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RPPR Final Report
as of 12-Jun-2018

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Proposal Number: 65627MS **Agreement Number: W911NF-14-1-0644**

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Final Report for Period Beginning 18-Sep-2014 and Ending 17-Sep-2017

Title: Diffusional Growth Control and Stabilization of Nano-sized Minority Phase Using Nanoparticles in Bulk Immiscible Materials during Solidification

Begin Performance Period: 18-Sep-2014 **End Performance Period:** 17-Sep-2017

Report Term: 0-Other

Submitted By: Xiaochun Li Email: xcli@seas.ucla.edu
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STEM Degrees: 3 **STEM Participants:** 5

Major Goals: The objectives of this proposal are to conduct fundamental study on diffusional growth control and stabilization of minority droplets using nanoparticles to obtain nano-sized minority phase in bulk immiscible material samples under practical cooling rates for casting (i.e. only up to a few hundreds of Kevin/s). Typical analog immiscible material systems, such as transparent succinonitrile (SCN)-carbontetrabromide (CTB), and etallic Zn-Bi and Al-Bi, will be used for the fundamental study. Fundamental knowledge gained through the proposed theoretical and experimental studies will provide a scientific guideline for unprecedented practical processing of numerous bulk immiscible materials with nano-sized minority phases, which will offer novel functionalities for important technical applications. This study could also push the frontier of diffusional growth control for nano-crystalline materials to a new level by providing a novel, general methodology.

Accomplishments: 1. Thermally stable nanoparticles are used to control Bi phase growth in immiscible Al-Bi alloy during solidification, producing Al-20Bi-TiC0.7N0.3 nanocomposites with homogeneously distributed Bi phases. Cu element and Al-5Ti-1B grain refiner were added to further strengthen the nanocomposite. Significant microhardness enhancement was achieved without deteriorating the distribution of Bi phase.

2. Immiscible Zn-Bi alloy has a good potential to replace lead-based alloys to serve as a running layer in plain bearings. However, it is still a major challenge to uniformly disperse Bi phase in Zn matrix during solidification processing since Bi droplets grow very fast in liquid state and readily coagulate to induce phase sedimentation. In this study, tungsten (W) nanoparticles were, for the first time, used and effectively incorporated into the Zn-Bi melt for phase control. Tungsten nanoparticles were able to self-assemble onto the Zn-Bi phase interfaces to slow down the growth of the Bi phase and prevent their coagulations, resulting in a significant size reduction of the Bi phase and microstructure refinement. Moreover, the incorporation of W nanoparticles into the Zn-Bi alloy enhanced its microhardness significantly. This new approach of using chemically-stable metal nanoparticles has a great potential for scale-up manufacturing of immiscible alloys for widespread applications.

3. Immiscible alloys, such as Al-Bi alloy, with a miscibility gap in the liquid state are not only scientifically important, but also they can offer unusual properties that can enable a wide range of applications. Moreover, if nanoscale minority phase can be obtained in bulk immiscible alloys, exciting properties can be realized for revolutionary technical applications. However, it is still a long-standing challenge to control the distribution and size of minority phase during cooling especially down to nanoscale in a scalable manufacturing approach. By applying a scalable molten salt assisted incorporation process, high volume fraction of well dispersed TiC nanoparticles can be incorporated in Al matrix to produce Al-TiC master nanocomposites, which can be readily used to process Al-Bi

immiscible alloy and restrict the size of minority Bi phase in large volume. TiC nanoparticles can be self-assembled on the Al-Bi interface and restrict Bi phase size substantially. In addition, combine the nanoparticles enabled phase control with the effect of higher cooling rates, nanoscale minority Bi phase can be achieved which breaks the fundamental and technical limits of processing immiscible alloys. Mechanical properties of Al-Bi immiscible alloys can be further enhanced by the addition of nanoparticles, Cu element and cold rolling.

Training Opportunities: This project was used to train one postdoc, 4 Ph.D. students, and two MS student on nanotechnology enabled immiscible alloy processing.

Results Dissemination: The results from this project has been demonstrated to industry, high school students, and public visitors in annual UCLA Open Houses.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: We have established active interactions with industry partners, such as Eck Industries, HRL Laboratories and MetaLi LLC for commercialization of the developed technology from this project. We are actively engaging in commercialization of immiscible bearing alloys with MetaLi LLC.

PARTICIPANTS:

Participant Type: PD/PI
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Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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Participant: Chezheng Cao
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International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Jiaquan Xu
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Project Contribution:
International Collaboration:
International Travel:

National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Chao Ma
Person Months Worked: 2.00 **Funding Support:**
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International Collaboration:
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National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Injoo Hwang
Person Months Worked: 2.00 **Funding Support:**
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Other Collaborators:

Participant Type: Graduate Student (research assistant)
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Participant Type: Graduate Student (research assistant)
Participant: Weiqing Liu
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Article Title: Phase Control in Immiscible Zn-Bi Alloy by W Nanoparticles
Authors: Chezheng Cao, Lianyi Chen, Jiaquan Xu, Jingzhou Zhao, Marta Pozuelo, Xiaochun Li
Keywords: Zn-Bi immiscible alloy; nanocomposites; phase control
Abstract: Zn-Bi alloy, a typical immiscible alloys with a liquid miscibility gap, has potential to work as the running layer in plain bearing to replace lead-based alloys. However, it is very difficult to uniformly disperse Bi phase in Zn matrix through conventional solidification process due to the fast growing rate of Bi droplets in liquid state and the density difference between Zn and Bi. Bi tend to sink down to the bottom of the crucible and cause phase sedimentation. Metal W nanoparticles are first time incorporated in to Zn-Bi melt to achieve phase control. The experiment results show that W nanoparticles could self-assemble at the Zn-Bi phase boundary at two liquid state to decelerate the growth rate of Bi droplets. Significant size reduction and microstructure adjustment was achieved by this nanoparticles enabled phase control. Moreover, the usage of W metal nanoparticle enable us to establish a more practical processing route for industrial production by taking advantages of the good w
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Authors: Chezheng Cao, Weiqing Liu, Zhiwei Liu, Jiaquan Xu, Ting-Chiang Lin, Injoo Hwang, Igor De Rosa, Xiac
Keywords: Scalable Manufacturing, Immiscible alloys, nanoparticles
Abstract: It is a long-standing challenge to control the distribution and size of minority phase in immiscible alloys during cooling especially down to nanoscale in a scalable manufacturing approach. Here we show that by applying a scalable molten salt assisted incorporation process, high volume fraction of well dispersed TiC nanoparticles can be incorporated in Al matrix to produce Al-TiC master nanocomposites which can be readily used to process Al-Bi immiscible alloy and restrict the size of minority Bi phase. TiC nanoparticles can be self-assembled on the Al-Bi interface and restrict Bi phase size substantially. addition, combine the nanoparticles enabled phase control with the effect of higher cooling rates, nanoscale minority Bi phase can be achieved which breaks the fundamental and technical limits of processing immiscible alloys. Mechanical properties of Al-Bi immiscible alloys can be further enhanced by the addition of nanoparticles, Cu element and cold rolling.
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Authors: Zhiwei Liu
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 12-Jun-2018

DIFFUSIONAL GROWTH CONTROL AND STABILIZATION OF NANO-SIZED MINORITY PHASE USING NANOPARTICLES IN BULK IMMISCIBLE MATERIALS DURING SOLIDIFICATION

W911NF-14-1-0644
Synthesis and Processing of Materials Program
ARO

PI: Xiaochun Li
Raytheon Endowed Chair in Manufacturing
Department of Mechanical and Aerospace Engineering
University of California, Los Angeles

Significant Results

- Scalable manufacturing of high performance Al-Bi bearing alloy
  - ➢ Self-incorporate nanoparticle into melt
    - --$KAlF_4$ flux break the oxide film on the melt surface
    - --TiC nanoparticles chemically stable above 820°C
  - ➢ Enable scalable manufacturing Al-Bi-TiC nanocomposites
    - --Ultrasonic processing is not necessary anymore
    - --Mechanical mixing can also achieve well distribution of Bi in Al
- Expand nanoparticles(NPs) selection scope
  - ➢ First utilize refractory metal NPs to realize rapid phase control in metal immiscible alloy system
    - --Use W NPs to realize rapid phase control in Zn-Bi immiscible alloy
    - --NPs feeding problem solved: excellent wettability compare with ceramic NPs
- Fundamental study and in-situ observation
  - ➢ Kinetic calculation in Zn-Bi-W NPs system and CTB-SCN-B_4C NPs system
  - ➢ First use transparent plastic crystal (CTB-SCN immiscible system) to simulate:
    - --Self-assemble process of NPs
    - --Interaction between minority droplet and solidification front
  - ➢ Design experiment for in-situ observation
    - --Suck sample in capillary rectangle glass tube
    - --Seal by high temperature resistant glue
    - --In-situ heating and solidification

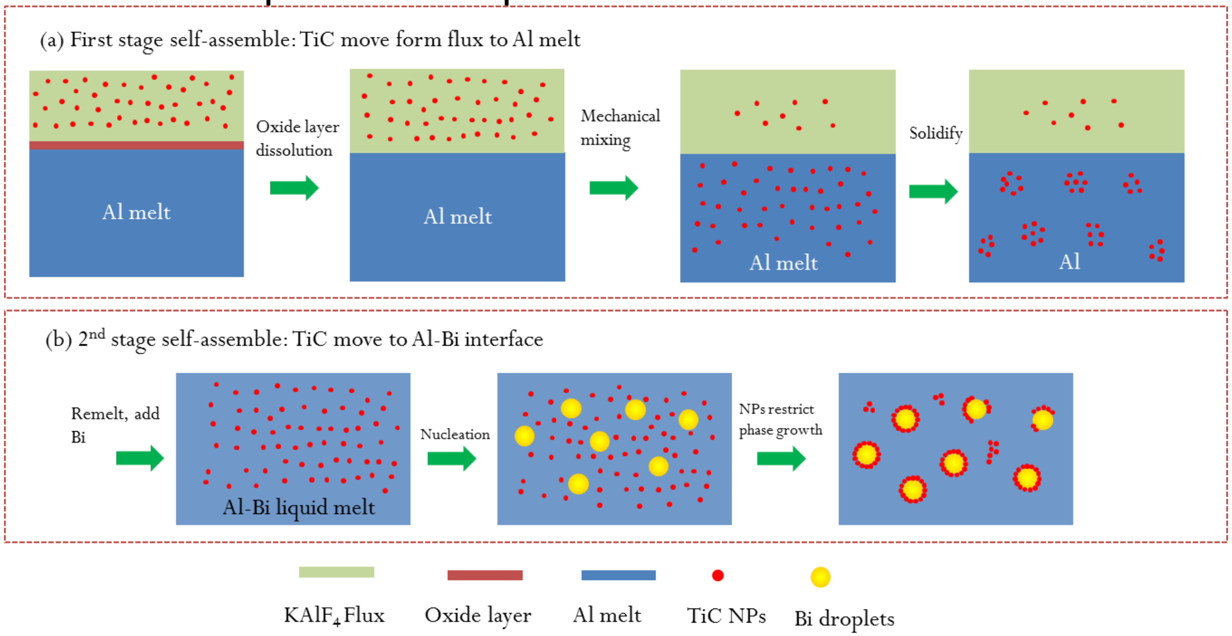
Significant Results

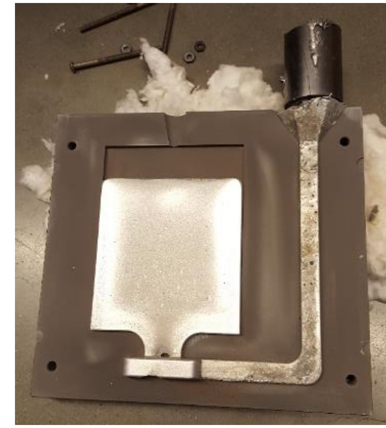
- Effect of Cooling Rate on Phase Growth Control of Al-Bi Immiscible Alloy by TiC Nanoparticles
  - Nanoparticles can substantially refine the size of minority phase
  - Ultra-fine size (< 1 μm) minority phase was achieved by tuning the cooling rate

Significant Results

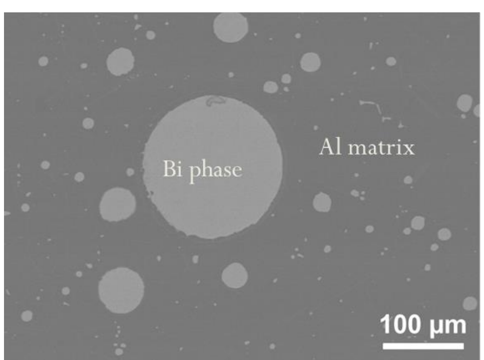
Scalable manufacturing of Al-Bi-TiC nanocomposites

- Self-incorporate nanoparticle into melt

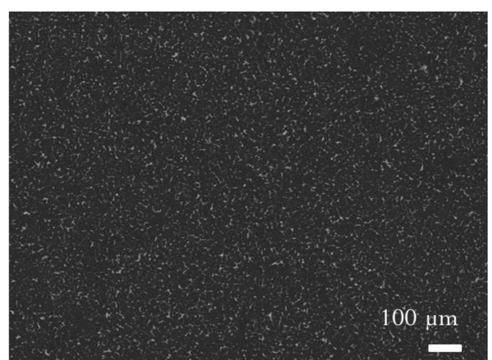




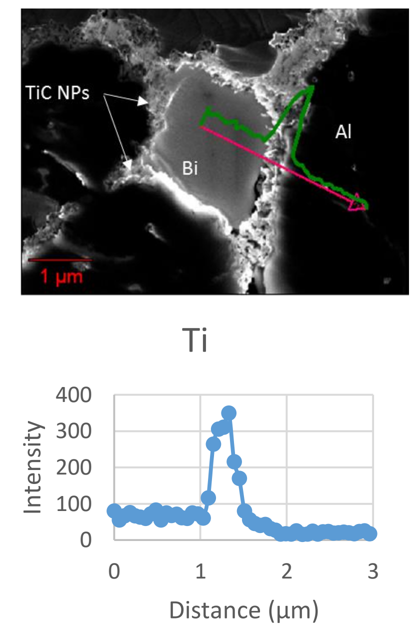
- Enable scalable manufacturing Al-Bi-TiC nanocomposites



Pure Al-20Bi



Al-20Bi-2vol.% TiC nanocomposites



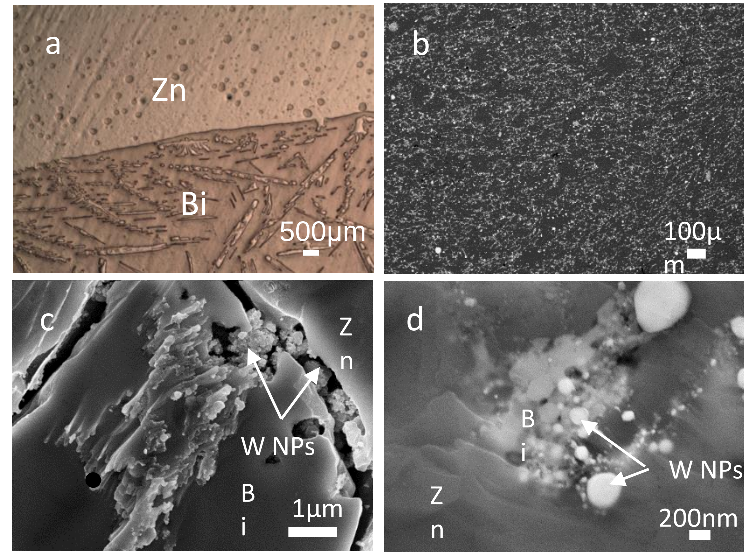
EDS line scan of Ti element

Significant Results

Nanoparticles selection and successful fabrication

- Zn-Bi system: W nanoparticles
  - ➢ Good wettability
  - ➢ Chemically stable
- CTB-SCN system: B4C nanoparticles
  - ➢ Mediate polarity
  - ➢ Low density: move fast

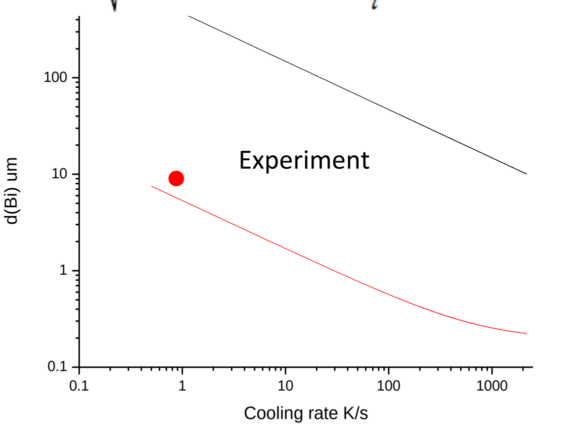
Refined Microstructure: Zn-Bi-W



(a) Pure Zn-6vol.%Bi; (b) Zn-6vol.%Bi-2vol.%W NPs; (c) W NPs assemble on Zn-Bi interface; (d) Sub-micron size Bi droplet.

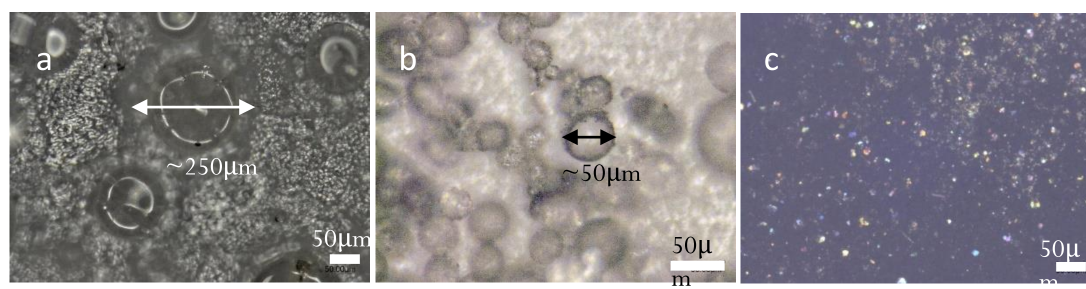
Theoretic Kinetic calculation: Zn-6vol.%Bi-2vol.%W system

$$d \approx 2\sqrt{2DSt_{np} + 2(1-f)DS\frac{T_d - T_m}{\tau}}$$



Diameter of Bi droplets as a function of cooling rate for Zn-6vol.%Bi.

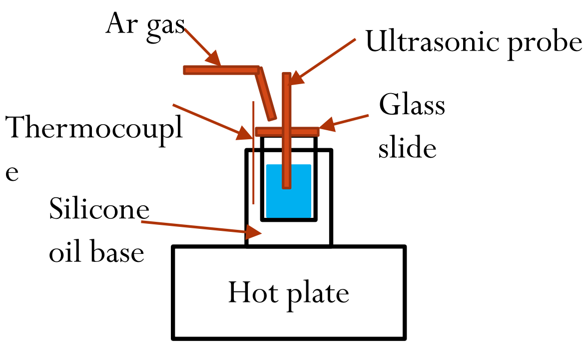
Effective phase control in CTB-SCN-B4C NPs system



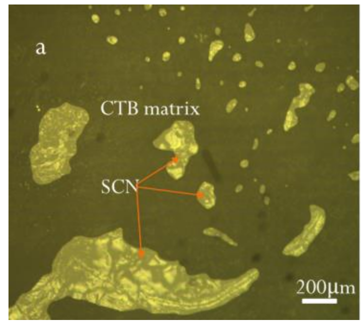
(a) Pure CTB-7.5mol.%SCN; (b)CTB-7.5mol.%SCN-0.1vol.%B4C NPs; (c) CTB-7.5mol.%SCN-2vol.%B4C NPs

Significant Results

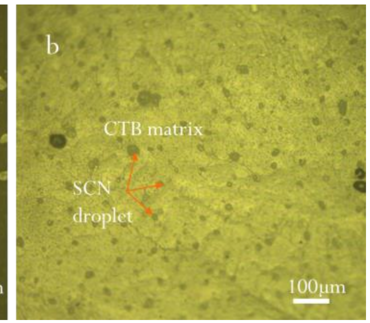
Phase Control in CTB-SCN by B_4C Nanoparticles



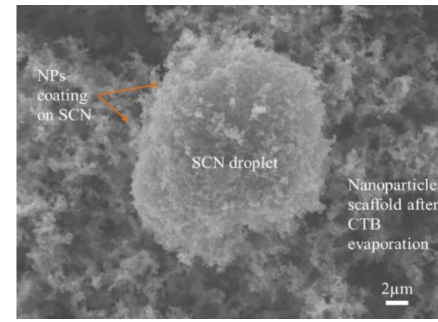
Experimental setup



Pure CTB-7.5mol.%SCN

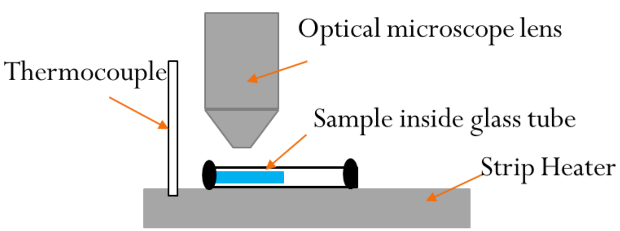


CTB-7.5mol.%SCN-2vol.%B_4C nanocomposites

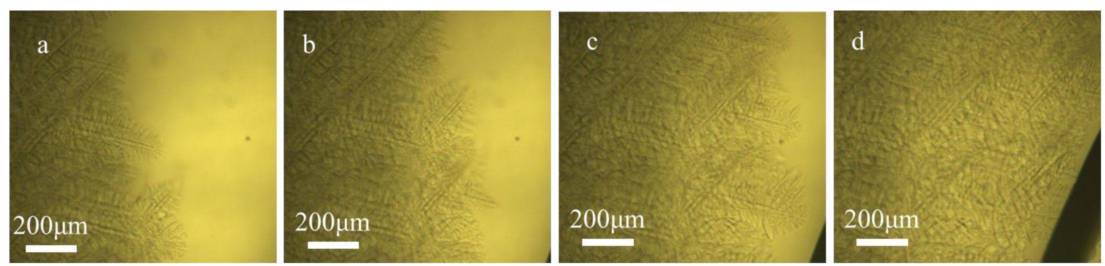


One SCN droplet of CTB-7.5mol.% SCN -2vol.% B_4C nanocomposites

In-situ observation during solidification of pure SCN



In-situ experiment setup



Dendrite growth of pure SCN under cooling rate about 3°C/min

Significant Results

- Nanoparticle-enabled phase control and effect of cooling rate on phase growth control in immiscible alloy system
- With the increase of cooling rate, the average diameter of Bi phase decreases gradually and Bi phase with ultra-fine size (around 800nm) can be obtained.