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EFFECTS OF TUNGSTEN NANOPARTICLES ADDITIONS ON THE DENSIFICATION OF MICRON SIZE TUNGSTEN POWDER

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Abstract. Low temperature activated sintering of 3 μm tungsten powder was studied. Sintering process was activated by vibration milling and by additions of W nanopowder of less than 10 nm in mean diameter, as well as combination of those techniques. There were no any additions of transition metals such Ni, Co or Fe. The blend of W micron size powder after mechanoactivation with 20% of W nanopowder showed sintering density up to 97% of theoretical density and high chemical purity.

1. INTRODUCTION.

Tungsten (W) and its alloys are one of the most important materials for high temperatures applications. Among other metals, it has highest melting point, lowest vapor pressure, and thermal expansion, and high thermal and electric conductivity. Through the years, it has been processed mostly using powder metallurgy (PM) techniques. To obtain densification, it is necessary to apply extremely high temperatures during sintering. By that reason, different ways to activate sintering process of tungsten powders in solid state had been suggested, such as activation by Ni [1], Pd, Fe, and Co additions [2]. However, it is difficult, even impossible, to receive a full density of tungsten by pressureless sintering at the temperatures below 2000 °C. Additionally, such activated sintering of refractory metals constantly results in significant embitterment of grain boundaries, which may relate to the existence of grain boundary's layers. Also mechanical activation of sintering process may be used to increase tungsten sintering density [3,4]. This paper considers tungsten activation sintering by using tungsten nanoparticles of less than 10 nm size synthesized by Chemical Vapor Condensation method as sintering activator. Such activating was applied for 3 micron size pure tungsten commercial powder and for same powder after mechanical activation. The potential aid is to improve densification of tungsten and decrease sintering temperatures without significant changes in chemical composition.

2. EXPERIMENTAL PROCEDURES

The blends of nano and micron W powder were used for sintering experiments. Initial "micron" size tungsten powder had the size of 2-6 μm, with the average size of 3 μm, and close to round shape of particles. As declared by manufacturer, tungsten purity was higher than 99.89%; oxygen and moisture content was less than 0.25%.

Crystalline nanosize W powder with the average size of about 10 nm was produced by Chemical Vapor Condensation (CVC) by using tungsten

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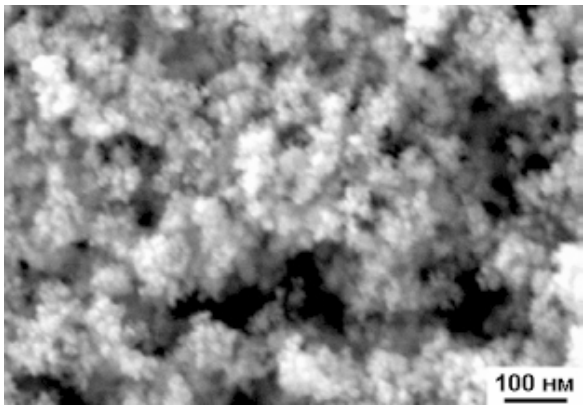


(a)

(b)

Fig. 1. Scanning (a) and transmission (b) electron micrographs of nanosize tungsten powder synthesized by Chemical Vapor Condensation method.

hexacarbonyl as a precursor [5]. The basic setup for CVC was similar to that already described in literature [6]. Particle has black or dark-grey color, close to round shape, and uniform size distribution. Slight agglomeration can be observed from the micrographs (Fig. 1). Particles of 8-10 nm joint together in 50-150 nm agglomerates. Chemical analysis of nanoparticles shows tungsten content of 96%, main admixtures are carbon (<1.5 wt.%), and oxygen.

Micron size tungsten powder was additionally activated by vibration milling for 40 h. In order to prevent contaminations, the vibration milling was done by W balls in isopropyl alcohol medium; reactor walls were protected by wear-resistive rubber. Wet blending with nanoparticles runs in rotated cylindrical reactor in benzene medium for at least 24 hours.

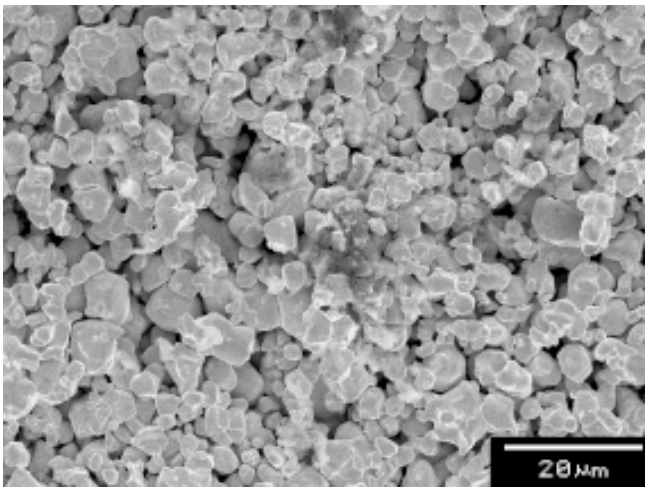
Powders were compacted in cylindrical molds of 8 mm in diameter and weight of approximately 5 g by the uniaxial cold pressing with pressure of 350 MPa. Prior to forming, the tungsten powder was mixed with benzine solution (20 cc/100 g) and 1.5 wt.% paraffin at the temperature of 40-60 °C. Sintering was carried out in vacuum dilatometer at 1850 °C for 15 min. Heating rate was 400 °C/h.

Particle size and shape were characterized by scanning electron microscopy (SEM) by using Zeiss SUPRA 55 VP-25-78 equipment. More detailed morphology and particles size distribution were determined by transmission electron microscopy (TEM) using JEOL JEM-2000FXII equipment. The powder for TEM investigations was ultrasonically dispersed in ethanol and dropped on a carbon coated copper grid. The phase and structural analysis of samples was carried out by DRON 2.0 diffractometer with using of monochromatic *K*a copper radiation. (λ = 0.154051 nm). Crystallite sizes (coherency length) and microstrains were estimated by Williamson-Hall method [7] by using four tungsten reflections ((110), (200), (211), and (220)). The lattice parameter of the BCC phase in as-quenched condition was determined by the extrapolation technique.

3. RESULTS AND DISCUSSION

3.1. Sintering behavior of initial tungsten powder

\It is well-known that it is difficult to obtain high density of pure tungsten by normal pressureless sin-



(a)

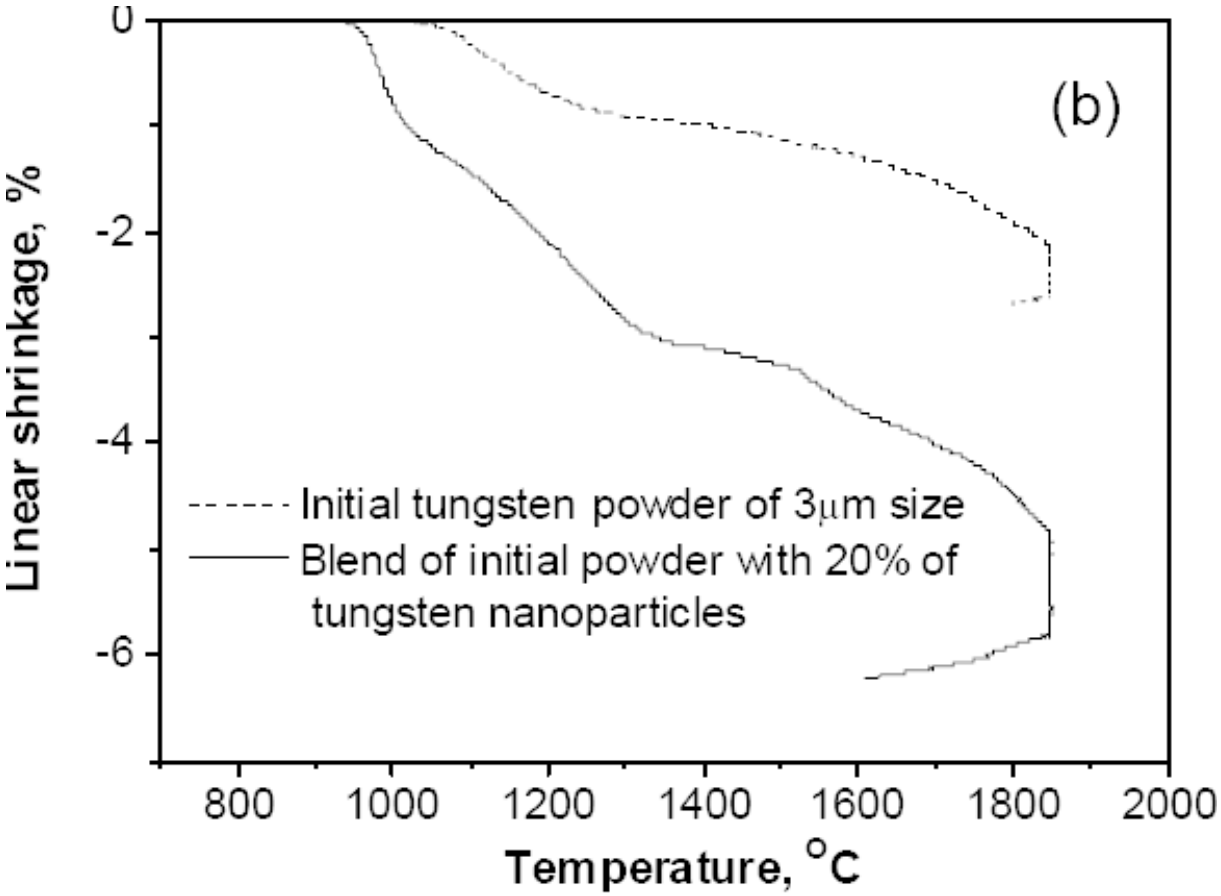


Fig. 2. SEM micrograph (a) and dilatometric curves (b) showed sintering behavior of initial tungsten powder.

tering at the temperatures below 2000 °C. For example, pure tungsten of 3 micron size powder couldn't be sintered in our experimental condition, see Fig. 2. The linear shrinkage was not higher than 3% at the sintering in dilatometer at 1850 °C for 15 min.

At the first step we add 20% of nanoparticles to the initial tungsten powder. Additions of nanopowder didn't influence green density of compact significantly; at pressure of 350 MPa green density decrease from 0.61 down to 0.585 for micron size powder and it blend with 20% of

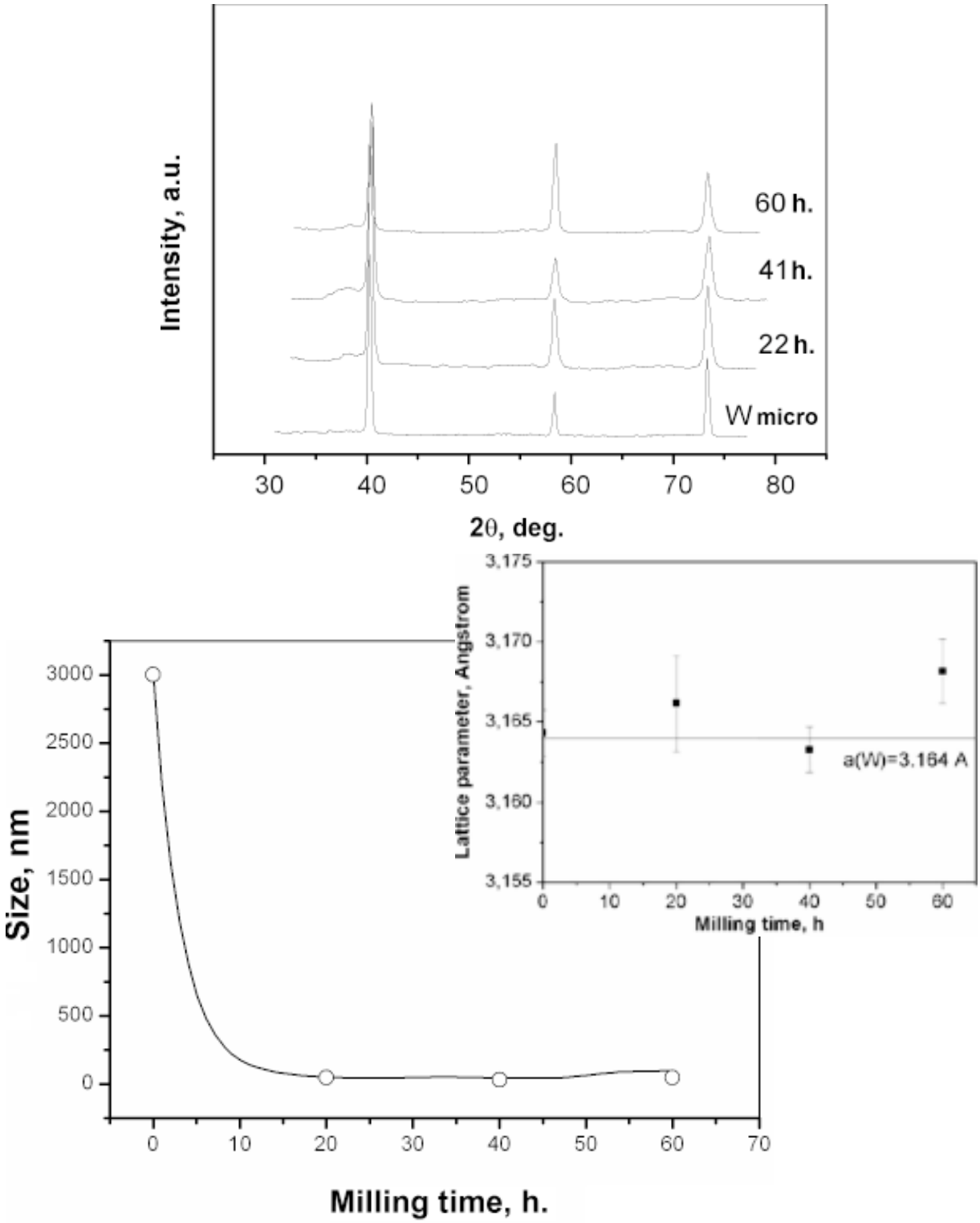


Fig. 3. X-ray diffraction patterns of mechanically activated powder (a) and calculated size decreasing (b). Insertion shows lattice parameter as function of milling time.

nanopowder respectively. It is clear from Fig. 2.that nanoparticles addition activate sintering process; linear shrinkage increased not only during heating process, but also during isothermal heat treatment and subsequent cooling. However, sintering density did not increase significantly; finally we received sintering density less than 0.7 after sintering for 15 min at 1850 °C. It means that nanoparticles addi-

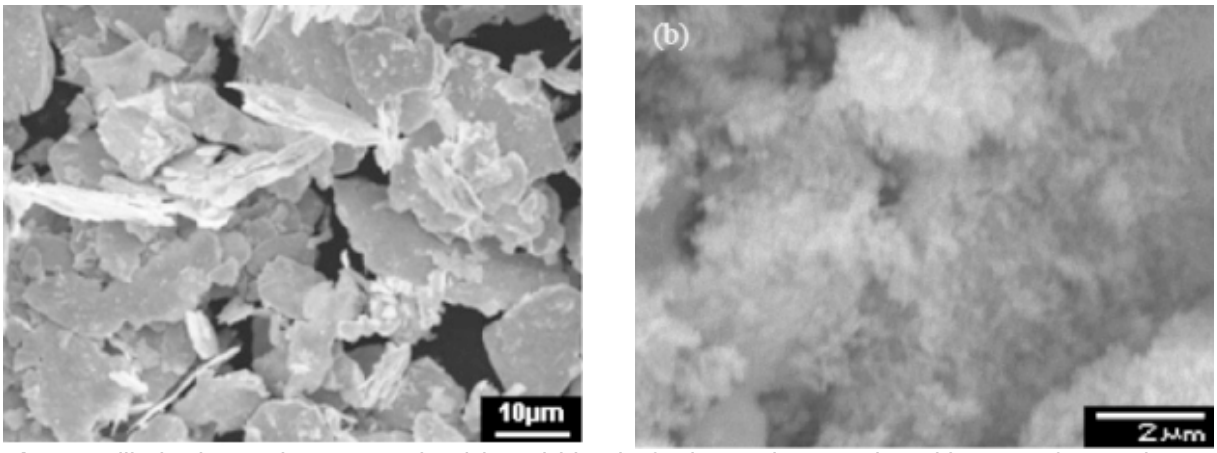


Fig. 4. Milled micron size W powder (a) and blend of micron size powder with 20% of nanosize W powder (b).

tion to rough tungsten powder can not activate sintering process significantly.

3.2. Mechanical activation of micron size tungsten powder

Next step was the use of additional mechanical activation of micron size powder by vibration milling. XRD study shows significant broadening of tungsten peaks as shown in Fig. 3a. Also, diffusive maximum at $2\Theta \cong 38°$ appears. It could be the evidence of some additional oxidation during the active powder after milling was exposed at atmospheric air. Calculation by Sherrer equation results in the average size of milled powder of 45, 32, and 47 nm at the milling time of 20, 40, and 60 h respectively (Fig. 3b), so all changes of apparent powder lies in the interval of method errors (about 20%). However, full-width at half maximum shows significant increasing after milling and subsequent small decreasing at 60 h milling that can be due to the coagulation of smallest particles and their agglomeration. Most significant size decreasing was observed in first 20 h of milling. Internal microstrains demonstrated rapid growth up to 0.2% with the milling time increase to 40 h and there was no significant growth of microstrains during the subsequent milling.

The lattice parameter of tungsten did not show any significant changes at the milling procedure, see Fig. 2, it was equal to lattice parameter of pure tungsten (0.3164 nm). It means that there are no any significant impurities, such as Ni or Fe, since iron and Ni additions leads to decrease in lattice parameter of tungsten.

However, SEM study of milled powder shows that “micron” size powders after vibration milling has mainly lamellar shape with the plate thickness of about or less 1 μm as shown in the Fig. 4a; small fraction of submicron size particles with the size of 300-500 mm may be also observed. Weight increase of powder after milling was usually about 10-15%.

Based on XRD results for the next study, we used powder after 40 h vibration milling due to the fact that the peak broadening was maximal at that condition. That powder was blended with additions of 10-30% of tungsten nanopowder. Fig. 4b shows SEM micrograph of the blend of micron and nanosize powders. The surface of big particles is fully covered by nanoparticles.

3.3. Effect of nanoparticles additions

Compacting experiments show that the green density of such blends after unaxial cold pressing is smaller as compared with initial micron size powder. The examples of compacting curves are shown in Fig. 5. It is impossible to get high green density of compacting bodies for pure nanopowder. In our experiments, green density for pure nanopowders was not higher than 0.41 d_{th}, even at the pressures higher than 1 GPa. Green density of mixed powder shows very small changes from 0.53 for milled micron size powder down to 0.47 at 30% of nanopowder additions.

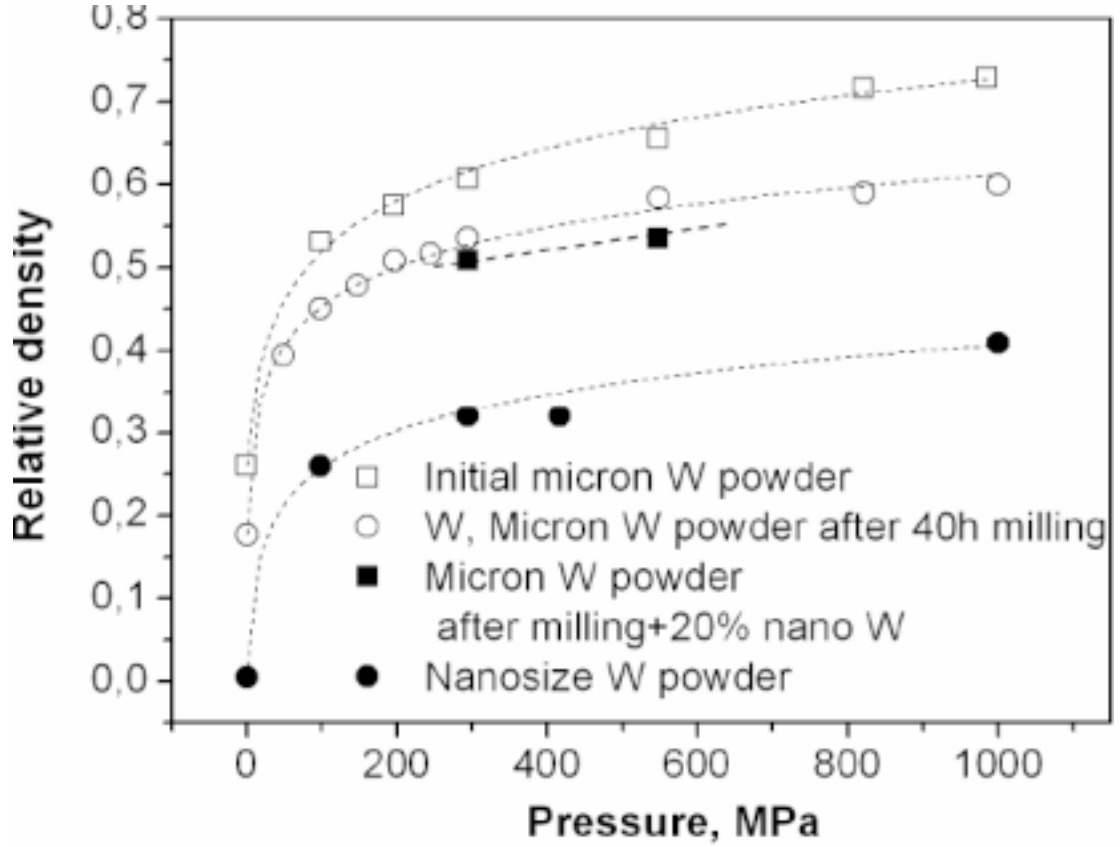


Fig. 5. Green density of compacted tungsten bodies.

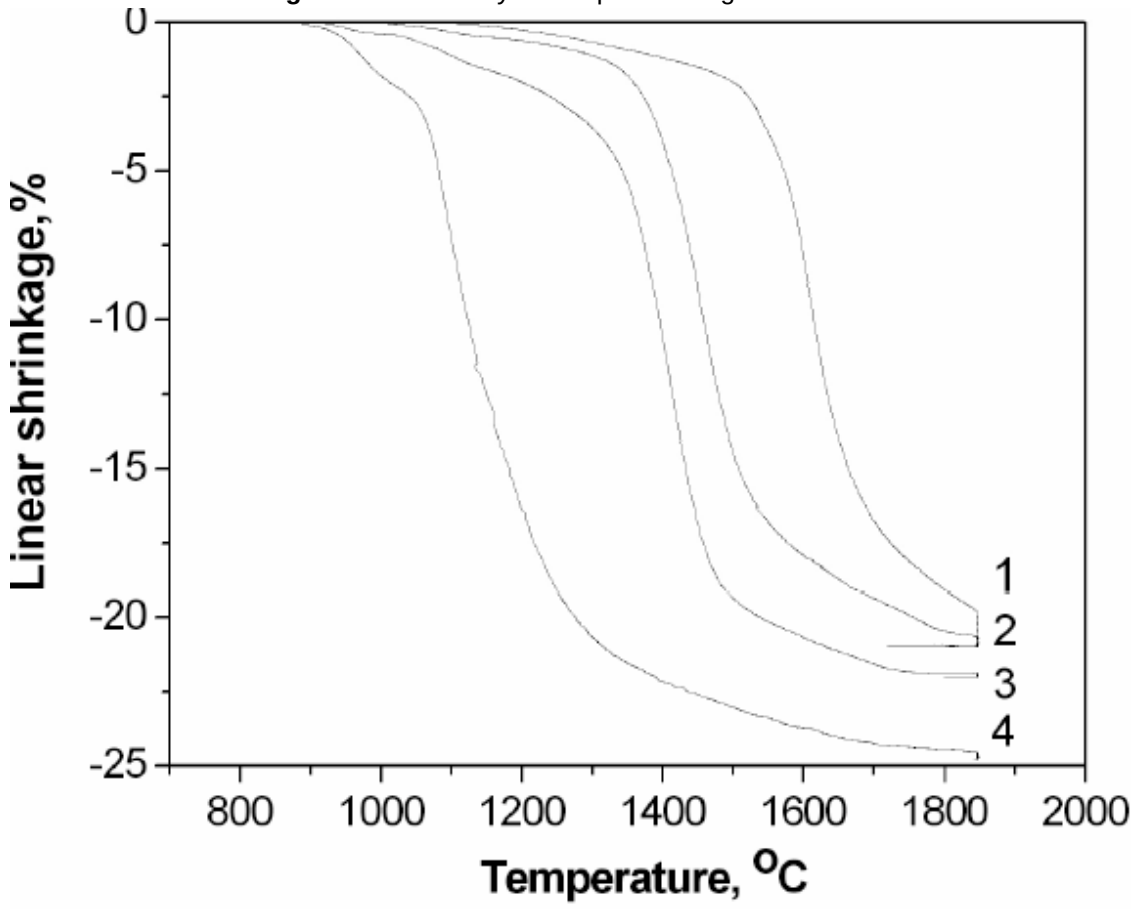


Fig. 6. Dilatometric results of sintering of milled W powder with nanopowder additions.
Curve 1 – tungsten powder after mechanoactivation for 40 h (powder 2); Curves 2, 3, and 4 – powder 1 with the additions of 10, 20, and 30 wt.% of nanosized W, respectively.

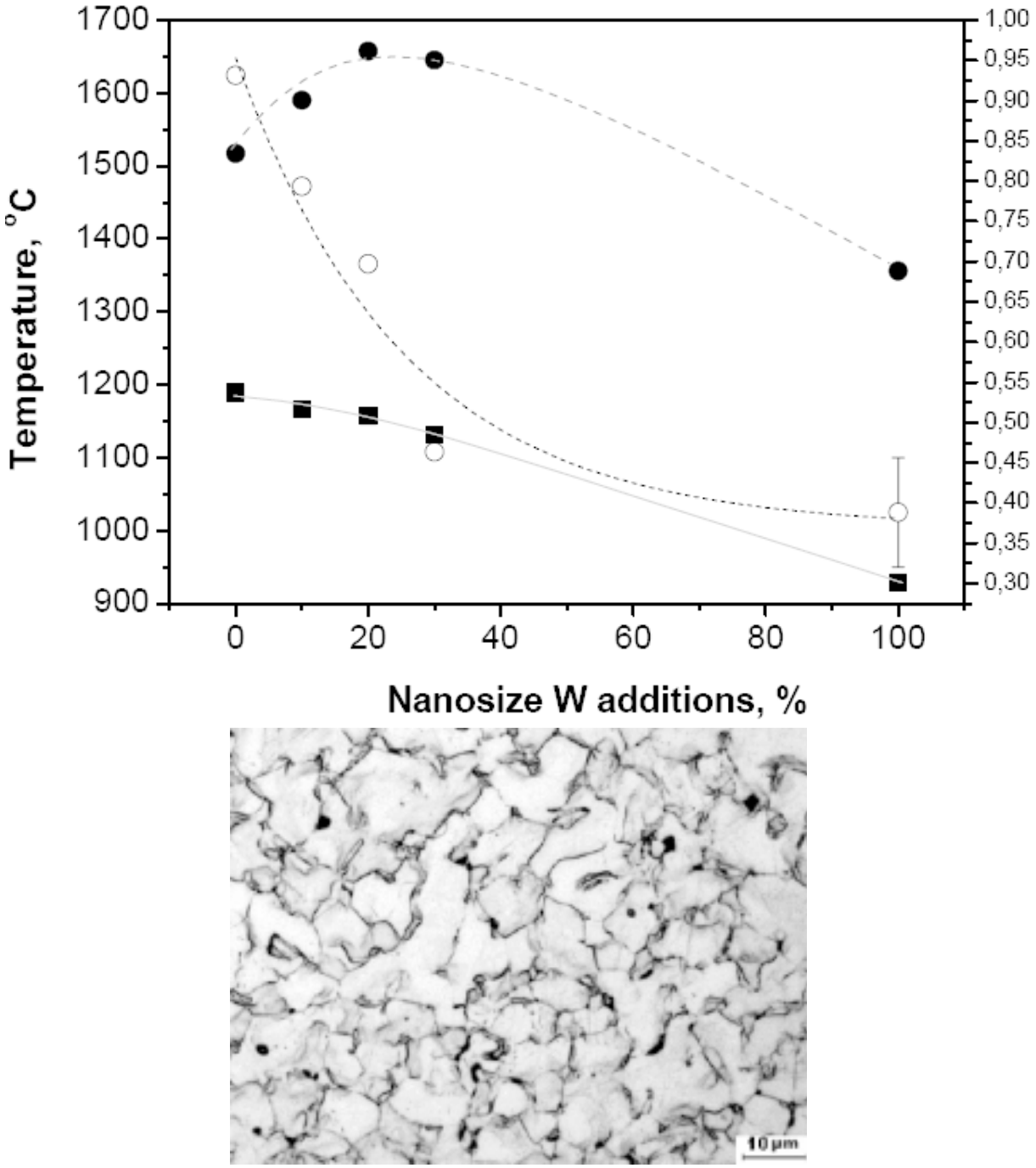


Fig. 7. The influence of W nanoparticles addition on green density (curve 1), sintering density (2), temperature of maximal sintering rate (3), and microstructure of sintered sample with 20% nanopowder additions.

The comparison of dilatometric results for the blends with 10, 20, and 30% of nanopowders and milled W powder are shown in Fig. 6. Maximal sintering rate for milled micron size powders is observed at temperatures higher than 1600 °C, and sintering processes proceeds intensively at maximal sintering temperature (1850 °C) (curve 1 in Fig. 6). The significant decreasing of sintering temperatures are observed with the additions of nanopowders up to 30%. The addition of 30% of nanopowder decreased sintering temperatures interval down to 1100-1400 °C and temperature of

maximal sintering rate decrease it for more than 450 °C. Shrinkage is not increased at the temperature of 1850 °C (curves 3 and 4 in Fig. 6). It is also possible to see the increase of the linear shrinkage with the additions of nanosize powders, that couldn't be explained only by increasing of initial porosity of compacts.

The comparison of green density before sintering, sintering density, and temperature of maximal densification rate are presented in Fig. 7. The green density of compacts and temperature of its maximal sintering rate are decreased continuously with the additions of nanoparticles. At the same time, sintering density has a maximum for the blend with additions of 20-30% nanoparticles. Sintering density of milled micron size powder usually is less than 0.85, maximal sintering density is observed at 20% nanoparticles additions (up to 0.97); the sintering density decreases at the higher amount of nanopowders.

Microstructure of samples are shown in Fig. 7b. It shows that the recrystallization of plate particles deformed by milling (Fig. 4b) are generally observed for all samples; however, the number of equiaxed grains in the structure was small, it means that recrystallization processes is not finished yet. Anyway, significant grain growth had been observed; grain size is about 10 μm. Chemical analysis shows that full content of admixtures is less than 0.4 wt.%, including the carbon content of about 0.02 wt.%, it is in good agreement with the purity of initial powders. We can suppose that such small carbon content in sintered bodies can be explained by reaction of oxygen with carbon at the comparatively low temperatures with CO or CO_2 formation or it can be partially dissolved and evaporated with tungsten oxides during heating for sintering in vacuum.

4. CONCLUSIONS

As-produced tungsten nanoparticles can be used as activator for sintering of micron size tungsten powder. By addition of nanoparticles up to 30% sintering temperature may be decreased by 400 °C with increasing tungsten sintering density. Additions of more than 30% nanoparticles can not decrease sintering temperature significantly. It is important to note that sintering can be activated without significant changes in chemical composition of sintered tungsten.

ACKNOWLEDGEMENTS

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