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Embrittlement of nanocrystalline nickel by liquid metals

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Metallographic and fractographic tests of liquid metal embrittlement are performed for nanocrystalline Ni–Hg systems. It is shown that the behaviour of nanocrystalline nickel under these conditions is close to that of ordinary polycrystalline materials. The presence of a stage of subcritical crack growth is demonstrated. As nanocrystalline grains have none of their own intrinsic dislocations, it is assumed that subcritical crack growth in liquid metal environment can be realized through the mechanism of dissolution of atoms from the crack tip. This dissolution–condensation model of liquid metal embrittlement, developed for polycrystals, can also be applied to nanocrystals.

1. Introduction

Liquid metal embrittlement (LME) is perhaps the most prominent example of environmental influence upon the mechanical properties of metals [1]. On the macroscopic level, LME is manifested in the decreased lifetime, strength and plasticity of metals being deformed in contact with a liquid metal as compared to those deformed in an inert medium [2]. It is established that fast fracture of a material by LME is caused by nucleation on the surface and subsequent subcritical crack growth (SCG) filled with melt [2, 3]. The kinetics and the micromechanisms of LME are still not clearly understood, which hampers the development of methods for combating the consequences of LME, which are often dramatic [2].

Two advanced concepts claim to describe the micromechanism of LME. The first, suggested by Glickman *et al.* [4, 5], is the dissolution–condensation model (DCM). Under DCM, the subcritical crack growth proceeds as follows. Atoms are dissolved at the tip of a crack, where chemical potential is higher due to stress. Their rapid diffusion in the liquid metal is followed by the condensation on stress-free walls of a crack [4, 5]. In this process, dissolving is effected by way of tangential growth of the solution centres, which are kinks on the atomic steps of the surface.

A second mechanism has been suggested by Popovich [6] and extensively developed by Lynch [7]: the mechanism of localized sliding. According to these authors, the creation of dislocations at the tip of a crack and their intense emission into the prefracture zone is facilitated by the adsorption of liquid metal atoms. The emitted dislocations interact with the dislocation structure existing in the plastic zone. This leads to the nucleation of microcracks — 'emissaries' which join subsequently to the main crack, maintaining its subcritical growth [7]. Unfortunately, there is insufficient experimental evidence to allow definite conclusions in favour of either of these concepts. The most outstanding distinction of the DCM model from that of localized sliding lies in the fact that, in general, the existence of dislocation of the material is not a necessary condition of crack growth through dissolution, whereas the other model implies that the fracture proceeds only through interaction between dislocations. Therefore an experiment with a material precluding the appearance of dislocations might help to illuminate the micromechanism of LME. The testing of such dislocation-free material under LME conditions will ascertain the existence of a stage of subcritical crack growth under the melt action; this process cannot be caused by the facilitation of dislocation emission from the tip of a crack.

Nanocrystalline materials are well suited for carrying out such an experiment. This material can be considered as a peculiar kind of dislocation-free model system [8, 9], and the very possibility of the dislocation structure formation in it is ruled out [10]. On the other hand, this new class of materials is poorly known, and experiments like that outlined above have much potential for yielding the information still lacking about its resistance to stress corrosion cracking under LME conditions. By this means, the peculiarities of the behaviour of nanocrystalline materials under such conditions, as compared with ordinary polycrystals, may be revealed.

In this work we have used nickel with nanocrystal size $d = 60$ nm. The absence of dislocation structure in this material after its plastic deformation has been demonstrated with the use of electron microscopy techniques and positron annihilation methods [10]. In this nanocrystalline nickel, grain growth begins at $T = 500$ K [11], therefore mercury was chosen as a liquid metal. In addition, it is known that no chemical

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compounds arise in the system Ni–Hg [12], and that polycrystalline nickel is susceptible to embrittlement by mercury [13, 14]. It should be noted that both these papers are devoted mainly to an investigation of the fracture surface in the zone of subcritical crack growth, and there is no evidence for the fracture kinetics of for the influence of mercury on the strength properties of nickel.

2. Experimental procedure

Nanocrystalline nickel test specimens with porosity of 5 to 6% were produced as disks 9 mm in diameter and 4 mm thick by the procedure described in [15]. How ever this shape of specimen is inconvenient to use in strength testing; therefore another mode of loading was adopted, namely console bending using the device IMASH 20–75. The speed of the active grid displacement was $1.86 \times 10^{-7}\ \mathrm{m\,s^{-1}}$, which corresponds to a bending rate of $0.002\,^{\circ}\,\mathrm{s}^{-1}$, or to a deformation rate of $\dot{\varepsilon} = 6 \times 10^{-5}\ \mathrm{s}^{-1}$. In deciding on a particular value, it was taken into account that the authors of [13, 14] had observed LME in the system Ni–Hg at a deformation rate close to ours. The loading was stopped if necessary, and this furnished testing under creep conditions.

The specimen surface was polished mechanically and wetted with concentrated hydrochloric acid, as described in [13, 14]. Mercury was then put on that side of the specimen which was to undergo extending. The main part of the experiments was performed at room temperature. After testing, the specimen was heated to 453 K in an argon environment to evaporate the mercury, whereupon its surface was cleaned with acetone. A MIM-10 optical microscope and a CamScan scanning electron microscope were used to perform the microscopic studies.

3. Results

Four sets of experiments were carried out. The first set was to determine the ultimate bending strength (σ_c) of nanocrystalline nickel under bending. Specimens without mercury coating were deformed to this purpose. The value of σ_c was found to be 450 ± 20 MPa, that is 4–5 times less than the value obtained on similar specimens for compression [10, 11]. In some specimens the nucleation of a crack occurred at deforming stress $\sigma = (0.7\text{–}0.8)\sigma_c$. This was registered by the relaxation of load on the deformation curve. In such cases the specimen was unloaded, and after determination of the crack length (l) by metallographic means it was loaded again up to break-down. This procedure enabled us to define the value of the fracture toughness K_c for nanocrystalline nickel. To calculate K_c the following formula was used [16]:

$$K_c = \frac{4.12 \times P_c L(\alpha^{-3} - \alpha^3)^{0.5}}{t b^{3/2}} \qquad (1)$$

where P_c is the critical fracture load, $\alpha = 1\text{-}\beta$, $\beta = l/b$, and b, t, L are geometrical dimensions of a specimen. We obtained $K_c = 3.5\ \mathrm{MPa\,m^{1/2}}$. This value is one to two orders of magnitude less than the fracture toughness of polycrystalline materials [17], but it is comparable to $K_{Ic} = 1.5\ \mathrm{MPa\,m^{1/2}}$ found for nanocrystalline rutile [18].

In the second set, the specimens underwent deformation immediately after coating with mercury. It turned out that the presence of liquid Hg alters neither the form of the deformation curve for nanocrystalline nickel, nor the value of its ultimate bending strength σ_c, in contrast to polycrystalline materials, where a drop in σ_c was observed at $\dot{\varepsilon} < 10^{-3}\ \mathrm{s}^{-1}$ by unaltered form of the deformation curve [1, 2]. Metallographic studies have revealed that in most nanocrystalline nickel specimens, as distinct from polycrystalline nickel [13], no cracks were created in the course of deformation under the influence of mercury up to the fracture. Even after 20 h of exposure at $\sigma = 0.7\,\sigma_c$ in the creeping mode, no nucleation of a crack in the specimen occurred. This fact, together with the fact that the value of σ_c for nanonickel proved not to be susceptible to the presence of mercury, demonstrates that liquid metal has no effect on the crack nucleation in nanocrystalline nickel.

In the third set of experiments carried out on specimens covered with mercury, we exploited the fact that, in some of these samples, the nucleation of a crack not connected with mercury influence occurs accidentally at $\sigma \approx (0.7\text{–}0.8)\sigma_c$. The melt flows in to such a crack [19], and the stress intensity factor does not reach the value of K_c. These circumstances made feasible the ‘classical’ tests for stress corrosion cracking [16].

Loading was stopped right after the nucleation of the crack. If the specimen was not fractured in the creep mode during 10^2 s, then it was unloaded and, once the mercury had been removed, deformed again up to its disruption. In both cases the fracture surfaces were qualitatively alike and consisted of three zones (see Fig. 1). Zones I and III (Fig. 2) were of the same morphology, no different from that observed in specimens fractured without mercury ([10] and in present work). This means that they were formed without the participation of mercury as a result of the nucleation

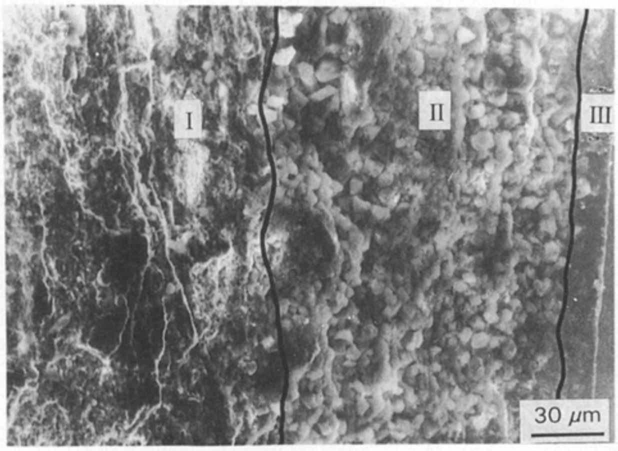

Figure 1 General view of the fracture surface of nanocrystalline nickel deformed in liquid mercury at room temperature. Three zones are recognizable: zone I is formed in the incipient crack, zone II appeared in the course of subcritical crack growth, and zone III arose when fracturing was completed.

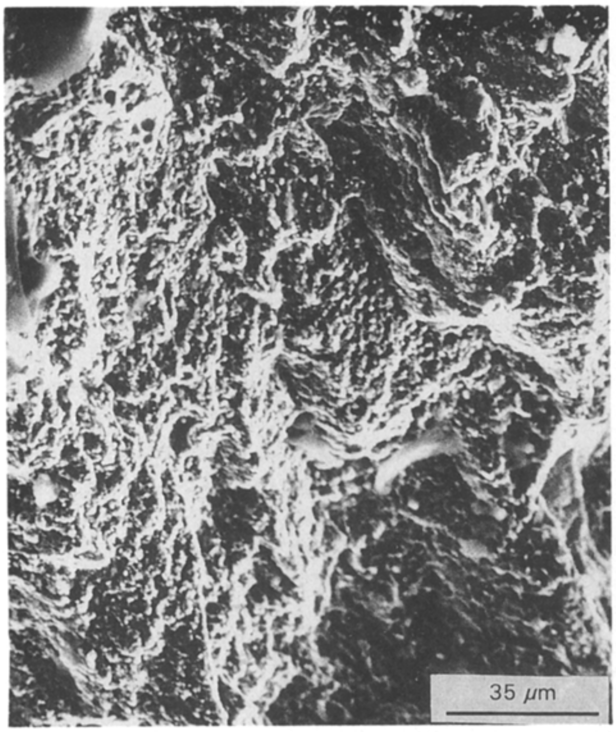

Figure 2 Minute view of zone I. The same view is seen for zone III and for specimens fractured in the ambient air with no mercury [10].

Figure 3 Minute view of zone II (zone of subcritical fracture growth).

of a crack (zone I) and the finishing fracturing of the specimen (zone III). It follows that zone II, which does not arise until a nucleated crack occurs, is formed by its subcritical growth under mercury. This zone measures 40–80 μm in the crack growth direction, i.e., the order of magnitude of the subcritical growth rate averages $10^{-6}\ \mathrm{m\,s^{-1}}$.

A detailed view of zone II is shown in Fig. 3. It bears some resemblance to the 'stone river' with the characteristic size of its 'stones' about 10 μm. This morphology of the fracture is a peculiar feature of nanocrystals and does not occur in any polycrystalline material fracture, including corrosive ones [20].

In the fourth set of experiments, specimens were not deformed. They were held in contact with mercury at temperatures of 300–400 K during various time intervals, up to 10^5 s. After the removal of mercury the surface of nanocrystalline nickel, originally plain and without any structure, appeared as a facetted surface of an ordinary polycrystal with grain boundaries etched away (Fig. 4). The mean size of the facets, measured by the line interception method, was 8–10 μm. This measurement proved to be independent of temperature and exposure time over all examined intervals (Fig. 5), and coincides with the size of the 'stones' in Fig. 3, seen on the fracture in the subcritical growth zone. The distance between the edges of neighbouring facets (which should correspond to the width of 'etched-away boundaries') was approximately 5×10^{-7} m. Nickel conglomerates precipitated from mercury at a size of $\cong 5 \times 10^{-7}$ m equal to the size of etched-away boundaries which were seen on the surface of a specimen, if it was not cleaned with acetone after the evaporation of mercury (see Fig. 6).

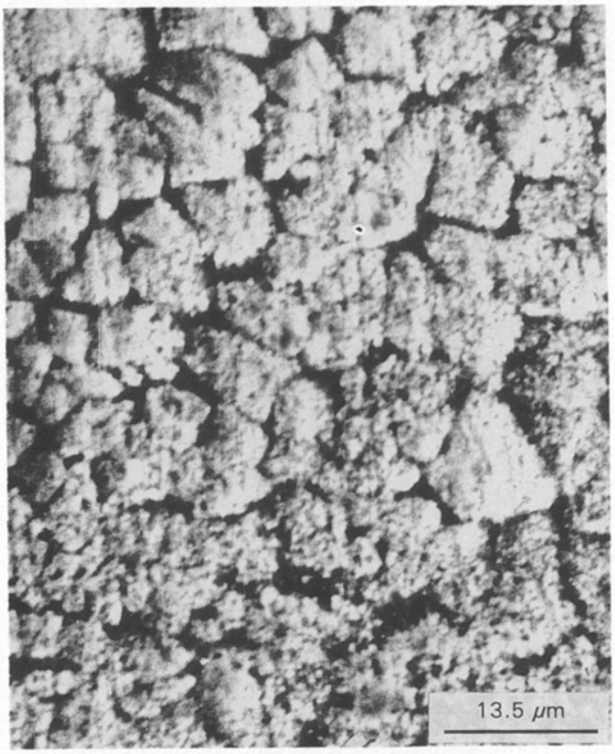

Figure 4 View of the nanonickel surface after long-term contact with mercury (10^3 s) at 355 K.

3. Discussion

It is well known that grooves like those of thermal etching are formed on the surface of a polycrystalline material in contact with molten metal, and the surface becomes facetted. This effect was particularly observed in the systems Cu–Bi [5] and α-brass–Hg [21].

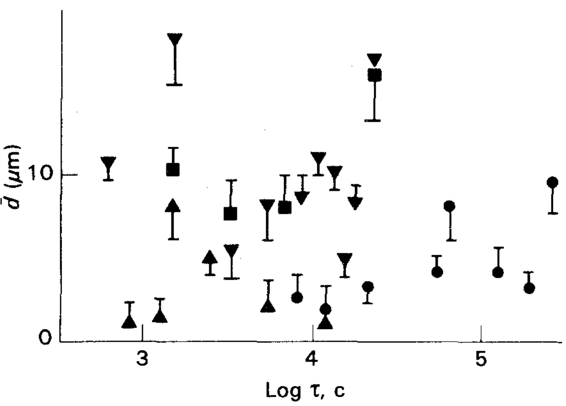

Figure 5 Mean size of the facets (d) developed on the nanonickel surface after contact with mercury as a function of the duration (τ) and temperature (T) of the experiment. T = ●, 300; ▲, 330; ▼, 355; ■, 400 K.

Figure 6 View of the nanonickel surface with conglomerates of powder particles precipitated from the evaporated droplets of mercury.

However, facetting of the surface of nanocrystalline nickel during its contact with mercury, and the independence of the mean size of facets from the exposure time and temperature, can presumably be explained only by the assumption that nanocrystalline materials have a peculiar kind of structure. In other words, nanocrystalline nickel supposedly has conglomerates of nanocrystals, i.e., grains of mean size about 10 μm in its inherent structure, which are separated by the mesh of grain boundaries. The latter, in their turn, consist of chains of finer grains. It is in this sense that a nanocrystal is similar to a polycrystal. In what follows we shall use this assumption, taking into account that the melt essentially penetrates along the boundaries of grains, and there are no dislocations in their bodies.

The susceptibility of a material to stress corrosion cracking stress is determined by the duration of the incubation period for the nucleation of a crack and by the duration of its subcritical growth [16, 22]. In this case the SCG under tension, together with the action of molten metal, is observed in the system under study (nanocrystalline nickel–mercury); this fact is of fundamental importance. The existence of the SCG stage in this model system can be considered as direct evidence that crack propagation under LME conditions occurs through the dissolving of atoms at the tip in the melt.

The notions of the DCM model [5, 22] can be applied for estimation of V_∞, the maximal velocity of the SCG under LME in nanocrystalline nickel, drawing on the above experimental results. Two peculiarities of the DCM model should be mentioned: firstly, the terrace-lattice-kinks model [23] of the crystal–melt interface is used to describe the structure of the dissolution site in a crack; secondly, it is assumed that the atoms while transferring to the melt from the tip of a crack, where their chemical potential is higher due to tensile stress, are condensed on the walls of the crack over a distance approximately equal to its tip opening displacement, δ (Fig. 7).

The equation for the SCG velocity in DCM is as follows [22]:

$$V = \frac{C_j D_L \omega^{1/3}}{h} \frac{C_0 [\exp[\mu/kT] - 1]}{\delta} \quad (2)$$

where

$$\mu = [K^2 - K_{scc}^2]\,\omega/RE \quad (3)$$

where C_j is the roughness of the crystal–melt interface, i.e., the concentration of kinks on the crystalline steps at thermodynamic equilibrium; D_L is diffusivity in the melt; C_0 is the solubility of nickel in the melt at equilibrium; ω is the atomic volume; h is the spacing between dislocation steps on the crack front; R is the width of the crack at its tip; K and K_{scc} are current and threshold of stress intensity factors determining the beginning of crack growth in the presence of melt, respectively; E is Young's modulus; and μ is the chemical potential of atoms at the tip of a crack.

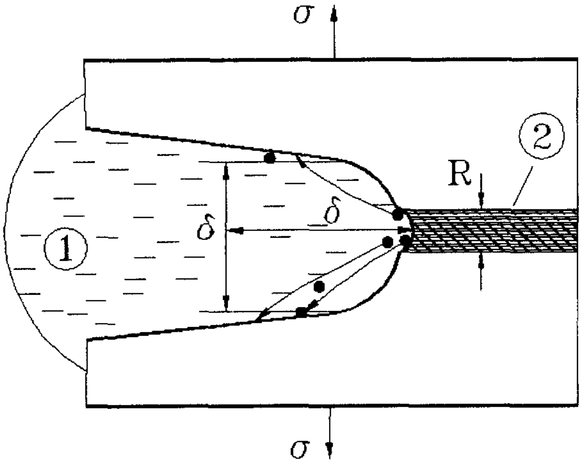

Figure 7 Schematic diagram of a crack filled with the melt (1) developing along the grain boundary (2) under action of stress, σ.

The estimate of an upper limit to the velocity of the subcritical crack growth under DCM conditions made for polycrystals [22] holds good for nanocrystals, as it is based on two additional assumptions. The local solubility of metal near the tip of a crack is assumed to be $C_1 = C_0 \exp(\mu/kT) \gg C_0$, and $C_1 \cong 1$ (per atom); this is true if the width of the crack is nearly equal to the width of the boundary, i.e. $R \cong 10^{-9}$ m, and the stress at the tip is high enough. The second further assumption is that $C_J \cong 1$, i.e. the roughness of the crystal–melt interface is high. This is reasonable if one takes into consideration the structure of nanocrystal surface as well as the low superficial tension on the crystal–melt interface.

In this case Equation 2 transforms into

$$V_\infty = \frac{D_L\, \omega^{1/3}}{\delta\, h} \tag{4}$$

To estimate the value of the crack opening displacement in nanocrystalline material, we insert the magnitude of the deforming stress σ into the relation $\sigma = K^2/\sigma_y E$ [16] instead of the value of yield point σ_y, and take into account that $K \cong \sigma\, l^{1/2}$. Then $\delta \cong \sigma\, l/E \cong 3.5 \times 10^{-7}$ m for the typical values $\sigma \approx 350$ MPa, $l \approx 10^{-4}$ m, and $E \cong 10^{11}$ Pa [24]. The resulting value does not differ from a similar estimate of δ for polycrystals [22].

The estimate of the spacing , h, between dislocation steps on the crack front is of basic importance. Violent emission of dislocations from the tip of a crack by polycrystals causes $h \cong \omega^{1/3}$ [22]. The situation in nanocrystals is radically different, as the emission of dislocations into grain bulk is impossible. Here a reasonable estimate is $h \cong d_0$, where d_0 is the size of a nanoparticle. Thus for typical values $D_L \cong 10^{-9}\,\mathrm{m^2\,s^{-1}}$, and $d_0 \cong 60$ nm we get

$$V_\infty = \frac{D_L\, \omega^{1/3}}{\delta\, d_0} \cong 10^{-5}\,\mathrm{m\,s^{-1}} \tag{5}$$

This value is in agreement with our experiment, but three orders of magnitude less than the subcritical crack growth velocity in polycrystals.

Hence the increase of spacing between dislocation sources and the corresponding decrease of their emission rate is the main cause for slowing down the crack growth in nanocrystalline materials, according to this model.

However, another estimate is possible which does not invoke any notion of dislocation emission. In the framework of this model a crack is developing owing to the flux of atoms through the melt from the tip to walls over a distance comparable to the size of a nanoparticle. This flux is induced by the stress, σ, at the tip of a crack and is equal in magnitude and opposite in sign to the flux of excess vacancies. Then

$$V_\infty = \frac{\sigma\, \omega D_L\, X_V}{k\, T\, d_0}\, \omega \tag{6}$$

where k is the Boltzmann constant and d_0 is the constant. For $T = 300$ K and vacancy concentration $X_V \cong 10^{-3}$–10^{-4} [25] this formula gives $V_\infty = 10^{-5}$–$10^{-6}\,\mathrm{m\,s^{-1}}$ in agreement with the experimental results as well.

In this model, the main physical cause of the fracture growth is the emission of excess vacancies, and the function of stresses is to determine the direction of the vacancies motion, hence that of crack propagation.

From fracture mechanics it is known that, if there is a well pronounced stage of the SCG, the lifetime τ_c (i.e. the susceptibility of a material to corrosion cracking) depends on the rate of this growth, which in turn, is a function of K, on the acting stress σ, and also on the fracture toughness K_c [26]:

$$\tau_c = \frac{2}{\pi\, \sigma^2} \int \frac{K\, \partial K}{V(K)} \tag{7}$$

We have estimated the lifetime of nano- (τ_{cn}) and polycrystals (τ_{cp}) for equal conditions of deformation under LME conditions, supposing that equation 5 holds, i.e., $V(K) \cong V_\infty f(K)$, which is true for real experiments [22], and $K_0 \cong K_{scc}$. The comparison of these estimates indicates that nanocrystalline material is at least not less resistant to the corrosive cracking at LME than the polycrystalline, mainly due to a lower rate of crack propagation in the first case.

The fracture surface formed in the growth zone of a crack was not observed in polycrystal fractures [20]. The formation of such a 'stone-river' is probably related to the peculiar features of nanocrystalline materials, and caused by the mode of relaxation of elastic stresses ahead of the tip of a crack in this material.

In polycrystalline materials, cracks grow blunt, i.e., the concentration of stresses drops, through the emission of dislocations from the tip [27, 28]. In contrast, such a mode of relaxation is impossible in nanocrystalline materials. But the presence of melt switches on an alternative mechanism of relaxation. In the zone in front of the tip of a crack, where the elastic stresses are concentrated, selective dissolution of the inherent mesh of grain boundaries proceeds. This leads to a falling out of the grains into the melt. Because of this, the radius of curvature of the tip increases, and the concentration of elastic stresses reduces. This process is similar to the microbranching of cracks observed in corrosion cracking of polycrystals [16]. But in such materials the magnitude of stress ahead of a crack is restricted by the value of yield limit σ_y, and in nanocrystalline materials it drops according to the law $\sigma \cong K r^{-1/2}$, where r is the distance from the tip [17], remaining all the time greater than σ_y. Therefore the mass character of the grains shedding as a consequence of the dissolution of boundaries is a unique feature in nanocrystalline materials.

4. Conclusions

The experiments reported above allow us to make the following inferences.

1. The fracture toughness, K_c, of nanocrystalline nickel equals approximately 3.5 $\mathrm{MPa\,m^{1/2}}$, and is at least one order of magnitude less than that of polycrystalline materials.

2. With respect to the embrittlement of nanocrystalline nickel by mercury, it can be conceived as a

customary polycrystal with the size of grains about 10 μm, disintegrating along the grain boundaries.

3. The existence of a subcritical crack growth stage in the course of LME for dislocation-free nanocrystalline material enables us to argue in favour of the DCM model, i.e. that the micromechanism of LME is the dissolution of atoms from the tip of a crack in the melt.

4. Our estimate of the ultimate rate of the subcritical growth of a crack is in agreement with the experimentally observed value.

5. The upper limit of the velocity of subcritical crack growth in nanocrystalline material at 300 K is three orders of magnitude less than in polycrystals, and the resistance of nanocrystalline materials to corrosive cracking is bound to be accordingly higher.

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References

1. V. I. LIKHTMAN, E. D. SHYKIN and P. A. PEBINDER, in "Physical-chemical mechanics of materials" (Izdatelstvo AN USSR, Moscow, 1962) p. 303.
2. W. ROSTOKER, J. M. MACCAUGHEY and M. MARKUS, in "Embrittlement by liquid metals" (Van Nostrand-Reinhold, New York, 1960) p. 162.
3. W. W. ROBERTSON, *Trans. AIME* **236** (1966) 1478.
4. E. E. GLICKMAN, J. V. GORJNOV, V. M. DEMIN and K. J. SAPICHEV, *Izvestiya VUZOV* (*USSR*) **5** (1976) 7.
5. E. E. GLICKMAN and J. V. GORJNOV, *Vestnic MGU* (*USSR*) **18** (1977) 551.
6. V. V. POPOVICH, *Phys.-Chem. Mech. Mater.* (*USSR*) **5** (1979) 4.
7. S. P. LYNCH, *Acta Met.* **36** (1988) 2639.
8. R. ARMSTRONG *et al. Phil. Mag.* **7** (1962) 45.
9. V. N. LAPOVOK, V. I. NOVIKOV, S. V. SVIRIDA, A. N. SEMENIKHIN and L. I. TRUSOV, *Phys. metals* (*USSR*) **57** (1984) 718.
10. L. I. TRUSOV, V. I. NOVIKOV, I. A. REPIN, E. E. KAZILIN and V. Y. GANELIN, *Metallophysics* (*USSR*) **10** (1988) 104.
11. V. G. GRYAZNOV, I. A. POLONSKY, A. E. ROMANOV and L. I. TRUSOV, *Phys. Rev. B* **44** (1991) 42.
12. M. HANSEN in "Constitution of binary alloys" (McGraw-Hill, New York, 1958) p. 1315.
13. C. E. PRICE and J. K. GOOD, *Trans. ASME* **106** (1984) 184.
14. S. P. LYNCH, *J. Mater. Sci.* **21** (1986) 692.
15. L. G. KHVOSTANTSEV *et al. High Temp.-High Press.* **9** (1977) 637.
16. O. N. POMANIV and G. N. NIKIFORCHIN, in "Mechanics of corrosion failure of constructional alloys", (Moscow, Metallurgiya, 1980) p. 240.
17. J. F. KNOTT, "Fundamentals of fracture mechanics", (Butterworths, London, 1973) p. 273.
18. H. J. HOFLER and R. S. AVERBACK, *Scripta. Met.* **24** (1990) 240.
19. P. GORDON, *Metal. Trans.* **9A** (1978) 267.
20. D. FELLOYZ (ed) "Metals Handbook", 8th Edition, Vol. 9, "Fractography and Atlas of Fractographs ASM" (Metals Park, Ohio, 1980) p. 782.
21. V. I. IGOSHEV, V. A. SOLDATENKOV and S. I. UTKIN in "Intercrystalline brittleness of steels and alloys" (Izevsk, 1989) p. 73.
22. E. E. GLICKMAN and V. I. IGOSHEV, in "Kinetics and mechanisms for liquid-metal embrittlement of polycrystalline materials" (Preprint IPTM AN USSR, IFDM, 1991) p. 50.
23. N. A. GJOSTEIN, in "Surfaces and interfaces: chemical and physical characteristics" (Syracuse University Press, 1967) p. 226.
24. H. GLEITER, *Prog. Mater. Sci.* **33** (1989) 223.
25. V. N. LAPOVOK, V. I. NOVIKOV, S. V. SVIRIDA, A. N. SEMENIKHIN and L. I. TRUSOV. *Solid State Physics* (*USSR*) **25** (1983) 1816.
26. H. LEIBOWITZ (ed.) "Fracture", Vol. 3, "Engineering Fundamentals and Environmental Effects" (Academic Press, New York, 1971) p. 753.
27. S. M. OHR and S. S. CHANG, *J. Appl. Phys.* **53** (1982) 5645.
28. I. H. LIN, *Mater. Sci. Engng* **81** (1986) 325.

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