}$ ) a structural rearrangement in the NiO film, seemingly related with the process by which local chemical equilibrium is attained at the interface, could be detected.



**Figure 1.-** EXAFS spectra of a sample that underwent a complete reaction cycle. The sequence is evaporation, oxidation, 1<sup>st</sup> treatment after 2 h at 1000 °C, 2<sup>nd</sup> treatment: after 4 h at 1000 °C; 3<sup>rd</sup> treatment: after 7 h at 1000 °C. Note the smooth transition from the NiO-like phase to the spinel-like phase through the three thermal treatments.



**Figure 2-** XANES spectra after different treatments; a: as grown NiO film; b: after 2 h at 930 °C; c: after 4 h at 930 °C; d: after 2 h at 1000 °C; e: after 4 h at 1000 °C; f: after 7 h at 1000 °C; g: after 9 h at 1000 °C; h = NiAl<sub>2</sub>O<sub>4</sub>. The inset shows the raw reflectivity spectrum of g for reference.