Effect of severe plastic deformation on the structure and properties of Ni-Cu alloys

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Abstract. The structure of Ni-Cu alloys processed by high pressure torsion by 5 revolutions at room temperature (saturation stage) has been studied by the methods of transmission electron microscopy and microhardness measurements. It is demonstrated that moving from copper possessing lower melting temperature and lower stacking fault energy (SFE) to nickel the melting temperature and SFE of which are considerably higher, the submicrorystalline structure of alloys is markedly refined (by about a factor of 2), whereas the microhardness increases by more than 1.5 times. The simultaneous effect of two factors (changing of homological temperature and SFE) results in the non-linear dependence of these parameters (crystallite sizes and microhardness) on alloy composition.

1. Introduction

Nowadays, great attention of materials science researchers is attracted by metal materials in which nanocrystalline (or submicrorystalline) state is obtained by severe plastic deformation (SPD), because these materials demonstrate new unique properties, such as enhanced strength, plasticity, specific diffusion properties, etc. [1]. However, it is not always possible to obtain a true nanocrystalline state, i.e. the structure in which crystallites the sizes of less than 100 nm with high-angle boundaries are dominating. The main limitation in fabricating the nanocrystalline structure is the onset of the so-called saturation state under the SPD, when with increasing strain there is no more refinement and strengthening of the material [3,4]. At this stage there is equilibrium between generation and annihilation of defects (vacancies, dislocations, high- and low-angle boundaries). The key process limiting structure refinement is migration of grain boundaries. The smallest grain sizes achievable under SPD are determined, first of all, by the type of a material, particularly, by its crystal lattice, melting temperature and stacking fault energy (SFE) [5]. Of not less importance are such factors as deformation temperatures, phase transformations and the possibility of two concurrent mechanisms of grain refinement, deformation twinning and dislocation activities, as demonstrated for steels in two recent publications [6,7].

Copper and nickel are quite plastic metals and can be deformed without fracture up to high strains at relatively low temperatures, which is necessary for the formation of ultrafine-grained (UFG) structure, and that is why their structure and properties after SPD were studied by numerous researchers [8]-[15] et al.. These studies have shown an important role of deformation temperature and material purity. Thus, in [9]-[11] it is demonstrated that when the deformation temperature is decreased from room to liquid nitrogen the average crystallite size in Ni and commercially pure Cu gets considerably smaller and the nanocrystalline structure is formed.

Another factor strongly affecting structure formation under the SPD is the stacking fault energy. There are experimental data on different effect of SPD on the materials with different SFE. In the
materials with high SFE the dominating role is played by dislocation glide [[16][6]-[17]. In such materials dislocation nets and low-angle boundaries develop into high-angle boundaries by dislocation redistribution and/or grain rotation. For materials with low SFE, in which twinning is dominating, the grain refinement was considered in less detail, but there are experimental data that at equal parameters of SPD the obtained grain sizes can be smaller in the materials with lower SFE [[5],[18]. The role of SFE in Cu, Cu-Al and Cu-Ni alloys subjected to ECAP and HPT is considered in [19-21], where it is demonstrated that homogeneous microstructures in materials with high or low SFE are much more readily achieved than in metals with medium SFE.

The Ni-Cu alloys considered in the present study are of interest because in this system composition and, consequently, SFE, can be changed continuously between constituent elements, which have relatively low SFE in Cu (78 mJ/m²) [5] and high SFE in Ni (160 mJ/m²) [22], which gives chance to analyze the effect of SFE on the structure formation under the SPD.

The goal of the present study is to analyze specific features of the structure of Ni-Cu alloys in its saturation state (refinement and strengthening) after high pressure torsion at room temperature, and to reveal factors responsible for their capability for nanostructuring.

2. Experimental
The Ni-Cu alloys of three compositions (10, 34 and 90 at. % Cu) were studied in the present paper along with polycrystalline Ni 99.6 % pure and commercially pure Cu, subjected to severe plastic deformation. Initial specimens of 10 mm diameter and 0.5 mm thick were deformed at room temperature by 5 revolutions of high-pressure torsion in Bridgman anvils. The average pressure of axis compression of disks was 6 GPa which reliably excluded their slipping at torsion; the angular velocity of anvils rotation was 0.3 rev/min. According to preliminary studies, in all the specimens under study this treatment results in the saturation state.

The structure of as-deformed specimens was studied in transmission electron microscopes JEM-200CX and Philips CM30 with following treatment of the images with the computerized program SIAMS-600. Microhardness was measurement by a special unit adjusted to optical microscope Neophot-21 and calculated by formula H=18192 P/C², MPa, where P is load in grams, and C is indentation diagonal in microns. Every value of C was averaged over not less than 9 indentations. The microhardness measurement error was in average about 2-3 % and did not exceed 5 % with confidence probability of 0.95.

3. Results and discussion
According to numerous publications (see, e.g., [23][3]-[24]), the structure fragmentation under deformation proceeds as follows. With the increasing strain dislocations are accumulated and localized in cell walls, and misorientation between cells is growing, which results in the formation of UFG structure, the basis of submicrorcrystalline or nanocrystalline grain structure. Further deformation causes activation of rotation deformation modes throughout a specimen bulk, ensuring the achievement of the steady-state deformation (saturation state). The determining factor in structure fragmentation is dislocation mobility, which can be decreased by two ways, by decreasing of SFE (for example, by alloying) and by lowering of deformation temperature (or by decreasing the homological temperature if one deals with different materials).

The structure of Cu after HPT is shown in Fig. 1. It is seen that the HPT by 5 revolutions of anvils results in the formation of non-uniform structure with wide grain size scattering (from 110 to 740 nm) and average grain size of ~ 280 nm. Analysis of this structure (drastic contrast changing in dark-field images, point-wise reflections in the Debye rings in the electron diffraction patterns, intricate dislocation contrast in some grains and its absence in the others, wide grain size scattering, the presence of coarse grains with low dislocation density) allows to conclude that under the HPT not only relaxation processes, but even dynamic recrystallization are possible in copper. In some grains one can see a striated contrast which, in an opinion of some authors [25], indicates the grain boundary structure
recovery. The results obtained are in agreement with the previous observations on high-pure and commercial-purity copper after room temperature HPT [14].

The structure of Ni-90%Cu alloy is shown in Fig. 2. It does not appreciably differ from that of copper. As in Cu, in some grain boundaries the striated contrast is observed, indicating relaxation processes and an approach of grain boundary state to equilibrium. There are areas with wide crystallite size scattering, and in small crystallites dislocation density is low and they have a polyhedron shape with high-angle boundaries. In neighboring coarser crystallites dislocation density is high, and smooth changing of contrast in dark-field images testifies the presence of low-angle boundaries. In the electron-diffraction patterns one can see a great number of point-wise reflections in the Debye rings and slight azimuth reflection blurring (insert in Fig. 2b).

![Fig. 1. The structure of copper after HPT by 5 revolutions at room temperature: a - bright-field image; b – dark-field image in (111)\textsubscript{Cu} reflection and electron diffraction pattern](image1)

In other areas coarse crystallites of polyhedral shape with low dislocation density are observed, and, in some of them, the dislocation contrast changes smoothly indicating the presence of low-angle boundaries. Thus, in general, it can be concluded that dynamic recrystallization is not suppressed in copper alloyed with 10 at. % of Ni. However, in the alloy the grain size scattering (130-470 nm) and the average grain size (250 nm) are lower compared to pure Cu.

![Fig. 2. The structure of Ni-90at.%Cu alloy after HPT by 5 revolutions at room temperature: a - bright-field image; b – dark-field image in (111)\textsubscript{Cu} reflection and electron diffraction pattern](image2)

Now let’s consider the effect of Ni alloying with Cu on the structure obtained at the steady-state deformation after 5 revolutions of HPT at room temperature. The structure of Ni after such treatment is shown in Fig. 3. It is characterized with appreciably curved crystallite boundaries, not always clearly seen, curved contrast inside crystallites and high dislocation density. All these features indicate high level of internal stresses and indirectly testify the specific non-equilibrium state of grain boundaries. In dark-field images one can see drastic change of contrast between neighboring crystallites characteristic of high-angle boundaries, and smooth contrast changing inside crystallites
indicating the presence of low-angle boundaries as well. The average grain size in Ni is 145 nm with grain-size scattering from 50 to 250 nm, i.e., as it was expected, the structure is much more uniform and dispersed compared to that of Cu and Cu-10at.%Ni alloy.

Fig. 3. The structure of Ni after HPT by 5 revolutions at room temperature: a - bright-field image; b – dark-field image in (111)_{Cu} reflection and electron diffraction pattern

When Ni is alloyed with Cu, one could expect, on the one hand, the formation of uniform and less dispersed structure, as the homological temperature of such alloy is increased due to much lower melting temperature of copper. On the other hand, the SFE is decreased as the SFE of Cu is almost by a factor of 2 lower than that of Ni, and this factor could affect the structure oppositely. The analysis of TEM data has shown that combination of these two factors results in practically no changes of structure when Ni is alloyed with 10 at.% of Cu and only slight changes of structure in case of alloying it with 34 at.% of Cu (Fig. 4).

Fig. 4. The structure of Ni-34at.%Cu after HPT by 5 revolutions at room temperature: a - bright-field image; b – dark-field image in (111)_{Cu} reflection and electron diffraction pattern

Figure 5a demonstrates dependence of average crystallite sizes on alloy composition. As mentioned above, when Cu is alloyed with 10 at % of Ni, the crystallite sizes and their scattering decrease, which could result mainly from the effect of two factors, decreasing of homological temperature (as Ni has much higher melting temperature) and changing of SFE (as the latter is 2 times higher in Ni). When the homological temperature is decreased, the structure is refined due to decreased dislocation mobility and suppression of relaxation processes. As seen from the structure obtained, these processes are really partly suppressed compared to those in pure copper, but not completely. On the other hand, alloying with Ni could increase the SFE and affect the structure oppositely. That is why some grain refinement in Ni-90at.%Cu alloy compared to Cu is most probably due to the decreasing homological temperature.

Absolutely another situation is observed when Ni is alloyed with Cu. When Cu concentration reaches 34 at %, the structure and crystallite average sizes change only slightly compared to pure Ni, but the crystallite size scattering somewhat increases. This slight influence of Ni alloying with Cu is
probably due to the effect of two factors acting oppositely. On the one hand, when Cu content in an alloy increases, its homological temperature gets higher, and it should result in coarser crystallite sizes. On the other hand, the decrease of SFE in this case must affect oppositely. Obviously, the effect of these two factors in Ni-rich alloys is compensated, and up to 34 at. % of Cu there is no appreciable change in crystallite sizes of alloys compared to those of pure Ni, and the average crystallite size obtained is considerably smaller than that predicted by the rule of mixtures.

![Graphs showing average crystallite size and microhardness](image)

Fig. 5. Average crystallite size (a) and microhardness (b) of Ni-Cu alloys after 5 revolutions of room temperature HPT versus their composition. Dashed line – rule of mixtures.

The composition dependence of microhardness (Fig. 5b) correlates with the dependence of average crystallite size. In Ni-rich alloys the growth of Cu concentration almost does not affect the microhardness, whereas from the side of Cu-rich alloys the microhardness drastically decreases when approaching to pure Cu, but it should be stressed that in all the composition range the microhardness is higher than that predicted by the rule of mixtures.

If only one parameter affected the crystallite average size and, consequently, microhardness, dependently on composition, for example, homologous temperature or SFE, then these parameters would change with composition linearly, i.e. in accordance with the rule of mixtures. The fact that it is not so, indicates that the structure and microhardness are affected by both factors. The results obtained allow to conclude that in Cu-rich alloys the determining role in structure formation is played by the homological temperature, whereas in Ni-rich alloys the changes of both homological temperature and SFE with composition to a great extent compensate each other acting in opposite directions.

4. Conclusion

The effect of composition of Ni-Cu alloys on their structure in the saturation state (steady-state deformation) obtained under room temperature HPT, has been studied and analyzed. It is demonstrated, that with composition changing average crystallite sizes and microhardness are changed non-linearly.

In Cu-rich alloys the increasing concentration of Ni results in considerable structure refinement and microhardness increase. The determining role in structural changes in this concentration range is obviously played by decreasing homologous temperature with increasing Ni content.

A completely different situation is observed in Ni-rich alloys. When up to 34 at. % of Cu are added to Ni, the crystallite sizes and microhardness change only slightly, which obviously results from the effect of two factors acting oppositely and to a great extent compensating each other, namely, the increase of homologous temperature and decrease of SFE.

The analysis of concentration dependences of average grain sizes and microhardness of Ni-Cu alloys has shown that the former are smaller and the latter is higher than those predicted by the rule of mixtures. It can be suggested that this results from a considerable effect of SFE changing dependently on alloy composition. Thus, the role of SFE in structure refinement and strengthening is an important factor, which must be taken into account in fabrication of alloys with a given complex of properties.
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