Nanostructuring of pure metals by severe plastic deformation at cryogenic temperatures

V V Popov¹, E N Popova, V P Pilyugin, D D Kuznetsov and A V Stolbovsky
Institute of Metal Physics Ural Branch of RAS, Ekaterinburg, Russia
¹E-mail: vpopov@imp.uran.ru

Abstract. In the present study the effect of severe plastic deformation by high-pressure torsion in liquid nitrogen on the structure of Cu, Ni and Nb and its thermal stability is analyzed. It is demonstrated that the room-temperature HPT of Cu is accompanied by its dynamic recrystallization. The latter can be suppressed if the deformation temperature is decreased to cryogenic, and the nanocrystalline structure can be obtained, but it degrades at room temperature due to the post-dynamic recrystallization. The HPT of Ni in liquid nitrogen results in nanocrystalline structure with average grain sizes of 80 nm and microhardness of 6200 MPa, this structure being stable at room temperature. In Nb subjected to low temperature HPT the average crystallite sizes are 75 nm, and the microhardness is 4800 MPa. The thermal stability of nanocrystalline structure in Ni and Nb, obtained by HPT in liquid nitrogen, is considerably lower than after the room temperature HPT. The grain growth starts in Ni at as low as 200°C and in Nb at 300°C. Thus, the HPT at cryogenic temperature enables to refine the structure and increase microhardness considerably, but the thermal stability of the as-obtained structures is quite low.

1. Introduction

At present nanocrystalline (nanostructured) materials, i.e. materials with average sizes of grains or other structural units below 100 nm, attract great attention of the researchers due to their unusual mechanical behavior, unique structure and properties [1, 2]. Bulk submicrocrystalline and nanocrystalline materials can be obtained by various techniques of severe plastic deformation (SPD) [3]. However, in pure metals it is quite difficult to obtain a true nanocrystalline state, when crystallites the sizes below 100 nm with high-angle boundaries dominate in the structure, because of the dynamic recrystallization or the onset of saturation state. At the latter no grain refinement and strengthening occur with increasing strain.

Among various techniques of SPD, high-pressure torsion (HPT) demonstrates a number of advantages which make it promising for an achievement of nanocrystalline structure when other methods, e.g. equal-channel angular pressing (ECAP), ensure only the submicrocrystalline state. The main feature of HPT is that it ensures extremely high strain not achievable by other methods. Besides, it should be noted that relatively brittle and high-strength materials may be treated by HPT, and by cooling or heating of anvils it is possible to carry out deformation in a wide range of accurately determined temperatures.

The main scenarios of the development of structure evolution at SPD are analyzed in Ref. [4], according to which the development of dynamic recrystallization is most probable at high T/Tm ratio. The second scenario, when the refinement is limited by the saturation state, is obviously more probable for most metals. According to R. Pippan with coauthors [5], the key process determining the onset of the saturation state preventing further refinement is grain boundary migration under stresses. Finally, the third possible scenario, referred to as amorphization, in case of SPD of pure metals is hardly probable and may be expected only at liquid helium temperatures.

In Ref. [6] R. Pippan et al. analyze the influence of various parameters on the strain at which the saturation state is achieved and on the sizes of structural elements at this state, and it is demonstrated that the deformation temperature has the strongest effect. In case of pure metals, low-temperature HPT is obviously the only way of achievement of the nanocrystalline state.
The goal of the present study is to analyze possibilities of obtaining nanocrystalline state in Cu, Ni and Nb by HPT, and to study thermal stability of the structures obtained.

2. Experimental

Single crystal Cu (99.98 % pure) and commercially pure (99.9 %) polycrystalline Cu was deformed by HPT at room temperature and in liquid nitrogen under the pressure of 4 GPa. Polycrystalline Ni of commercially pure (99.6 %) was deformed by HPT in liquid nitrogen at the pressure of 6 GPa. The specimens of Cu and Ni were 10 mm in diameter. The specimens of Nb 10 mm in diameter were deformed at room temperature under 5 GPa and Nb disks of 6 mm in diameter were deformed in liquid nitrogen under 8 GPa. The initial thicknesses of all specimens were about 0.5 mm and the deformation rate was 0.3 revs/min. To study the thermal stability all the specimens were annealed in the oil-free vacuum at the pressure of 10^{-5} Torr in the range of 100-800°C for 1 h. The structure of deformed and annealed specimens was studied by TEM in JEM-200CX and Philips-CM30 microscopes with subsequent treatment of images by the computerized program SIAMS-600. The standard deviation was ± 10 %.

Microhardness was measured by a special unit in the optical microscope Neophot-21, under the load of 50-100 g, and calculated as \( H = 18192 \cdot \frac{P}{C^2} \), MPa, where \( P \) is load in grams, and \( C \) is the indentation diagonal in \( \mu \)m. Every value of \( C \) was calculated as an average of not less than 9 indentations. The measurement error was ± 2 %.

3. Results and discussion

Since copper is a relatively easily melted metal, its melting point being 1356.6 K, the development of the first scenario, i.e. dynamic recrystallization under SPD is most probable in it. Let’s consider the effect of temperature and purity on the structure of Cu after HPT at room temperature and in liquid nitrogen. Figure 1 demonstrates dependences of microhardness of high-purity Cu on the strain at these two temperatures.

![Fig. 1. Effect of strain by HPT (the number of revolutions, N) and temperature on microhardness of high-purity Cu](image-url)

For the room temperature the \( T/T_m \) ratio is 0.22. It is quite a high value, and thus relaxation processes are quite possible in copper at this temperature. In this case the microhardness at first slightly increases and then drastically drops and remains at one and the same level up to
the highest strains studied. After the HPT by 1-3 revolutions the structure consists mainly of submicrocrystalline grains the average size of about 250 nm. In TEM images an intricate diffraction contrast indicating high level of internal stresses characteristic of the structures obtained by HPT is observed in some grains, but the number of such grains is not large and the dislocation density in most grains is relatively low. There are also some coarse grains (the sizes of up to 600 nm) which testifies that along with the dynamic recovery the dynamic recrystallization is also possible in the case considered.

With the strain increasing up to 5 revolutions the structure of Cu changes considerably, a nonuniform structure forming with wide grain size distribution. Grain boundaries are thin and straight and dislocation density in grains is low, which testifies an intensive dynamic recovery and dynamic recrystallization. Note, that at this strain the microhardness drastically drops. At further strain increase up to 10 revolutions the structure and microhardness practically do not change, as the saturation stage is achieved.

To suppress dynamic recovery and recrystallization HPT was carried out at -193°C (in liquid nitrogen), the T/T_m ratio being only 0.06 for this temperature. As seen from Fig. 1, the microhardness behavior in this case considerably changes from that of observed at room temperature. In the strain range of 1-5 revolutions the microhardness gets markedly higher and practically does not change with the increasing strain. The structure in this case is strongly distorted and consists of grains with the average size of about 200 nm (Fig. 2a). It is more uniform than after the same deformation at room temperature, and there are no coarse dislocation-free grains in it. When the strain is increased up to 10 revolutions, the microhardness drastically drops down much lower level, than after the room temperature HPT (Fig. 1), and the structure changes as well. It consists mainly of recrystallized dislocation-free grains the sizes of about 500 nm (Fig. 2b), testifying the post-dynamic recrystallization.

It should be noted that in specimens deformed at -193°C by 1-5 revolutions the microhardness decreases at room-temperature ageing. It means that in these specimens the post-dynamic recrystallization also occurs though much slower than after the higher strain (10 revolutions).

Along with the deformation temperature decrease the recovery and recrystallization are considerably affected by the presence of impurities. Figure 3 demonstrates the microhardness of commercially pure copper (99.9 %) versus the strain by HPT at room temperature and in liquid nitrogen. For the room temperature deformation the microhardness behavior does not differ substantially from that of high-purity Cu, but the absolute values of the former are considerably higher. In the range of 1-3 revolutions the
microhardness changes only slightly, and at higher strains it markedly drops, though not as drastically, as in high-purity Cu, and the saturation state is not achieved. In case of low-temperature deformation of commercially pure copper the microhardness markedly increases with the increase of strain from 1880 MPa after 1 revolution up to 2070 after 10 revolutions (Fig. 3). Thus, it can be concluded that the dynamic and post-dynamic recrystallization is really retarded by the impurities present in the commercially pure Cu, and it is confirmed by TEM studies. An average size of crystallites in the commercially pure Cu directly after the low-temperature HPT by 10 revolutions is 60-70 nm (Fig. 4a), i.e. a true nanocrystalline structure is formed. However, this state is unstable, and at room temperature ageing the microhardness drops and grain sizes increase. After only 10 days of room-temperature ageing the microhardness drops down to 800 MPa and grain sizes get microcrystalline (Fig. 4b).

![Fig. 3. Effect of strain by HPT (the number of revolutions, N) at room temperature and in liquid nitrogen on microhardness of commercially pure Cu](image_url)

![Fig. 4. Structure of commercially pure copper directly after the HPT in liquid nitrogen by 10 revolutions (a) and after the further room-temperature ageing for 10 days (b)](image_url)
Thus, it is possible to obtain the true nanocrystalline structure in the commercially pure Cu by HPT at cryogenic temperatures, but this structure is unstable even at room temperature. It is of interest to compare the results obtained in this work for Cu subjected to HPT at room temperature with those published in [7] for Cu-4.9%Co alloy after similar treatment. In the cited paper it is demonstrated that independently on the initial microstructure and phase composition the steady-state is reached after 1-2 anvil rotations, whereas in our experiments this state is reached in high-purity Cu after 5 revolutions (see Fig. 1) and in commercially pure Cu the microhardness decreases gradually beginning from 3 revolutions, but the steady-state is not achieved even after the HPT by 10 revolutions (Fig. 3). Moreover, the difference is not only in the earlier onset of the steady state in the Cu-Co alloy, but in the level of properties characteristic of this state. In the alloy the torsion torque increases with the growth of strain up to 1-2 anvil rotations and then remains unchanged. In high-purity copper the microhardness reaches high level after 1 revolution, then it practically does not change up to 3 revolutions, decreases with strain growth to 5 revolutions and does not change with further increasing of strain. These regularities can be explained as follows. In copper both high-purity and commercially pure the first scenario of structural evolution under SPD is realized, i.e. the steady-state is reached due to dynamic recrystallization. In Cu-based alloys, particularly in Cu-4.9% Co alloy, the second scenario is realized, because the dynamic recrystallization is retarded by the doping element present both in solid-solution and precipitates. In this case the steady state is achieved when the Cu-matrix reaches its stable composition and contains 2.5 % of Co in the solid solution due to partial decomposition or precipitation of Co under HPT.

The melting temperature of Ni is 1726 K, which is much higher than that of Cu, and for Ni the $T/T_m$ ratio at room temperature is 0.17. Thus, the room temperature deformation of Ni is hardly accompanied by the post dynamic recrystallization, though the processes of dynamic recovery and recrystallization cannot be completely excluded. The structure of Ni after the HPT at room temperature was studied in a number of publications [8-11], and it was demonstrated that a uniform submicrocrystalline structure can be formed, but the nanocrystalline state is not achieved because of the saturation state. It was also demonstrated that the dispersivity of structure and its thermal stability increase with the decrease of the material purity.

As demonstrated in the present study, the microhardness of Ni (99.6 % pure) after HPT in liquid nitrogen by 5 revolutions is as high as 6200 MPa and practically does not vary along a specimen’s radius. The microstructure is also uniform along radii, with the average grain size of 80 nm. The formation of uniform structures and constant microhardness after the HPT with high enough strains was reported in a number of studies. For example, in Refs [12, 13] it was found in Ni and Al after the room temperature HPT, and in [13-15] in Nb after the HPT in liquid nitrogen. Note, that in the present study the higher microhardness and more dispersed structure have been achieved compared to Ni deformed by HPT at room temperature [10, 11].

The typical electron micrographs of the structure of Ni after the HPT in liquid nitrogen by 5 revolutions are shown in Fig. 5. On the first sight, the structure obtained seems uniform, consisting of equiaxed grains and subgrains, especially in the bright-field images (Fig. 5a). All the electron-diffraction patterns are ring-wise, with a large number of reflections in the Debye rings, which testifies small crystallite sizes and high-angle misorientation. However, a peer view of a number of dark-field images shows that there are also the traces of microbands in the structure, divided into fragments with gradually changing low-angle misorientation (Fig. 5b).
Curved grain boundaries, not always clearly seen, and distorted contrast inside crystallites resulting from high dislocation density are characteristic of the high-strained structures. These features indicate high level of internal elastic stresses and indirectly evidence a specific non-equilibrium state of grain boundaries. We observed an analogous structure in Nb subjected to HPT at room and cryogenic temperatures [14-18], and the specific state of grain boundaries was confirmed by the Mossbauer studies [19-21].

Based on the results of TEM studies it can be concluded that in Ni at low temperature HPT the deformation microbands with localization of strain along their boundaries are formed along with the formation and refinement of cellular structure. With the accumulation of high strain the fragmentation of microbands results in their gradual disappearance, but they don’t completely vanish at the strain studied.

Thermal stability of the structure obtained in Ni by HPT in liquid nitrogen was studied by TEM and microhardness measurements. The structure is absolutely stable at room temperature. Neither grain growth nor microhardness decrease was observed after its several months ageing, i.e. it does not undergo the post-dynamic recrystallization. However, its thermal stability is not high. Only at the lowest annealing temperature (100°C) the structure and microhardness practically do not change compared to the strained state.

Thermal stability of Ni deformed by HPT at room and cryogenic temperatures is compared in Fig. 6. We compare our results on Ni after the HPT in liquid nitrogen with those obtained in [10] for Ni of almost the same purity, subjected to HPT at room temperature. As seen from this figure, the microhardness of Ni deformed in liquid nitrogen only slightly changes at annealing up to 200°C, indicating only the recovery processes in this temperature range. On the other hand, noticeable changes in the structure are observed after the annealing at this temperature. Thin fragmented deformation microbands are not observed any more. There are still areas with fine crystallites, curved boundaries and high dislocation density, but along with them one can see areas of other type, with coarser grains. The average crystallite size increases to about 140 nm, though, judging from TEM, the recrystallization does not proceed at this temperature. The driving force of recovery and recrystallization is a system’s tend to reduce the elastic energy, whereas the driving force of grain boundary migration is its tend to reduce the energy of crystallite boundaries. According to the classical view, transformations of structure in a strained metal at annealing begin from recovery followed by recrystallization at higher temperatures, and the normal grain growth is possible only after that. In ultrafine-grained (UFG) materials processed by SPD the sequence of structural transformations may be somewhat different. In such materials the crystallite boundaries energy must be high enough, especially taking into account their specific non-equilibrium state with an enhanced energy. As a result, it is quite possible that migration of boundaries of some crystallites may...
take place simultaneously with recovery and start before recrystallization. It is just the case at 200°C annealing of Ni specimens deformed by HPT in liquid nitrogen. An analogous situation, the superposition of recovery and grain boundary migration, was observed at annealing of high purity Ni after the room temperature HPT [10].

The further grain growth and considerable decrease of microhardness are observed at the increase of the annealing temperature up to 300°C. Taking into account the TEM data, demonstrating an appearance of relatively coarse crystallites with low dislocation density and thin straight boundaries, one can conclude that at this temperature the recrystallization starts.

At the 400°C annealing the microhardness drastically drops down to 2700 MPa, and the completely recrystallized microcrystalline structure is formed.

According to Fig. 6, the temperature dependences of microhardness and grain sizes of Ni deformed by HPT at room and cryogenic temperatures are in general similar, but the changes of these parameters in the latter are observed at lower annealing temperatures. Thus, after the HPT in liquid nitrogen grain growth and microhardness drop are obvious at as low annealing temperature as 200°C, whereas in Ni deformed at room temperature these changes are found only at 400°C.

Consequently, it can be concluded that the thermal stability of structure of Ni deformed at cryogenic temperature is considerably lower than in case of the room temperature deformation.

![Fig. 6. Microhardness (a) and average grain size (b) of Ni 99.6 % pure (1) after the HPT in liquid nitrogen (present work) and of Ni 99.5 % pure (2) after the room temperature HPT (ref. [10]) versus the annealing temperature](image)

Thus, the decrease of HPT temperature from room to cryogenic ensures more intensive refinement of structure in commercially pure Ni, but on the other hand the structure obtained is less stable at further annealing.

Niobium is a refractory metal, its melting temperature being 2741 K. For room temperature the T/T_m ratio is 0.11, and for liquid nitrogen it is as low as 0.03. That is why dynamic recovery and recrystallization at SPD of Nb is excluded even at room temperature.

As shown in [17, 18], the room temperature HPT of Nb results in the structure intermediate between submicro- and nanocrystalline, with average crystallite sizes of 100-120 nm and
microhardness of about 2500 MPa. The onset of the saturation state was found at HPT by 5 revolutions.
In case of HPT in liquid nitrogen much higher microhardness and more dispersed structure are achieved, and the saturation state starts from 3 revolutions. At such deformation mode the nanocrystalline structure, uniform along specimen radius, with crystallite sizes of 75 nm and microhardness of 4800 MPa is formed in Nb. This structure is absolutely stable at room temperature and does not degrade for several months, i.e. it does not undergo post-dynamic recrystallization, but its thermal stability, as in case of Ni deformed in liquid nitrogen, is not high.
Figure 7 demonstrates microhardness and crystallite sizes of Nb after HPT in liquid nitrogen versus the annealing temperature.
After the annealing at 100-200°C microhardness of nanocrystalline Nb somewhat decreases, whereas the structure and crystallite sizes practically do not change. In most of grains the curved contrast is retained after the annealing and all electron diffraction patterns are ring-wise. Thus, it may be concluded that the microhardness decrease is exclusively due to recovery.

![Figure 7](image.png)

Fig. 7. Microhardness (circles) and average grain size (triangles) of Nb after HPT in liquid nitrogen versus the annealing temperature

With the increase of the annealing temperature up to 300°C the average grain size does not noticeably change, but along with the grains the sizes of less than 100 nm there appear relatively coarse recrystallized grains with low dislocation density, the sizes of more than 300 nm (Fig. 8a). Thus, it can be concluded that in this case the grain growth starts at as low as 300°C, though the microhardness does not drastically drop, because the fraction of recrystallized grains is small.
After the annealing at 400°C the fraction of the recrystallized grains increases, and the structure gets submicrocrystalline (Fig. 8b), and further decrease of microhardness is observed.
At higher annealing temperatures, beginning from 500°C the intensive grain growth is observed, and grain sizes are about 1 μm and even coarser (Fig. 8c). The microhardness drastically drops, and it can be concluded that the structure is completely recrystallized.
It is of interest to compare the thermal stability of the structure of Nb deformed at room and cryogenic temperatures. After the room temperature HPT the structure is stable up to 600°C,
and an intensive grain growth is observed only at 700°C [18], whereas in specimens deformed in liquid nitrogen the intensive grain growth starts at as low as 400°C. Thus, the low temperature HPT of Nb, similarly to Ni, enables to obtain the true nanocrystalline structure, but this structure demonstrates low thermal stability.

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![Fig. 8. Structure of Nb after HPT by 3 revolutions at -193°C and further annealing at 300 (a), 400 (b) and 500°C (c)](image)

**Fig. 8. Structure of Nb after HPT by 3 revolutions at -193°C and further annealing at 300 (a), 400 (b) and 500°C (c)**

**Conclusions**

In most cases the decrease of HPT temperature down to that of liquid nitrogen enables to obtain in pure metals the nanocrystalline structure with non-equilibrium grain boundaries, high internal stresses and record-breaking high microhardness. However, the thermal stability of this structure is low. In cases of metals with low melting point (Cu) the nanocrystalline structure degrades even at heating up to the room temperature because of post-dynamic recrystallization. In metals with higher melting temperatures (Ni and, especially, Nb) the structure is stable at room temperature, but at annealing it degrades at lower temperatures than that after the room temperature HPT.

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