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# Experimental Study of the Interactions Between Oxidation and Structural Defects

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**Abstract.** A multiscale study of the high temperature oxidation effects on high purity polycrystalline nickel behaviour is presented. In situ tensile tests have been carried out at room temperature on preoxidised thin foils. The results obtained lead to a better understanding of the strengthening effect of the oxide layer.

Detailed examinations of the metal microstructure are also made after high temperature oxidation treatment. Atomic Force Microscope (AFM), Secondary Ion Mass Spectroscopy (SIMS), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) are used to characterise the microstructure. Formation of voids at grain boundaries as well as vacancy injection are then discussed.

## Introduction

The influence of chemical environment on mechanical properties and behaviour of materials can be illustrated by many examples. After high temperature air exposure, the embrittlement of nickel-based alloys and pure nickel is well documented and has been previously discussed and reviewed [1-6]. Oxygen has been demonstrated to be a damaging species and it has been shown that grain boundaries were embrittled far ahead of any matrix internal oxidation [7,8].

However, most of these studies have been carried out on thick specimens and the role of sample geometry on mechanical and microstructural properties has not been examined in detail. Therefore, the present work was undertaken with the objective to set out some original results on the effect of oxidation on nickel samples of different thicknesses and shapes. Moreover experimental evidence is reported showing that surface oxidation affects the metal properties over a large range of length scales. At a macroscopic scale, this is shown by the modification of mechanical properties of oxidised foil, related to the behaviour of the oxide scale, as observed during in-situ deformation in a SEM. Metallographic observations of cross sections prepared from oxidised samples of different geometries show that the microstructure is affected because oxidation introduces numerous voids at grain boundaries. Finally Atomic Force Microscope (AFM) measurements reveal that point defects, such as vacancies, must be injected in the metal and are transported over quite large distances.

## Materials

The investigations were conducted on high purity nickel foils (125  $\mu\text{m}$  and 1mm thick) and wires (1mm diameter) with the chemical composition given in Table 1. Before oxidation treatments, all the samples were annealed one hour at 1000°C in a mixture of argon and hydrogen (Ar-5 vol% H<sub>2</sub>) to stabilize the microstructure (or at least to minimize subsequent

grain growth). The mean grain size obtained was about 300-400  $\mu\text{m}$  for the three types of specimens. The samples were then polished (except for nickel wires which were set to the as-received state) by diamond pastes down to 1 $\mu\text{m}$  before being cleaned through ultrasonic waves first in acetone then in ethanol.

Table 1. Chemical composition of the studied material – Concentrations in ppm weight (bold text shows elements whose concentrations were determined in this study. The others are given by the producer)

Element	Co	Cr	Cu	Fe	Mg	Mn	Si	Ti	C	S	O	N	Ni
Concentration [wt ppm]	8	8	10	10	10	10	8	10	2	<b>0.40</b>	<b>1.20</b>	<b>0.02</b>	bal

In situ tensile tests were conducted in the SEM with a specific apparatus developed in the laboratory [11] (the tensile test samples were cut out through electrodischarge machining). Examinations of the metal grain boundaries were conducted with SEM, AFM and SIMS.

### Experimental results and discussion

**Oxide microstructure.** The nickel foils were oxidised at 1000°C in laboratory air which led to the formation of a NiO duplex microstructure irrespective of the treatment's duration (Fig. 1). The scale, observed after electrolytic dissolution of nickel in nitric acid, consists of an inner layer of equiaxed grains showing few voids and a compact outer layer of columnar grains. The thickness ratio (outer layer/inner layer) is close to 1.5 whatever the treatment duration. These results differ from those obtained by Peraldi et al. [9] who, at that temperature, observe the formation of a compact simplex layer. As mentioned in [10], this difference can be explained either by the chemical composition of the material or by the nature of the environment (laboratory air in our case and pure oxygen for previous results [9]). Note also that the oxide surface shows many faceted grains and some large plates in few cases as was observed by Peraldi [9].

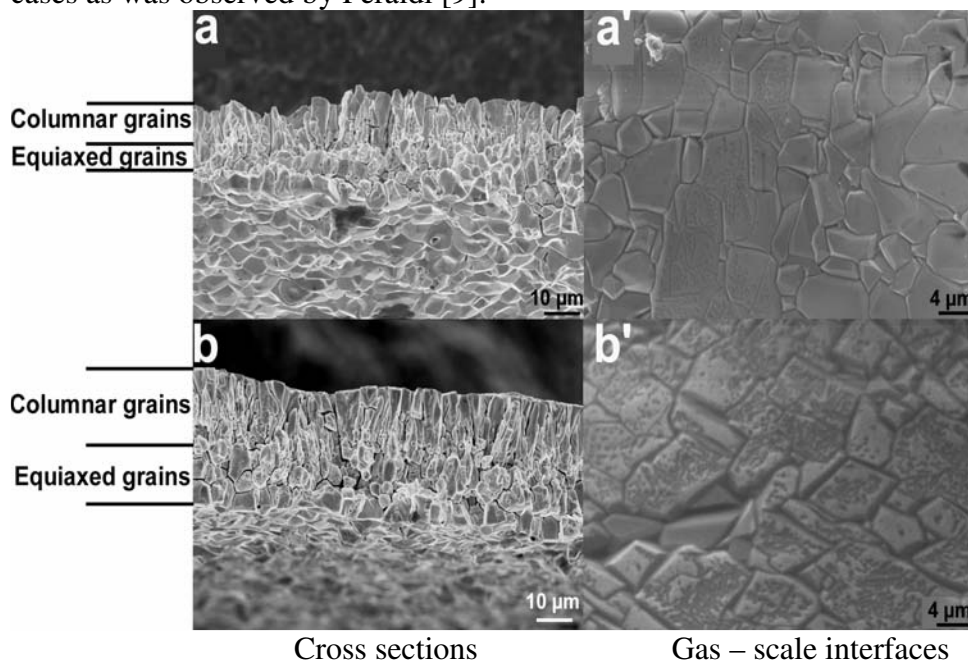


Fig. 1. Morphologies and microstructures of NiO scales grown at 1000°C in laboratory air after two oxidation times : a,a': 15h – b,b': 48h

**Effect of the oxide layer on the tensile mechanical properties of thin specimens.** Tensile tests were carried out on high purity oxidised foils (initially 125  $\mu\text{m}$  thick). The treatment (1h/1000°C in laboratory air) resulted in the formation of a 5 $\mu\text{m}$  thick oxide layer and a mean in-plane grain size of 400  $\mu\text{m}$  for the metal substrate. Consequently, the specimens exhibit a "bamboo" (or "ladder") structure.

The tensile tests were firstly realised in a Jeol 840 SEM at room temperature to follow the behaviour of the oxide scale throughout the deformation. Characteristics of this in-situ set-up are presented in a previous article [11]. An example of a stress-strain curve showing the true stress versus the total applied strain that was obtained with this apparatus is shown on Fig. 2. Tensile tests were stopped at several strain levels to take high resolution images of the oxide scale cracking (which caused the presence of little hooks on the curve). The first cracks observed appeared at 0.6% of true stain. A statistical study [11] of the inter-cracks spacing has shown that new cracks form throughout the plastic deformation contrary to previous results concerning bending tests and which have shown a threshold in inter-crack spacing [12-13].

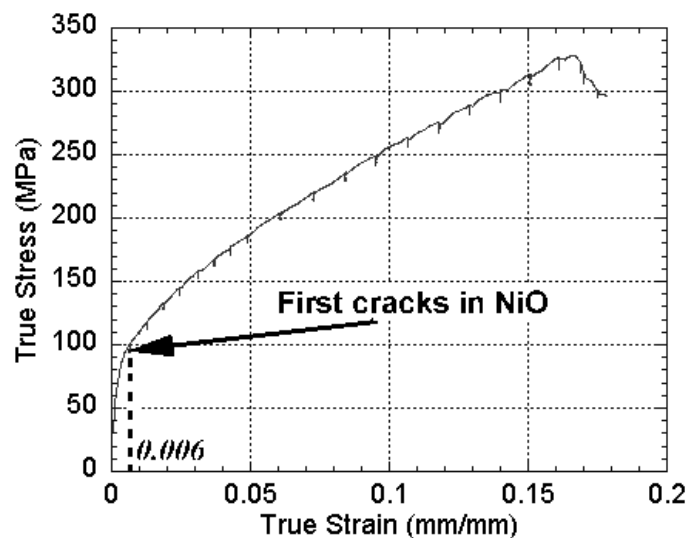


Fig. 2. Stress-strain curve of nickel oxidised one hour at 1000°C in laboratory air – Room temperature

Tensile mechanical properties of the oxidised specimens were then compared to the properties of samples annealed 1h at 1000°C in dynamic secondary vacuum ( $10^{-3}$  Pa). Those tensile tests were performed in a machine dedicated to mechanical tests (and not in the SEM). It is worth noticing (Fig. 3) that tensile stress levels are higher and that the failure strain is highly reduced for the oxidised sample as compared to the annealed one. In each case (oxidised and annealed samples) three tensile tests were realised and results were quite well reproducible.

Relaxation tests have been performed which did not show any difference between the two samples indicating that the same mechanism is involved in both cases. Moreover, Fig. 3 shows ductile transgranular rupture in both cases. The strengthening effect and the lower failure elongation seem to be directly linked to the presence of the oxide scale. From a mechanical point of view, the oxide scale does not affect the elastic behaviour since Ni and NiO exhibit similar Young Modulus [14-15]. But in the plastic domain, NiO hardens the material by a composite effect. This strengthening effect decreases as deformation proceeds because the oxide cracks (see above) moving from a "long fibre" composite to a "short fibre" one. The composite effect must then be effective all along the tensile test which is confirmed by in-situ observations presented before. Indeed, the mean inter-cracks spacing continuously

diminishes until the sample breaks, which is the proof that even quite small oxide islands can bear stress. The lower failure elongation on oxidised samples would then be explained by the extreme sensibility of thin specimens to localisation of the deformation between oxide islands for example.

From a mechanistic point of view, the oxide layer, which is adherent to the substrate in the case of the Ni/NiO system, can constitute a barrier to the emergence of dislocations during tensile test. Interactions between dislocations lead to the hardening of nickel and the localisation of deformation can appear between two oxide islands leading to the early rupture of the material.

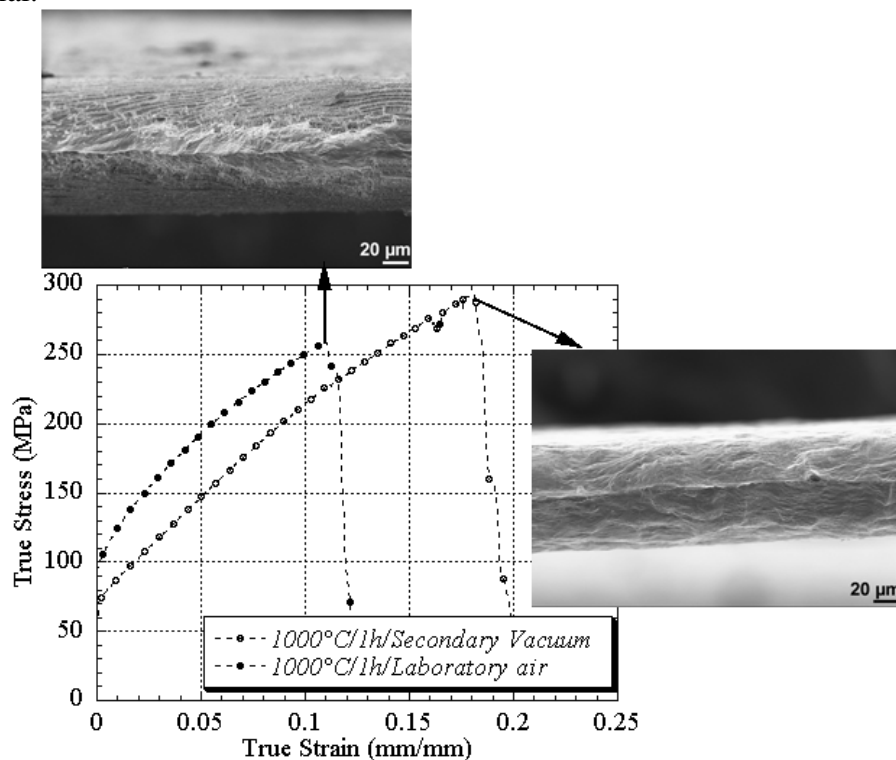


Fig. 3. Tensile tests realised at room temperature on nickel oxidised 1h at 1000°C in air (a) and on nickel annealed 1h at 1000°C in secondary vacuum (b)

**Formation of voids in thick oxidised specimen.** Keeping in mind the embrittlement of nickel-based alloys after high temperature exposure presented in the introduction, a careful examination of grain boundaries has been performed after oxidation treatments of 1mm thick nickel foils. Cross sections of these plates (oxidised 48 hours at 1000°C in laboratory air) were made and observations of the metal undertaken using SEM, TEM and SIMS techniques. It has been verified that the specimen does not creep under those conditions by using a laser extensometer. As illustrated in Fig. 4, the metal shows many voids localised at grain boundaries which didn't exist in the as-received material. Note that these voids were only observed after chemical etching in a mixture of nitric and acetic acids. The mean size of these voids is 10μm and voids smaller than 1μm have not been observed even by using TEM. The largest ones are localised at the oxide-metal interface and are most of the time connected to the oxide scale by mean of intergranular oxides. One of the most striking observation is that voids are also observed in the middle of the sample, that is to say 500μm under the metal-oxide interface. EDX analysis revealed the presence of oxygen in each void but as the oxygen peak was always associated with a silicon peak it was difficult to conclude if the presence of oxygen had to be related to the oxidation treatment or if it was just due to the sample's preparation.

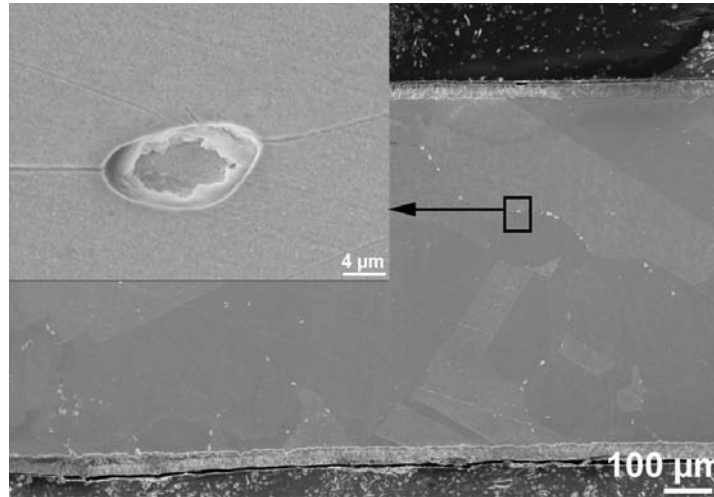


Fig. 4. Voids observed in a 1mm thick nickel foil oxidised 48 hours at 1000°C in air

SIMS experiments have then been undertaken in order to check the presence of oxygen in voids. Indeed, the SIMS technique allows the ionic sputtering of the sample's surface as well as the detection of chemical elements with a high resolution. Thanks to this technique, the problem of sample's contamination due to sample's preparation is suppressed because after few minutes of abrasion, voids localised in the bulk material can be observed. Experiments were realised with a CAMECA IMS4F6 apparatus using a  $\text{Cs}^+$  ions source. Fig. 5 shows images of  $^{16}\text{O}^-$  taken at the metal-oxide interface and in the middle of the sample. The areas enriched in oxygen are always localised at grain boundaries and their mean size is around 10  $\mu\text{m}$ . This is consistent with the mean size of voids observed with the SEM. Note that no trace of silicon has been detected in those regions enriched in oxygen which is the proof that this phenomenon is not due to the sample's preparation. Depth profiles have been carried out and do not show any trace of oxygen in grain boundaries even between voids.

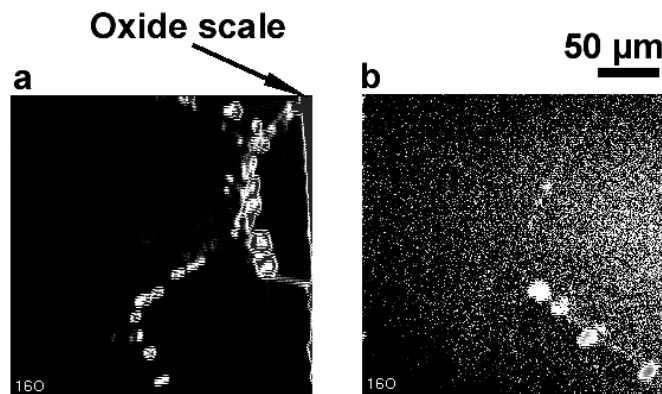


Fig. 5. SIMS images ( $^{16}\text{O}^-$ ) of nickel foil oxidised 48h at 1000°C in air a: Metal-oxide interface, b: Metal bulk

One may well wonder whether or not the enrichment in oxygen associated with intergranular voids is due to the presence of nickel oxide or to the presence of oxygen in solid solution. An answer to this question can be given by following the signal of nickel which is really higher in a region enriched in oxygen than anywhere else: indeed, this enhancement of the nickel signal is the proof of a change in the nature of nickel chemical bonds which is itself attributed to the presence of nickel oxide. Moreover, TEM diffraction investigations have clearly demonstrated the presence of nickel oxide in voids.

The same work has been done for nickel wires of the same purity, oxidised 48 hours at 1000°C in laboratory air. On a cross section of this oxidised wire (Fig. 6), intergranular

oxidation appears as well as voids in the centre of the wire. Note also that the oxide layer seems to have lost contact with the substrate. SIMS characterisation of voids is under progress to detect or not the presence of oxygen in the centre of the sample but it is already clear that the geometry of the sample affects the extent of internal voids as already demonstrated [16]. From the microstructural observations, mechanical properties of nickel wires should be more affected by oxidation than the mechanical properties of thin sheets.

In the present case and as a concluding remark, it can be stated that mechanical softening, which is often associated with void formation is most likely eliminated due to the presence of an oxide scale on the wall of the voids.

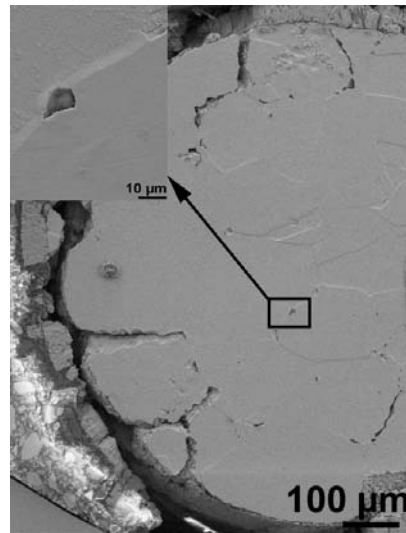


Fig. 6. Voids observed in a 1mm thick nickel wire oxidised 48 hours at 1000°C in air

**Original experiment to explore vacancy injection phenomenon.** The formation of voids presented before is the subject of a controversial debate for several decades. Two main theories are well documented in the literature. The first one [17-20] considers that these voids are the consequence of vacancies condensation in grain boundaries (the vacancy injection phenomenon is described elsewhere [21-22]) and the second one assumes that voids result from the reaction between carbon initially present in the metal and oxygen diffusing in the metal [7-8]. In the present study, even if the carbon content in the material is really low (<10ppm), the occurrence of carbon segregation in grain boundaries cannot be ignored. An original set-up has then been developed to go further in the understanding of voids formation. The experimental set-up, inspired from previous work [23], is described on Fig. 7. In this experiment, it is possible to oxidise only one side of a sheet by passing an argon and hydrogen mixture (5 vol% H<sub>2</sub>) inside the chamber. A specimen placed in the chamber and then entirely protected from oxidation plays the role of a reference sample. The sample's preparation is described in [22].

The face protected from oxidation was examined using SEM and AFM techniques. The SEM observations performed on a 1mm thick nickel foil oxidised 48 hours in laboratory air show grooves at grain boundaries intersecting the protected face. The AFM technique allows precise measurements of depth and width of the grooves. An example of views and profiles obtained with the AFM technique is shown on Fig. 8. It is worth noticing that grooves developed on the oxidised sample are deeper than grooves developed on the reference sample. The difference in mean depth is estimated to be around 200 nm. Thermal grooving theory by Mullins in 1957 [24] explains the mean groove's depth of the reference but not the

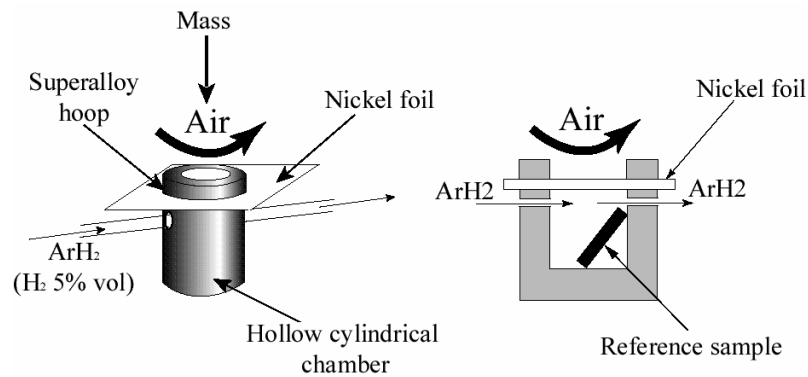


Fig. 7. Set-up used for the oxidation of nickel foils on one side – General view and cross section of the system

deeper grooves measured for the oxidised sample. The deeper grooves formed on the opposite side of the oxidising surface could be explained by the migration of metal vacancies from the metal-oxide interface to the metal-ArH<sub>2</sub> one where they would be annihilated. Moreover, the self-diffusion coefficient of nickel at grain boundaries at that temperature [25-26] is compatible with diffusion of nickel vacancies through the whole foil's thickness (1mm in the present case).

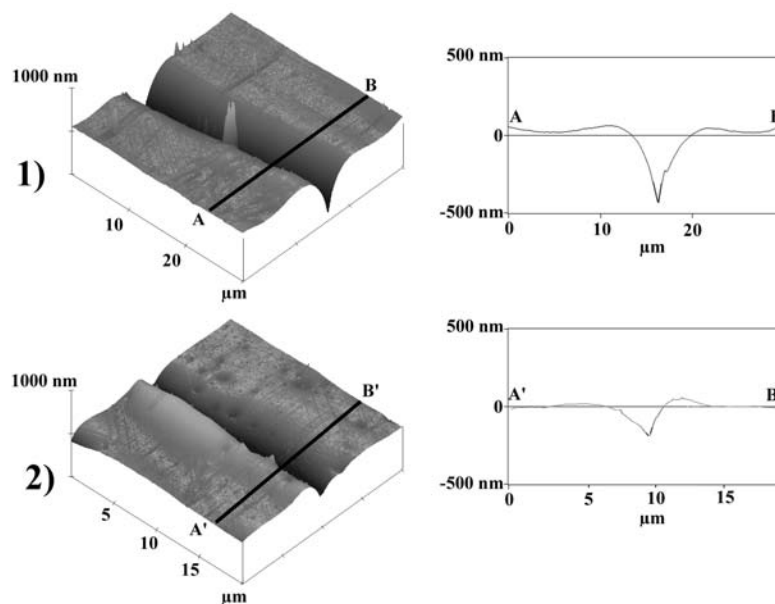


Fig. 8. AFM views and corresponding sections:

- 1) Face protected from oxidation
- 2) Reference sample

Nickel foils (1mm thick) - 48h at 1000°C

## Conclusions

This work proposes a multiscale study of the oxidation effects on high purity polycrystalline nickel including macroscopic mechanical properties, microstructure modification and point defects injection and diffusion. Although thin compared with the whole specimen thickness, the nickel oxide scale generates dynamic and static effects. Some of them, essentially static, have been tackled in this study.

Tensile mechanical tests conducted at room temperature have clearly demonstrated that NiO scale strengthened the Ni substrate. In the case of thin specimens, a decrease of the strain to fracture is evidenced for oxidised sample. Original results concerning the NiO scale cracking are also exposed: indeed, it is shown that new cracks form all along the plastic



deformation contrary to previous results concerning bending tests. A composite effect of NiO is then suspected.

At the microstructure scale, intergranular voids in high purity nickel are observed together with the formation of an external oxide scale. These voids are localised at grain boundaries at the metal-oxide interface as well as 500  $\mu\text{m}$  under this interface. Moreover, they are partially filled with NiO. It is then difficult to conclude whether these voids have a softening or a strengthening effect.

Finally, diffusion of structural defects such as vacancies is highlighted following oxidation treatments of nickel foils. Most of the topics presented in this paper are still under investigation by the authors.

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