2nd Sino-German Workshop on PWI in Fusion Devices

Properties of TaC dispersion-strengthed tungsten sintered by spark plasma sintering

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Tungsten as plasma facing materials (PFM)

- Tungsten will be the favoured choice for plasma facing components (PFCs).
- Among the high-Z materials, tungsten is the only one with a relatively short activation decay time.
- In contrast to carbon, the erosion of tungsten by low energy hydrogen atoms is small.

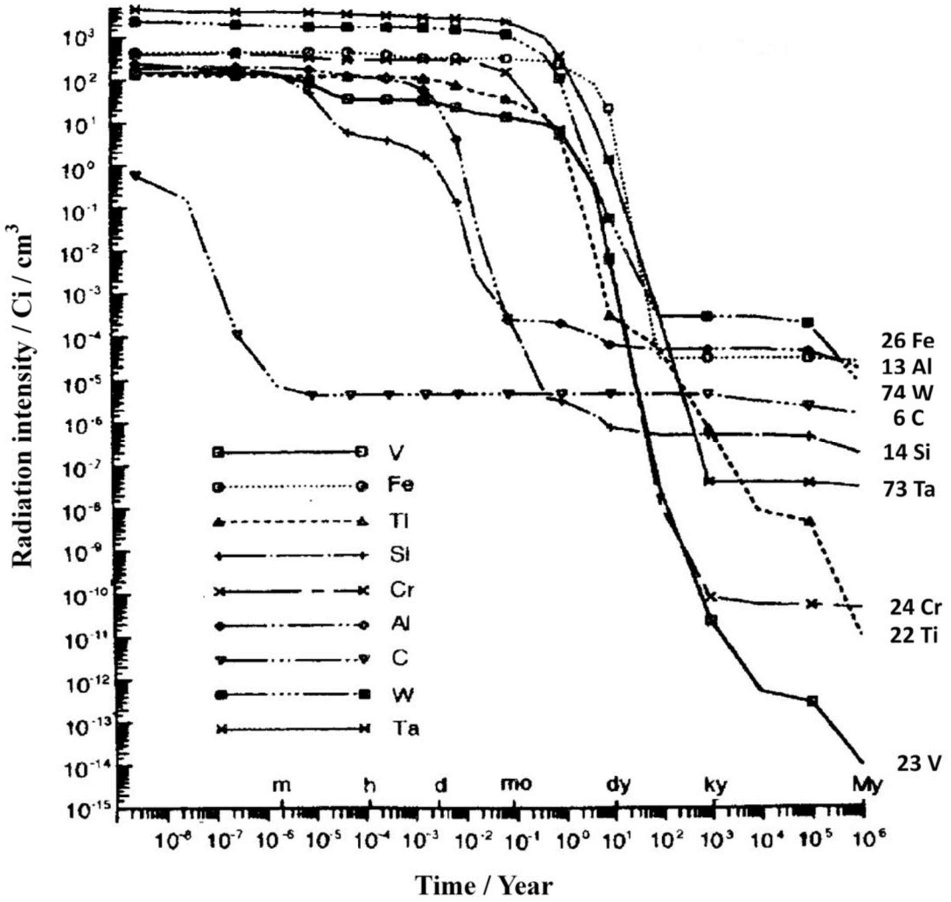
Dispersion strengthened W by oxide

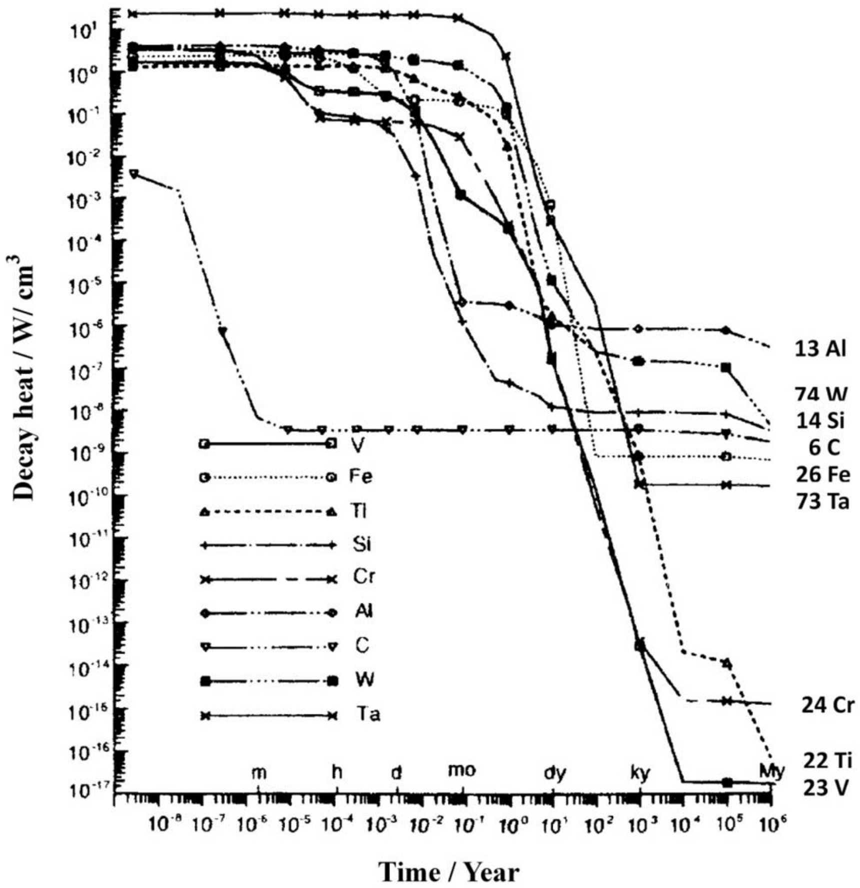
- W-ThO_2, CeO_2, La_2O_3, Y_2O_3, etc.
- The dispersoids are stable at the high sintering temperature and do not dissolve in the tungsten matrix. They pin the grain boundaries during the later stages of sintering.
- A rod containing 0.75% of thoria has a grain size of 5000 to 10,000 grains per square millimeter, as compared to 1500 grains per square millimeter for a similar rod of pure tungsten.
- Thoriated tungsten is used at 1700 to 1800 ^{o}C.

[1] Erik Lassner and Wolf-Dieter Schubert, Tungsten-properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds, 1999 Kluwer Academic/ Plenum Publishers, New York

[2] Xiaoli Xi, et al, Study on preparation and emission properties of nano-composite W–La_2O_3 material, Applied Surface Science 251 (2005) 134-138

Dispersion strengthened W by carbide

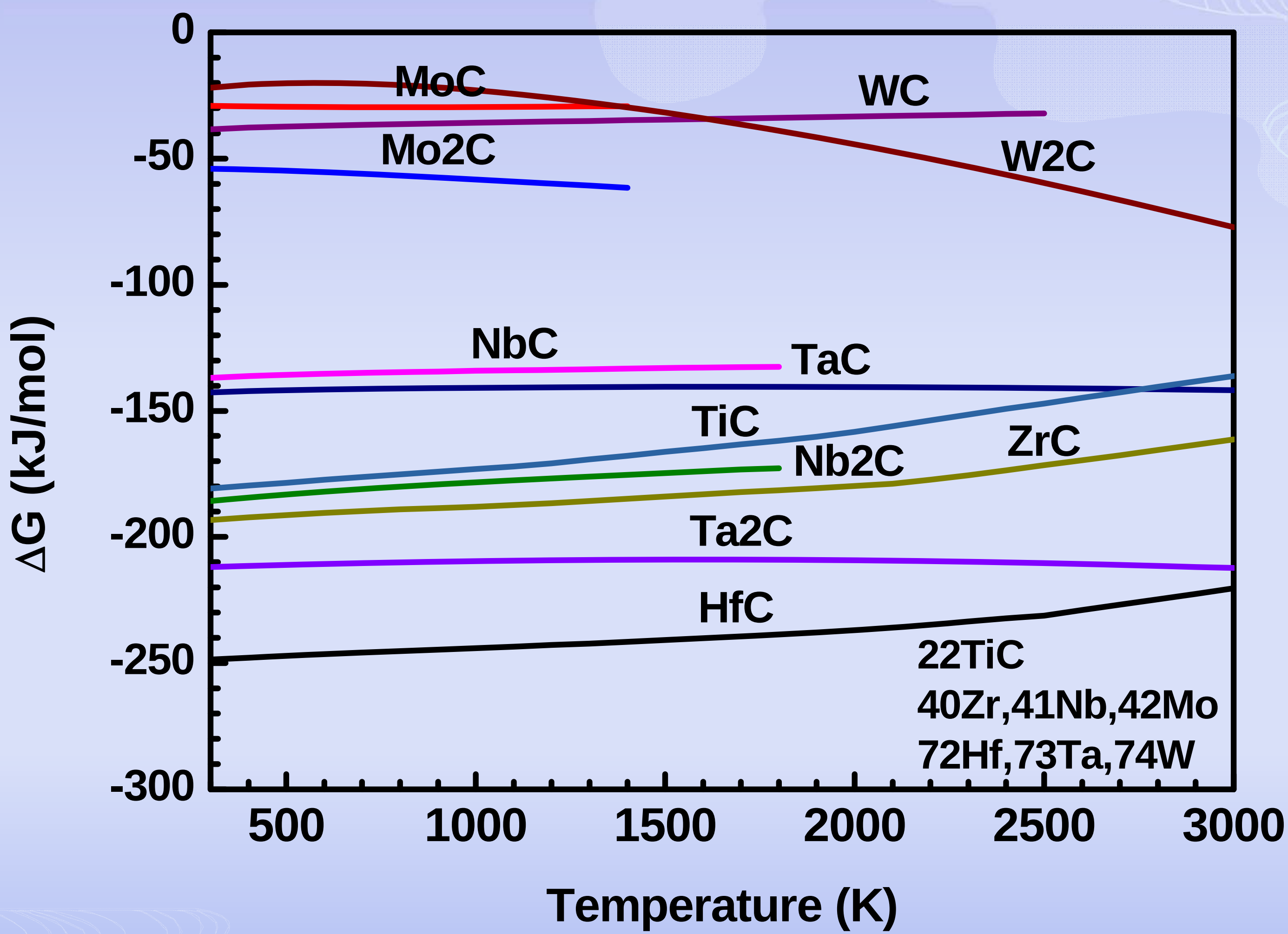




Induced radiation (left) and decay heat (right) of selected materials by typical neutron spectrum in fusion reactor.

Both tantalum carbide and titanium carbide are composed of low-Z or high-Z and reduce-activated elements.

Gibbs free energy of carbide-forming



Tantalum carbide is stable near to titanium carbide. Bitantalum carbide is stable near to hafnium carbide. Atomic number of Tantalum only inferior to tungsten.

Abundance of elements in Earth's crust

Element	Chemical symbol	[1]	[2]	[3]	[4]	[5]	annual production
tungsten	74W		160.6 ppm	190 ppm		1.25 ppm(?)	45,100 tons
hafnium	72Hf		5.3 ppm	3.3 ppm		3.0 ppm	50 tons
tantalum	73Ta		2 ppm	1.7 ppm		2.0 ppm	840 tons
zirconium	40Zr		190 ppm	130 ppm	250 ppm	165 ppm	7,000 tons
niobium	41Nb		20 ppm	17 ppm		20 ppm	15,000 tons
molybdenum	42Mo	trace	1.5 ppm	1.1 ppm		1.2 ppm	80,000 tons
titanium	22Ti	0.44%	5,600 ppm	0.66%	0.62%	0.56%	99,000 tons

Annual production of tantalum is higher than hafnium.

References

1.^ "Elements, Terrestrial Abundance". www.daviddarling.info. http://www.daviddarling.info/encyclopedia/E/elterr.html. Retrieved 2007-04-14.
2.^ Barbalace, Kenneth. "Periodic Table of Elements". Environmental Chemistry.com. http://environmentalchemistry.com/yogi/periodic/. Retrieved 2007-04-14.
3.^ "Abundance in Earth's Crust". WebElements.com. http://www.webelements.com/webelements/properties/text/image-flash/abund-crust.html. Retrieved 2007-04-14.
4.^ "List of Periodic Table Elements Sorted by Abundance in Earth's crust". Israel Science and Technology Homepage. http://www.science.co.il/PTelements.asp?s=Earth. Retrieved 2007-04-15.
5.^ "It's Elemental — The Periodic Table of Elements". Jefferson Lab. http://education.jlab.org/itselemental/index.html. Retrieved 2007-04-14.

Tantalum carbide for a strengthener of tungsten

- Tantalum carbide (TaC) is a potent strengthener for tungsten at elevated temperature below 1900 ^{o}C.
- Particle size and interparticle spacing must be small in order to lead to an effective strengthening.
- This occurs as a result of dislocation pinning through the fine (50-100nm) TaC particles, which inhibits the slip of atom planes and the migration of grain boundaries.

Impurities in tungsten

- Embrittlement of tungsten is increased by the presence of small amounts of interstitially soluble elements, such as O, **C**, and N, which lead to intergrannular precipitation, thereby further weakening the grain boundary strength.

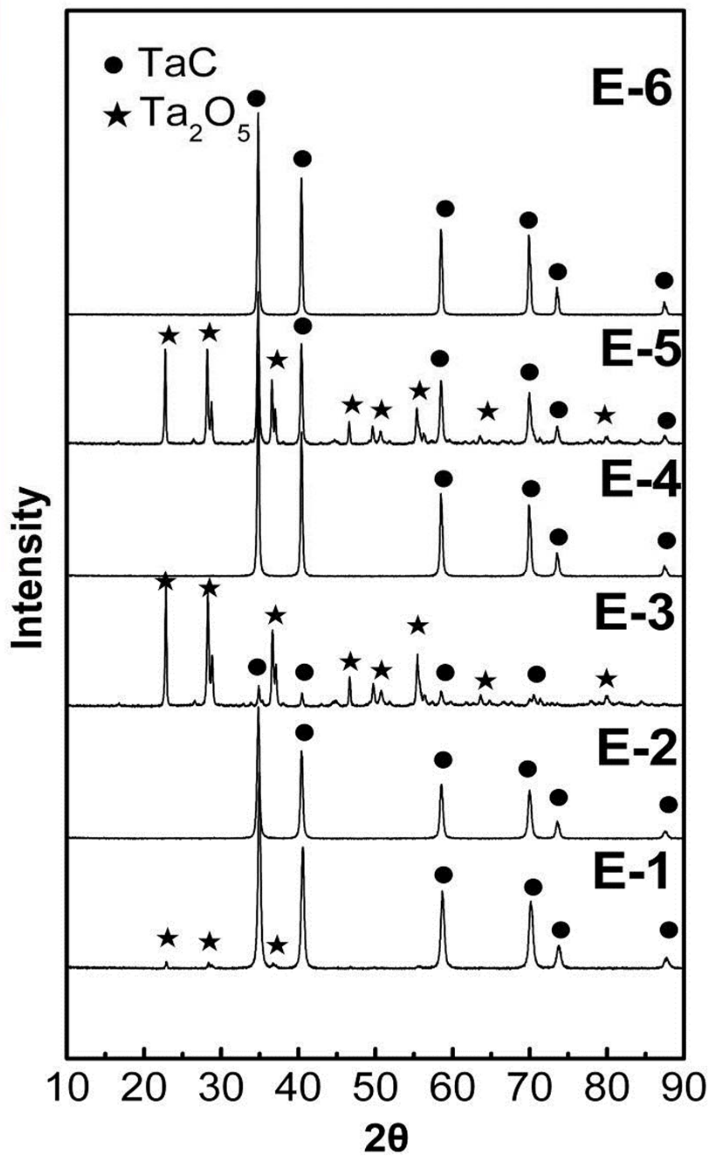
Self-preparation of TaC nanopowders

- TaC nanopowders were prepared using tantalum chloride ($TaCl_5$) and 24nm activated carbon by a liquid-phase process with ethanol.
- Residual Ta_2O_5 in synthetic TaC nanopowders was eliminated by mixing C and Ta in the ratio of 6 to 1.
- Free carbon in synthetic TaC nanopowders was eliminated in boiled strong nitric acid.

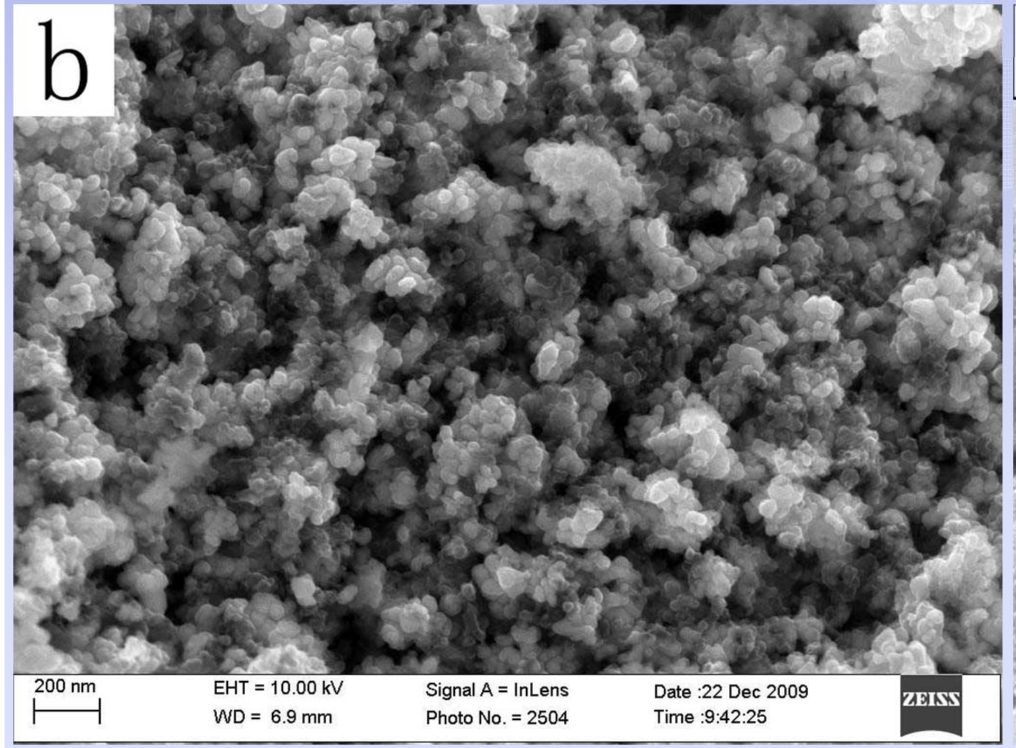
Preparation of TaC nanopowders

Sample	Temperature (^oC)	Time (h)	Activated carbon (g)	Atmosphere	BET (m^2/g)
E-1	1200	0.5	0.10	Vacuum	
E-2	1300	0.5	0.10	Vacuum	28.399
E-3	1200	0.5	0.10	H_2	
E-4	1300	0.5	0.10	H_2	12.146
E-5	1300	0.5	0.10	Ar	
E-6	1400	0.5	0.10	Ar	**61.140**

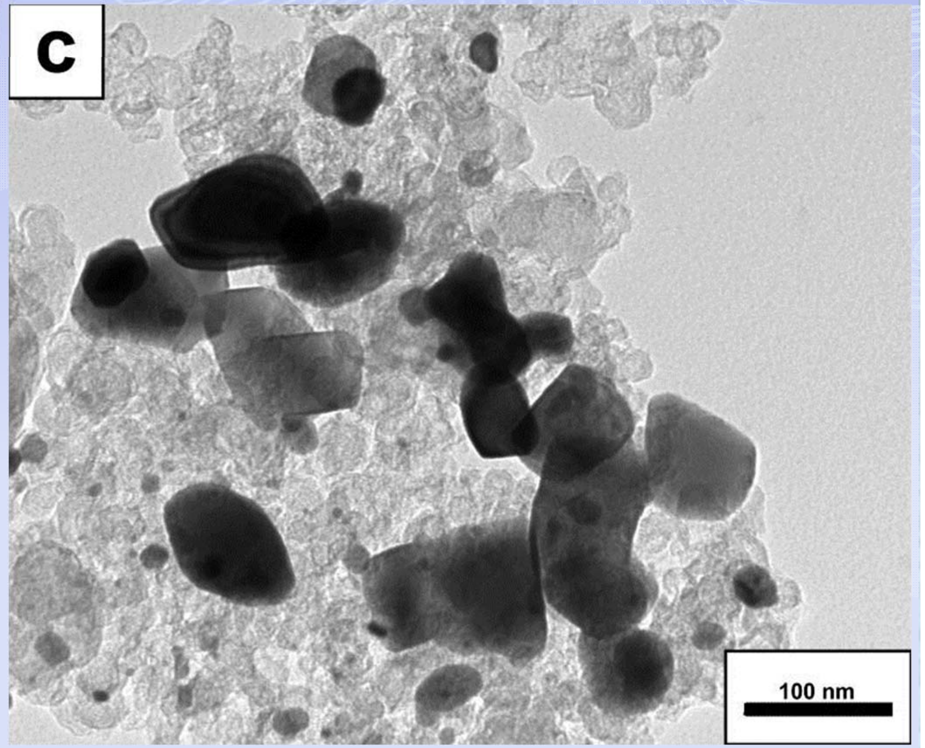
- Optimum processing condition is 1400 ^oC in argon, next is 1300 ^oC in vacuum or hydrogen.



Preparation of TaC nanopowders



Scanning electron micrograph of TaC nanopowders eliminated free carbon



Transmission electron micrograph of TaC nanopowders prepared in Ar at 1400 ^{o}C

Mass percent, %	Ta	Total C	Free C	O	N
Before decarburation	80.5	18.8	13.5	0.5	0.2
After decarburation	88.5	10.2	4.3	0.8	0.5

Blending procedure of nano-TaC with tungsten powders

commercial tungsten powder

Powder size	30 nm	200 nm	3 μm
Oxygen content	1.20%	0.50%	0.06 %

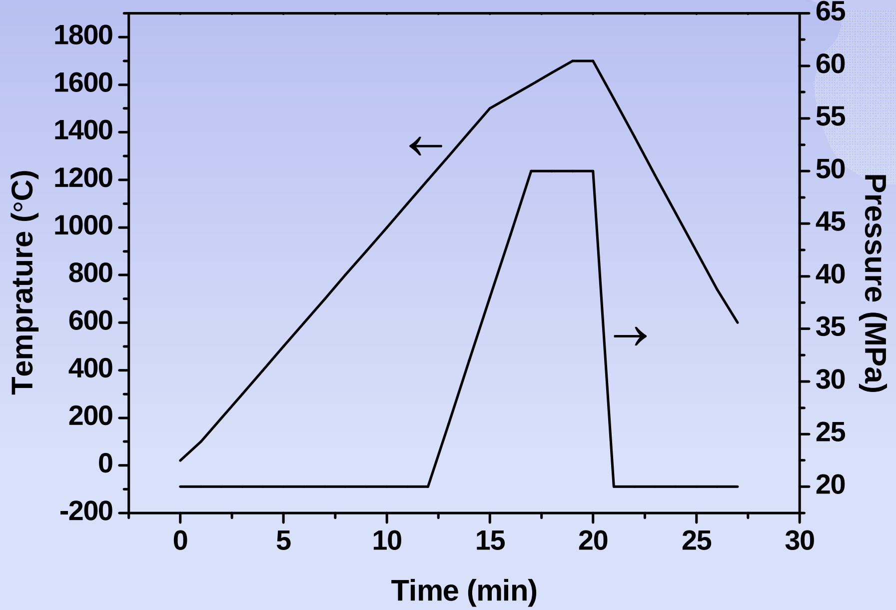
- Self-made nano-TaC powder
- ultrasonic dispersion
- Tungsten balls and nylon jars
- By a horizontal planetary ball mill

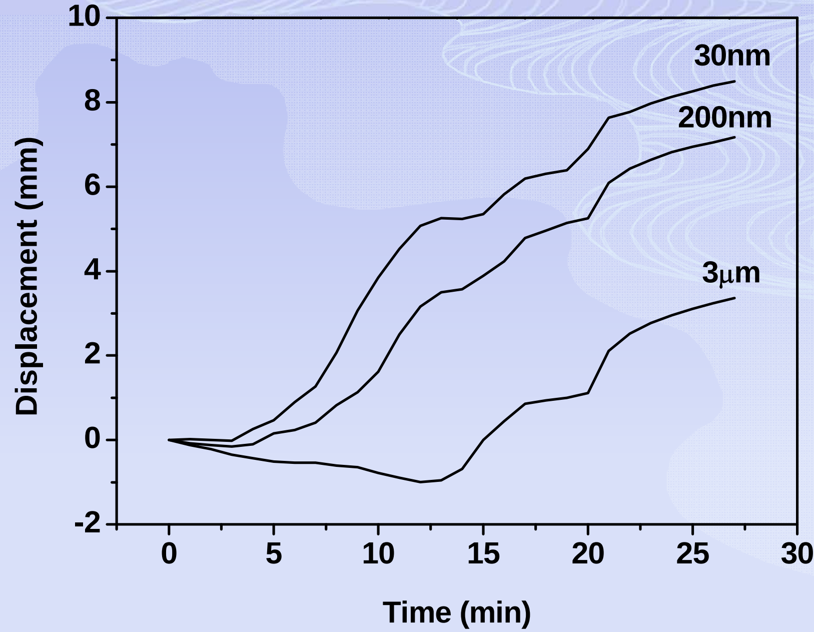
Sintering of pure tungsten

	Temperature (^{o}C)	Pressure (MPa)	Time (min)	Density (%)
Direct sintering	3000	0	50-120	88-96
Indirect sintering	2000-2700	0	480-1440	90-98
RSUHP	1900	9000	1-2	98
SPS	1700	30	30	96.4
SPS+RSUHP				99

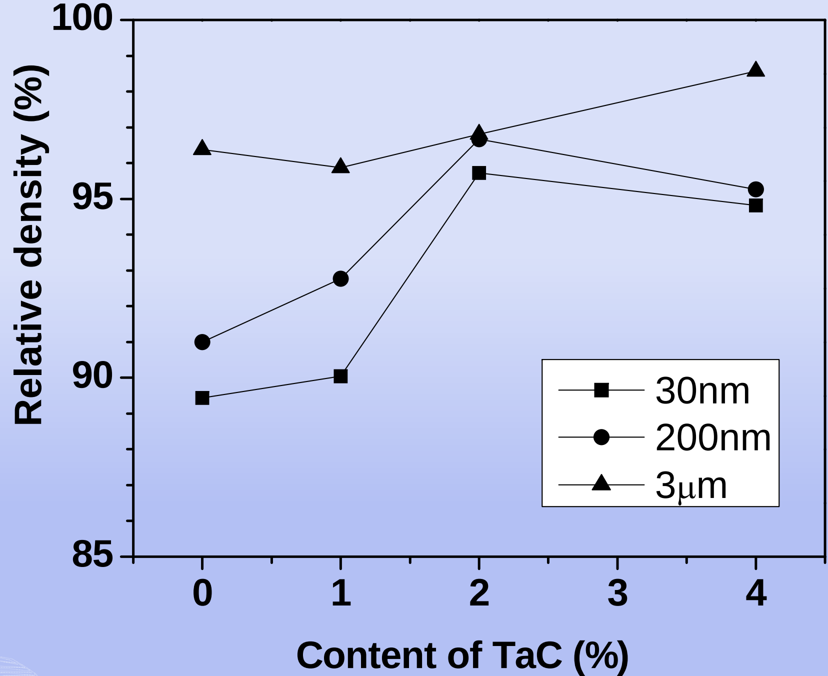
Resistance sintering under ultra-high pressure, RSUHP
Spark plasma sintering , SPS

Spark plasma sintering of TaC dispersion-strengthed tungsten

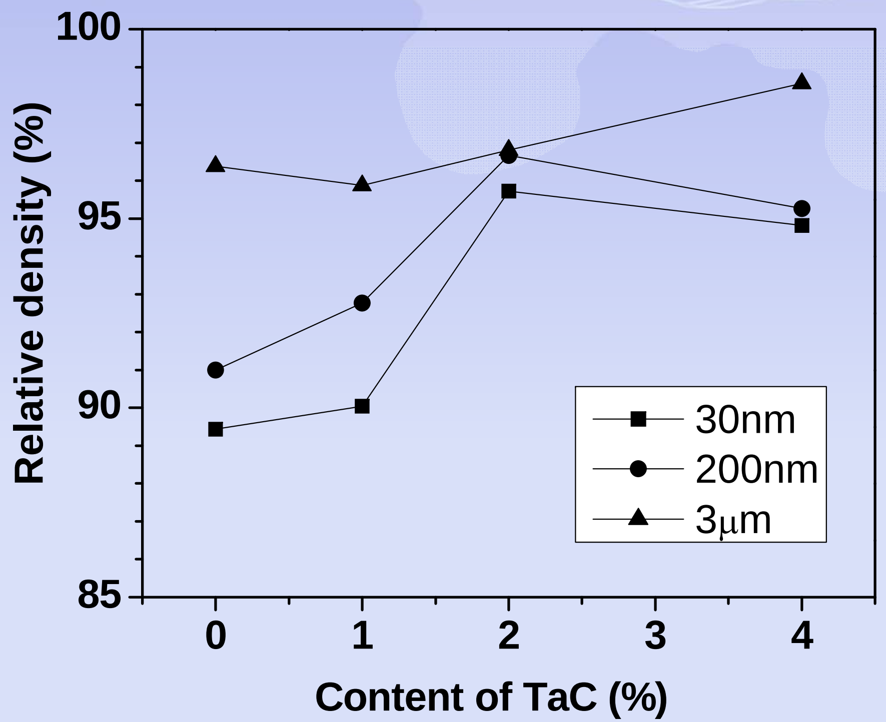




Green compact of tungsten is 20mm in diameter and about 6mm in thickness. Spark plasma sintering of samples is at 1700 °C under 50 MPa for 5 minutes. The finer tungsten powder is, the lower relative density of the sample is.



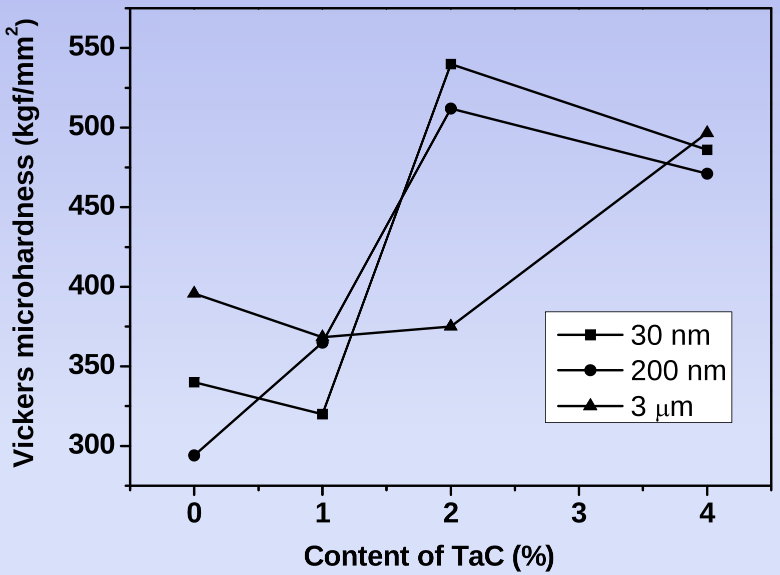
Sintered density of TaC dispersion-strengthed tungsten

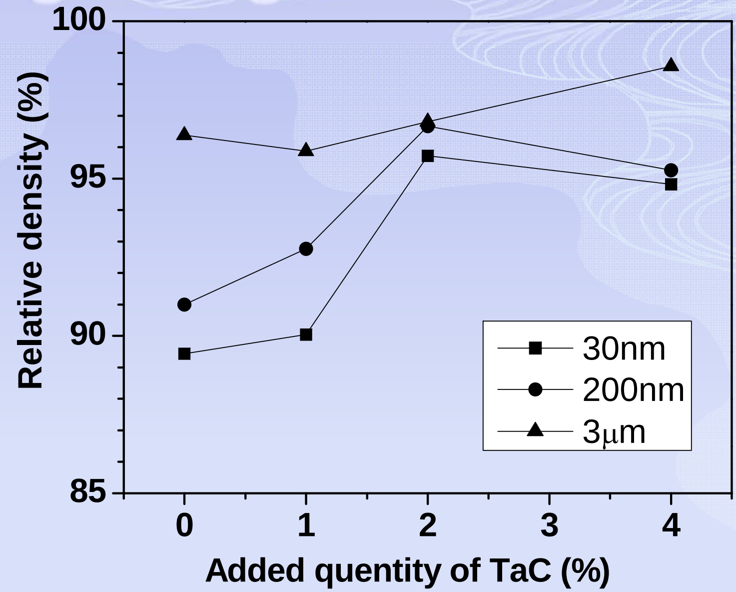


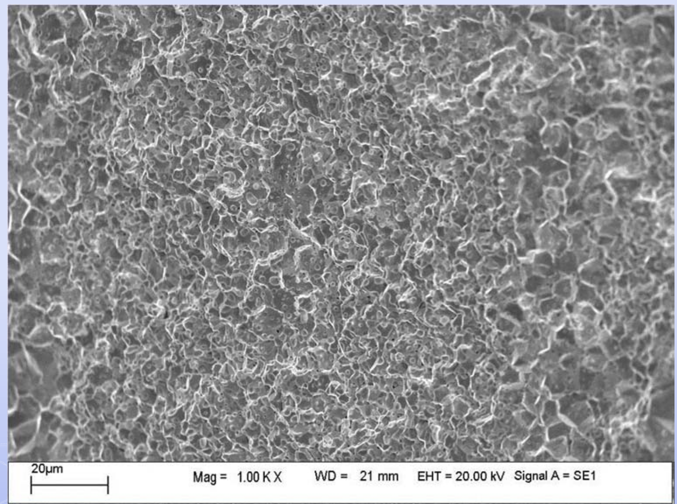
Material	Melting Point (°C)	Electrical Resistivity (μΩ·cm) (20 °C)	Thermal conductivity (W/m·K) (300 K)	Specific heat capacity (J/mol·K) (25 °C)
W	3422	5.5	173	24.297
TaC	3880	30.3	180	36.789

- **Difference of resistance between W and TaC promotes activated spark plasma sintering of W. Relative density of W+nano TaC is 98.6% which is higher than 96.4% of pure tungsten.**

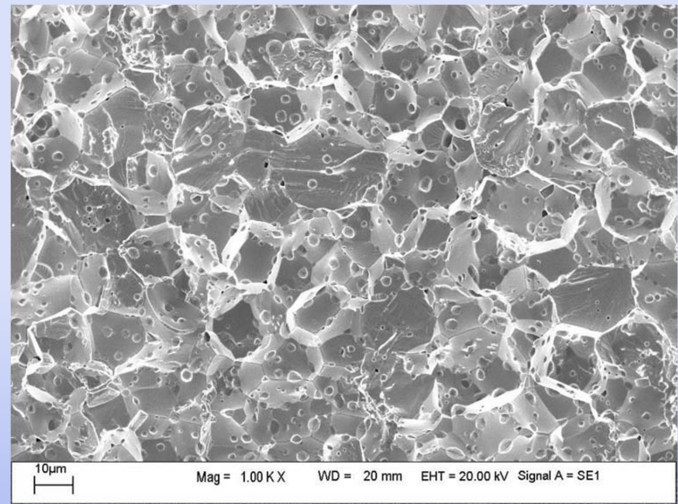
Vicker's microhardness, relative density and fractograph of TaC dispersion-strengthed tungsten







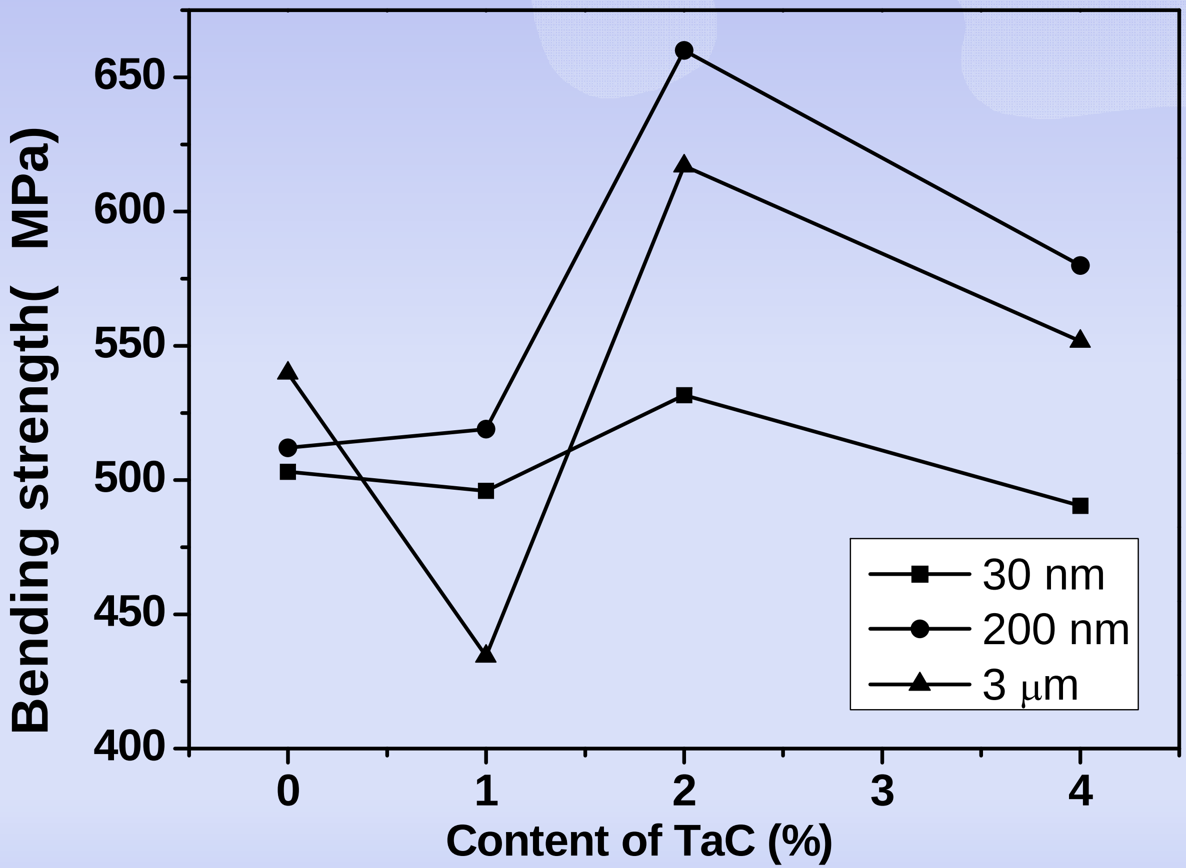
30 nm tungsten with 2% nano-TiC



3µm tungsten with 2% nano-TiC

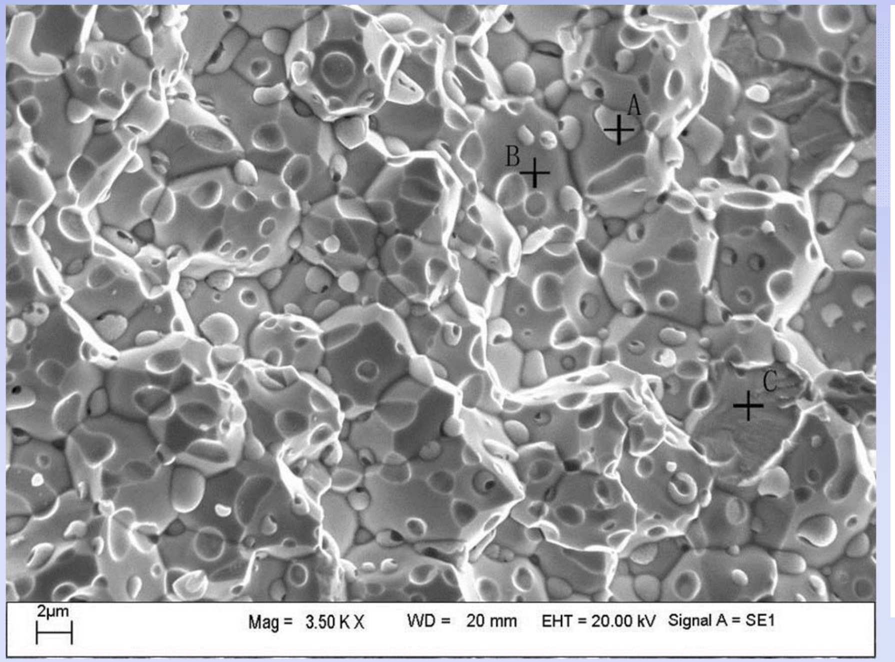
Grain size of 30nm tungsten with 2% nano-TaC is 5µm, that of 3µm tungsten is 15 µm. The smaller grain size is, the higher Vicker's hardness is.

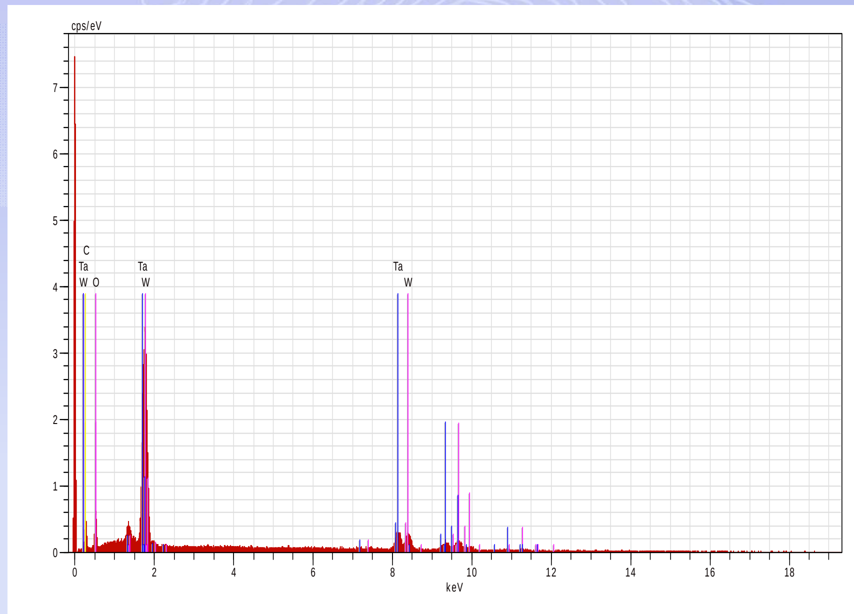
Bending strength of TaC dispersion-strengthed tungsten



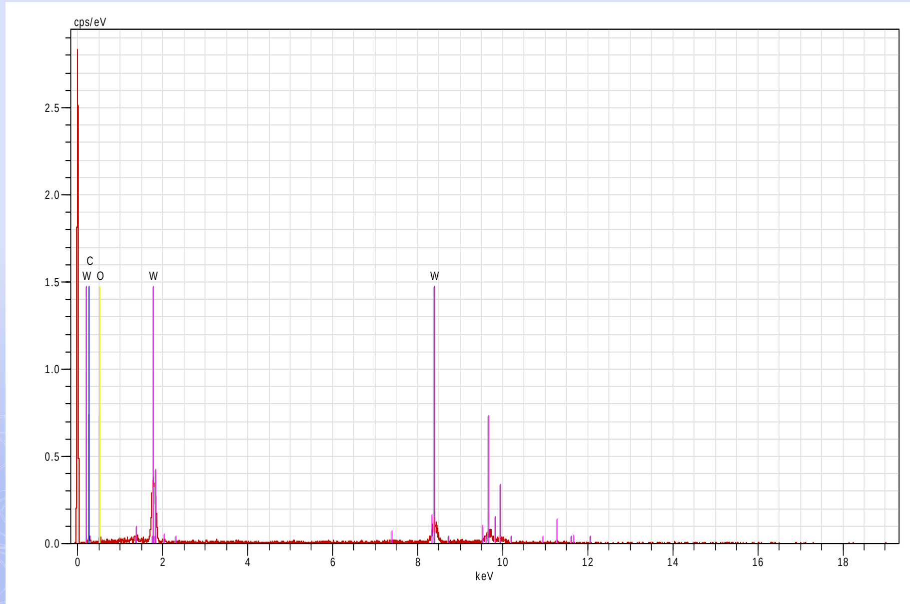
- Samples of 200nm tungsten powder gain highest bending strengths.
- Samples of 30nm tungsten powder gain lower bending strengths because higher content of oxygen.

Energy Dispersive Spectrometry of 200nm W with 2% nano-TaC

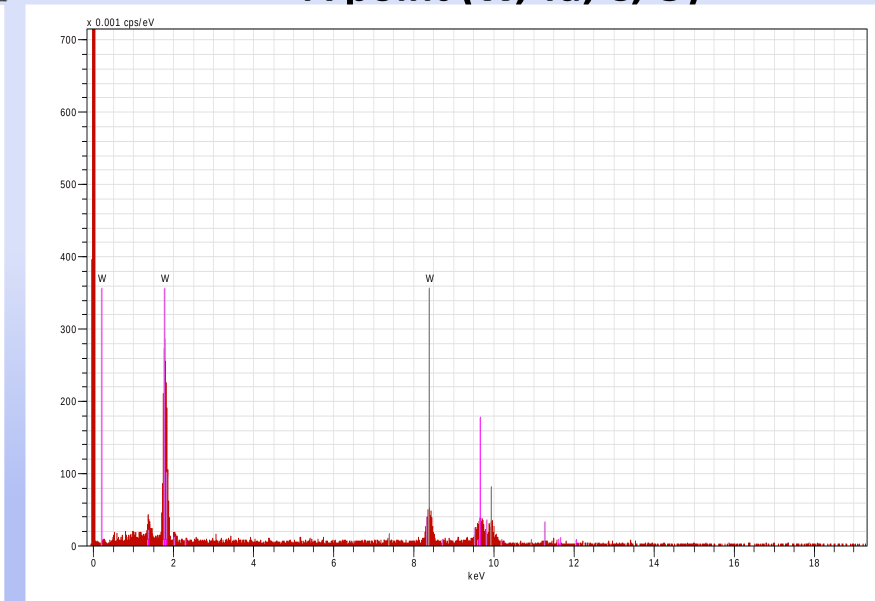




A point (W, Ta, C, O)

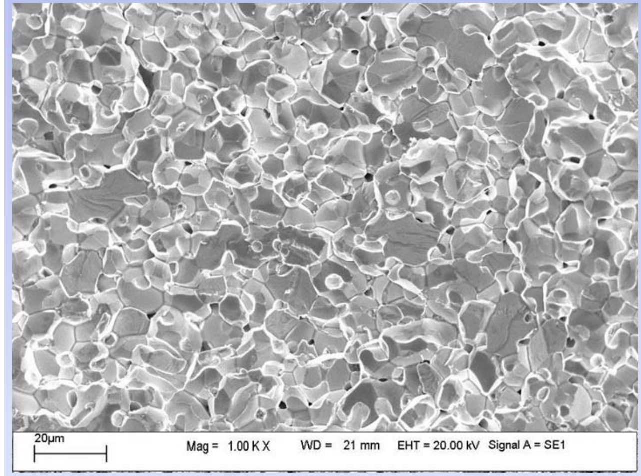


B point (W, C, O)

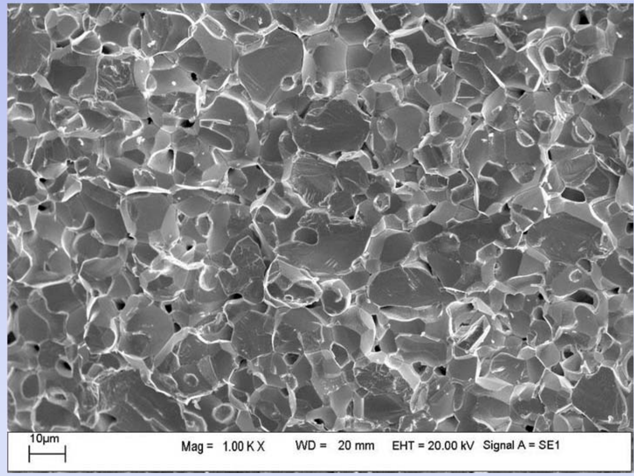


C point (W)

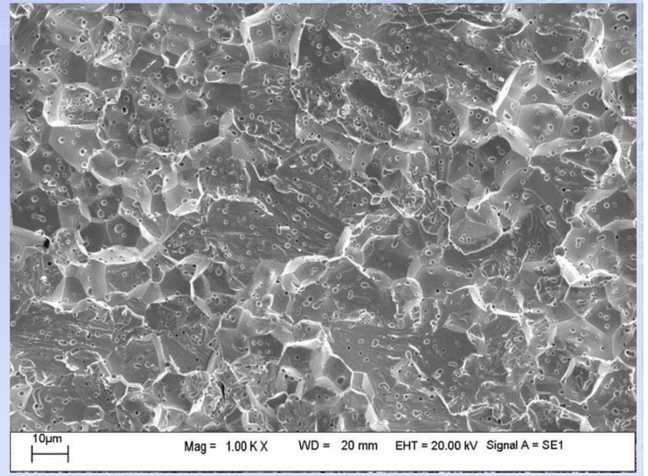
Nano-TaC for grain growth inhibition of sintered tungsten



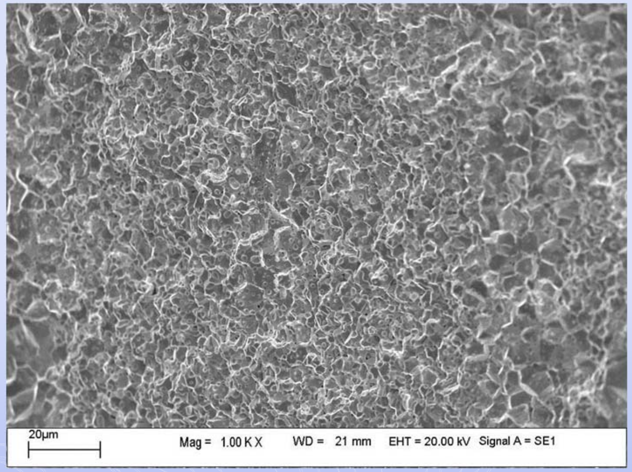
30nm W



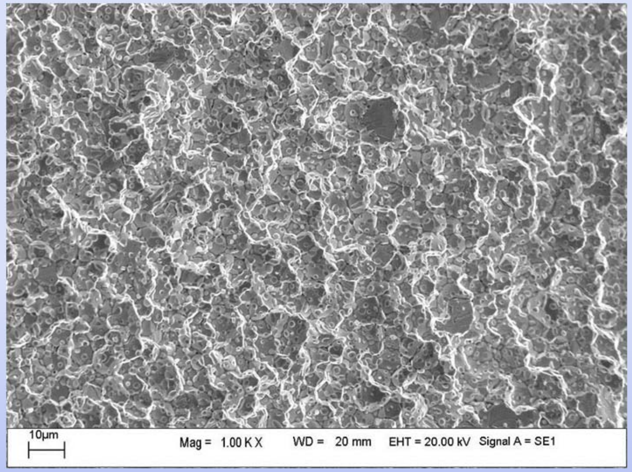
200nm W



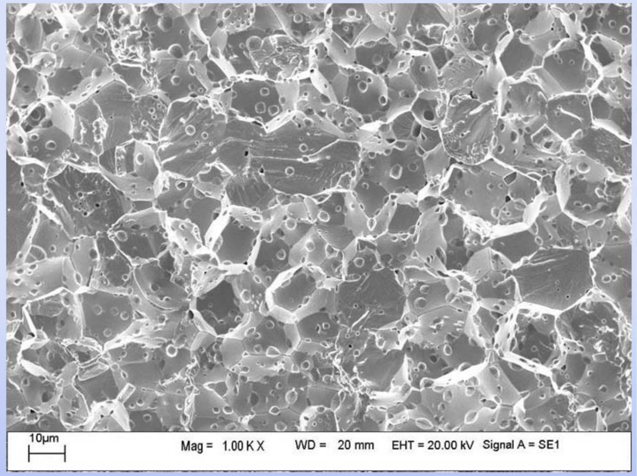
3µm W



30nm W+2% TaC



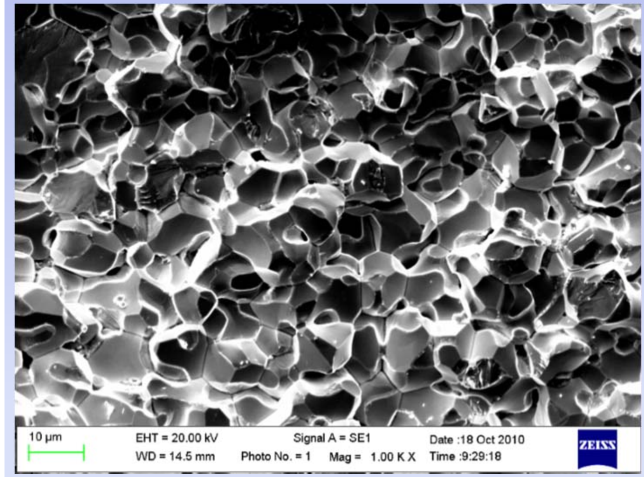
200nm W+2% TaC



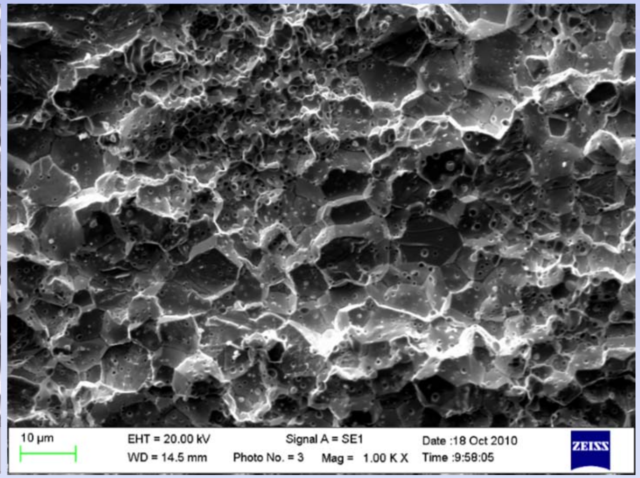
3µm W+2% TaC

Compare pure tungsten with W+2%TaC, Nano-TaC inhibits grain growth of sintered tungsten. (fractrograph)

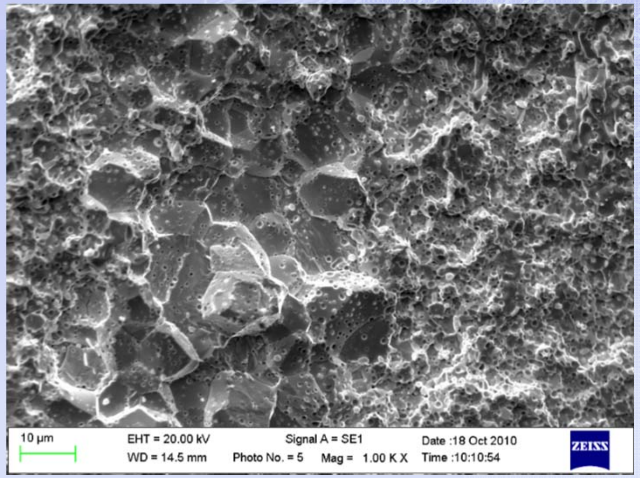
Grain growth of TaC dispersion-strengthed tungsten in heat treatment with 10 °C/min to 1600 ^{o}C for 2h



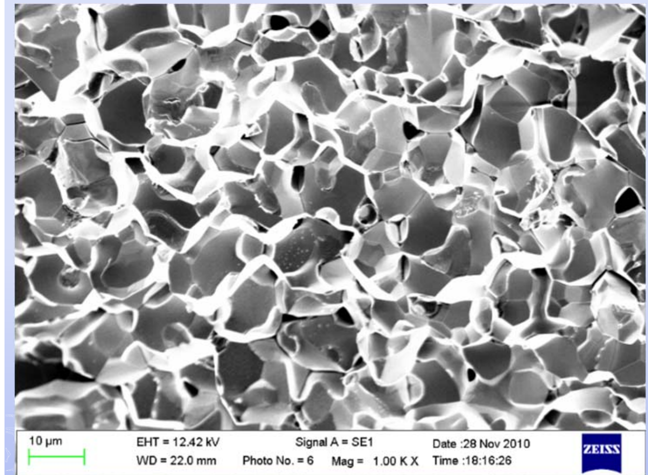
30nm W before heat treatment



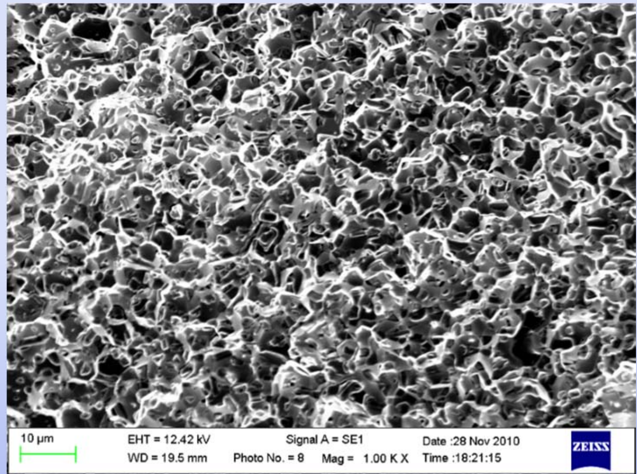
30nm W+2%TaC before heat treatment



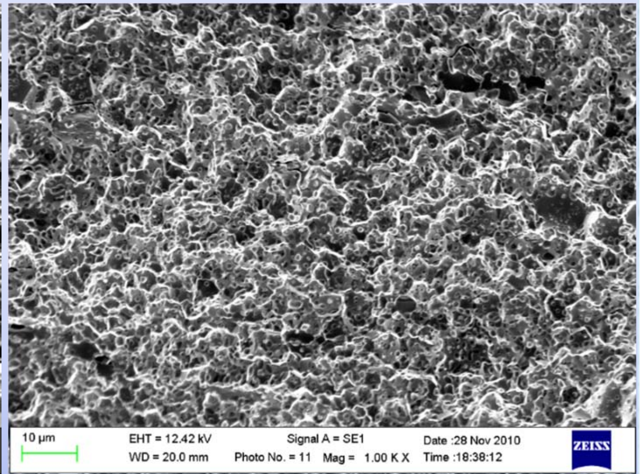
30nm W+4%TaC before heat treatment



30nm W after heat treatment



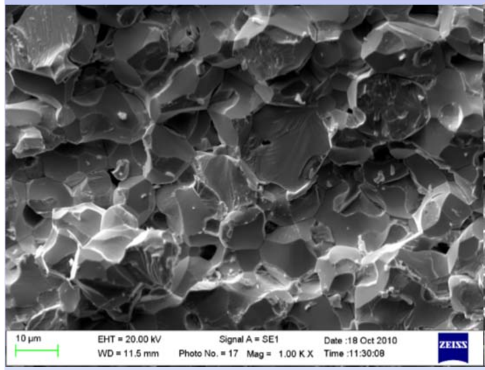
30nm W+2%TaC after heat treatment



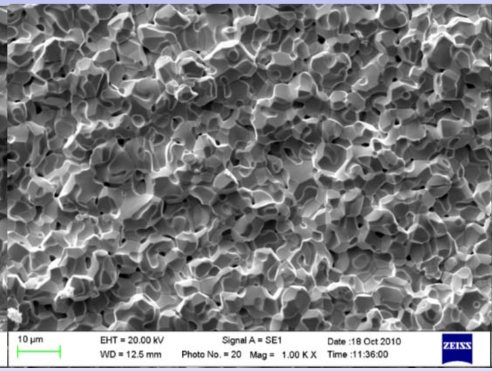
30nm W+4%TaC after heat treatment

30nm W+nano-TaC inhibit grain growth of tungsten in heat treatment. (fractrograph)

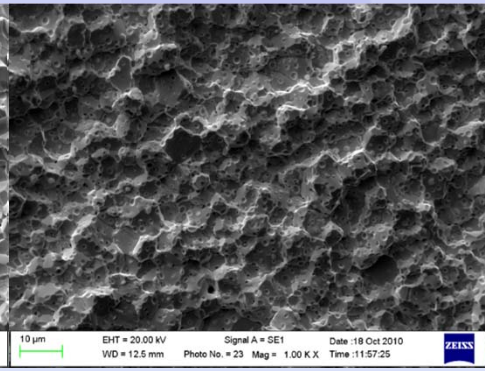
Grain growth of TaC dispersion-strengthed tungsten in heat treatment with 10 °C/min to 1600 ^{o}C for 2h



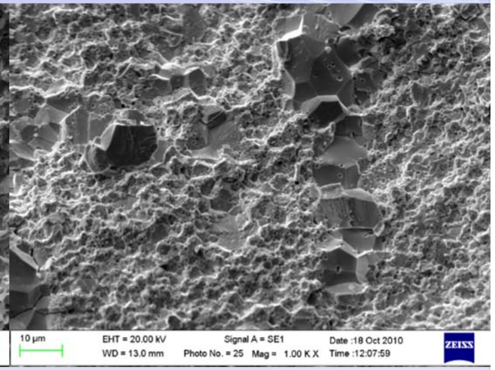
200nm W before heat treatment



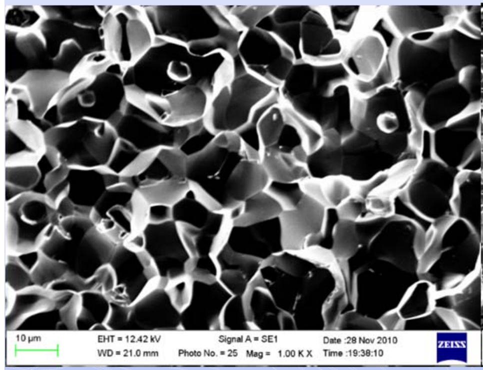
200nm W+1%TaC before heat treatment



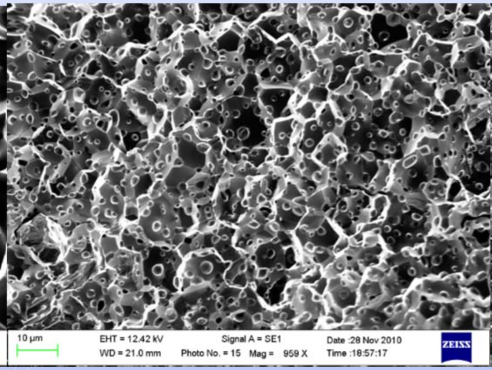
200nm W+2%TaC before heat treatment



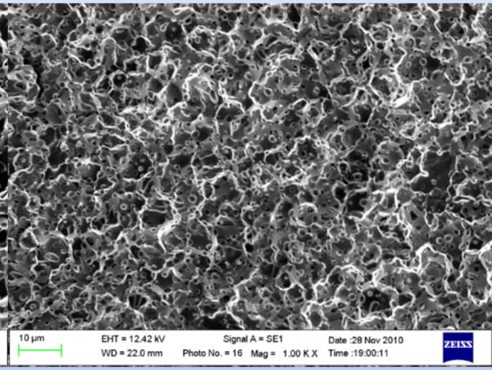
200nm W+4%TaC before heat treatment



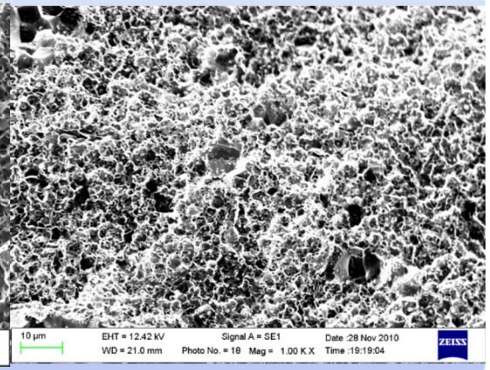
200nm W after heat treatment



200nm W+1%TaC after heat treatment



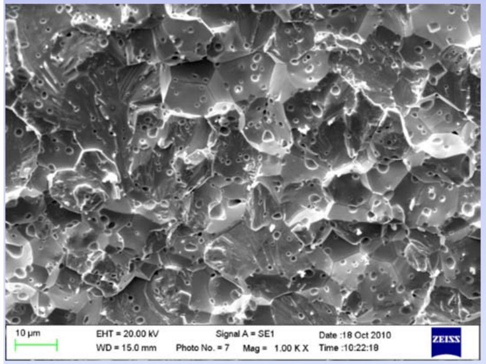
200nm W+2%TaC after heat treatment



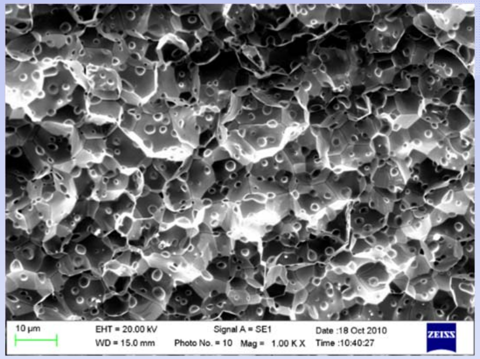
200nm W+4%TaC after heat treatment

200nmW+nano-TaC inhibit grain growth of tungsten in heat treatment. (fractrograph)

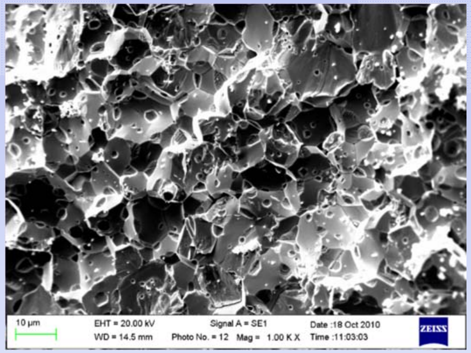
Grain growth of TaC dispersion-strengthed tungsten in heat treatment with 10 °C/min to 1600 ^{o}C for 2h



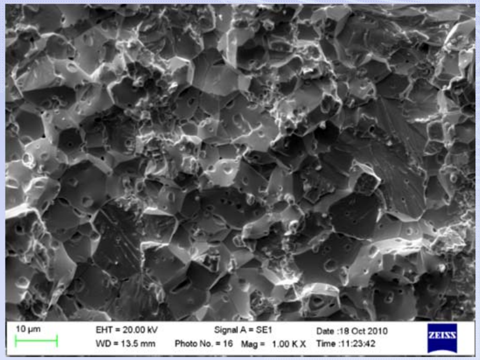
3μm W before heat treatment



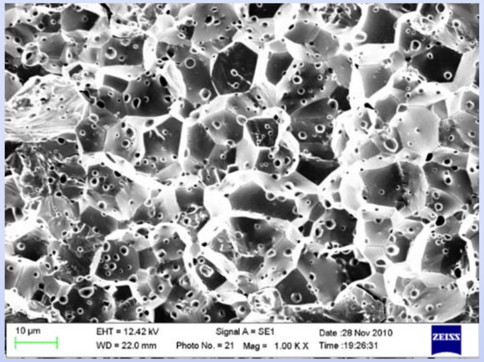
3μm W+1%TaC before heat treatment



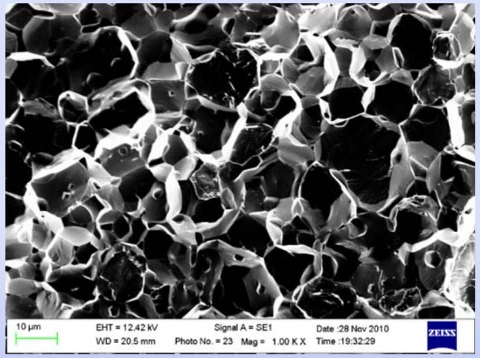
3μm W+2%TaC before heat treatment



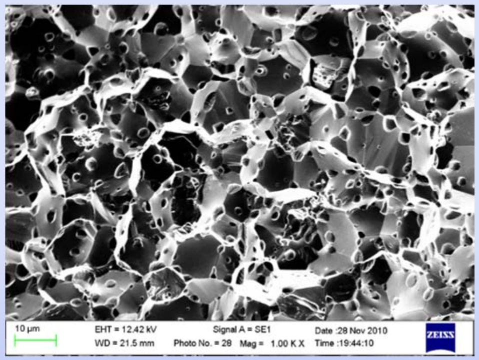
3μm W+4%TaC before heat treatment



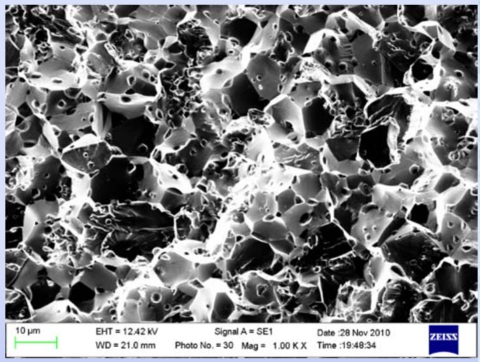
3μm W after heat treatment



3μm W+1%TaC after heat treatment



3μm W+2%TaC after heat treatment

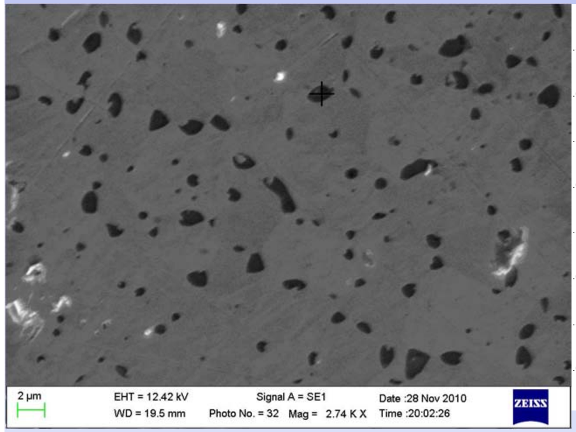


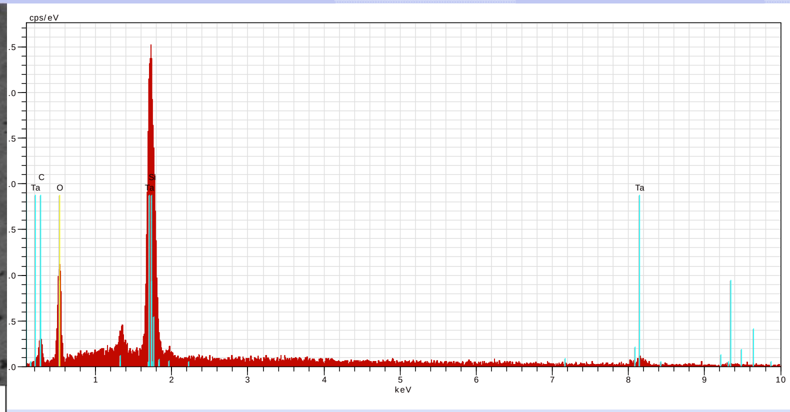
3μm W+4%TaC after heat treatment

3μm W is not compared with 30nm W and 200nm W in inhibiting grain growth of tungsten in heat treatment. (fractrograph)

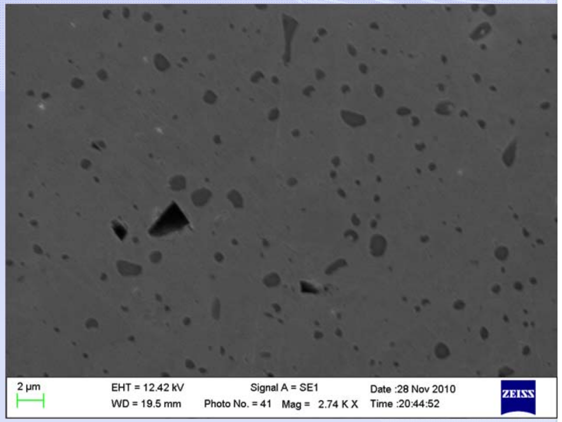
Radiation damage of TaC dispersion-strengthed tungsten by high-energy Helium

He of 0.02MeV and $2\times10^{17}cm^{-2}s^{-1}$ for 6h at ambient temperature by a linear accelerator

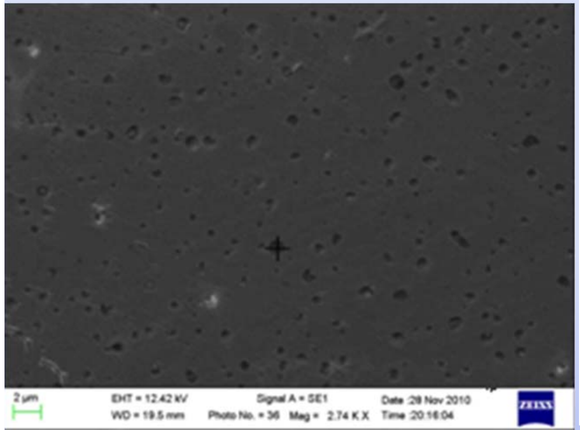


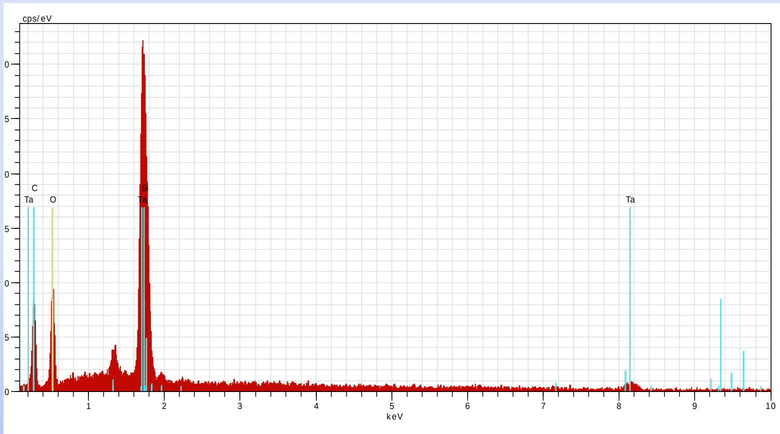


200nm W+2%TaC before irradiation

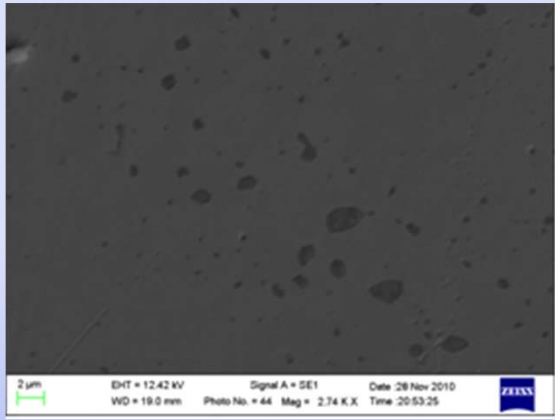


30nm W+2%TaC before irradiation





200nm W+2%TaC after irradiation



30nm W+2%TaC after irradiation

He blistering is not seen, but TaC particles drop out from tungsten surface because their interfacial strength is weaker than the damaging stress by high-energy He. However, the TaC particles in tungsten can not drop out.

Conclusions

- Nano-TaC powders can be prepared by a liquid phase process from tantalum chloride dissolved in ethanol and nano activated carbon powders.
- Difference of electric resistance in W and TaC promotes activated spark plasma sintering of W. Relative density of tungsten with nano-TaC reaches 98.6% which is higher than 96.4% of pure tungsten.
- Bending strength from 30nm tungsten powders is lower than that made from 200 nm tungsten powders because its higher content of oxygen.
- Nano-TaC inhibits grain growth of minus 200nm tungsten in sintering and thermal treatment.
- He blistering is not seen, but TaC particles drop out from tungsten surface radiated by He of 0.02MeV and $2\times10^{17}cm^{-2}s^{-1}$ for 6h at ambient temperature with a linear accelerator.

Acknowledgement

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Thanks for your attention