Development of strains in nanocrystalline TiN under high pressures and high temperatures

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Titanium Nitride (TiN) is an important material with diverse applications due to its unique properties (e.g., electrical conductivity higher than that of Ti-metal, high melting point of about 3000 ºC, the hardness close to that of diamond, significant chemical corrosion resistance). TiN powders in nanosized range were synthesized by the application of an anaerobic „imide” route (10-50 nm, low oxygen content) [1] and aerosol synthesis (40-80 nm) [2]. No known reports address sintering of nano-TiN under HP-HT conditions. Preliminary studies on recrystallization and lattice relaxation were performed at HASYLAB, MAX80 Cubic Anvil Press (F2.1 station) [3], to optimize the sintering conditions to obtain high-density/low oxygen TiN ceramics.

In this report we present continuation of examination of two powders of TiN, one with 5 nm average grain size that was synthesized at 500 ºC and another with 26 nm grain size that was obtained at 800 ºC. Generation and relaxation of microstrains was traced by analyzing the changes of FWHM of Bragg reflections, macrostrain was measured from weighted positions of Bragg reflections. The diffraction data were collected in energy dispersive geometry. Sodium chloride was applied as a pressure marker and no pressure medium was used.

Below we present the results of examination of samples compressed up to the pressure of 6 GPa and thermal expansion of 5 and 26 nm TiN powders under the pressure of 6 GPa.

Compression

Fig.1 shows compression of TiN powders under the pressure of 0-6 GPa measured for (200) reflections calculated for their weighted positions. The specific shape of the plots is due to the core-shell structure of individual grains. Referring to a core-shell model of a nanocrystalline grain we assume that there are two distinctive volumes of the sample corresponding to the core and the shell, which obviously show different elastic properties [4]. What one measures in an experiment as a Bragg reflection is a combination of two components of its shape, corresponding to the core and shell of the grain [5].

Figure 1 (a) shows that at ambient pressure, d_{200} (thus also the corresponding lattice parameters) values of both samples are about same, d/d_0 ≅ 0.99, and they are about 1% smaller than that of bulk TiN (d_0 = 2.13 and corresponds to crystalline TiN). At the initial stage of compression, up to about 25-30 kbar, the 5 nm sample compresses very strongly, and 26 nm sample shows no compression. At this stage, there is a strong increase of micro-strains in 5 nm sample, Fig. 1(b) but no increase of strains is observed in the 26 nm sample. The origin of this behavior is in different elastic properties of cores and shells of the grains (softer shells and harder cores) and in different ratios of the sample volume corresponding to the shells and cores. The pronounced compression of soft shells has a strong effect on the position of Bragg reflection of 5 nm sample, but contribution from the compressed shell to Bragg peak positions for 26 nm sample is very small. At the initial stage most of the strain energy is accumulated in the shell, which hardens and protects the inner part of the grains, the cores, from being...
compressed [5]. At the second stage, above 30 kbar, the material becomes homogenous (the densities of cores and shells become equal) and the measured compression of both samples is similar.

Thermal expansion

The samples annealed under pressure show that there is a characteristic temperature which divides the examined temperature interval in two parts where TiN shows different thermal expansion. Up to temperature of about 500°C the thermal expansion coefficient is about that observed for single crystalline material; the inlet shows the lattice expansion corresponding to \( \alpha = 10^{-6} \, \text{K}^{-1} \). Above 500°C the thermal expansion increases very strongly, and this is accompanied by a very rapid relaxation of microstrains, Fig.2 (b). After full relaxation of microstrains (above 800°C the broadening of Bragg reflections, FWHM, is only due to grain size), during cooling, the thermal expansion coefficient (here: compression) is again that of TiN lattice.

The reasons for a very large thermal expansion measured for nanocrystalline TiN above 400-500°C are obviously connected with core-shell structure of the grains. One has to remember that in a diffraction experiment one measures positions of intensity maxima, which one routinely treats as Bragg reflections with corresponding specific d-values. One has to remember, however, that information which one gets is only about this part of the sample volume which contributes to Bragg reflections. Considering that a nanocrystal shows a core-shell structure, Bragg reflections are combinations of two components corresponding to the core and the shell, thus there might be a part of the sample volume which, due to strains or disorder might not contribute to Bragg maxima. The plots of Figs. 1 and 2 present average compression and average lattice expansion as measured from weighted positions of the reflections. One might assume that the real d-values of the examined materials are those measured for the relaxed samples after pressure and temperature treatment, i.e. \( d_{200}/d_0 \) for 5 nm grains is about 0.99, and for 26 nm – 0.995. After densification at 6 GPa the d-values measured before heating are obviously not representative for the whole sample volume: they correspond to this part of the sample volume which is very strongly compressed, probably at the contacts between individual grains, while this part of the sample volume which is strained but located in the pores do not contribute to Bragg reflections and do not affect their positions. The real average d-value for the whole sample volume is larger (by the value H shown in Fig.2 a) than that measured before heating under pressure. A very “fast” relaxation above 400-500°C observed in Fig.2(b) describes the process of rearrangement of individual nanograins and disappearance of porosity in the material.

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References