Science Advances
AAAS

Bulk ultrafine grained/nanocrystalline metals via slow cooling

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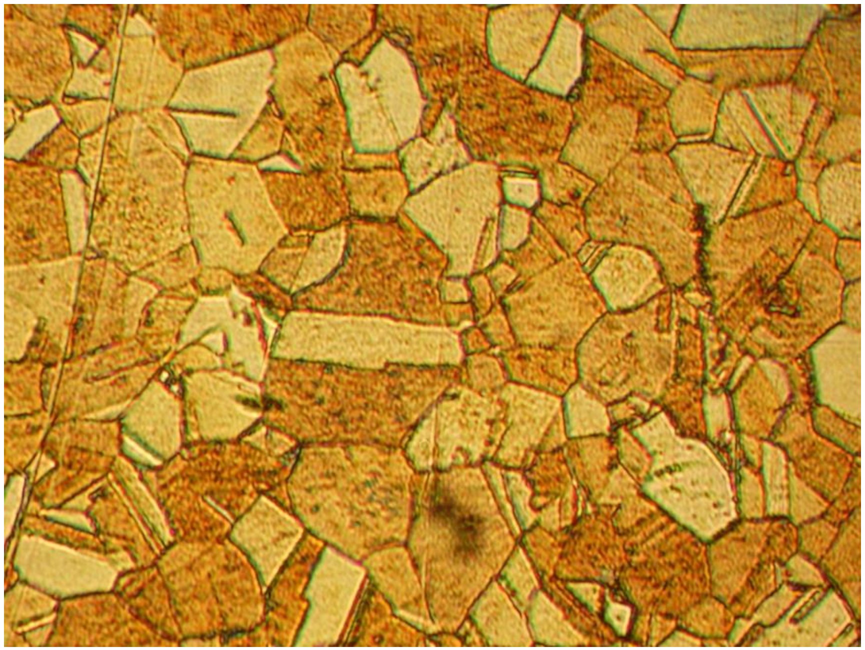
Terminologies

- **Grain and grain boundary** :

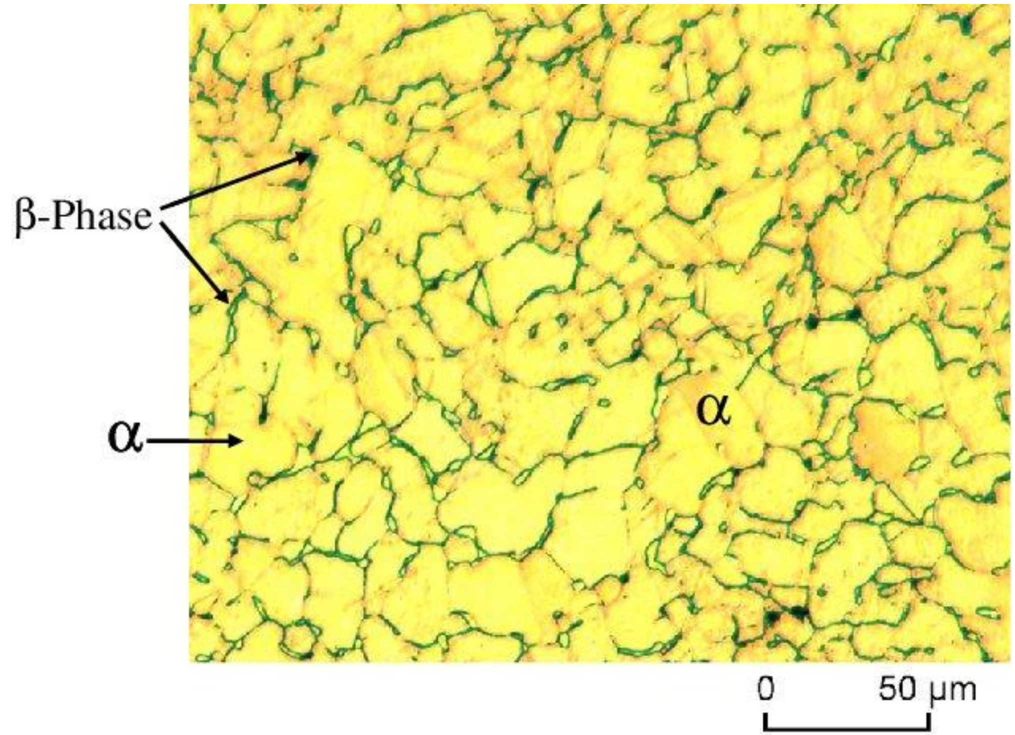
  Metals used for manufacturing process consist of crystals of different orientations i.e. polycrystals. Each of the crystal goes into a crystalline orientation or **Grain**. So each grain consists of either a single crystal or polycrystalline aggregate.

  The surface that separates individual grains from each other are called **Grain Boundaries.** The crystal orientation changes abruptly across the grain boundary.

Relevance to our group



Microstructure of annealed brass.



Microstructure of cold drawn brass.

Background work

ADVANCED MATERIALS

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Simultaneously Increasing the Ductility and Strength of Ultra-Fine-Grained Pure Copper**

By *Yong-Hao Zhao, John F. Bingert, Xiao-Zhou Liao, Bao-Zhi Cui, Ke Han, Alla V. Sergueeva, Amiya K. Mukherjee, Ruslan Z. Valiev, Terence G. Langdon,* and *Yuntian T. Zhu**

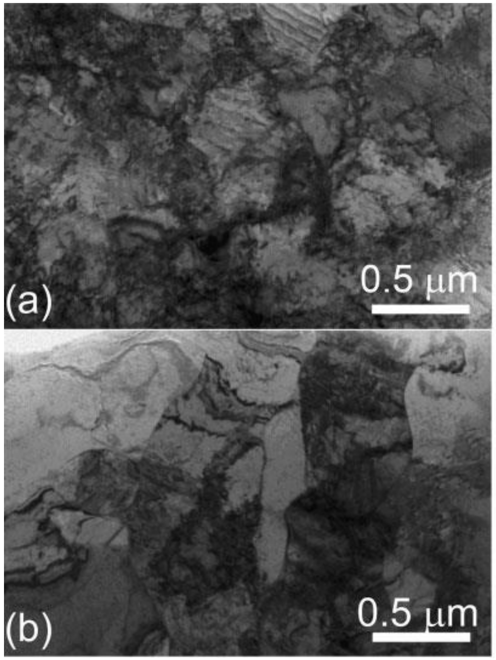


Figure a,b: Typical bright-field TEM images for the UFG_{ECAP} and $UFG_{ECAP+D+R}$ Cu samples, respectively. It is apparent that the grain boundaries in the $UFG_{ECAP+D+R}$ sample are sharper and straighter than in the UFG_{ECAP} sample.

Equal channel angular pressing (ECAP)
Cryodrawn (D) and cryorolling (R)

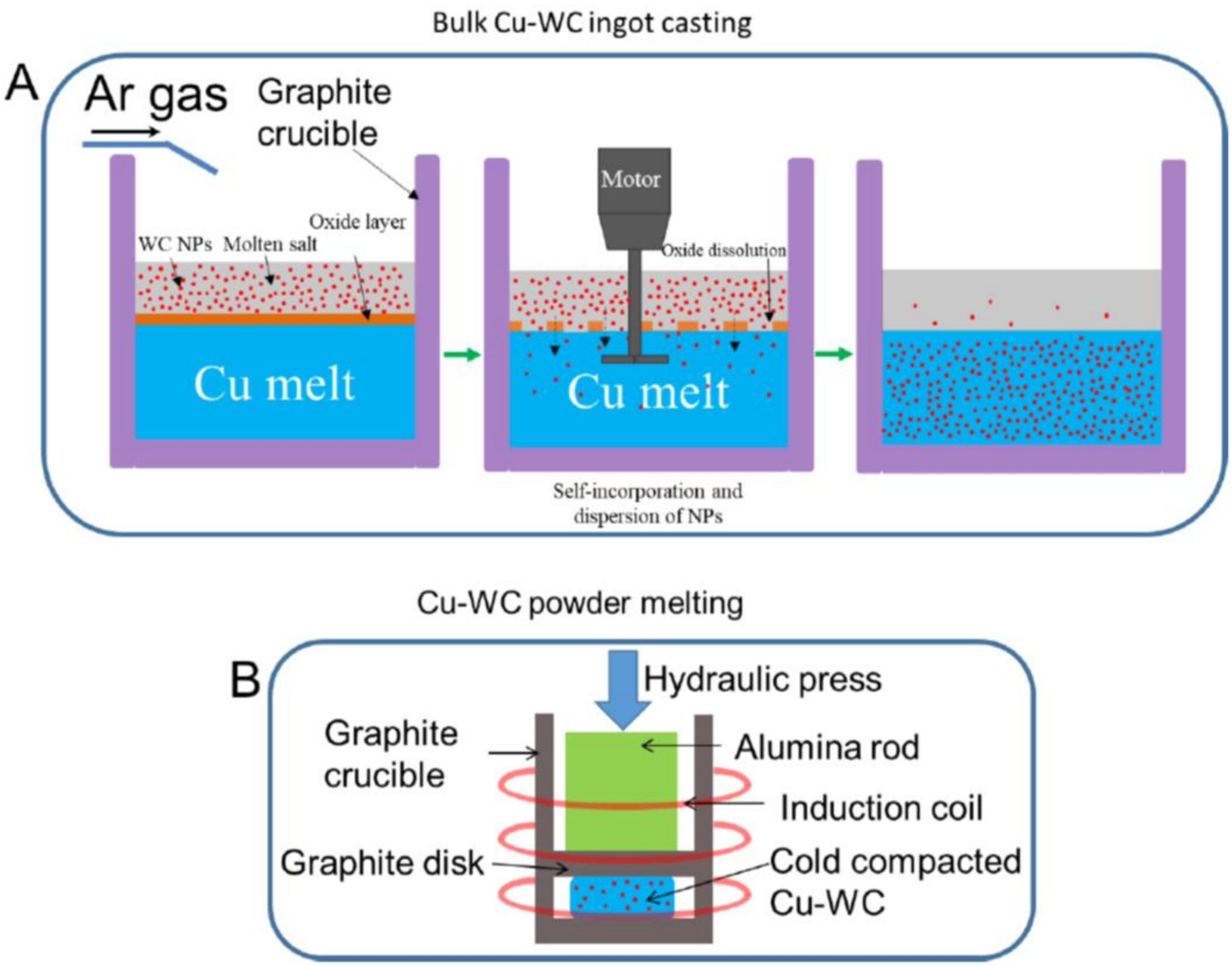
Introduction

- Grain refinement in metals during solidification is of great interest due to the enhanced mechanical properties, more homogeneous microstructure, and improved processability of refined microstructures.

- Here, they report a new discovery that nanoparticles can refine metal grains down to ultrafine or even nanoscale by instilling a continuous nucleation and growth control mechanism during slow solidification.

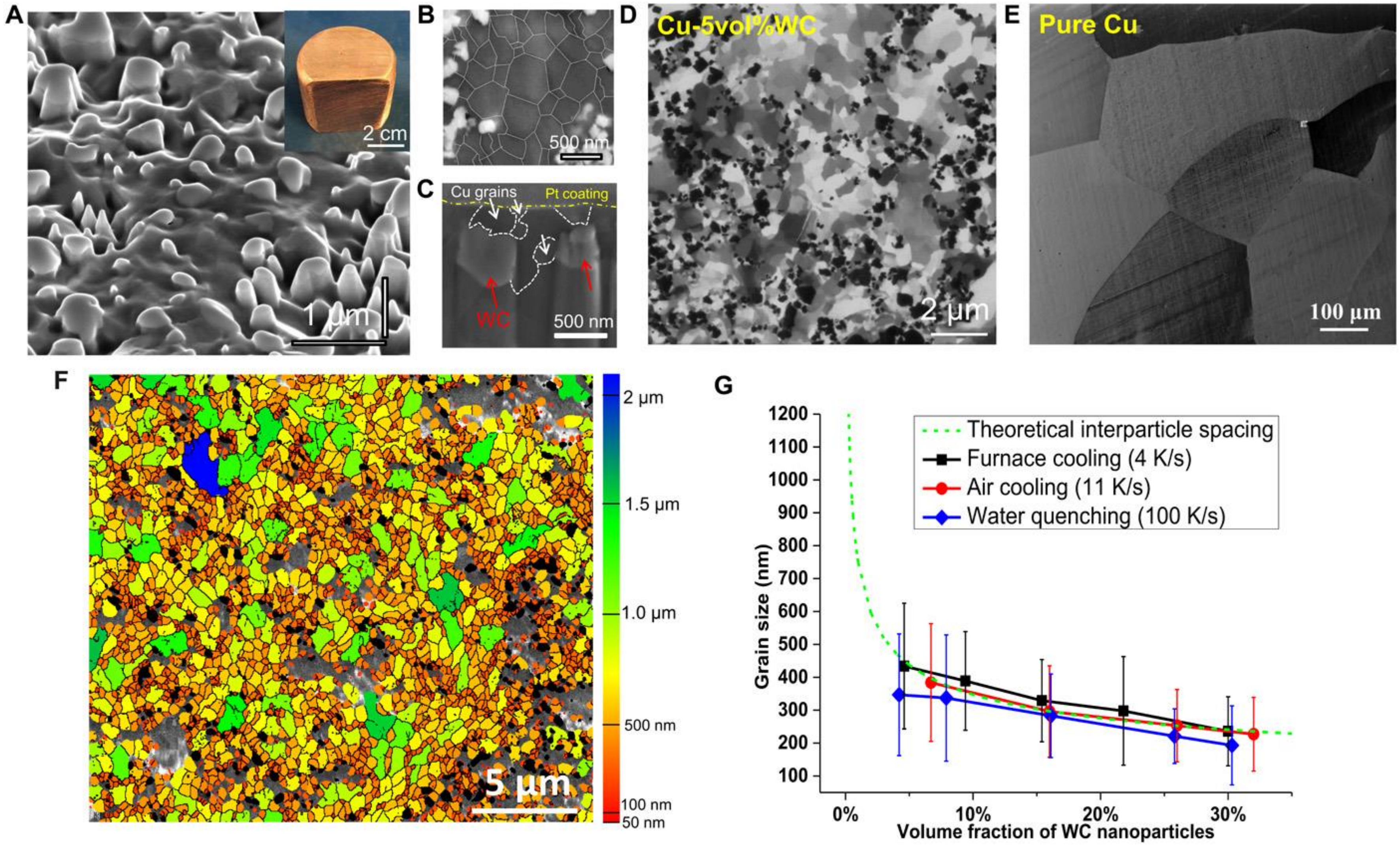
- When casting pure Cu with tungsten carbide (WC) nanoparticles, the grain sizes of Cu are refined substantially down to ultrafine and even nanoscale.

- This revolutionary method paves the way for the mass production of bulk stable UFG/nanocrystalline materials that may be readily extended to any other processes that involve cooling, nucleation, and phase growth for widespread applications.

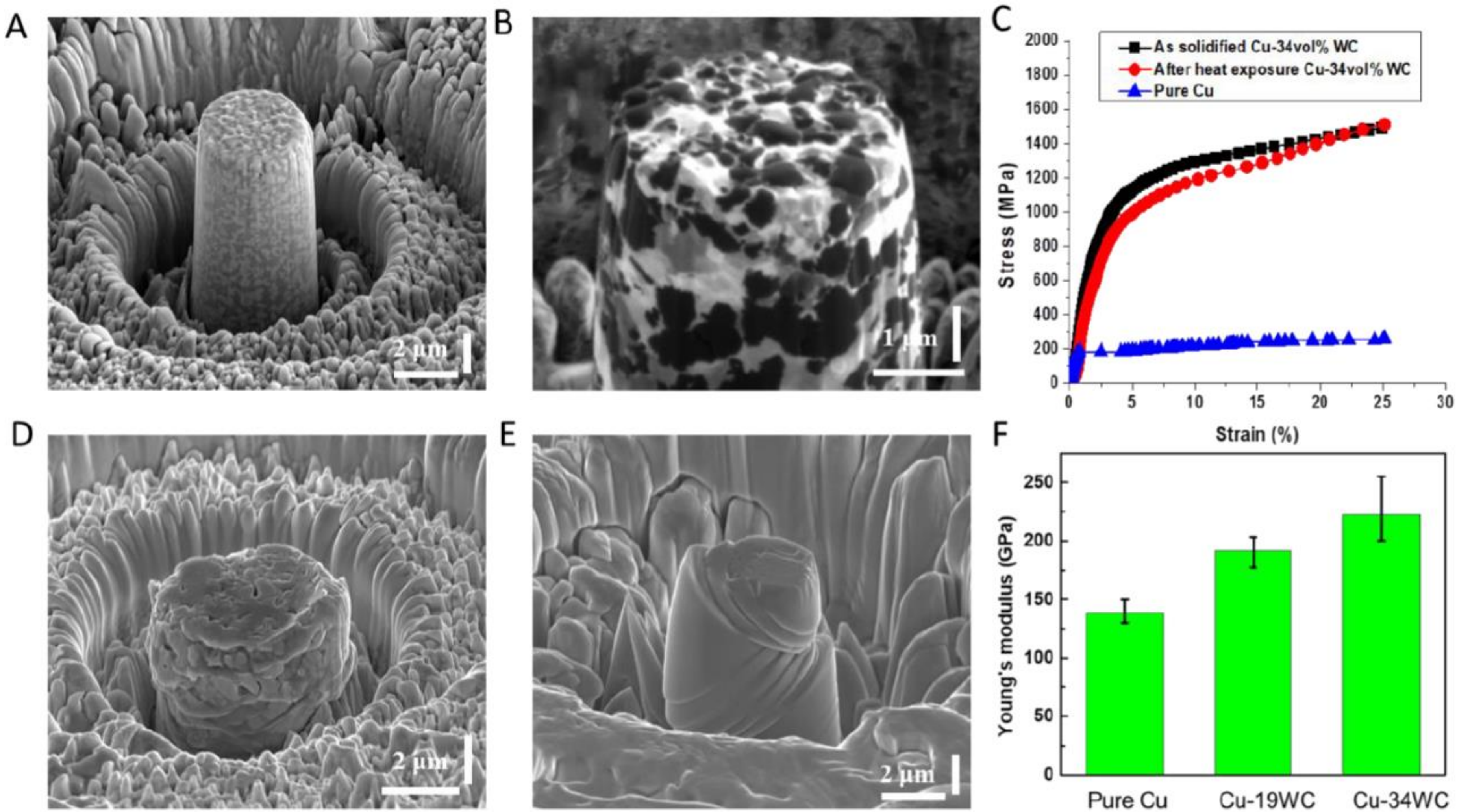


Fabrication of Cu-containing WC nanoparticles. (A) Schematic illustration of the salt-assisted self-incorporation for Cu-WC before casting bulk ingots. (B) Schematic illustration of the powder melting method to cast Cu containing WC nanoparticles.

Fig. 1 Microstructure of bulk UFG/nanocrystalline Cu-containing distributed WC nanoparticles.

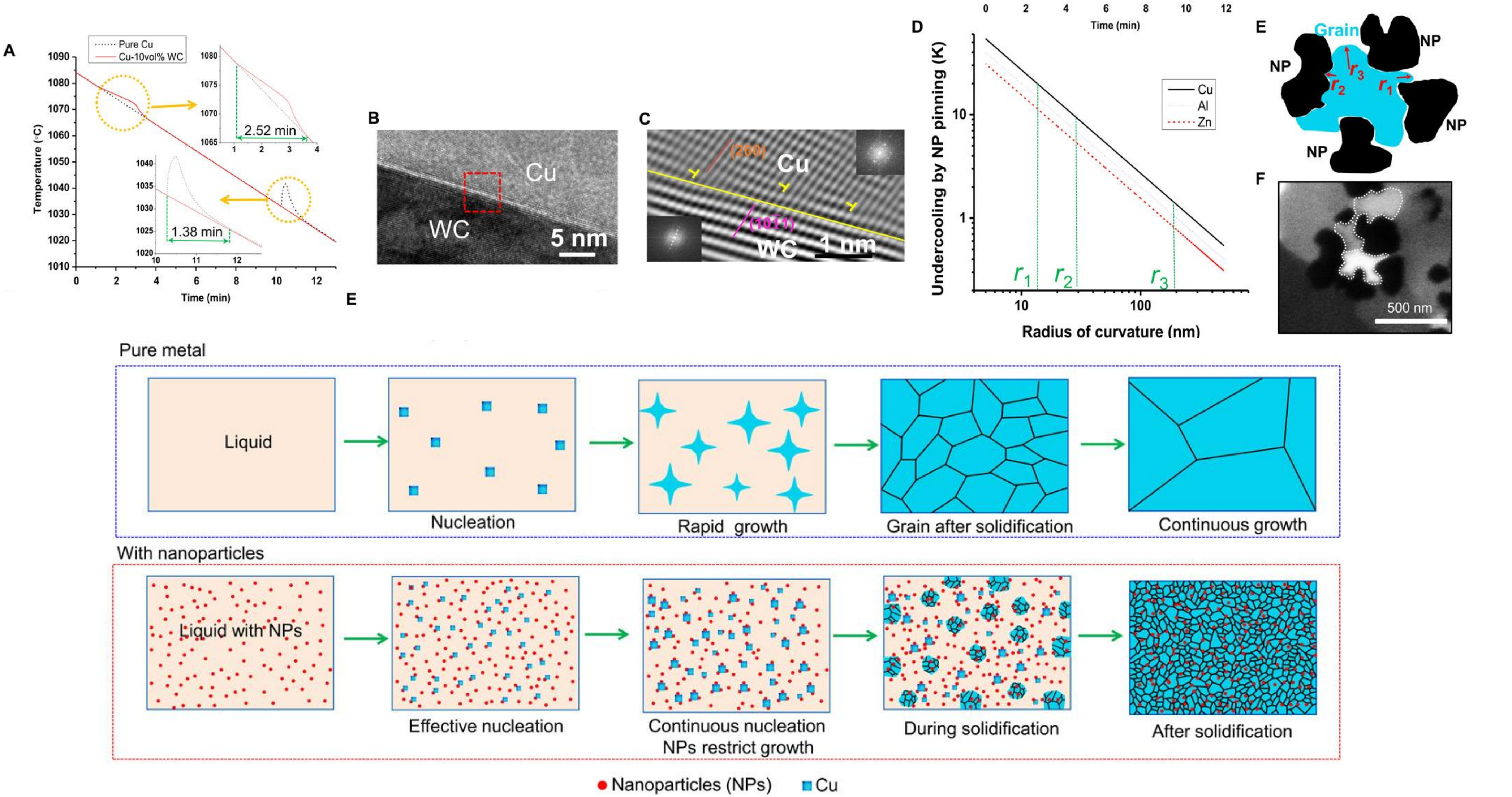


Microstructure of bulk UFG/nanocrystalline Cu-containing distributed WC nanoparticles. (**A**) SEM image of Cu-5vol%WC (by a cooling rate of 4 K/s) acquired at 52° showing well-dispersed WC nanoparticles in the Cu matrix. Inset is the image of a typical as-cast bulk Cu-5vol%WC ingot with a diameter of 50 mm. (**B**) Magnified SEM image of Cu-5vol%WC (4 K/s) showing the ultrafine and nanoscale Cu grains. (**C**) SEM image of the cross-section showing the UFG Cu matrix and the WC nanoparticles present beneath the surface of the sample. (**D**) Typical FIB image of Cu-5vol%WC (4 K/s) showing the UFG/nanocrystalline microstructure. (**E**) FIB image of pure Cu cast under the same condition showing coarse Cu grains. (**F**) EBSD image of Cu-5vol%WC (4 K/s) with grain size color code. Black phases are WC nanoparticles, red grains are smaller than 100 nm, and yellow and orange grains are smaller than 1 μm. (**G**) Summary of the average Cu grain sizes for different volume fractions of nanoparticles under different cooling rates. Error bars show the SD.



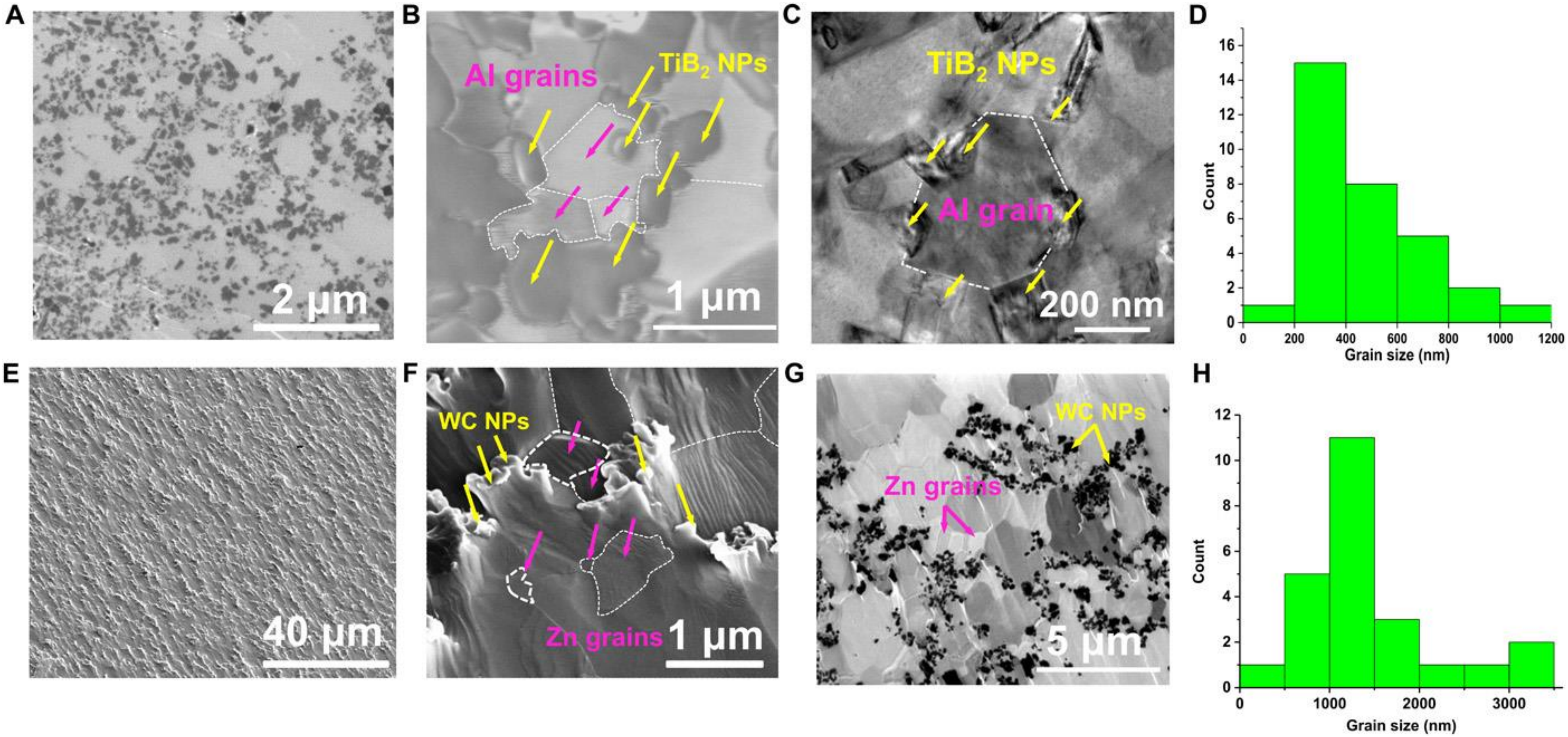
Mechanical properties of UFG/nanocrystalline Cu-containing WC nanoparticles. (A) SEM image of a Cu-34vol%WC micropillar machined by FIB. (B) FIB image of the micropillar showing polycrystalline Cu matrix with WC nanoparticles. (C) Engineering stress strain curves of as-solidified pure Cu samples (blue), with nanoparticles (black) and heat treated sample (red). (D-E) SEM images showing the morphology of post-deformed samples with (D) and without (E) nanoparticles. (F) Young's modulus of pure Cu, Cu 19vol%WC and Cu-34vol%WC.

Fig. 2 Nucleation and grain growth control mechanisms by nanoparticles.



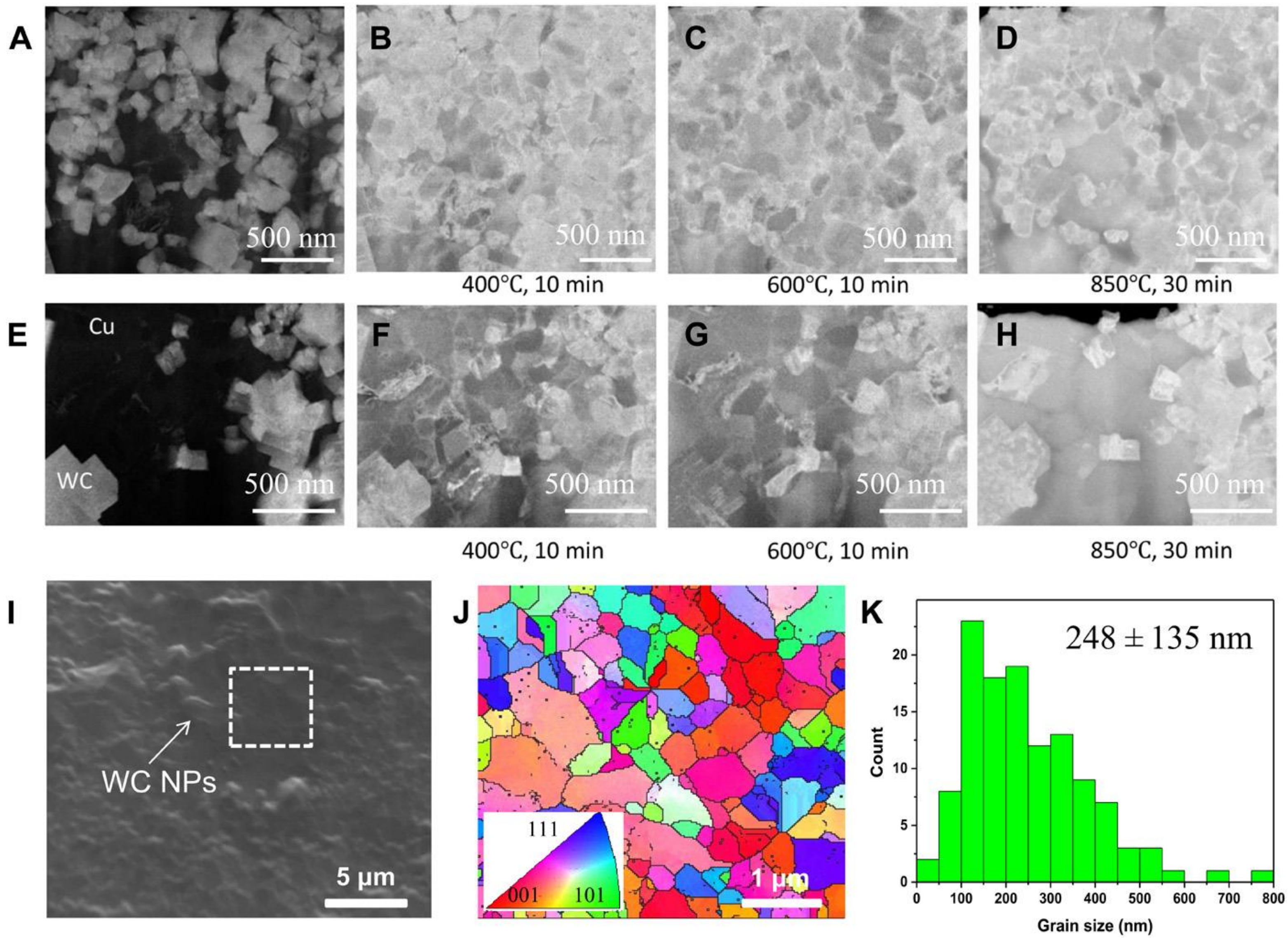
Nucleation and grain growth control mechanisms by nanoparticles. (**A**) Typical DSC scanning result during the cooling of pure Cu and Cu-10vol%WC. (**B**) Typical TEM image of the Cu-WC interface showing the interface between the Cu matrix and the WC nanoparticle. (**C**) Fourier-filtered high-resolution TEM image of the marked red rectangle area in (B) showing a characteristic interface between the WC nanoparticle and the Cu matrix. Insets are the fast Fourier transformation of the Cu matrix (top right) and the WC nanoparticle (bottom left). (**D**) Undercooling requirement to overcome Gibbs-Thompson pinning effect for Cu, Al, and Zn. (**E**) Schematic illustration of the nanoparticle pinning effects. (**F**) SEM image of a Cu grain refined by WC nanoparticles. (**G** and **H**) Schematic illustrations of phase evolution during solidification of pure metal (H) and metal with nanoparticles (I).

Fig. 3 Nanoparticle-enabled grain refinement in other materials systems.



Nanoparticle-enabled grain refinement in other materials systems. (**A** and **B**) FIB images of Al-10vol%TiB_2 cast by furnace cooling (0.7 K/s) showing the distribution of TiB_2 nanoparticles and ultrafine Al grains. (**C**) TEM image of Al-10vol%TiB_2 (0.7 K/s) showing one ultrafine Al grain surrounded by TiB_2 nanoparticles. (**D**) Al grain size distribution of Al-10vol%TiB_2 (0.7 K/s). (**E** and **F**) SEM image of Zn-5vol%WC by air cooling (3.7 K/s). (**G**) FIB image of Zn-5vol%WC (3.7 K/s). (**H**) Zn grain size distribution of Zn-5vol%WC (3.7 K/s).

Fig. 4 Thermal stability of ultrafine/nanocrystalline Cu-containing WC nanoparticles.



Thermal stability of ultrafine/nanocrystalline Cu-containing WC nanoparticles. (**A** to **D**) STEM images of an area with a high percentage of WC nanoparticles at room temperature, 400°C, 600°C, and 850°C, respectively. (**E** to **H**) STEM image of an area with a relatively low percentage of WC nanoparticles at room temperature, 400°C, 600°C, and 850°C, respectively. (**I**) SEM image of Cu-34vol%WC after heat treatment (750°C for 2 hours). (**J**) EBSD image corresponds to the marked white rectangle in (I). (**K**) Cu grain size distribution of the heat-treated Cu-34vol%WC sample.

Conclusion

- In summary, a revolutionary approach to effectively control nucleation and grain growth down to ultrafine/nanoscale during slow solidification was discovered using dispersed nanoparticles in molten metals.

- The nanoparticle-enabled new grain refinement mechanisms, which combine continuous nucleation and grain growth control, break the fundamental limit of conventional grain refinement methods.

- As-cast bulk UFG/nanocrystalline metals with nanoparticles also show exceptional strengths and Young's modulus enhancement. Furthermore, this general approach is valid for different materials systems such as Al-TiB2 and Zn-WC. This approach will have a profound impact not only on the solidification processes for metals but also on numerous applications such as biomedical, chemical, and atmospheric sciences.

Thank you ☺