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Low temperature stress relaxation of nanocrystalline nickel

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Stress relaxation in nanocrystalline nickel within the temperature range 523–673 K in a uniaxial compression regime is studied in the present investigation. The results obtained for coarser grained nickel are given for comparison. An average strain rate of nanocrystalline nickel within the investigated range of temperatures is 1.75×10^{-5}–3.03×10^{-5} s^{-1}. The presence of two types of stress relaxation dependencies are shown. The most likely strain mechanism is grain boundary sliding controlled by grain boundary diffusion for temperatures between 623 and 673 K.

1. Introduction

As shown in [1, 2] the presence of an extremely developed system of internal interfaces in nanocrystalline (NC) materials leads to qualitative changes in the processes of morphological and structural relaxation. These processes become evident in recrystallization, sintering, pore formation and formation of chemical compounds by solid phase reactions. At the same time the processes of boundary sliding and migration determine mechanical properties to a great degree. Thus, qualitative alteration of the stress–strain curve takes place in NC Ni, compared with polycrystal Ni [3]. At the initial stage of strain the curve is parabolic in type, with downward curvature. Theoretical analysis [4] has shown that this behaviour may be explained by alteration of the strain mechanisms. As long as dislocations are absent from the bulk of the NC Ni grain, traditionally, for polycrystals, the initial grain channel of intragranular strain is closed and grain boundary (GB) sliding becomes dominant at the initial stage of strain. A hardness study of NC materials, depending on the grain size, shows good agreement with the Hall–Petch relationship ($H_V = H_0 + kd^{-1/2}$, where H_V is Vickers hardness, H_0 is the hypothetical single crystal hardness, k is a constant and d is the grain size) [5, 6]. However, in some investigations [7, 8] negative inversion of the Hall–Petch relation ($k < 0$) is observed. This is attributed by the authors [8] to changes in the mechanism of strain, i.e. grain boundary sliding. The possibility of a high rate of diffusional creep at room temperature is described in [7, 9]. But, an experimental study [10] of creep in NC Pd and Cu has shown that the rate of diffusional creep high (10^{-8}–10^{-9} s^{-1}) is not at room temperature. High rates of creep (10^{-5} s^{-1}) at 0.5–0.6 T_m have been described in [11], which is dedicated to a study of creep in NC TiO_2. The conclusion stated that creep kinetics was more likely to have been controlled by GB processes, rather than by diffusion. This conclusion has been considered as preliminary.

The present investigation studies stress relaxation in nanocrystalline Ni when a compressed load is used in the temperature range 523–673 K (0.17–0.27 T_m), where T_m is the melting temperature.

2. Experimental procedure

2.1. Sample preparation

Samples of cylindrical shape, with a diameter of 5 mm and a height of 4 mm, made of ultrafine nickel powder were utilized in the NC Ni mechanical property tests. Powder with a mean size of 65 nm was obtained by evaporation–condensation techniques in an inert gas atmosphere (argon). Compact NC Ni samples, with a mean grain size of 70 nm, were prepared by a three step process:

1. ultrafine Ni powder was compacted under 200 MPa to 50–60% of theoretical density of Ni;
2. the tablets obtained were encapsulated into Ni foil; and
3. workpieces were pressed by sintering under pressure in high pressure chambers of 'toroid' type [12] under 4.4 GPa and at a temperature of 773 K. The obtained density was 94–96%. In order to compare the results of the mechanical tests Ni samples with a mean grain size of 150 nm and a density of 95–96% were obtained. At 4.4 GPa, the temperature was 1073 K. In both cases the duration of heating was 3 min and the pressure was lowered only after cooling to room temperature.

2.2. Stress relaxation tests

Stress relaxation tests were carried out on an Instron test machine within the range 523–673 K, under uniaxial compression in vacuum at 10^{-4} Torr. The initial imposed loads corresponded to the initial part of the stress–strain curve with dependence, where δ is the stress, A is the constant ε is the strain and exponent $n \cong 2$ [3].

In order to retain the initial nanocrystal structure, the samples were loaded and then heated to test temperature; this was necessary because recrystallization in ultrafine medium, with mean grain size < 0.1 μm at 0.2–0.3 T_m, was two to three orders-of-magnitude higher than in polycrystalline materials. Vickers hardness (with a load of 5 kg) of the NC samples was 4.66–4.73 GPa, and the hardness of samples with growing grains (mean grain size of 150 nm) was 2.86–3.10 GPa.

The information about the defect structure of the samples prior to and following testing has been obtained by transmission electron microscopy (TEM) of thin foils treated preliminarily by ion bombing. The foils were cut from large samples using a diamond saw. The edge of the wedge-like foil was thinned to the grain size, so that pictures of grain projections would not overlap. The mean grain size was determined by the section method. Fig. 1a, b shows the initial NC Ni with a mean grain size of 70 nm. The grain size is within the range 40–100 nm. Grains have crystallographic shapes. The smallest pores are angular, and form from triple junctions of grains . Twins occur very seldomly, and when present the thickness of the interlayer twins is 20–40 nm; the pore size being not more then 40 nm. Fig. 2a, b shows the structure of Ni with growing grains, the size of which is about 100–300 nm. The mean size of the grain is 150 nm. The structure of coarser grain Ni is characterized by more morphological asymmetry of grains and by the absence of twins. Complexes of dotted defect, which look like speckles, are evident in the initial samples of NC Ni and Ni with coarser grains. This defect is characteristic of the metal foil, thinned by ion polishing. It has been assumed that this structure has been caused by loops, nets of dislocation having a very high density distribution; but it is impossible to come to this conclusion, even at × 190 000 magnification. Besides, the picture of dislocation is not evident even in pure, not-etched grains, if the microscope angle is about 40°. This proves that the material has an undislocated structure in the grain volume.

3. Results and discussion

According to experimental data (Fig. 3) a several times increase of internal stress (upward curvature) takes

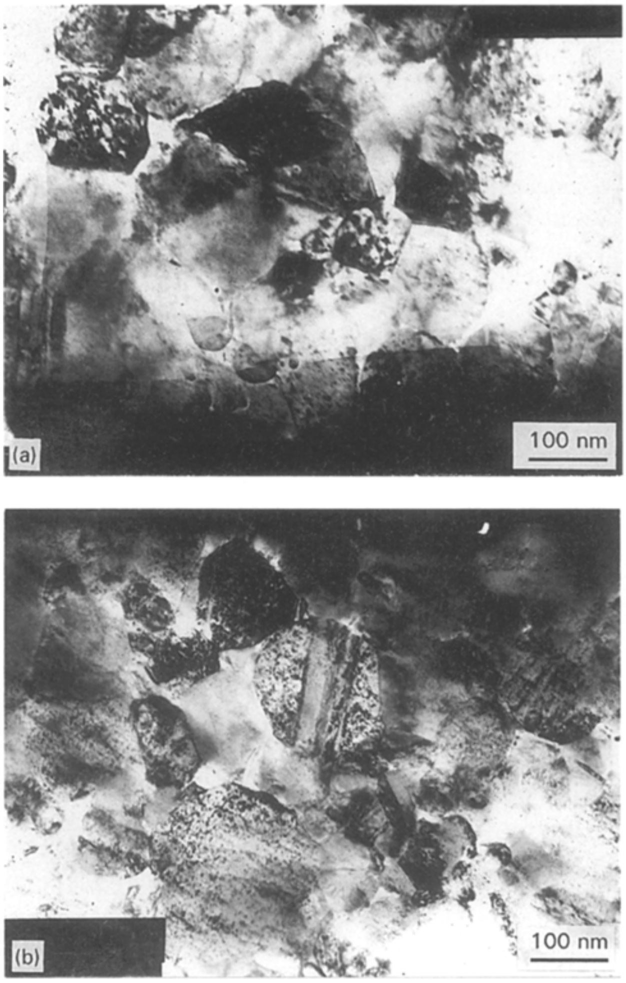

Figure 1 (a, b) TEM of the initial nanocrystalline Ni with mean grain size of 70 nm.

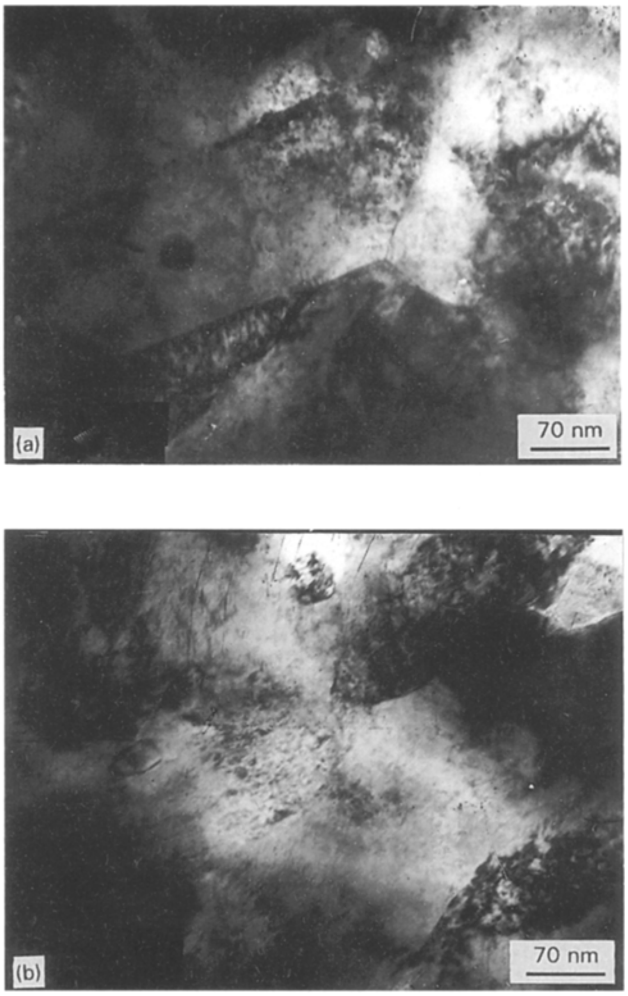

Figure 2 (a, b) TEM of the initial Ni with growing grains. Mean grain size of 150 nm.

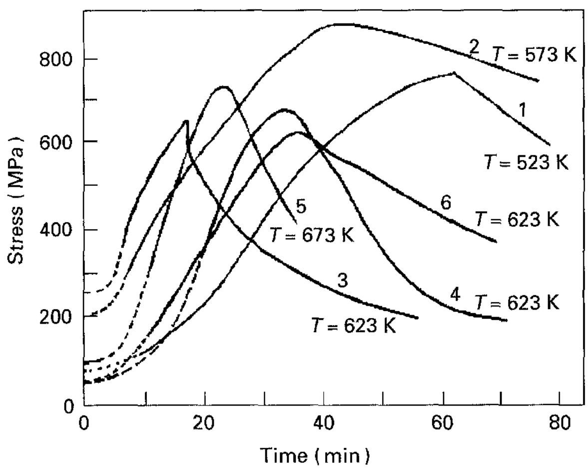

Figure 3 Stress–time plots for a compressive load under a temperature range of 523–673 K; stress relaxation test on nanocrystalline Ni and Ni with growing grains: (– – –) heating, (——) isothermal.

place if compression loads are used at the initial stage of the stress–time curve. Then, following the relaxation of stress, unloading occurs (downward curvature). The dotted line on the stress relaxation curve shows heating of samples up to the test temperature. Table I shows the main data of every experiment. The simplest explanation for stress growth at the initial stage of the stress relaxation tests is the development of thermal stress in every particular part of the loading unit, i.e. in stocks made of molybdenum alloys, which like the sample itself are heated to 523–673 K and transfer the increased load to the sample. The coefficient of thermal linear extension, α, of stocks made of molybdenum is $6\times10^{-6}\,1\,\mathrm{K}^{-1}$, so 50 cm long stocks, L, pressed in a grip, change their length by

$$\Delta L = L\times\alpha\times\Delta T \cong 9\times10^{-2}\,\mathrm{cm}$$

(if the difference in temperature between the stocks and the sample is ~ 300 K). This change in stock length is added to the edges of the sample which has a height of $L_i = 4$ cm, and makes strain, ε, equal to

$$\Delta L/L_i \cong 2.2\times10^{-2}$$

and stress compression

$$\Delta P_1, \varepsilon E \cong 60\,\mathrm{MPa}$$

where $E = 2.63$ GPa; the value of Young's modulus is determined experimentally from the stress–strain curves. These relatively small values of ΔP_1 cannot explain the effects observed.

Another possible explanation of the experimental data is the development of internal stress during loading and heating. Such stress may be found, for example, within the system of pores near triple junctions of boundaries, which are subject to interval pressure from dissolved gaseous impurities (oxygen, nitrogen, water) collected there. An effect close to the one observed in this investigation has been found in [13] for NC Cu, and has been explained by separation of oxygen in the pores.

It is necessary to estimate the value of the internal stress connected with gaseous impurities in the pore system. The contribution of impurities to the inner pressure in a pore is determined as

$$\Delta P_2 = Q\times(RT/V_\mathrm{p}),$$

where Q is the quantity of moles of the agent, R is the Boltzmann constant and V_p is the pore volume.

According to [14], the distance between oxygen molecules on the nickel's surface in air is $x \cong 2$ nm. If one takes a pore volume, V_p equal to $4\pi/30\,D^3 \cong 10^{-16}\,\mathrm{cm}^3$ (where D is the pore diameter), and one also assumes that at strain an impurity is collected into a pore from an area approximately equal to the area of one initial particle, then $Q = 1.5^{-20}$ mol. Taking this into consideration, estimation of the inner pressure in a pore, to oxygen conveyance is

$$\Delta P_2 \cong 1\,\mathrm{MPa}$$

The time required for creation of corresponding stress is relatively short because of the great value of the oxygen diffusion coefficient in Ni [15]

$$D_\mathrm{ox} = 4.9\times10^{-2}\exp[-164\,(\mathrm{kJ\,mol}^{-1})/RT]$$
$$\cong 10^{-14}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$$

The time required for conveyance of the impurities to the pore is

$$\tau_\mathrm{ox} \sim d^2/D_\mathrm{ox} \sim 5\times10^3\,\mathrm{s}$$

where d is the grain size. The stress obtained and time conveyance required for impurities to the pore are much less than the value observed experimentally.

The most important factor that influences the creation of internal stress may be the dilatation effect, caused by a great concentration of non-equilibrium vacancies formed during the process of recrystallization. These dynamic vacancies are condensed into microvacancied clusters, which have been found to exist by experimentation [16]. The recrystallization scheme is shown in Fig. 4. According to [17] a dilation, effect owned to the presence of non-equilibrium recrystallizing vacancies with a concentration of $\sim 10^{-4}$ atomic units causes strain, $\varepsilon \sim 6\times10^{-2}$. The pressure connected with the dilatations of distortion is estimated to be $\Delta P_3 \cong \varepsilon\times E \cong 160$ MPa. This value is more than the combined values of the effects mentioned above, and close to those obtained during experimentation.

The existence of two types of stress relaxation curves for NC Ni may be marked within the range of investigated temperatures (523–673 K). The first is a sharp curve of stress relaxation for temperatures of 623–673 K, and the second is a relaxation curve with a flat maximum at lower test temperatures of 523–573 K. A preliminary calculation has been performed to estimate the strain rate ($\dot{\varepsilon}$) provided by the different mechanisms. According to this estimation, the maximum strain rate controlled by GB selfdiffusion of vacancies ($\sim 10^{-4}\,\mathrm{s}^{-1}$) is provided by sliding under experimental conditions. The rate of diffusional creep is small. The strain rate for the Nabarro–Herring mechanism of creep is about $10^{-11}\,\mathrm{s}^{-1}$ and for Coble mechanim of creep it is $10^{-6}\,\mathrm{s}^{-1}$. Analysis

TABLE I Tabulation of data from stress relaxation test on nanocrystalline Ni and Ni with coarser grains: T, test temperature; $\dot{\varepsilon}$, average strain rate

Sample	Grain size (nm)	T (K)	Rate heating (°C min^{-1})	Initial imposed load (MPa)	Maximal stress (MPa)	$\dot{\varepsilon}$ ($\times 10^{-5}$ s^{-1})
1	70	523	25	78.8	778.4	2.64
2	70	573	50	200.0	878.9	1.75
3	70	623	50	253.6	624.0	3.36
4	70	623	17	61.5	684.9	3.03
5	70	673	40	83.0	721.6	1.95
6	150	623	30	74.8	617.9	2.87

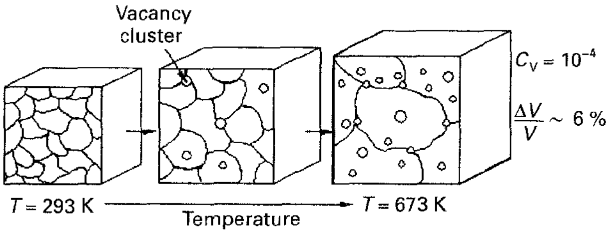

Figure 4 The recrystallization scheme of nanocrystalline Ni according to [17]: C_v, concentration of non-equilibrium recrystallizing vacancies (atomic units), $\Delta V/V$, strain.

of the stress–strain curve of NC Ni [3] within the range of well known models [4] shows the presence of GB zones in nanocrystals, capable of sliding under the influence of relatively low stress. Therefore, while explaining the experimental data at the unloading stage (downward curvature), it is assumed that a system of surfaces, which have the ability to slide with the assistance of diffusion vacancies under the influence of stress, exists in the nanocrystalline material. The equation shows GB sliding controlled by GB diffusion, if one assumes that it is performed by a system of intercrystal dislocations [18]

$$\dot{\varepsilon} = HD_{GB}\frac{Gb}{kT}\left(\frac{b}{d}\right)^3 \times \left(\frac{\sigma}{G}\right)^2, \quad H = 8\times 10^5 \quad (1)$$

where d is the grain size, D_{GB} is the coefficient of grain boundary diffusion, G is the shear modulus, b is Burger's vector, k is the Boltzmann constant, T is the test temperature and σ is the internal stress. Calculations using Equation 1, for stress relaxation curves at temperatures of 623–673 K, have shown good correlation between theoretical and experimental results (Fig. 5a–c) shows a theoretic approximation of the results obtained during calculation, with the help of Equation 1.

At lower test temperatures (523–573 K) a good correlation between theory and experimentation has been obtained for plastic strain by the power law creep (where exponent $n = 4.5$) according to the Weertman model, where a strain is the result of sliding of edge dislocations which overcome the obstacles by climbing [19]

$$\dot{\varepsilon} = \alpha\frac{D_{GB}}{b^{3.5}\times M^{0.5}}\left(\frac{\sigma}{G}\right)^{4.5} \times \left(\frac{G\Omega}{kT}\right) \quad (2)$$

where Ω is an activate volume, M is the density of dislocation sources, and α is a constant.

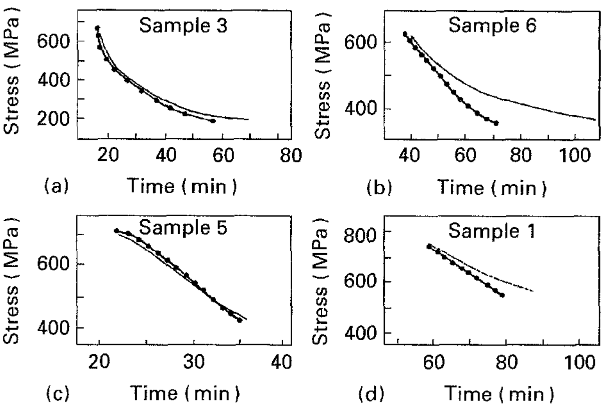

Figure 5 Theoretical approximation of stress relaxation curves obtained by calculation with Equation 1a for NCNi tests at 623 K, (a) at 673 K (c); for Ni with growing grains at 623 K (b), and by calculation with Equation (2) for NcNi at 513 K (d). Where (—) is experiment, (●—●—●) is theory.

Fig. 5d shows the theoretic approximation of results obtained during calculation, with the help of Equation 2.

It is necessary to remark that the change of shape of the maximum from sharp to flat (at 623 K), and consequently a certain decrease in the strain rate for the sharp angle dependence of the stress relaxation curve happens under the following conditions

1. lower rate of heating 17 °C min^{-1} (curve 4);
2. presence of more coarse grains, ~150 nm (curve 6); and
3. increase in temperature to 673 K (curve 5).

Once more, at 623–673 K plastic strain (at the unloading stage) occurs by a GB sliding mechanism, controlled by GB diffusion. However, it may be assumed that in all the above-mentioned cases, strain happens with great help from diffusion processes, which influence a certain decrease of the strain rate (Table I). TEM data proves the theoretical calculation. A structural investigation of NC Ni performed 2 min after maintaining a constant temperature of 623 K (Fig. 6a, b) shows that a number of twins increase, their grain boundaries are not always rectilinear, some wedge-like twins are met. A lot of microcracks connect neighbouring triple junctions, and even more extent cracks exist. Areas with a great amount of microcracks are alternated with areas where cracks are not yet formed. As a result of testing (sample 3, a curve with sharp maximum) the following

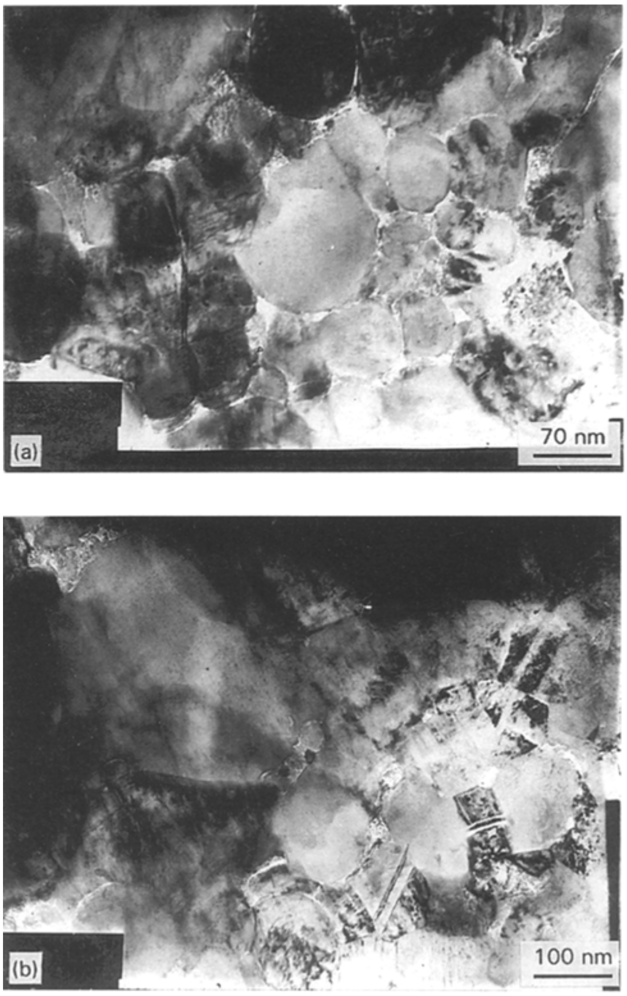

Figure 6 (a, b) TEM of nanocrystalline Ni performed 2 min after keeping a constant temperature of 623 K.

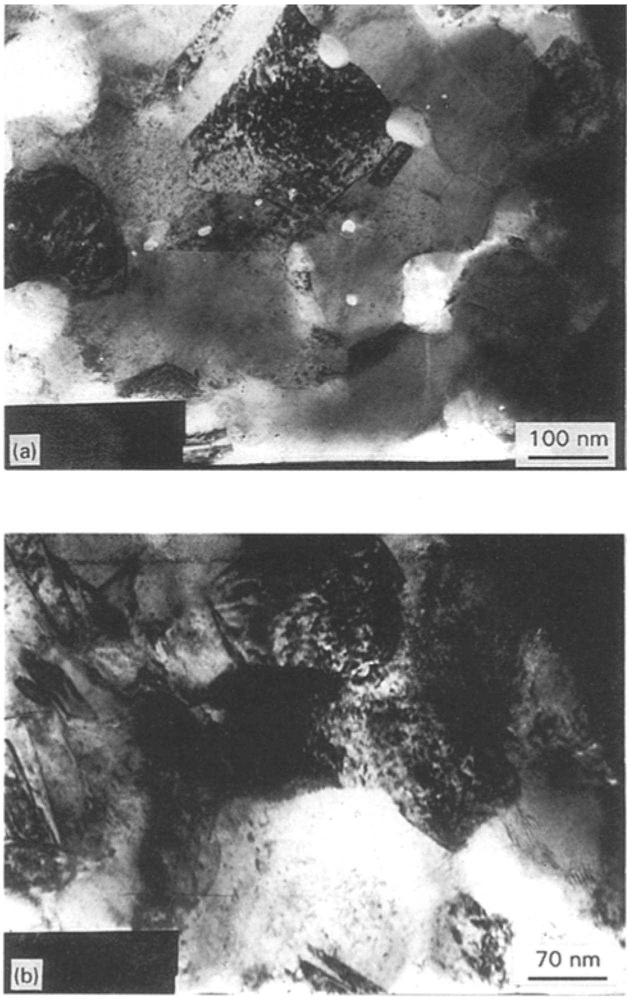

Figure 7 TEM of nanocrystalline Ni after testing at (a) 623 K and (b) 673 K.

results are obtained (Fig. 7a): the grain becomes uniaxial; micropores are formed, not only at triple junctions, but along boundaries as well as within the grain; the thickness of microcracks grows; oxidation and formation of the smallest NiO crystals in pores take place. Despite the low test temperature, a collective recrystallization takes place selectively in samples, resulting in the formation of large round (about 1 μm) monocrystals or double particles of Ni. A break in density is observed around them, evidently caused by great thermal stresses. The conclusion is, that at the initial stage (upward curvature), formation of pores and microcracks is observed. After this stress process is completed, curves go down sharply (downward curvature). Samples which have a smoother maximum on the stress relaxation curve, as has been supposed, have microstructure, proving that the diffusion process is more active under these conditions. A sample tested at 673 K (Fig. 7b) has the following features: welde-like twins, the presence of which shows the complicated character of initial tension distribution and high gradients of stress distribution. Grain coalescence takes place, but as far as the morphology of the grains grown together are concerned, the changes are only in the places contact; it is evident that migration of high angle boundaries within grains, with subsequent reorientation of the neighbouring crystal, is observed. This process is activated by stress. Newly formed large particles are not spheroidal. The desire to minimize the surface energy manifests itself in the disappearance of some boundaries, and in the acceptance of a round shape. Porosity in triple junctions is not observed. It is possible that the material is characterized by high strength boundaries, in which GB diffusion is hardened. A set of structural elements altering with stress relaxation is more unlikely in coarser grained materials (Fig. 8, stress relaxation curve 6). Quite large voids are formed. Microcracking is not observed. The stress relaxation here is caused by diffusion.

On the basis of TEM data it is possible to come to the conclusion that, of known types of strain, i.e.,

1. intergrain sliding,
2. direct diffusion of vacancies,
3. dislocation movement,

the two first types may occur in nanocrystal samples. A field of initial tension is formed after loading. There partial relaxation happens by twinning of grains conveniently orientated towards the acting forces. Usually twins' boundaries are rectilinear, their deflection is caused by formation of twinning dislocations. It is known that multiple twinning occurs in crystals at very high tension. Twins may cross each other and form strange shapes. Such an effect is not observed here.

Figure 8 TEM of Ni with growing grains (150 nm) after testing at 623 K.

The mechanism of twinning corresponds to the initial flat part of the dependence curve, $\sigma(t)$ (Fig. 3), and the process of cracking takes place practically at the same time. Pores were observed when samples were in the initial state. Consequently, there was a great gradient in the concentration of vacancies. Therefore, a directed flow of vacancies appears when loading is applied. Due to GB diffusion, angles with two facets become round, the degree of asymmetry becomes smaller and as a result conditions for grain rotation and sliding, i.e. intergrain sliding, are created.

Some features proving the possibility of NC Ni superplasticity should be discussed. It is known that the mechanism of "running neck" is characteristic of superplastic materials. The stress is not equally distributed and reaches a maximum either in this or in some other part of the sample. Microcracks, partial removal of stress and initial sliding occur in places with a maximum level of stress. Then, this process happens in another place. This is an explanation for non-homogeneity in the NC Ni structure: areas with a large amount of microcracks alternate with areas without them.

One of the characteristics of superplasticity is the strain rate sensitivity of the stress (the exponent m for $\sigma = A\dot{\varepsilon}^m$). To determine m in NC Ni, sample tests at constant rate and temperature of 623 K (0.25 T_m) in a 10^{-1} Torr vacuum, were carried out. Comparison of loads P_1 and P_2 before and after graded changes of rate from V_1 and V_2 was made. This change of arbitrary strain is taken as momentary and it is assumed that $m = (\ln P_1/P_2)/(\ln V_1/V_2) \cong \partial \ln \sigma / \partial \ln \dot{\varepsilon}$. The value of m for NC Ni at the strain rate, $\dot{\varepsilon} = 10^{-2}$–$10^{-3}\,\text{s}^{-1}$ is within the range $-5.51 \leq m \leq 0.48$, if $\varepsilon = 1\%$; and $-1.33 \leq m \leq 0.47$, if $\varepsilon = 8\%$, and at the rate $\dot{\varepsilon} = 10\,\text{s}^{-1}$ is within the range $-0.48 \leq m \leq 0.86$, if $\varepsilon = 1\%$. It may be marked that the value of m is close to the strain-rate sensitivity of the stress which are characteristic of superplasticity. Really, if a superplasticity regime is assumed, the sensibility of a material to the strain rate sensitivity of the stress is within the range $0.5 \leq m \leq 0.7$, while $m \leq 0.2$ if conventional strain is assumed. Though the data of these experiments do not show the presence of superplasticity in NC Ni, but taking into account the above facts, such as high real rates of stress relaxation (about $10^{-5}\,\text{s}^{-1}$) at 0.17–0.27 T_m, the type of dependence showing stress relaxation [$\dot{\varepsilon}(\sigma)$ with $n = 2$] and mechanism of plastic strain, i.e. GB sliding, as well as value of strain-rate sensitivity of the stress, it may be assumed that Ni being in a nanocrystalline condition may be superplastic at certain temperature – rate regimes. It should be marked that conventional superplasticity is observed at $T \sim 0.5$–$0.7\ T_m$, and as a rule for heterophase two components systems, while superplasticity of one component materials is possible at $T \sim 0.25\ T_m$ for nanocrystalline nickel.

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