Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information For

Eutectic Solidification Applied to Nanofabrication: a Strategy to Prepare Large-Scale Tungsten Carbide Nanowalls and Nanowires

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1. Experimental facility

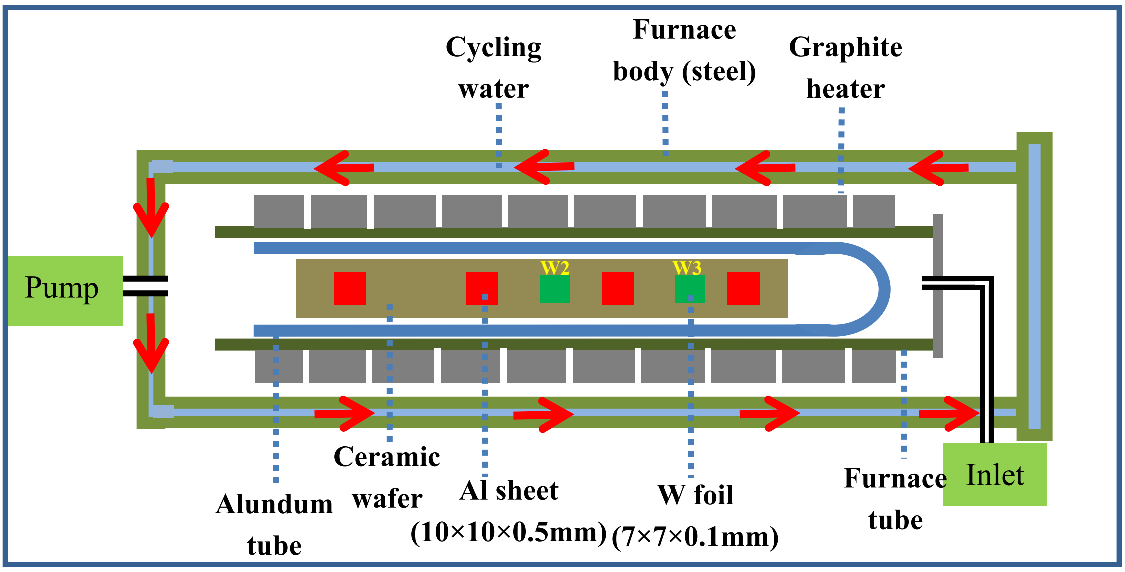

Figure S1 The furnace setup and resource location of the experiments

Figure S1 illustrates the detailed structure of the furnace used. The whole shell is made of hollow cast steel, inside of which is cycling water for cooling the chamber. All of the subassemblys including graphite heater, furnace tube, and protecting alundum tube are in the big chamber which is pumped by molecular pump. In the experiment, the sizes and location of precursors are shown in the figure too.

2. TEM analysis of WC nanowires cleaned by NaOH solution

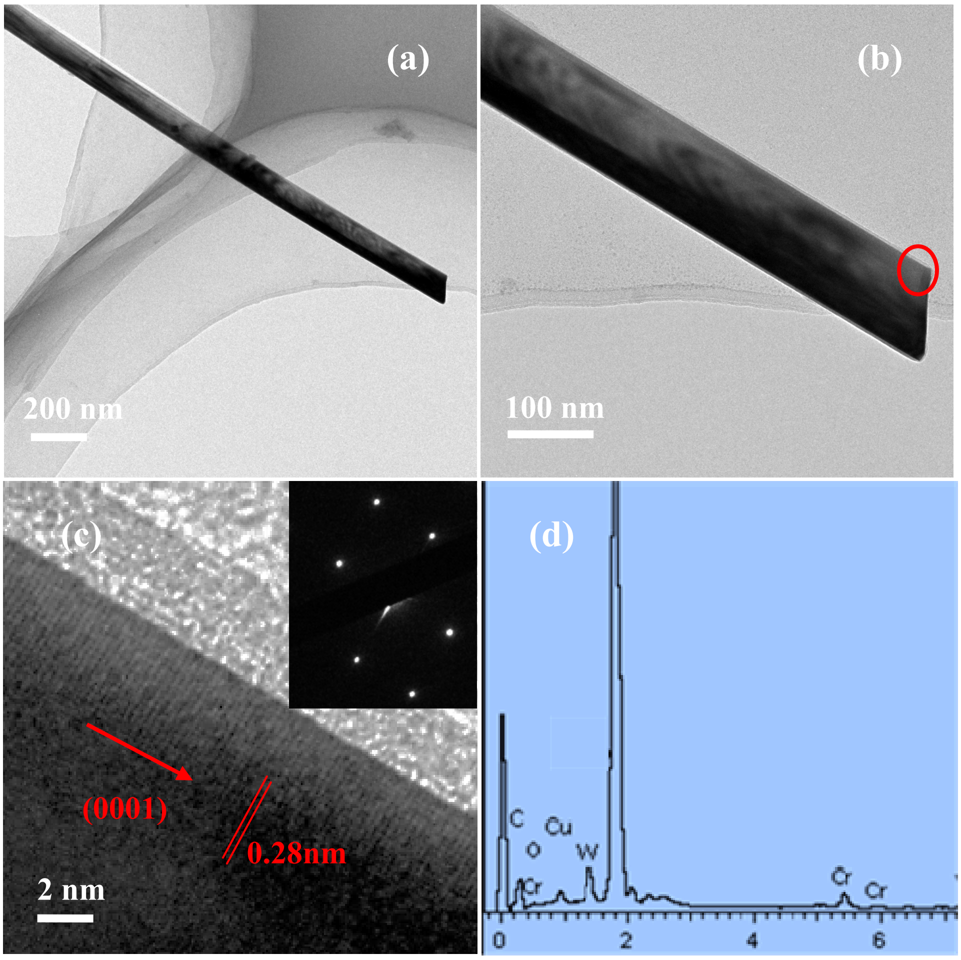

Figure S2 TEM analysis of WC nanowires cleaned by NaOH solution

As shown in **Figure S2**, after bath in NaOH solution, the WC nanowire is free of surficial intercrescence and no Al signal could be detected by EDS measurement.

3. Contrastive experiments

1. Influence of Oxygen

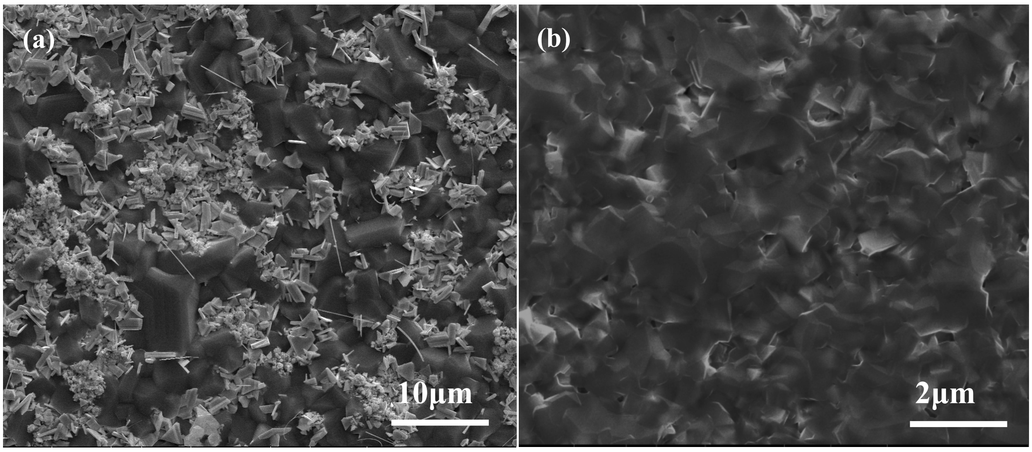

Figure S3 images from W2 and W3 on condition of too much Oxygen

As comparament, we do experiment on condition of residual Oxygen. In detail, only mechanical pump was used in the pretreatment process, the ultimate pressure was about 10Pa when the heating process began. As shown in **Figure S3**, WC nanowalls with high quality couldn't grow out under overmuch Oxygen environment. (a) discribes the sample from the centre of ceramic sheet (W2), which has some nanowires and other pell-mell WC structures growing out, just similar to the sample in **Figure 4(a).** however, there is no abvious structure except for a layer of close-grained Al2O3 film in W3 position. In case of overmuch Oxygen, amounts of Al would combine with O, forming Al2O3 crystal layer which covers the W substrate, preventing the contaction of Al and W. it is abvious that sample shown in (b) received more Al2O3, leading to a almost completely coverage of substrate.

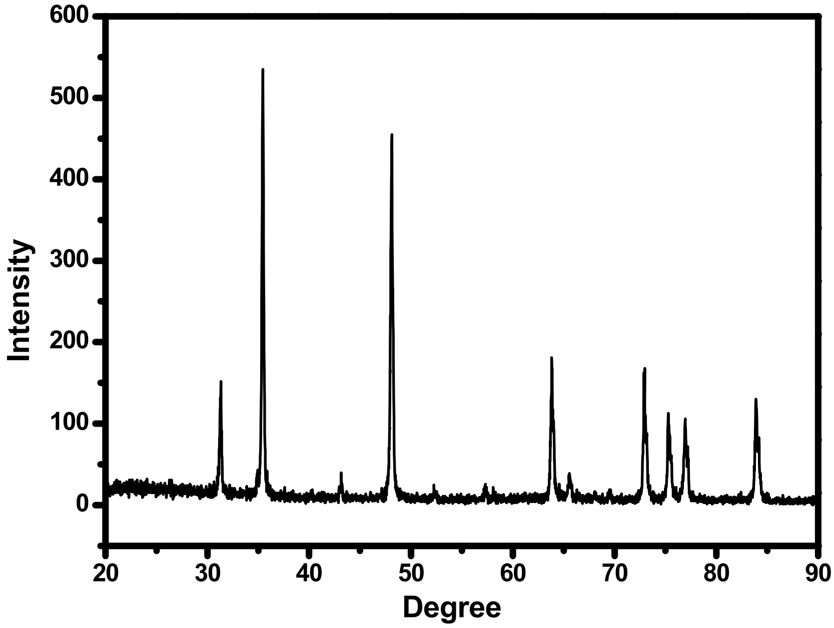

Figure S4 XRD result from nanowires sample shown as **Figure S2 (a)**

XRD test was empoyed to confirm composition of W2, which is shown as **Figure S4**. Aacording to the result, signal of Al_2O_3 is more abvious than nanowalls sample, but signals of WC and W_2C decrease, which is reasonable because large area of substrate is covered by Al_2O_3 crystal layer.

2. Influence of Al

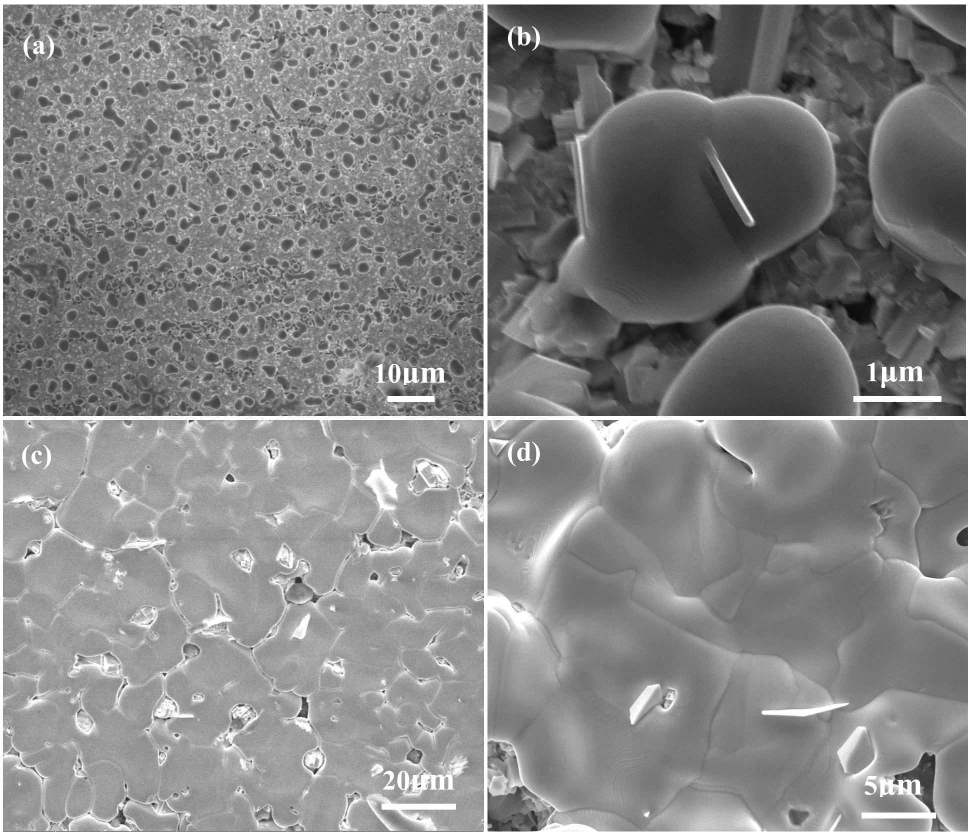

Figure S5 (a, b) images of samples from insufficient Al precursor, (c, d) images of samples from excessive Al precursor

Figure S5 shows the images from samples grown with different amount of Al precursor. We first used Al sheet about 10×5×0.5mm, on this situation, very few WC nanostructures emerged, but isolated droplet-like islands distributed on the substrate with mussy morphologies just as (a) and (b). In fact, relative amount of O in the atmosphere would rise in case of low level of Al vapor, which is to say that Oxygen would influence the growth process more actively. In detail, on one case, high level of O would prevent W substrate from contacting with Al vapor further through consuming more Al atoms in the atmosphere. On the other, low level of Al can only etch W substrate in very small areas forming W-Al-C liquid which are easy to solidify as a result of Al shortage, which is how those mussy structures come. However, these WAlC structures would cut down the W atoms supplement from substrate to a great extent even for regular formed liquid droplets, leading to excessive of Al atoms in these droplets which is hard for WC nanostructures to separate out, which would keep liquid state till the temperature decreased to freezing point. That is why we only could see morphology like that.

Figure S5(c), (d) shows images from samples grown on the condition of excessive Al precursor. In this case, four Al sheet in size of 10*10*1mm were set every sites. After reaction, W substrate deformed seriously as a result of alloying of W and Al in large area shown as (c). There are no WC nanostructures grow out on this condition either, but alloying liquids combined into liquid layer in large area. The liquid layer, with so high level of Al, was hard to solidify and and precipitate WC nanowalls and nanowires.

4. W-Al-C ternary phase diagram and W-Al phase diagram

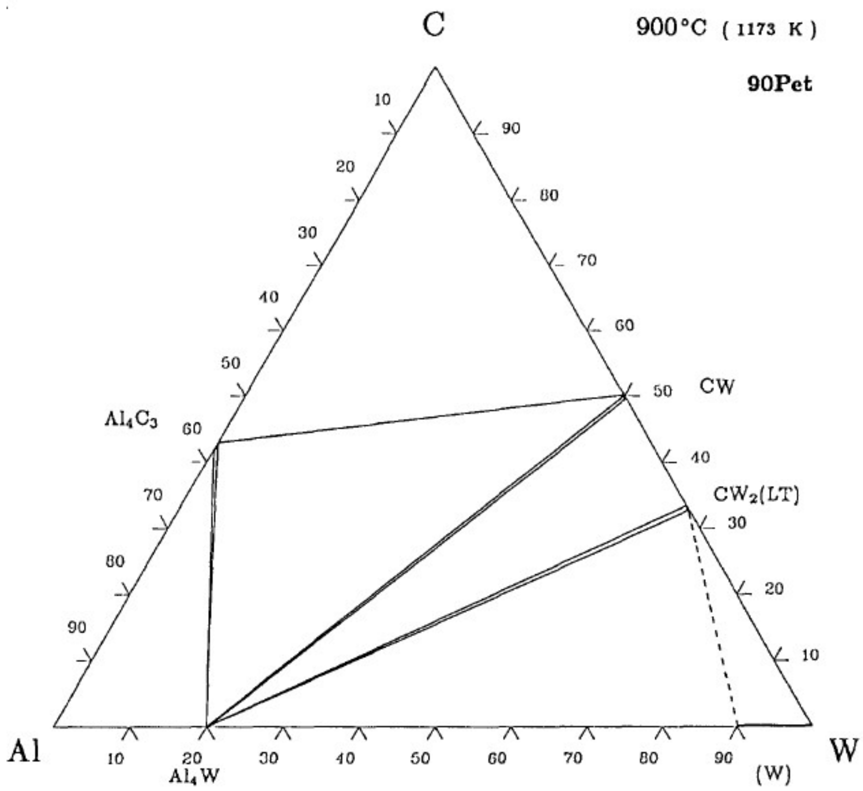

Figure S6 W-Al-C ternary phase diagram at 1173K

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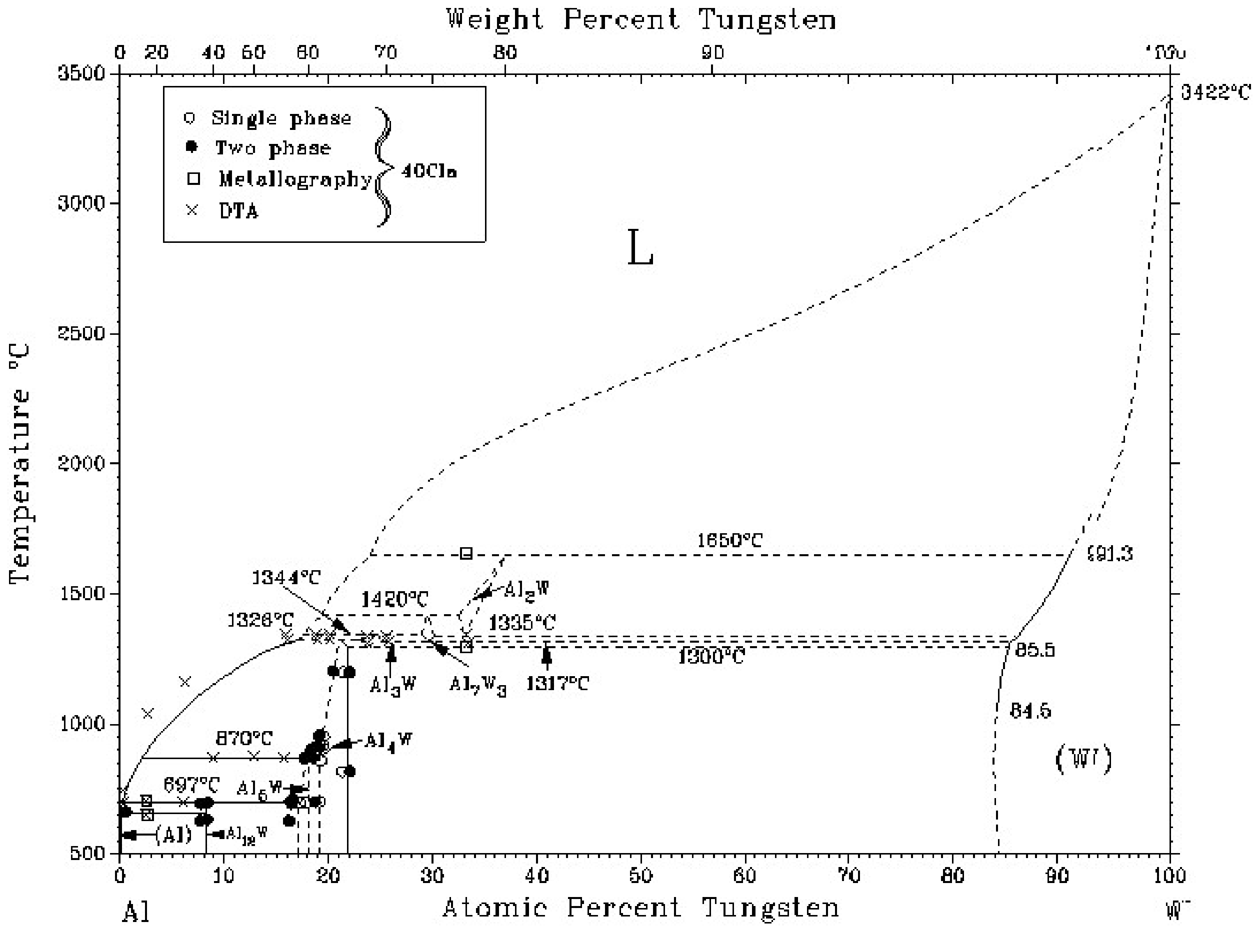

Figure S7 W-Al phase diagram