Hot pressing of nanocrystalline tantalum using high frequency induction heating and pulse plasma sintering

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Abstract. The paper presents the results of nanocrystalline powder tantalum consolidation using hot pressing. The authors used two different heating techniques during hot pressing: high-frequency induction heating (HFIH) and pulse plasma sintering (PPS). A comparison of the structure, microstructure, mechanical properties and corrosion resistance of the bulk nanocrystalline tantalum obtained in both techniques was performed. The nanocrystalline powder was made to start from the microcrystalline one using the high-energy ball milling process. The nanocrystalline powder was hot-pressed at 1000 °C, whereas, for comparison, the microcrystalline powder was hot pressed up to 1500 °C for proper consolidation. The authors found that during hot pressing, the powder partially reacts with the graphite die covered by boron nitride, which facilitated punches and powder displacement in the die during densification. Tantalum carbide and boride in the nanocrystalline material was found, which can improve the mechanical properties. The hardness of the HFIH and PPS nanocrystalline tantalum was as high as 625 and 615 HV, respectively. The microstructure was more uniform in the PPS nanomaterial. The corrosion resistance in both cases deteriorated, in comparison to the microcrystalline material, while the PPS material corrosion resistance was slightly better than that of the HFIH one.

1. Introduction

Many components used in advanced industry require high-tech materials that are resistant to high temperature, corrosive media or radiation. These components are usually made using, inter alia, refractory elements. However, refractory metals, alloys and composites based on Ta, W, Nb, oxides and nitrides [1-5] are technologically problematic materials that require high temperature processing, i.e. high sintering temperature. These materials are usually made using powder metallurgy [6,7]. In terms of powder metallurgy, the conventional process is usually based on the following stages: (1) preparation of a powder of required composition, size and shape, (2) high pressure compaction for green compact formation and (3) sintering for green compact consolidation [8]. To provide good mechanical properties of sintered material, i.e. strength and low porosity, high pressure and high temperature are required, which is unfavorable in terms of the grain growth at elevated temperature and high requirements for the pressing/sintering equipment. The conventional powder metallurgy process can be successfully used for microcrystalline powders. For nanocrystalline powders, however, other processing routes are required such as hot pressing [8], in which the stages of pressing and
sintering are carried out simultaneously. Thus, the process has many advantages including lower pressure, temperature and shorter sintering time. Finally, the hot-pressed material has a greater density, lower porosity and smaller grain size, which ensure better mechanical properties. The hot pressing process has many possible variants of heating. One of them is high frequency induction heating (HFIH), resistance heating (RH), spark plasma sintering (SPS) or pulse plasma sintering (PPS) [1,9-11]. The PPS is a relatively new technique [11,12] developed for the consolidation of high melting temperature compounds [13]. The PPS technique for fast powder heating during pressing, utilizes the pulses of high electric current generated by discharging high voltage capacitors. This allows acceleration of the heating to the steady temperature and shortening the time of sintering. The process is useful in the obtainment of high-density and fine-grained materials [13]. Tantalum can be used in different technical elements, which works in hard conditions [14] and it is very resistant in acidic environments. High corrosion resistance is a consequence of a passive Ta$_2$O$_5$ oxide film [15]. Tantalum is an unfavourably expensive element used in very hard operating conditions: in aviation and in the space industry, for chemical, energy-related and biomedical applications. Beside the high cost, which limits its widespread use, one of the downsides of tantalum is its high melting point and difficulties during processing. The powder metallurgy applied to tantalum is a good choice for the production of bulk elements, however, high sintering temperature leads to an increase in the size of the grains. It is commonly known that, according to the Hall-Petch equation, the smaller grain size leads to material strengthening [16]. Therefore, small grains of nanometer size, before the consolidation stage, are much desired to limit the final grain size in the consolidated materials after the sintering process. The formation of nanostructure tantalum can be promising in terms of its strengthening. Decrease of the grain diameter leads to larger volume of the boundaries between them. The nanostructure tantalum powder can be successfully consolidated to form bulk parts of high density, close to the theoretical value. The application of hot pressing limits the grain growth at elevated temperatures (which is lower in hot pressing compared to a conventional sintering process) and should provide nanocrystalline or ultrafine tantalum of greater strength in comparison to microcrystalline counterparts.

The first study of the nanocrystalline tantalum sintering was carried out in 1999 by Yoo et al [17]. They found that large surface area of the nanoparticles improves the densification process in comparison to the microcrystalline powder. At high strain rates, tantalum nanograins exhibit ductile deformation behavior without significant fracture and the tantalum nanograins tend to get softer [17]. Ductility and flow stress increase significantly as the initial particle size is reduced below 100 nm. Thus, the nanocrystalline tantalum not only has better mechanical properties but is more susceptible to process in comparison to microcrystalline powder.

The nanocrystalline tantalum was investigated by other researchers [18,19], however, the material still needs further investigation. In this work, we compare properties of HFIH and PPS hot-pressed nanocrystalline tantalum. This is a preliminary study for further preparation of nanocrystalline tantalum based alloys. The new methods of nanomaterials formation can provide new data and properties useful in extending theirs application. Different techniques were successfully used for tantalum nanopowders consolidation [8,10]. The work attempted to determine whether the applied method of hot pressing affects the properties of tantalum.

2. Experimental data

The nanocrystalline tantalum was produced in the process of high energy ball milling (HEBM). The milled powders were next hot pressed. The starting Ta powder (AlfaAesar, Germany) has a size <44 μm. The impurities do not exceed 0.03%. The powder was stored and handled in Unilab glove box (MBraun, Germany). The HEBM process was run using SPEX8000M mill (SpexSamplePrep, USA). Milling time was set experimentally at 48 h. Room temperature (RT) was a standard condition of the process. Powders after HEBM were hot-pressed in vacuum (<10$^{-2}$ Pa). The consolidation was done using graphite equipment (die as well as upper and lower punches), which were covered by BN layer (HeBoCoat, Germany). The BN layer improves punches moving and powders consolidation. The
authors used two different heating modes during consolidation: high-frequency induction heating (HFIH) and pulse plasma sintering (PPS). The consolidation temperature was 1500°C and 1000°C for micro- and nanocrystalline powders, respectively. The time of sintering at a constant temperature was 5 s. The lower temperature of hot pressing was choosing for nanocrystalline material, which has better sinterability and to avoid its excessive grain growth [17,20]. The pressure exerted on the powder had a value of 50 MPa. In the PPS process the pulses of high electric current going through the die and the powder. The current pulses in the module are generated by discharging of a 250 F capacitor, charged to a voltage of maximum 8 kV. The pulse duration during sintering process is automatically controlled due to a temperature measurement by a pyrometer direct on the upper punch. Voltage, pulse frequency, force, temperature, and real-time vacuum were automatically controlled during the sintering procedure.

The structure was checked using Empyrean XRD (Panalytical, The Netherlands) with a crystalllographic database ICDD-JCPDS. The investigations were performed using CuK radiation (45 mV, 40 mA). The crystallite size was calculated by the Scherrer’s equation.

The microstructure was recorded by SEM (Tescan, Czech Republic), operated at 20 kV in the secondary electrons mode as well as by AFM (Quesant, USA). The AFM works in the wavemode (SSS-NCLR premounted Nanosensors probe, 145 kHZ probe frequency, and scan speed 3 lines/s, total 1024 lines for image formation). For the microstructure evaluation the hot-pressed samples were grinded, polished and chemically etched in a H₂SO₄ + HNO₃ + HF mixture.

The mechanical properties were measured using Picodentor HM500 (Fischer, USA) nanoindention tester. The HV – Vickers hardness and E₁− indentation modulus were measured at loading. The indentations were made using diamond indenter at the force of 300 mN acting for 20 s.

The corrosion resistance was measured on hot-pressed materials using Solartron 1285 Potentiostat (Solartron Analytical, England). The potentiodynamic mode was applied, starting at -0.5 V and finishing at 3 V vs OCP. The scan speed was 0.5 mV/s. The bulk tantalum was the working electrode, graphite was the counter electrode and Ag/AgCl/Cl⁻ was the reference electrode. The corrosion resistance was measured in the Ringer’s solution containing the following ion concentrations: 147.2 mmol l⁻¹ Na⁺, 4.0 mmol l⁻¹ K⁺, 2.2 mmol l⁻¹ Ca²⁺, 155.7 mmol l⁻¹ Cl⁻.

3. Results and discussion
The microcrystalline tantalum powder shows a cubic-type Im-3m structure (reference code 01-0894901). The material is single-phase (figure 1(a)). During high-energy ball milling for 48 h (figure 1(b)) a significant decrease of the crystallite size to 20 nm occurred. The reduction of intensity of peaks and their broadening points formation of nanostructure or even partial amorphization (figure 1(b)). The ball-powder-ball hits results in the introduction of material stress, formation of dislocations and subgrains. These finally lead to cold strengthening, material crushing and nanostructure formation. During hot pressing, a significant relaxation of stress occurs and the provided energy results in grain growth (figures 1(c) and 1(d)). Because of high reactivity of the amorphous/nanocrystalline metallic material, high temperature and residual gases under vacuum, the powder partially reacts with the gases as well as the graphite die (figures 1(c) and 1(d)) and forms intermetallic phases. However, given their properties, these Ta-C, Ta-O or Ta-B type compounds can have a positive effect on the final properties of the bulk nanocrystalline tantalum. The precipitations can strengthening of the tantalum as well as inhibit grain growth at elevated temperature [5,7,8]. In the case of the PPS material, the XRD peaks for additional phases are smaller, indicating that the PPS process does not significantly support the reaction of Ta with the B, C or O elements as is in the case of the HFIH material. The microcrystalline hot-pressed material (figure 1(e)) shows no additional phases, for both HFIH and PPS hot-pressed samples (due to the same spectrum for both PPS and HFIH materials, for comparison, figure 1(e) shows the HFIH sample only).
In the HEBM process, the tantalum powder undergoes a grain size reduction, however, the powder during milling undergoes not only crushing but strong plastic deformation and cold welding (the powder particles are hit and trapped between the balls and the wall of the milling vial), which results in the formation of powder agglomerates of relatively large size (figure 2(a)). The agglomerates are composed of smaller particles, hence the SEM image (figure 2(a)) shows agglomerate particles (composed of nanograins) rather than nanoparticles. The XRD shows (peaks broadening and decreasing their intensity) that the material after intense milling transforms into nanocrystalline. As the reference material, the authors chose hot-pressed microcrystalline 325-mesh powder. The obtained consolidated microcrystalline sample has large grain size of the average value of 15 µm and low porosity (figure 2(b)). After mechanical milling, the nanocrystalline powders were hot-pressed using HFIH (figure 2(c) and 2(d)) and PPS (figures 2(e) and 2(f)). The hot-pressed nanomaterials have a slightly larger porosity following the pressing of the agglomerates, however, due to limited time of the hot pressing and a relatively low temperature, the metastable nanocrystalline material has insufficient energy for significant grain growth. After the HFIH slight porosity forms around the hot-pressed agglomerates (figure 2(c)). The higher magnification shows ultrafine structure (figure 2(d)). The PPS process results in a lower porosity and more uniform microstructure. The density of hot-pressed
microcrystalline tantalum was 15.6 g/cm$^3$, whereas for HFIH and PPS hot-pressed nanocrystalline tantalum was 14.9 g/cm$^3$ and 15.3 g/cm$^3$, respectively. These densities are 95%, 91% and 93% of the theoretical value, respectively.

**Figure 3.** AFM images of tantalum: nanocrystalline powder after mechanical milling (a), nanocrystalline hot-pressed using HFIH (b), nanocrystalline hot-pressed using PPS (c) and microcrystalline hot-pressed (d).

**Figure 4.** AFM grain size histogram of tantalum in the nanocrystalline powder after mechanical milling (a), nanocrystalline hot-pressed using HFIH (b), nanocrystalline hot-pressed using PPS (c) and microcrystalline hot-pressed (d).
The nanocrystalline materials were investigated using AFM. For comparison, the microcrystalline was also checked. Taking into account the AFM images (figures 3(a)-3(d)), grain size histograms were calculated (figures 4(a)-4(d)). For grain size analysis, we take the AFM pictures of 12 m² summarized area. The analysis was done on the pictures recorded on 3 different places to avoid sample inhomogeneity. The mechanically milled tantalum powders are shown in figure 3(a). The presented image shows agglomerated particles of relatively high homogeneity. However, the measured grain size distribution has a relatively broad range from approx. 30 to above 180 nm. The calculated average grain size is 70 nm (figure 4(a)). The hot pressing using HFIH results in the grain growth (figure 3(b)), but the grains are not larger than 230 nm (figure 4(b)). The calculated average grain size is 170 nm. The PPS process results in a smaller grain growth during the consolidation of the powders (figure 3(c)) and the average grain size is 165 nm (figure 4(c)). The microcrystalline sinter has large grains and, due to limited scan size, a relatively low surface area with only few grains in the frame was scanned (figure 3(d)). The mechanical properties were measured using a nanoindentation tester (figure 5 and table 1). Figure 5 shows example load-displacement curves recorded for nanocrystalline tantalum. The results have a relatively broad spectrum of the curves that do not overlap one another, indicating some inhomogeneity and porosity of the hot-pressed material. The hardness of the nanocrystalline materials is twice as high compared to the microcrystalline and significantly higher than commercially available tantalum (100 HV for annealed and 200 HV for cold-worked). In both, HFIH and PPS nanomaterials, the mechanical properties are comparable. The high hardness in nanocrystalline tantalum can be attributed to the nanostructure as well as hard precipitations formed at elevated temperatures after contact with boron nitride-coated graphite die. The indentation modulus is comparable for all hot-pressed samples and is slightly lower in comparison to bulk commercial tantalum (186 GPa). Generally the porosity deteriorates the modulus.

![Figure 5. Example load-displacement curves recorded for nanocrystalline PPS tantalum.](image-url)
The corrosion resistance was measured for microcrystalline and nanocrystalline hot-pressed materials. It is commonly accepted that the microcrystalline and single-phase structure favour better corrosion resistance in comparison to nanostructure of large volume grain boundaries (smaller grains) and multiphase materials [15,21]. It is, thus expected that nanomaterials have worse corrosion resistance in comparison to microcrystalline materials. The OCP (open circuit potential) and polarization curves are shown in figures 6A and 6B, respectively. OCP for the microcrystalline Ta (a) shows a significantly more negative value in comparison to the nanocrystalline Ta (b, c). The more positive value of OCP suggests a formation of a more stable passive layer. An increase in OCP to a more positive value with time indicates that the material undergoes overall corrosion (a), whereas constant OCP or its slight decrease denotes a stable passive layer (b, c).

The polarization curves shown in B point to better corrosion resistance of the microcrystalline Ta (a) in comparison to the nanocrystalline Ta (b, c). The microcrystalline Ta has a corrosion current density of $I_{corr} = 3.108 \times 10^{-8}$ A/cm², whereas for the hot-pressed nanocrystalline HFIH and PPS Ta, the $I_{corr} = 3.625 \times 10^{-7}$ A/cm² and $1.198 \times 10^{-5}$ A/cm², respectively. The lowest $I_{corr}$ denotes better corrosion resistance. For the nanocrystalline Ta, the $I_{corr}$ has a significantly higher $I_{corr}$. The high $I_{corr}$ is related to greater volume of the grain boundaries and a smaller grain size. The current in the passive range is significantly higher for the case of nanocrystalline material.

### 4. Conclusions
The paper has shown the results of nanocrystalline tantalum consolidation using different heating techniques during hot pressing. To prevent excessive grain growth at elevated temperature, the nanocrystalline powders, made using HEBM process were hot-pressed applying induction heating and pulse plasma sintering. Both methods give comparable results, i.e. small average grain size in the range of 165-170 nm and good mechanical properties with the hardness of approx. 620 HV, twice higher compare to the hot-pressed microcrystalline Ta. PPS tantalum exhibits a slightly better corrosion resistance in comparison to HFIH tantalum, however, the microcrystalline tantalum has a best corrosion resistance.

### Table 1. Mechanical properties of the hot-pressed microcrystalline and nanocrystalline tantalum

| Parameter | Microcrystalline (HFIH) | Nanocrystalline (HFIH) | Nanocrystalline (PPS) |
|-----------|-------------------------|------------------------|----------------------|
| HV [HV]   | 346.4±29.8              | 625.2±132.1            | 615.2±149.5          |
| $E_{IT}$ [GPa] | 180.3±5.8              | 180.4±22.8             | 182.2±23.1           |
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