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EFFECT OF AN OXYDE LAYER ON THE TENSILE BEHAVIOR OF PURE NICKEL FOILS

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Articolul prezintă consecințele oxidării asupra comportării mecanice la tracțiune a foliilor de nichel pur. Prezența unui film de oxid durifică metalul la grade mici de deformare şi îi micşorează ductilitatea. Măsurătorile volumelor de activare efectuate în cursul experimentelor de relaxare a tensiunilor au arătat că mecanismul deplasării dislocațiilor nu este afectat de prezența oxidului ci că acesta se bazează pe intersecția cu pădurea de dislocații. S-a arătat că principala contribuție a oxidului constă în faptul că acesta acționează ca o barieră pentru dislocații. In acest mod are loc un proces de accelerare a aglomerării dislocațiilor şi de mărire a densității acestora, ceea ce produce efectul de durificare a metalului.

We present in this paper the consequences of an oxide scale grown on pure nickel on the mechanical behaviour. The presence of the oxide layer hardens the metal for low strain level, and reduces the ductility. Activation volumes as measured during stress relaxation experiments show that the dislocation motion mechanism is not affected by the presence of the oxide and it relies on forest interactions. It is shown that the main contribution of the oxide is to act as a barrier for dislocations and accelerates the storage of dislocations thus increasing the total dislocation density which causes hardening of the metal.

Keywords: oxide, barrier, work hardening rate, dislocation storage

1. Introduction

The formation of an oxide scale at the metal surface is very useful for the metal protection against further oxidation or corrosion. It is also recognised that oxide layers may affect the mechanical properties of metals. More generally the influence of any coating on the mechanical properties of metals has been addressed for a long time and is still a subject of numerous studies [1–4]. In the present paper, we study the case of polycrystalline pure nickel plasticity during tensile tests, by comparing the response of a naked metal and an oxidized one, which have undergone the same thermal history. The oxidation of nickel which forms in air nickel oxide NiO is widely studied and considered as a model system. The oxidation kinetics and oxide growth mechanisms in the system Ni/NiO have

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been examined in details in our laboratory. It was shown that the formation of NiO is a mixed cationic and anionic mechanism [5] and that this formation implies injection of vacancies in the metal [6]. We have also shown that the adhesion of NiO layer on Ni is very good [7] and this makes the couple Ni/NiO an excellent candidate for studying the role of adherent oxide scales on the plasticity and tensile behaviour of the metal.

2. Experimental details

The investigations were conducted on high purity nickel foils (125 µm thick) with the chemical composition given in table 1. Tensile test samples, with a gauge length 20 mm X 3 mm width, were cut out through electro discharge machining. After cutting the samples surfaces were grinded then polished (up to diamond paste 3 µm). All the specimens were then heat treated 1h at 1000°C in reducing atmosphere (argon containing 5% vol. of hydrogen: Ar-H_2), which implied a growth of the nickel grains up to 360 µm in average diameter without oxidation of the metal surface. Note that since the grain diameter is larger than the foil thickness, only one single grain is present in the thickness of the foil. Some of these non oxidized samples were then directly mechanically tested; they will be referred as “naked” samples or annealed nickel. The other samples were further heat treated in laboratory air at 1000°C for various durations in order to form oxide layers of thicknesses 5, 10 and 15 µm.

Table 1

Chemical composition of the studied material –
(bold text shows elements whose concentration was determined during the study.
The other results come from a typical analysis given by the producer)

Element	Co	Cr	Cu	Fe	Mg	Mn	Si	Ti	**C**	**S**	**O**	**N**	Ni
Concentration (ppm weight)	8	8	10	10	10	10	8	10	**2**	**0.40**	**1.20**	**0.02**	bal

Tensile mechanical tests were performed at room temperature with an imposed strain rate of 7×10^{-4} s^{-1}. Some stress relaxation tests were carried out at various strain level in order to study the evolution of activation volume during plastic deformation. After straining some specimens were prepared for observation by transmission electron microscopy. Small squares 3 mm in diagonal were cut in the foil plane, then they have been thinned by electrolytic polishing system Tenupol® using a solution of perchloric acid and 2 – butoxyethanol in methanol, at – 5 °C under 22 V. Observations were performed with a Jeol JSM 2010 microscope, from the TEMSCAN (centre for microscopy of the Paul Sabatier University, Toulouse).

3. Results

The tensile curves of the different specimens that were tested are shown in Fig. 1. For the oxidized samples, since it was shown [7] that the oxide forms cracks during very early plastic strain, the oxide layer was not considered as a bearing section and the stress was calculated from the measured load by considering only the surface of the remaining metal. It appears that the naked nickel foil curve (denoted annealed nickel in the fig. legend) is always situated below the curves corresponding to the oxidized specimens. The elastic limit is about 70 MPa for the naked nickel while it is between 90 and 100 MPa for the oxidized samples. However the maximum stress is about the same for all samples.

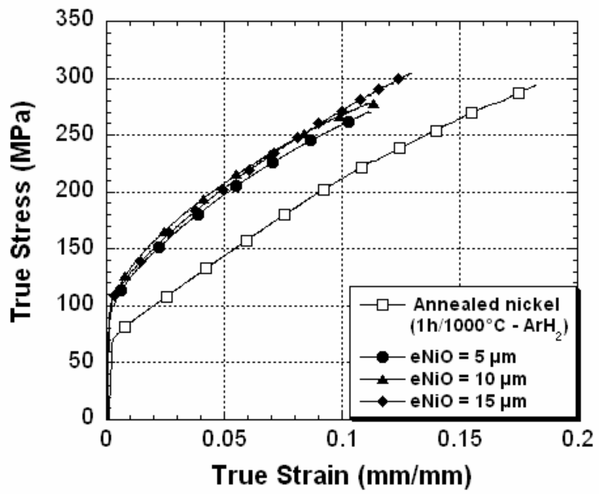

Fig. 1. Tensile curves at room temperature for naked and oxidized nickel (with various indicated oxide thickness)

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The difference is also marked for the ductility. Indeed the non oxidized sample presents homogeneous plastic strain which extends up to 18 % whereas this deformation is limited to 11 – 13 % for oxidized samples. The curves are shown up to the maximum stress only, because for all samples a necking occurs associated with a very rapid (within less than 1% strain) drop of the stress after the maximum of the tensile curve. It is worth noting that tensile curves of the three tested oxidized samples are very close one to another. There exists a slight difference between the curves for oxide thicknesses varying from 5 to 15 µm; the thicker the oxide, the higher the flow stress, but the amplitude of this difference is very small (10 MPa from the 5 µm thick to the 15 µm) as compared to the difference between oxidized and naked curves (more than 50 MPa). So that what matters is the existence or not of an oxide and not the thickness of the scale itself.

The work hardening rate (WHR) of the different samples have been obtained by differentiation of the tensile curves, and it is shown versus the applied stress in Fig. 2. As for the tensile curves, one can notice that two types of very different behaviour are revealed depending on the presence or not of an oxide layer. The thickness of the oxide layer itself seems to have only a very limited effect, if any, on the WHR as it was already noticed for the tensile curves. For the oxidized samples the WHR continuously decreases all along the tensile curve. In contrast, the naked foil shows two regimes of WHR. At the beginning of deformation, WHR rate is constant, much lower than the corresponding values for the oxidized samples. For stress levels higher than 180MPa (which correspond to about 7 % plastic strain for naked samples) WHR rate starts to decrease and show values very similar to the oxidized samples.

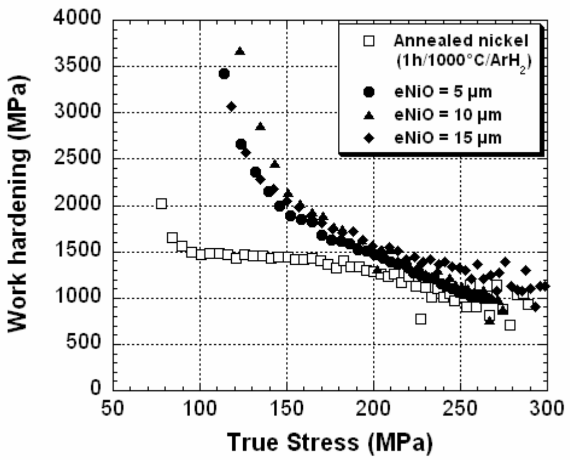


Fig. 2. Work hardening rate versus the applied stress for the naked and oxidized samples.

In order to study the microscopic mechanisms responsible for the plastic deformation of the samples, apparent activation volumes V_a have been determined by stress relaxation tests performed along the tensile curve for the non oxidized and oxidized samples (oxide thickness : 5 µm). The stress decrease $\Delta\sigma$ during the relaxation was fitted to the relation [8]:

$$\Delta\sigma = \frac{kT}{V_a} \ln\left(1 + {}^{t}\!/_{c}\right) \qquad (1)$$

where k is the Boltzmann constant, T the absolute temperature, t the time and c a constant for the fit. The activation volumes are expressed in terms of b^3, where b is the Burgers vector of ½<110> dislocations, so that 1 b^3 approximates the atomic volume and the magnitude of V thus represents roughly the number of atoms involved in the dislocation mechanism [9]. Values of the activation volume determined along the tensile curve are shown versus the applied stress (stress level at the beginning of the relaxation) in Fig.3. It is remarkable that the volume measured on both naked and oxidized foil follow exactly the same curve which decreases with stress. Such stress dependence of the activation volumes clearly proves that the same dislocation mechanism is involved for the plastic deformation of both naked and oxidized samples [10].

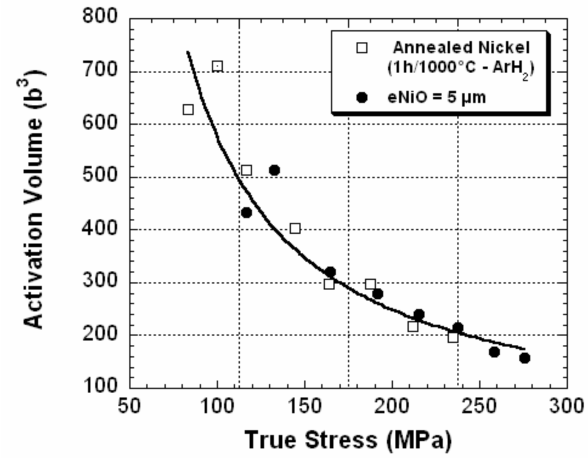
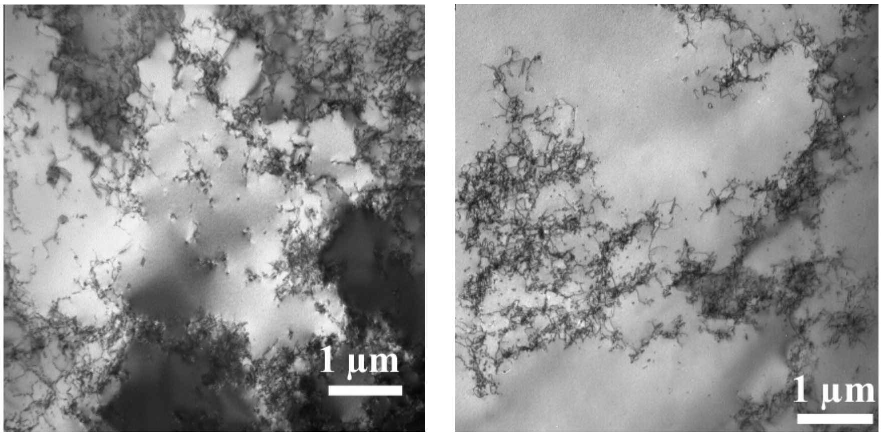


Fig. 3. Activation volume measured at different stress levels for the naked and oxidized metal.



(a) (b)

Fig. 4. Typical dislocation microstructure observed in pure nickel foils, either naked (a) and oxidized (b) after tensile testing interrupted at the stress level 150 MPa. Bright field, g = 111.

Dislocation microstructures have been observed by transmission electron microscopy on both naked and oxidized samples on specimens for which the tensile test was interrupted at a stress level of 150 MPa. The images presented in Fig. 4, show quite a similar dislocation structure for both the naked and oxidized samples. One can see that dislocations are widely tangled and start to form some cell structure. It is remarkable that very similar structures are obtained for both samples despite the fact that the interruption at a given stress level corresponds to very different plastic strain amounts for both conditions. Indeed plastic strain is about 6 % for the naked sample and 2 % for the oxidized sample, meaning that observed microstructure necessitates much less plastic deformation to be formed in the case of the oxidized sample.

4. Discussion

The modification of the tensile behaviour of pure nickel foil has been observed repeatedly. The oxide layer increases the yield stress and the work hardening rate at the beginning of the plastic deformation. In terms of microscopic phenomena it appears that identical dislocation mechanisms are operating whatever the foils were oxidized or not. This is supported by direct observations of the dislocation microstructures and measurements of the activation volume along the tensile curve which fit the same curve as seen in Fig. 3. As commonly observed in pure face centred cubic metals it is likely that the main mechanism which controls plasticity is the interaction of mobile dislocations with the dislocations forest. In this case, the flow stress is related to the total dislocation density (ρ) by the so – called Taylor equation [11]:

$$\sigma = \alpha\mu\sqrt{\rho}\,. \tag{2}$$

where μ is the shear modulus and α a dimensionless coefficient.

In many cases some friction term σ_0 may be added to the dislocation hardening [12]. The corresponding activation volume can be written $V = b^2d$, where d is the main distance between forest dislocations which turns to be the reverse of the dislocation density square root $\left(d = 1/\sqrt{\rho}\right)$. So finally we can reformulate the expression for the activation volume :

$$V = \frac{\alpha\mu}{\left(\sigma - \sigma_0\right)} \tag{3}$$

This can be fitted to the experimental values of the activation volume, and actually the curve in Fig. 3 corresponds to the equation (3) with the fitted parameters : $\alpha = 0.367$ and $\sigma_0 = 24$ MPa. It is remarkable that these parameters are in excellent agreement with the values currently reported in the literature. Indeed various literature reviews based on either theoretical models or experimental results have shown that the parameter α from the Taylor relation ranges between 0.2 and 1 [12]. Some threshold stress σ_0 was reported for pure nickel, in the expression of the Hall Petch relation of the flow stress with grain size; Thompson [13] reported $\sigma_0 = 21.8$ MPa.

Since we have shown that the plastic deformation is governed by the interaction of mobile dislocations with the forest in both naked and oxidized nickel foils, the role of dislocation storage is obviously predominant [11]. The different tensile behaviour of the naked nickel foil as compared to the oxidized samples must be understood in that frame. In both type of samples, the metal subjected to a heat treatment for 1 hour at 1000°C, has reached a very large grain size (360 µm), larger than the foil thickness. The resulting microstructure is of bamboo type : in any place, only one grain crosses the thickness of the specimen, or in other words all the metal grains possess two large free surfaces. It is obvious that the dislocations are attracted by these surfaces due to image forces [14], and so many dislocations can escape the foil in the case of naked nickel. This simply explains why both yield stress and WHR are lower at the beginning of the deformation for the naked foil as compared to the oxidized ones.

In the general case of oxidized samples the surface elastic force problem is not trivial and some model refinement are still discussed nowadays [15]. However for the case of interest in this study, namely NiO layer on nickel, the elastic stiffness of the oxide is similar to the metal one. In this case we have calculated that the image force is nearly not affected and that even the oxidized surfaces attract dislocations [16]. Nevertheless, the structure of the oxide layer itself, as well as its very good adherence on the metal, constitute an obstacle to dislocation motion and thus impede their escape at the specimen surface (which is not free any more). So that in the case of oxidized nickel foils the dislocation storage will be much more rapid than in the case of naked specimens, and the yield stress and WHR are thus higher. After some amount of plastic strain, the dislocations entangle in the core of the sample, leading to some dislocation cell structure (as seen in Fig. 4). Once this structure is set up the dislocations move in this cell structure, that is the mean free path of dislocation is of the order of the cell size, much lower than the foil thickness. In this case the nature of the surface (either free surface or oxidized barrier) has no more incidence on the whole mechanical behaviour. At the macroscopic scale, after some plastic strain has been achieved, the behaviour of oxidized and naked nickel foils are identical. Indeed the WHR values are the same for both types of specimens and the rupture stress is also identical. The amount of plastic strain which is necessary to set up the dislocation cell structure is simply higher in the case of naked specimens, explaining why the latter have a better ductility than the oxidized ones.

5. Conclusions

The presence of an oxide layer at the surface of pure nickel foils (125 µm thick) strongly affects the mechanical properties of the metal during tensile testing. This effect is not related to the oxide thickness, i.e. similar effects are measured for 5, 10 and 15 µm thick oxide layers. We have shown through activation volume measurement that the deformation mechanism is the same in both naked and oxidized samples; the dislocation motion seems to be controlled by forest hardening, as suggested by activation volume values and stress dependence and by TEM observations. The oxide layer on the surface of the metal acts as a barrier for dislocations and impedes dislocations escape at the beginning of the plastic strain. This effect accelerates quite strongly the storage of dislocations and thus increases the WHR, so that the dislocations form well defined cells for relatively low strain levels. For high strain level, i.e. when the cell structure of dislocations is achieved in the naked sample, the behaviour of both metals is the same. However the delay for setting the dislocations cell structure in the naked sample implies a better ductility since more strain is necessary to reach the rupture stress. This work shows that the barrier role of the oxide scale can be effective even when there isn't any elastic stress or interaction. It also highlights the importance of considering dislocations storage rate for modelling plastic deformation of metals.

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