Structural features, strength and mechanisms of deformation of nanocrystalline materials

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Abstract. Results of recent original studies of structure and properties of nanocrystalline metals and alloys produced by severe plastic deformation and by nanocrystallization of amorphous alloys are considered. High resolution transmission electron microscopy, scanning electron microscopy, and in situ deformation in the column of an electron microscope were used to analyze the structures and the mechanisms of plastic deformation of nanocrystalline materials.

1. Introduction
Metals and alloys can be considered as nanostructured materials if the size of one or several structural parameters such as crystal grain, layer thickness of multilayers, diameter of a tube or a filament in multifilamentary composites, does not exceed 100 nm. These materials can be produced by different processing methods, namely, evaporation-condensation of nanosized particles with further compaction, mechanical activation, super fast quenching from a melt with further crystallization, severe plastic deformation (SPD) [1–6]. It is commonly accepted that a nanocrystalline grain in a nanostructural multiphase material does not exceed a nanophase size (≤ 100 nm). The specific feature of the nanocrystalline materials is the fact that the volume fractions of grain boundary interlayers and of grains bodies are neighbors. Due to their unique strength and functional properties the nanocrystalline materials undoubtedly are of much interest among material researchers. The present paper is aimed to analyze structural features, strength characteristics and plastic deformation mechanisms in a number of nanocrystalline materials.

2. Experimental
Nanocrystalline metals (Ni, Cu, Fe, Ti) and alloys (Al+0,1%Zr, Al+1%Hf, Al+0.5%Ce, Al+0.2%Nb, Al+0,5%Re, Al+10%Mg, Al+1%Hf+0.2%Nb+0.2%Sn, Al+0.5%Ce+0.12%Zr+0.5%Re) produced by severe plastic deformation (SPD) and alloys (Fe73.5Cu7.5Si13.5B9, Fe60Cr18Ni5SiB12 and Fe50Ni10Si3B110) produced by nanocrystallization of amorphous alloys were studied. The structures of nanocrystalline metals and alloys are analyzed by transmission electron microscopy (TEM) JEM – 200KX. Mechanical properties (their strength and plasticity), the hardness of nanocrystalline materials were studied and in situ deformation in the column of an electron microscope was used to analyze the mechanisms of plastic deformation.

3. Structural features of nanocrystalline metals and alloys
The investigation by TEM and by high resolution TEM have shown that FCC nanocrystalline metals (Ni, Cu, Fe, Ti) processed by SPD, are characterized with a high level of internal distortions within a nanosized grain body, which increase with approaching the grain boundary, and a non-equilibrium state of grain boundaries attributed to high dislocation density [1–3, 7–10]. Nanocrystalline Mo and W processed by SPD have “wider” grain boundary interlayers with high dislocation density than FCC-metals [7,9], which is most likely due to low dislocation mobility in BCC metals. Finally, nanocrystalline SPD processed Ti and Co have two types of boundaries in their structure, interphase and grain ones, which, in turn, results in different dislocation densities in them. Unlike the spectrum of disorientation of a conventional crystal the spectrum of disorientation of nanosized grains is shifted to a low angle range [7,9].

The structure of nanosized grains and grain boundaries of nanocrystalline multiphase SPD processed alloys has been investigated in a number of publications [7–13]. Different processing schemes (modes) of nanosized grains formation and phase generation in such alloys were proposed in [7–9,12,13]. It is shown [14,15] that plastic deformation within the range of high strains results in formation (transformation) of internal structure of different alloys by at least three ways (mechanisms), namely, continuous refining of structure, non-monotonous refining with a “threshold” of internal elastic distortions overcoming of which results in structure refining and combination of phase formation and structure refining.

Reasoning from the results of HRTEM studies [7,9,10] one can assume that the crystal lattice of a nanosized grain and a precipitating nanosized phase can be defect-free, with defects, or elastically stressed. According to these publications, the crystal lattice of nanosized grains of alloys with internal elastic distortions similar to that of pure metals is distorted most of all at nanosized grain boundaries. Evidently, only nanosized phases of the smallest size (4–6 nm) may be free of defects. As to grain boundaries of nanosized grains and phases, they can be quasi-amorphous, heavily-distorted crystalline, of a twinning type or ones with incompatibility dislocations similar to a transition layer with another chemical composition.

4. Mechanical properties (strength and plasticity), the hardness of nanocrystalline materials

Mechanical properties of nanocrystalline materials are determined mainly by the nanograin size $d$ and the state of nanograin boundaries. Thus, with decreasing $d$ from 1500 to 5 nm the microhardness $H$ of pure metals may increase by a factor of 2–6 [7,9] (table 1). The yield strength $\sigma_{0.2}$ and ultimate tensile strength $\sigma_u$ of nanocrystalline metals also grow compared to those of the coarse grain state, while the low temperature plasticity $\delta$ decreases (table 1).

| Metal | $d$ change, nm (from – to) | $H$ change, GPa (from – to) | $\sigma_{0.2}$ change, MPa (from – to) | $\sigma_u$ change, MPa (from – to) | $\delta$ change, % (from – to) |
|-------|--------------------------|-----------------------------|-------------------------------------|----------------------------------|--------------------------|
| Ti    | 50000–40                 | 0.8–6.7                     | 275–980                             | 420–1310                         | 29–5                     |
| Fe    | 10000–80                 | 1.8–4.5                     | 375–1010                            | 480–1100                         | 25–15                    |
| Cr    | 1500–70                  | –                           | 313–780                             | 485–960                          | –                       |
| Al    | 1500–200                 | 0.3–1.2                     | 13–26                               | 42–176                           | 20–2                     |
| Mo    | 500–50                   | 1.0–6.0                     | –                                   | –                                | –                       |
| W     | 200–40                   | 3.0–6.2                     | –                                   | –                                | –                       |
| Cu    | 200–70                   | 0.9–1.4                     | 60–365                              | 120–650                          | 60–30                    |
| Cu    | 70–20                    | 1.4–1.8                     | –                                   | –                                | –                       |

Researchers assume that the deviation from the Hall-Petch law at small grain sizes to be connected with modification of deformation mechanism in nanocrystalline materials. This assumption is possible, since it’s known that the stress needed to actuate a dislocation source is rather high in a nanosized grain, e.g. for Ni with a grain size (dislocation source size) of 140 nm it is 870 MPa, the
shear modulus of nickel being 95 MPa. Mechanical properties of some nanocrystalline multiphase alloys are presented in table 2. It is seen that in alloys, similar to pure metals, the transition to a structure with sub-micro- or nanosized grains is accompanied by the increase in microhardness and strength. Besides, there is observed an increase in plasticity in the alloys in the state of superplasticity at high temperatures [9]. Similar to pure nanocrystalline metals, the Hall-Petch dependence for nanophase alloys is valid not within the whole nanophase size range [5,7,9]. In most cases the Hall-Petch law is not valid for alloys with a grain size of 30 nm and less, the coefficient k having a negative value. The possible causes for violation of the Hall-Petch law for nanocrystalline alloys are the same as for pure metals, namely, modification of the plastic deformation mechanism and the weakening of nanograin boundaries.

Table 2. Nanograin size (d), microhardness (H), yield strength (σ_{0.2}), ultimate tensile strength (σ_B) and relative elongation (δ) of coarse-crystalline and nanocrystalline SPD obtained alloys.

| Alloy                  | d change, nm (from – to) | H change, GPa (from – to) | σ_{0.2} change, MPa (from – to) | σ_B change, MPa (from – to) | δ change, % (from – to) |
|------------------------|---------------------------|---------------------------|---------------------------------|----------------------------|-------------------------|
| FeCuNbSiB              | 200–6                     | 6,0–15,0                  | 140–2180                        | 140–2280                   | 0–0.8                   |
| CoFeSiB                | 100–25                    | 10,5–13,0                 | 945–1880                        | 950–2100                   | 0–2.6                   |
| VT-6                   | 25–8                      | 13,0–9,0                  | –                               | –                          | –                       |
| Fe-12%Cr-18%Ni-10%Ti   | 3000–150                  | –                         | 500–1600                        | –                          | –                       |
| Fe-12%Cr-25%Ti         | 2000–50                   | 1,8–6,5                   | –                               | 1500–2500                  | –                       |
| AlNiCeFe               | 2000–80                   | –                         | –                               | 120–1560                   | –                       |
| Al-10%Mg               | 2500–900                  | 0,3–0,5                   | 120–170                         | 180–275                    | 0,5–1,1                 |
| Al-1%Re                | 2000–440                  | 0,3–0,6                   | 30–150                          | 35–180                     | –                       |
| Al-1%Hf                | 2500–760                  | 0,3–0,4                   | 30–160                          | 40–180                     | –                       |
| Al-1%Hf-0,2%Sn         | 2000–110                  | 0,4–0,8                   | 40–140                          | 60–200                     | 0,3–4,8                 |
| 0,2%Nb-0,2%Sn          | 110–60                    | 0,8–1,8                   | –                               | –                          | –                       |
| Al-0,5%Ce-0,1%Zr       | 2000–150                  | 0,4–0,65                  | 40–180                          | 80–220                     | 0,1–5,2                 |
| AlMgLiZr               | 500–20                    | –                         | –                               | 490–680                    | –                       |
| Ni_3Al                 | 1000–60                   | –                         | –                               | 780–3000                   | –                       |

5. Plastic deformation mechanism of nanocrystalline materials

The results of “in situ” deformation investigations [7,9,14,15] show that tensile deformation of nanocrystalline nickel with the grain size of 40–70 nm is realized both through dislocation creep (slip, sliding) and nanograin turn. There arise dislocation pile-ups near grain boundaries in coarser grains. In fine nanograins dislocations are immobile and nanograins undergo the turn which, as a rule, is accompanied by the growth of density of grain boundary dislocations and the formation of a deformation band along grain boundaries of a number of nanograins.

Deformation of nanocrystalline copper with a grain size of 30 nm is realized mainly through a turn of grains relative to each other [9,14]. It has been determined that grains turn relative to each other through the angle from 0.5 to 30° with increasing strain from zero up to failure. The turn of nanograins is evidently caused by internal stresses which are accumulated and concentrated in triple junctions of nanograins and are rearranged and partially decreased after such a turn.

During deformation of nanocrystalline copper the dislocations observed within the grain interior remain immobile. At the same time the amount of defects at nanograin boundaries appreciably increases and nanograin boundaries become “broader” that indicates an active character of deformation processes occurring along nanograin boundaries. The turn of nanograins is most likely accompanied by the occurrence of discontinuities along grain boundaries. Microcracks and micropores are accumulated at grain boundaries, combined and lead to failure.
During tensile deformation of nanocrystalline Ti there also occur an activation of rotation deformation modes and formation of deformation shear bands at boundaries of a number of nanograins. Along with, there also occurs formation of microtwins of similar orientation in nanograins of nanocrystalline Ti with increasing strains [9] that is evidently due to the activation of deformation rotation modes resulting in an enhancement of the material plasticity. Figures 1a–d and 2a–c demonstrate TEM images of one and the same site of microstructure of Al+1% Hf (figure 1) and Al+1%Hf-0.2%Nb-0.2%Sn, and Al-0.5%Ce-0.5%Re-0.1%Zr (figure 2) [9] nanocrystalline alloys subjected to tensile deformation at different strain values increased successively (“in situ” method). As can be seen from figures 1 and 2 the deformation is realized by the dislocation-rotation mechanism (with increasing strain value there occurs a turn of nanograins and the density of grain boundary dislocations increases). Particles of a phase, no more than 10 nm in size, are observed at nanograin boundaries. On the one hand, the phase particles evidently retard with strain the movement of dislocations, and, on the other hand, these particles undergo “dissolution” while interacting with grain boundary dislocations. Concurrently there occurs formation of disperse phases, no more than 1 nm in size, within the nanograin interior that surely results in strengthening of nanograins.

![Figure 1](image1.jpg)

Figure 1. TEM successive images of one and the same area of nanocrystalline Al–1% Hf alloy (d = 60 nm) deformed in the electron-microscope column

a – δ = 9.0; b – δ = 14.5; c – δ = 24.5; d – δ = 36.8%.

![Figure 2](image2.jpg)

Figure 2. TEM successive images of one and the same area of nanocrystalline alloy Al–0.5%Ce–0.5%Re–0.1%Zr (d= 40 nm) deformed in the electron-microscope column

a – δ = 9.0; b – δ = 24.5; c– δ = 67.5%.

The proposed mechanism of plastic deformation of a nanocrystalline material assuming a turn of nanograins and their displacement along boundaries is apparently most close to the actual mechanism of deformation. One should take into account the dependence of strength and plasticity on concentration of the second nanophase in a nanocrystalline alloy. The second nanophase is formed in
the deformation process of material. The elastic modulus changes appreciably with changing a quantitative ratio of matrix and the second phase concentration.

Typical micrographs of fracture surface of nanocrystalline Mo and Cu are presented in [8,9,11,12]. In both cases failure occurs along nanograin boundaries. The only difference is that in the nanocrystalline Cu the microcrack develops at the grain boundary of several similarly oriented grains, which ensures a higher low temperature plasticity of the nanocrystalline Cu.

6. Conclusions
The grain size refinement to several tenths of nanometers in nanocrystalline metals and alloys is accompanied by the considerable growth of their strength and hardness.

The “in situ” study of deformation of FCC, BCC and HCP nanocrystalline materials made it possible to conclude that during tensile deformation of a nanocrystalline material resulting in a decrease of a nanograin size the rotation modes occur which cause the development of mesoscopic deformation shifts at grain boundaries due to their cooperative character. Development of the rotation deformation modes in nanocrystalline materials leads to initiation of rotation plasticity in the form of grain boundary mesoscopic shifts.

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