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Title: Texture development in a nanocrystalline Pd-Au alloy studied by synchrotron radiation

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Abstract: Using synchrotron radiation, a comparison is made between torsion textures formed in nanocrystalline (nc) and coarse grained (cg) samples of the Pd-10at.%Au alloy after identical shear strains. Intensities of characteristic components of shear texture are several times stronger in the cg sample than those in the nc one, which is regarded as evidence of increased activity of grain boundary mediated deformation in the nc sample. Dislocation slip and twinning do not significantly contribute to the plasticity of the nc alloy.

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Dear Editor

please find enclosed the manuscript of an article entitled "Texture development in a nanocrystalline Pd-Au alloy studied by synchrotron radiation" by Yu. Ivanisenko, W. Skrotzki, R. Chulist, T. Lippmann, L. Kurmanaeva which we would like to submit for publication in "*Scripta Materialia*". Using synchrotron radiation, a comparison was made between torsion textures formed in nanocrystalline (mean grain size of 13 nm) and coarse grained samples of the Pd-10at.%Au alloy after identical shear strains. We found that intensities of characteristic components of the shear texture were several times stronger in the coarse grained sample than those in the nanocrystalline one, which was regarded as evidence of increased activity of grain boundary mediated deformation in the nc sample. Dislocation slip and twinning did not significantly contribute to the plasticity of the nc alloy.

Analysis of the texture formed during plastic deformation could be very helpful in estimating the contributions to strain of various deformation mechanisms. Despite of it texture measurements are used very seldom for that purpose: to our best knowledge there are only four papers describing the texture development in truly nanocrystalline materials, i.e. when the grain size is less than 30 nm. Our investigation demonstrated the lack of texture in nanocrystalline sample after shear strain as large as 1, which is an ambiguous evidence of dominance of grain boundary sliding at such a small grain size. This is very important finding, which will be interesting for scientists doing their research in the field of nanostructured materials and their mechanical behaviour.

We believe that our paper would be ideal for publication in "*Scripta Materialia*". All authors are in agreement with the submission of the manuscript. This would be the first publication of this manuscript, and it is not being under consideration for publication elsewhere. We look forward to hearing from you shortly in response to our submission.

Yours sincerely

Yulia Ivanisenko (corresponding author, on behalf of the five authors)

Dear Professor Ke Lu,

thank you very much for sending us the reviewer's report to our manuscript. It addresses very important question about the contribution of partial dislocations and twinning to plasticity of nc Pd alloy. Indeed several MD simulations made in the group of Prof. Yamakov, predicted partial dislocation activity in nc metals. On the other hand, H. Swygenhoven et al. in Nat Mat 3(2004)399 conclude that "The high-stress/short-time restrictions inherent to MD make it impossible to determine the true rate-limiting processes, and therefore it is not obvious whether the observation of extended partial dislocations as the dominant deformation mechanism in some of the f.c.c. materials would be expected during experimental observations. Therefore, atomistic simulations on their own are at present not suited for setting up a deformation map analogous to that used in constitutive plasticity for nanocrystalline structures, where the suggested mechanisms are quantified in terms of applied stress and grain size ". Indeed, twins and partial dislocations were observed in cold rolled Pd by Makmann et al, as well as after HPT deformation in our previous works [Yu. Ivanisenko, L. Kurmanaeva, J. Weissmueller, K. Yang, J. Markmann, H. Rösner, T. Scherrer, H.-J. Fecht. Acta Mater. 2009;57:3391, Yu. Ivanisenko, W. Skrotzki, R. Chulist, T. Lippmann, K. Yang, L. Kurmanaeva, H.-J. Fecht. J. Mater. Sci. 2010;45:4571]. But observation of twins in some grains does not give us an answer about the quantitative contribution of twinning to plasticity of nc material. Twins can produce a total shear deformation $\gamma_{tw} = s_{tw} f_{tw}$, where s_{tw} is the twinning shear, $s_{tw} = 0.7$ for fcc lattice, and f_{tw} is a volume fraction of twins. Therefore even if we suppose that 100% of deformed material experienced twinning, we can obtain a shear strain of 70%. But reviewer writes about "very fine nanoscale twins"! How much can they contribute?

Though it is very difficult to make an accurate estimate of f_{tw} for grain sizes as small as 15-20 nm, we roughly calculated the number of twinned grains after HPT deformation for $\gamma = 1$ in several TEM micrographs. It appeared that only 2 to 3% of the grains contain very narrow, 1-2 nm thick, twins. Thus, the volume fraction of twins is very small and their contribution to shear strain in nc Pd-10% alloy is negligible. That is why the texture components resulting from twinning were not revealed in the ODFs of this alloy, even when based on synchrotron measurements. In our previous paper (Yu. Ivanisenko, et al J. Mater. Sci. 2010;45:4571) we observed a weak texture formation with components corresponding to deformation twinning. But in the samples used there, strain induced grain growth took place simultaneously with the mean grain size increasing to 24 nm and the amount of grains >30 nm being larger than 30%, while in the as-igc state it was less than 1%. Therefore we believe that both dislocation slip and twinning can take place in larger grains with the size >30 nm. To compare, in present investigation a slight strain induced grain growth was also observed, but the fraction of grains with the size >30 nm was less than 10%. It should be also mentioned that [Wu and Zhu, 2008, Zhu, 2012] experimentally observed an inverse grain size effect on twinning, i.e. for grains smaller than an optimum grain size which depending on the material is about several tens of nanometers becomes more difficult. The grain size in our investigation seems to be below this optimum grain size. We added the discussion on this subject in the manuscript (pages 4 and 5, highlighted with a blue color).

Texture development in a nanocrystalline Pd-Au alloy studied by synchrotron radiation

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Abstract

Using synchrotron radiation, a comparison is made between torsion textures formed in nanocrystalline (nc) and coarse grained (cg) samples of the Pd-10at.%Au alloy after identical shear strains. Intensities of characteristic components of shear texture are several times stronger in the cg sample than those in the nc one, which is regarded as evidence of increased activity of grain boundary mediated deformation in the nc sample. Dislocation slip and twinning do not significantly contribute to the plasticity of the nc alloy.

Keywords: nanocrystalline metal, inert gas condensation, high pressure torsion, grain boundary sliding, texture

There is still a lack of understanding of the deformation mechanisms operating in nanocrystalline (nc) materials. The results collected until now are controversial. On the one hand, theoretical considerations [1], MD simulations [2,3], and some experiments [4,5] favour grain boundary mediated processes, on the other hand, very low ductility and relatively low strain rate sensitivity (order of 0.05) typically revealed in nc metals point towards dislocation mediated mechanisms [6,7,8,9]. Analysis of the texture formed during plastic deformation could be very helpful in estimating the contributions to strain of various deformation mechanisms, because such processes like dislocation slip and mechanical twinning occurring in specific crystallographic planes and directions lead to preferred orientations depending on different factors like stacking fault energy, deformation temperature and others. On the other hand, in general grain boundary sliding leads to randomization of the existing texture. Texture analysis has been frequently used in studies of conventional superplastic straining [10,11], and several such attempts were also undertaken recently in nc materials [12,13,14,15]. In particular, in a previous paper synchrotron radiation was used to study the texture development in a Pd-10at.%Au alloy as a result of shear deformation under high pressure (after high pressure torsion, HPT) with a shear strain of 15. It was found that the intensity of typical shear texture components was generally lower in the nc sample as compared with that in the coarse grained (cg) counterpart. This was interpreted as indication for grain boundary sliding in the nc sample [15]. However, the difference in texture intensities was not very pronounced, most likely because the shear strain of 15 was large enough to give rise to some stress-induced grain growth in the nc sample from about 13 nm to 24 nm. On the other hand, the mean grain size of the cg sample was refined from 100 μm to 315 nm. In fact, the initial microstructures were too different as compared with the final ones. In order to eliminate this problem, experiments were performed under the same HPT conditions as described in Ref. [15], but to much lower shear strain. As expected, the texture formation was significant in the cg sample, while it was practically negligible in the nc one. At the same time, neither the mean grain size nor the grain size distribution in nc sample had changed so much as a result of HPT.

Nanocrystalline Pd-10at.%Au samples with a diameter of 8 mm and thickness of typically 0.3 mm were produced by inert gas condensation (igc) using parameters and procedures as described in Refs. [16, 17].

As-igc samples had a very uniform nc microstructure with a mean grain size of 13(1) nm (Fig. 1a,b). Careful inspection reveals very few twin boundaries (about 6% of grains contain

single fine twin lamellae) in the as prepared samples. Dislocations can only be observed in a small fraction of grains. Triple points exhibit angles near 120° characteristic of an equilibrated grain structure. As reference, a cg Pd-10at.%Au specimen with a mean grain size of about 100 μm and the same dimensions was produced by annealing. Quasi-hydrostatic HPT was conducted under a pressure of 4.5 GPa in a SchenckTM testing machine. As-igc and coarse crystalline samples were twisted at a constant rotation rate of 5 deg. s^{-1} for 5° .

For local texture measurements small pins (1.5 mm $\times$ 0.2 mm $\times$ 8 mm) were cut by spark-erosion from the disc-shaped HPT specimens in radial direction as shown in Fig. 2. Quantitative texture measurements in a 0.08 mm³ (nc) and 0.12 mm³ (cg) volume of the pin were performed with high energy (100 keV synchrotron radiation at beamline HARWI II at DESY-HASYLAB (Hamburg, Germany) in the HPT disc centre as well as at locations corresponding to $r = 1.1$ mm, 2.2 mm and 3.3 mm from the centre as indicated in Fig. 2 in order to follow the texture development in nc and cg samples with increasing shear strain γ . For these distances shear strains estimated with $\gamma = \theta r/t$ ($\theta \equiv$ angle of twist in HPT, in radians; $r \equiv$ distance from the centre and $t \equiv$ specimen thickness) are 0, 0.35, 0.65 and 1, respectively. A detailed description of the synchrotron texture measurement is given in [18]. The orientation distribution function (ODF) was calculated on the basis of the measured (111), (200) and (220) pole figures using LABOTEX software [19]. The Euler angles were used in Bunge notation [20]. To account best for the monoclinic symmetry of simple shear, the crystal and sample reference systems are defined as X $\parallel$ shear direction (SD), Y $\parallel$ shear plane normal (ND), Z $\parallel$ transverse direction (TD) [21]. The textures are represented by $\varphi_2 = 0^\circ$ and $\varphi_2 = 45^\circ$ ODF sections, which for face-centred cubic (FCC) metals contain all major shear components (Table 1).

The initial texture of the as-igc Pd-10at.%Au specimens is practically random with an orientation density varying between 1 and 2 m.r.d (multiples of a random distribution). Due to poor grain statistics in the cg specimen, it was difficult to analyze the initial texture quantitatively. However, it seems also to be random.

In HPT deformation the shear plane is parallel to the HPT disc plane and the shear direction is normal to its radius. It is known that simple shear textures of FCC metals are characterized by two partial fibres: (i) $\{111\} \parallel \text{ND}$ containing $A/\bar{A}$, A_1^* , A_2^* ideal components and (ii) $\langle 110 \rangle \parallel \text{SD}$ containing $A/\bar{A}$, $B/\bar{B}$ and C ideal components [22]. Crystallographic indices of the ideal components are given in Table 1. Figs. 3a, b represent the $\varphi_2 = 0^\circ$ and φ_2

= 45° ODF sections corresponding to all sites shown in Fig. 2 for cg and nc samples, respectively. The positions of the simple shear ideal orientations for the respective ODF sections are indicated in the key figures in the top of Fig. 3. The texture develops very differently in the cg sample as compared with that in the nc one. In particular, after a shear strain of $\gamma = 0.35$ a very pronounced texture typical for simple shear is observed in the cg sample with the intensity of the components being as large as 24. However, for this small shear strain the grain statistics is still too small for a quantitative texture measurement, even with synchrotron radiation. At higher shear strains due to grain fragmentation the data are more reliable. At the same level of strain, the texture in the nc sample is still random. Remarkably, with increasing shear strain the texture strength decreases in the cg sample (Fig. 3a, Table 1). A further decrease was observed for higher shear strains ($\gamma = 15$) due to grain refinement [15]. At $\gamma = 1$ the most intense components are $B, \bar{B}$, C and cube. In contrast, the nc sample still shows no pronounced texture formation at all strains. This is a direct indication of very limited dislocation activity in the nc sample. Furthermore, the intensity of the $B, \bar{B}$ components, usually observed in torsion textures of low stacking fault energy FCC metals and related to deformation twinning [23,24,25], are also close to random (Table 1). This indicates that twinning as well, has not made any notable contribution to the plasticity of the nc Pd-Au alloy. Twins can produce a total shear deformation $\gamma_{tw} = s_{tw} f_{tw}$, where s_{tw} is the twinning shear, $s_{tw} = 0.7$ for fcc metals, and f_{tw} is the volume fraction of twins. Despite it is very difficult to make an accurate estimate of f_{tw} for grain sizes as small as 15-20 nm, we roughly calculated the number of twinned grains after HPT deformation for $\gamma = 1$ in several TEM micrographs taken in the sample cross section normal to the radial direction using a Phillips CM 30. It appeared that only 2 to 3% of the grains contain very narrow, 1-2 nm thick, twins. Thus, the volume fraction of twins is very small and their contribution to shear strain in nc Pd-10% alloy is negligible. That is why the texture components resulting from twinning were not revealed in the ODFs of this alloy, even when based on synchrotron measurements. In our previous paper [15] we observed a weak texture formation with components corresponding to deformation twinning. But in the samples used there, strain induced grain growth took place simultaneously with the mean grain size increasing to 24 nm and the amount of grains >30 nm being larger than 30%, while in the as-igc state it was less than 1% (Fig. 1b). In comparison, in the present investigation a slight strain induced grain growth up to 20 nm was observed, too, but more important, the fraction of grains >30 nm was less than 10% (Fig. 1d). It is also worth noting that grains remain equiaxed even after larger shear

strain in HPT [15]. These facts point towards a significant contribution of grain boundary sliding to plasticity in the nc state, which is in a good agreement with other texture measurements [12,13,15] and atomistic simulation studies [2,3]. Both dislocation slip and twinning can take place in grains larger than 30 nm. It should be also mentioned that [26, 27] experimentally observed an inverse grain size effect on twinning, i.e. for grains smaller than an optimum grain size which depending on the material is about several tens of nanometers becomes more difficult. The grain size of the present work seems to be below this optimum grain size.

Additionally, a relatively strong oblique cube component $\{100\}\langle 100\rangle$ is present in the cg sample (Fig. 3a, Table 1). This texture typically forms in FCC metals during recrystallization, either dynamically or after pressure release.

In summary, the present investigation of texture development in the cg and nc Pd-10at.%Au alloy as a result of high pressure torsion deformation clearly demonstrates that dislocation slip and deformation twinning is practically negligible in the nc sample for shear strains $\gamma \leq 1$ and grain sizes < 20 nm. Thus, it is assumed that grain boundary sliding is the dominating deformation mechanism in the nc sample leading to no essential texture development.

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Figure captions:

Figure 1. Typical dark field TEM images of the Pd-10at.% Au alloy microstructure (a,c) and corresponding grain size distributions (b,d): as igt state (a,b) and after HPT straining for $\gamma = 1$.

Figure 2. Schematic diagram showing how the pins for texture measurements were cut from the HPT discs. Numbers indicate the distance from the HPT disc centre. Arrows show shear direction in HPT. (SD $\equiv$ shear direction, TD $\equiv$ transverse direction, ND $\equiv$ normal direction)

Figure 3. $\varphi_2 = 0^\circ$ and $\varphi_2 = 45^\circ$ ODF sections of cg (a) and nc (b) samples processed by HPT at 4.5 GPa for shear strains as indicated. The positions of simple shear ideal orientations are indicated in the key figures in the top.

Figure(s)

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(b)

Figure(s)

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(d)

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Table 1. Ideal texture components in simple shear [22] observed in cg and nc Pd-10at.%Au specimens after HPT deformation and corresponding ODF intensities of near-by maxima.

Component designation	Miller indices (hkl) shear plane, [uvw] shear direction	Intensity/m.r.d.					
		$\gamma = 0.35$		$\gamma = 0.65$		$\gamma = 1$	
		cg	nc	cg	nc	cg	nc
<i>A</i>	(11 $\bar{1}$)[$\bar{1}10$]	0.2	0.8	0.7	0.9	0.5	0.9
$\bar{A}$	($\bar{1}\bar{1}1$)[$\bar{1}10$]	0.2	0.8	0.7	0.9	0.7	0.9
<i>B</i>	(11 $\bar{2}$)[$\bar{1}10$]	11.1	0.9	4.8	0.9	4.3	0.9
$\bar{B}$	($\bar{1}\bar{1}2$)[$\bar{1}10$]	4.2	0.8	3.3	0.9	4.0	0.9
<i>C</i>	(100)[011]	7.6	0.9	3.2	0.9	1.8	1.6
A_1^*	(11 $\bar{1}$)[$\bar{2}\bar{1}1$]	23.8	1.1	4.5	1.2	0.5	1.3
A_2^*	($\bar{1}\bar{1}1$)[$\bar{2}\bar{1}1$]	5.1	1.1	4.2	1.2	0.4	1.1
Cube	(001)[100]	8.0	0.8	6.5	0.8	5.1	1.8