Annual Review 2005

DEVELOPMENT OF BULK NANOCRYSTALLINE WC-Co FOR INDUSTRIAL APPLICATIONS

A Industrial Materials of the Future Program
by the Office of Industrial Technology of the
US Department of Energy

The Team

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Bulk Nanocrystalline WC-Co for Industrial Applications (CPS# 16949)

Goal: Develop bulk nanocrystalline WC-Co materials for industrial manufacturing tools and wear resistant applications.

Challenge: Nanocrystalline bulk materials shows promising superior mechanical properties. However, there is no commercially viable processes for sintering nanoscaled powders without sacrificing nanoscale characteristics.

Benefits: Prolonged tool life saves energy and improves productivity of all manufacturing operations.

Potential End-User Applications: Machining, oil exploration, mining, electronics manufacturing, and wear components. Technology will also be applied to the synthesis and consolidation of other nano powders.

FY05 Activities: a) Design and build a chemical vapor synthesis reactor system, b) Design and build a ultrahigh pressure rapid hot consolidation press system, and c) Comprehensive study of densification and grain growth mechanisms during sintering of nanoscaled WC-Co powders.

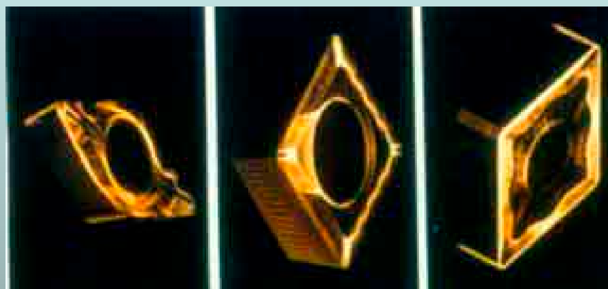
Product and technology

This is an "incremental" (not radical) nano technology that will

- Dramatically improve industrial tools and
- Bring economic benefit in shorter term
- Nano technologies for manufacturing industries are more sustainable

Market and Applications

Metal machining



Electronics manufacturing

Mining and construction

Wear parts

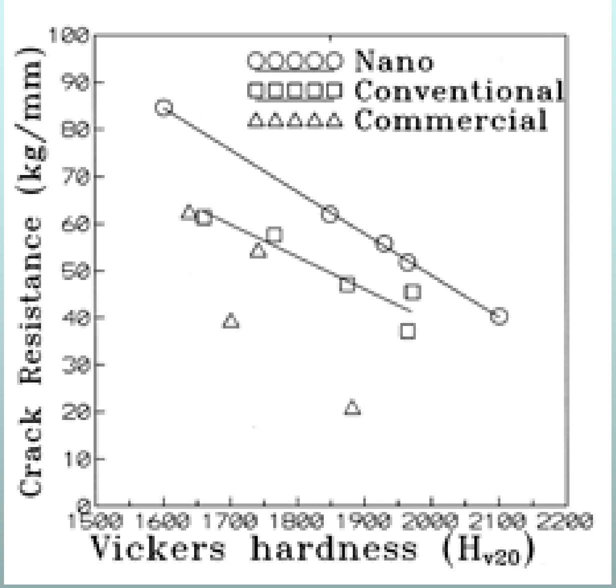
Oil and gas drilling

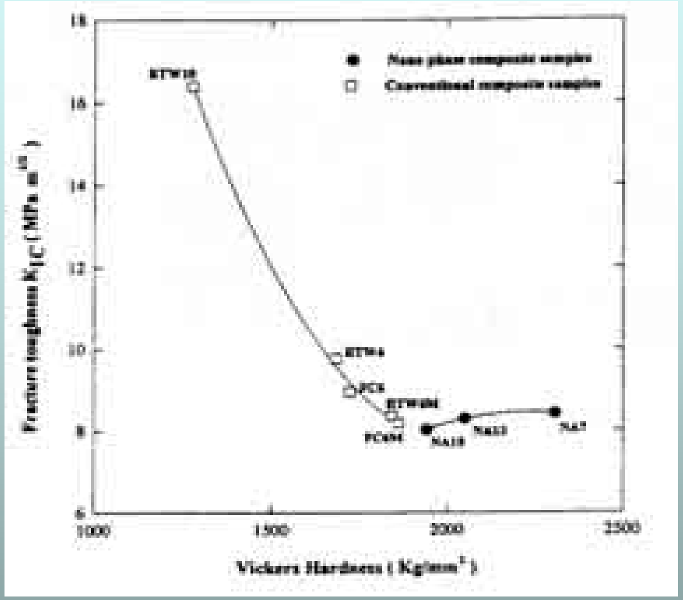
Barriers

- Lack of method in keeping grain size of bulk materials below 100 nm after sintering
- Lack of knowledge about the feasibility of producing nanosized Co coated WC powders
- Lack of information on the mechanical properties of bulk structures with nanoscale grain size.

Background

Regarding mechanical properties





- Encouraging deviations from the norm, but, not enough
- Grains size the materials that these properties are measured on are > 100 nm
- Mechanical properteis of WC-Co with true nanoscaled grain sizes remain unexplored.

Background

Questions / motivations

- Is properties of nanocrystalline WC-Co better?
- What would be the properties of WC-Co if grain sizes are <30 nm?
- How do we make WC-Co with <30 nm grain sizes?

Goals of sintering nanocrystalline powder is not only to achieve full densification, but also to retain nanoscaled grain sizes.

Challenge: How?

-Challenges-

Availability of nanoscaled powders raises possibility of superior properties, but sintering at high temperatures causes grain growth and coarsening, - lost nano characteristics.

- *How to prevent coarsening?*
- *How to produce bulk* nanocrystalline materials *cost effectively*?

Technical Approach

Meet the challenges

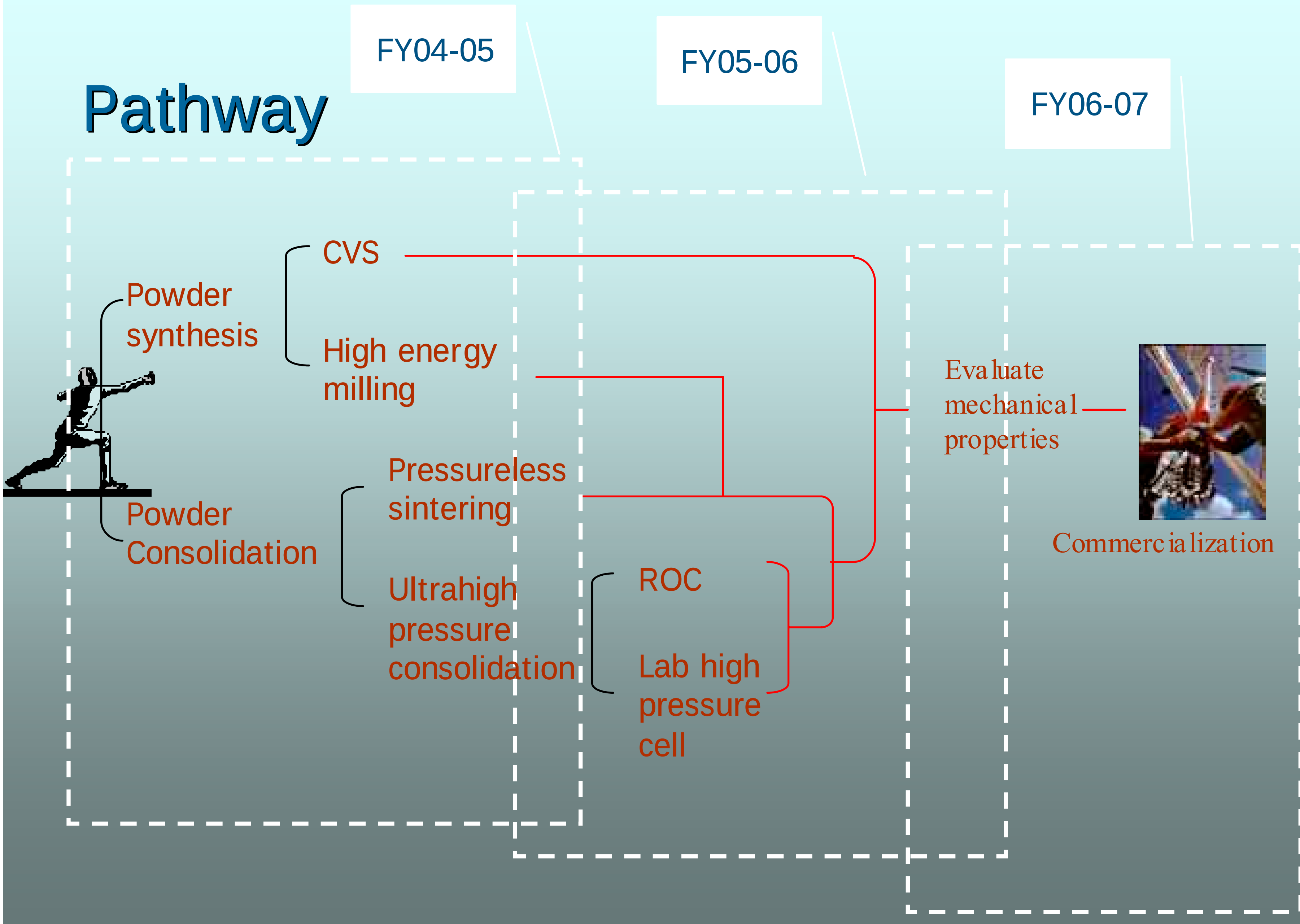
- Understand mechanisms and interplays of grain growth and densification
- Vapor phase synthesis - *produce nano cobalt coated WC composite powders – minimizing grain growth*
- Rapid heating + Ultrahigh pressure

  fully densify nano powders with minimum grain growth

Critical Metrics

- Particle / grain size of nanocrystalline WC/Co must be below 50 nm, with chemical compositions within commercial tolerable range,
- Consolidated bulk WC-Co composite must have grain size below 100 nm,
- The powder synthesis and consolidation processes must be at least 20% more energy efficient than the corresponding conventional processes.

Pathway


FY04-05
FY05-06
FY06-07
Powder synthesis
CVS
High energy milling
Powder Consolidation
Pressureless sintering
Ultrahigh pressure consolidation
ROC
Lab high pressure cell
Evaluate mechanical properties
Commercialization

FY 04-05 Plan Activities

- Design and build a customized CVS system,
- Identify critical processing variables of CVS
- Design and build a rapid heating system
- Design and build a laboratory ultrahigh pressure cell: 500MPa – 1GPa
- Study fundamentals of densification and grain growth

Major Milestones to date

1. Powder synthesis:

   CVS experimental systems - established

   Initial results including high energy milling

2. Ultrahigh pressure rapid hot consolidation

   Ultrahigh pressure cell - complete

   Rapid plasma heating - complete

3. Understanding mechanisms of densification and grain growth of nano powder

   More in-depth understanding – more chance for success!

Major Milestones to date

1. Powder synthesis: *Chemical Vapor Synthesis*

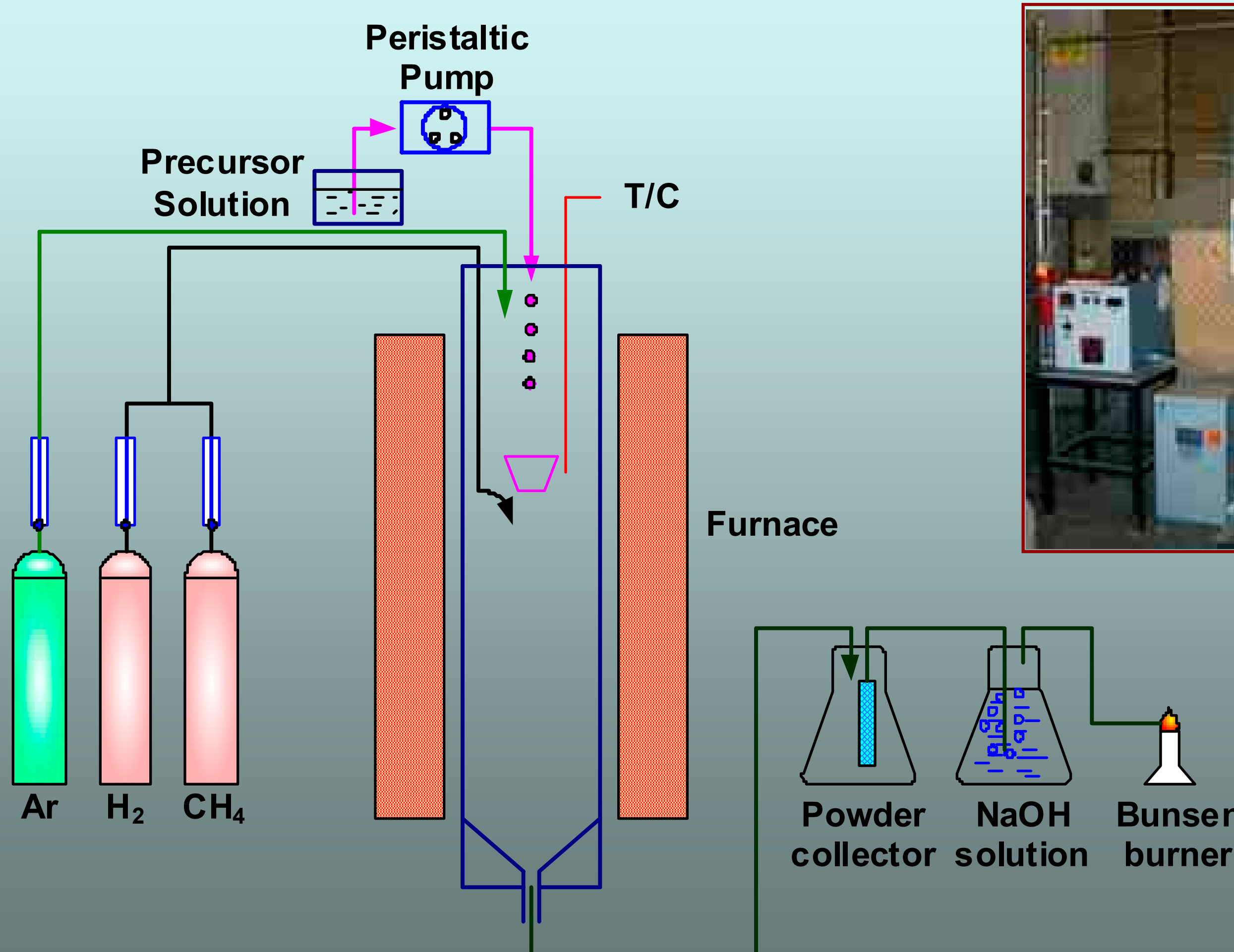
Chemistry

$$WCl_6(g) + xCoCl_2(g) + CH_4(g) + (x+1)H_2(g)$$
$$= WC(s) + xCo + (2x+6)HCl(g)$$

$\Delta G^o = -(151+13x)$ kcal at 1200 °C; $\Delta H^o = -(10.5+20.2x)$ kcal

- Uniform mixture of WC and Co powders
- Energy-efficient process (fast, exothermic reaction)

Experimental Set-up



Continuous Feeding

Slurry Feeding

(Ground WCl_6 and $CoCl_2$ powder in heptane)

Clogging

Low yield

Solution Feeding

(Solution of WCl_6 and $CoCl_2$ in methanol)

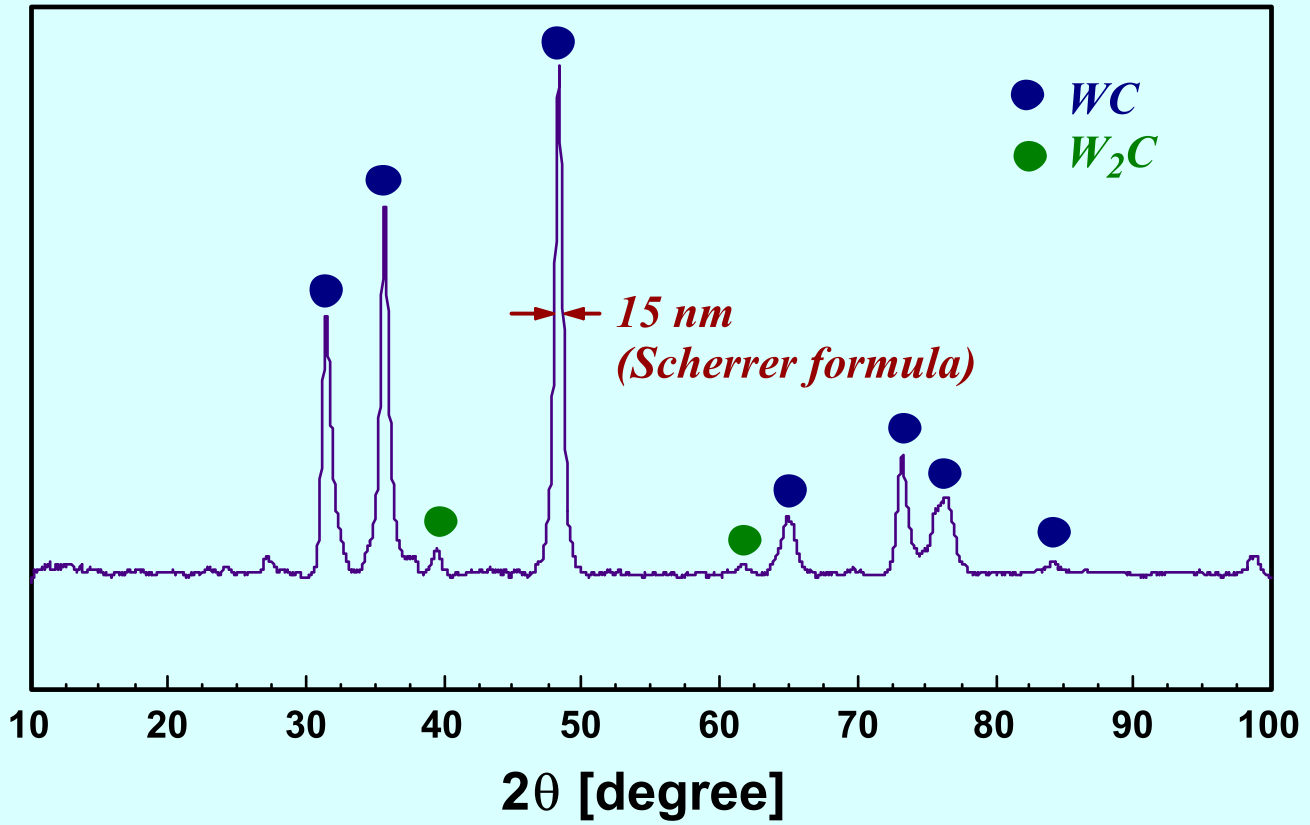
Low yield

Aerosol Feeding

(Atomized solution using a nebulizer)

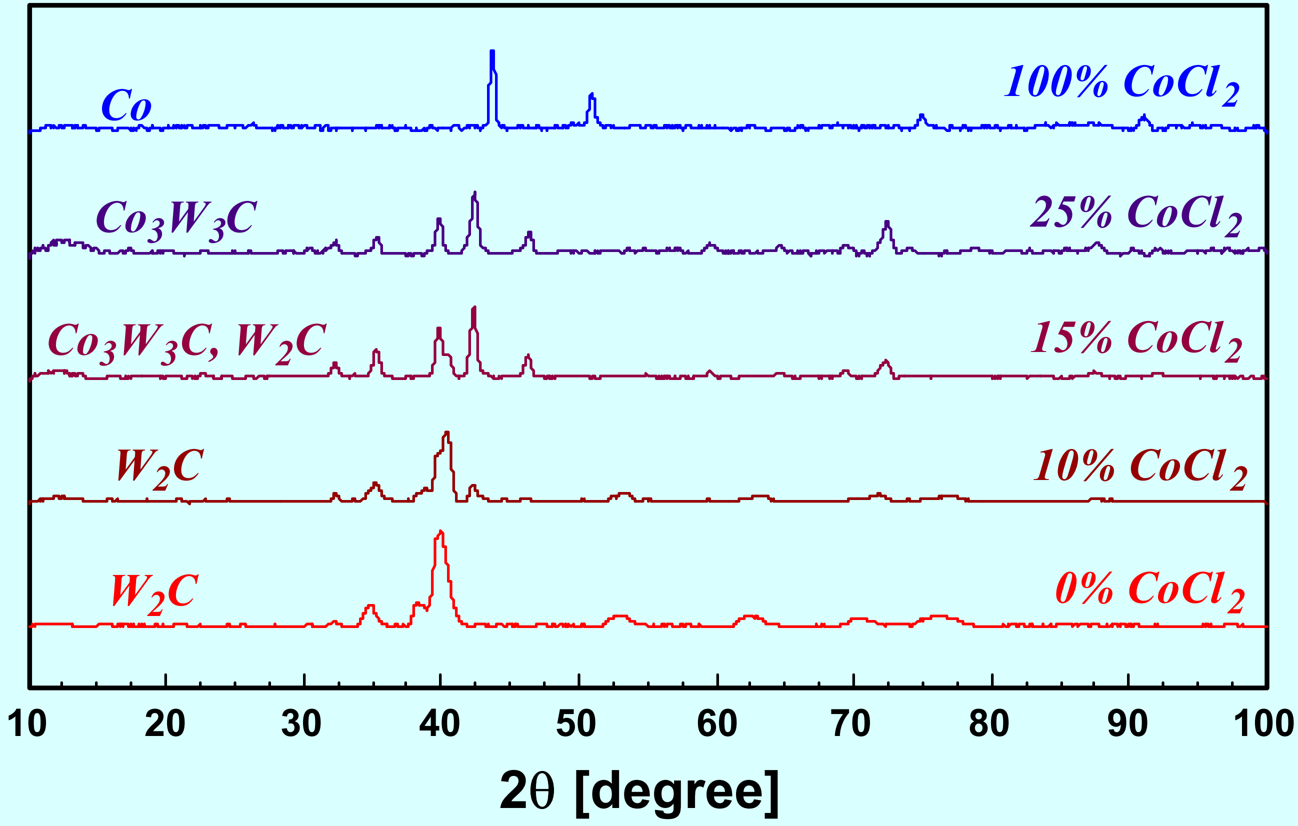
WC Production

$WCl_6(g) + CH_4(g) + H_2(g) = WC + 6HCl(g)$ at 1400°C

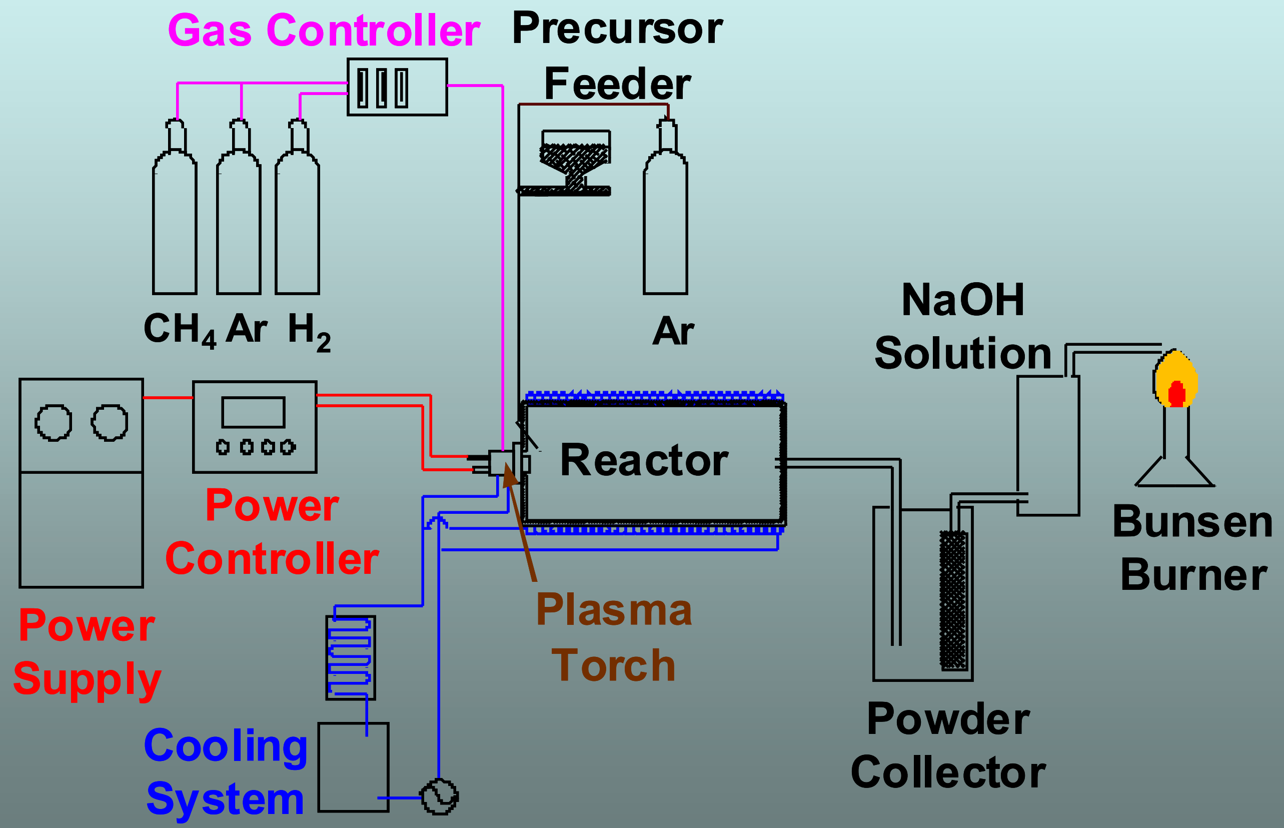


Co-Content Effects

$WCl_6 + xCoCl_2$ at 1150°C



Plasma Reactor System
(65 kW DC Non-transferred Thermal-plasma System)



Plasma Reactor System
(65 kW DC Non-transferred Thermal-plasma System)

- **Much higher temperatures and reactivity**
  - Rapid chemical reaction,
  heat and mass transport
- **Rapid quenching from high temperature**
  - Fine particles
- **Possibility of using other precursors**

► In the process of fabricating the system

Future Plans

- **Evaluation of produced powders**
  - effect of T and reactant concentrations

- **Original objective**
  - one-step synthesis of uniformly mixed powder

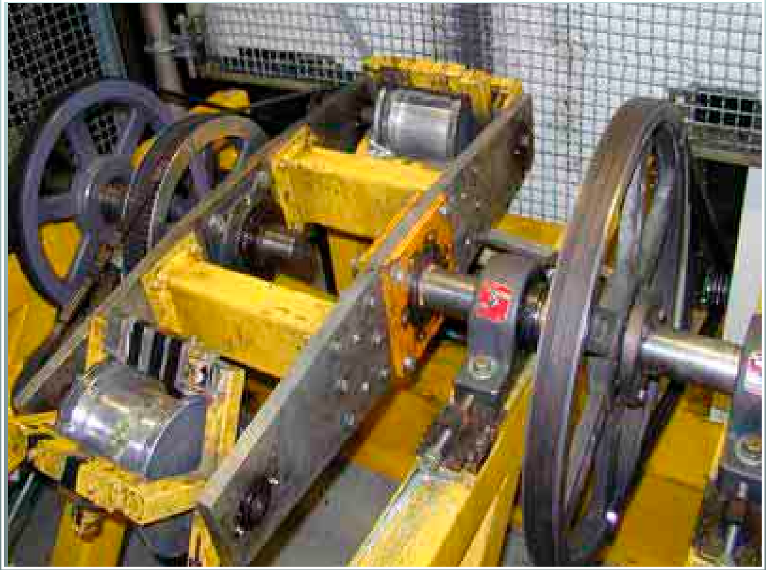
- **Back-up approach**
  - separate synthesis of "WC and Co" or "W_2C and Co_3W_3C" nanopowder
  → composite powder by mixing

- **Production of composite WC-Co powder using a flame-reactor system and a plasma-reactor system**

Major Milestones to date

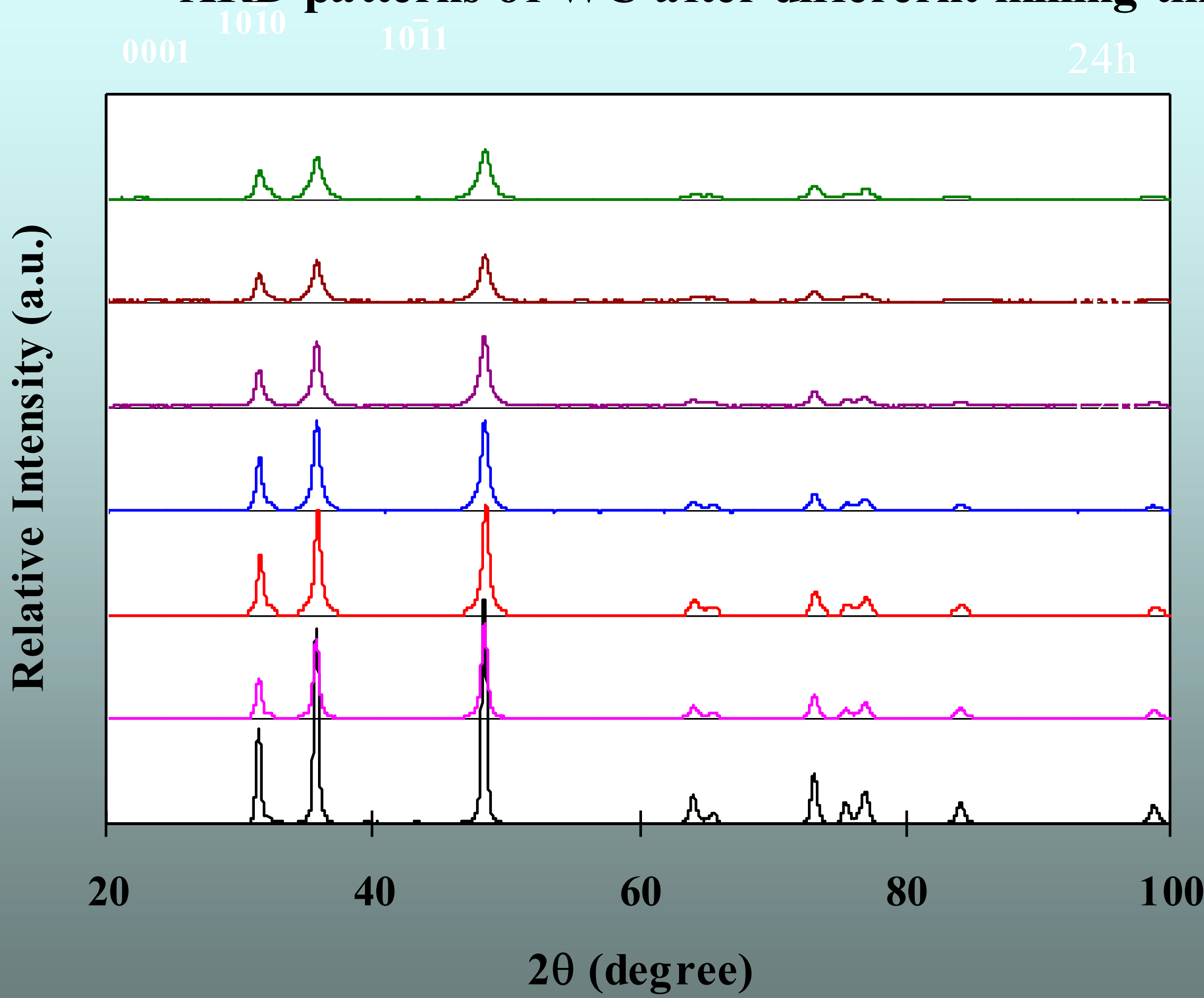
1b. Powder synthesis -*High energy milling*

The Dual Drive Double Planetary Mill

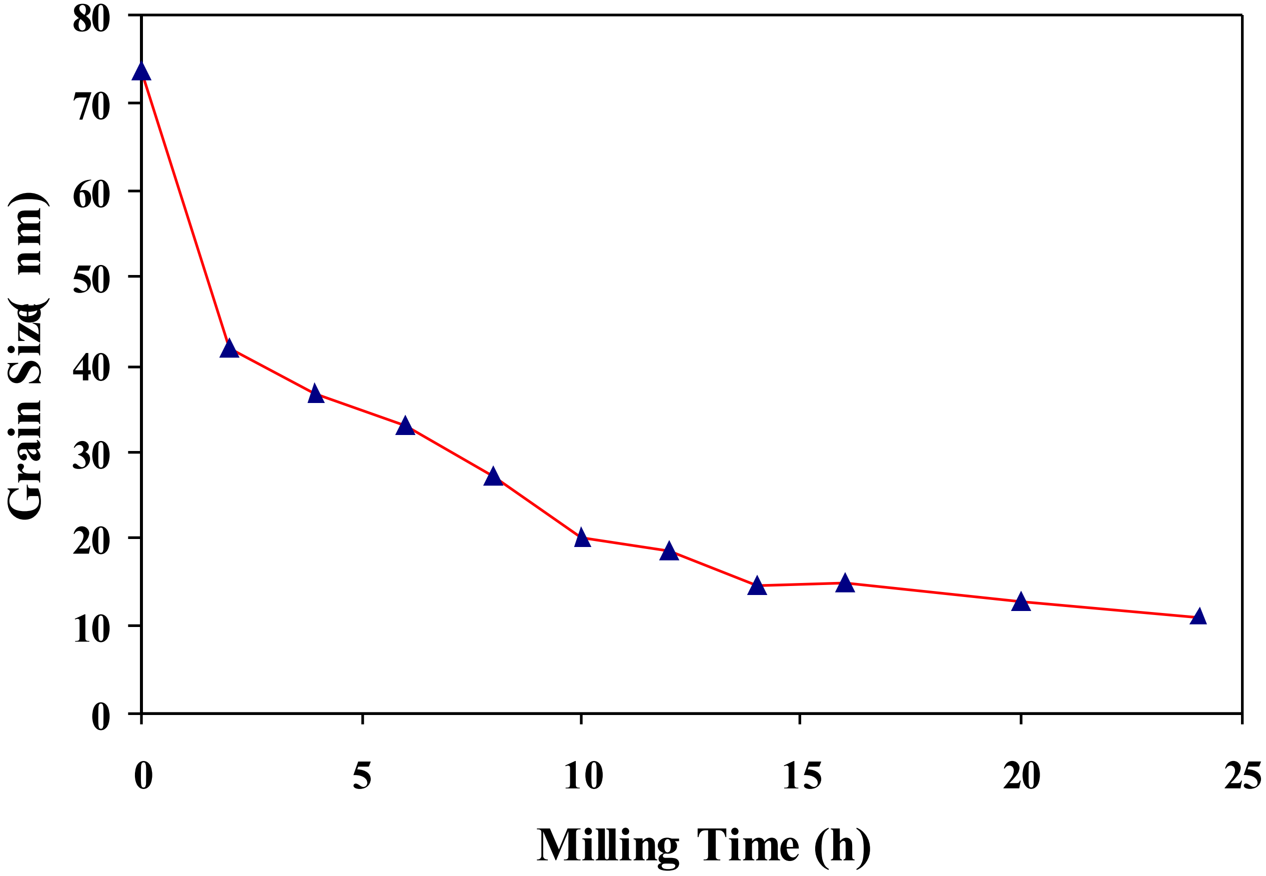


- 60-100g force
- 64% critical speed
- 0.5 mm milling media
- Reduction of 800 nm to 10 nm in 10 hours
- Produce 400 gram batches regularly

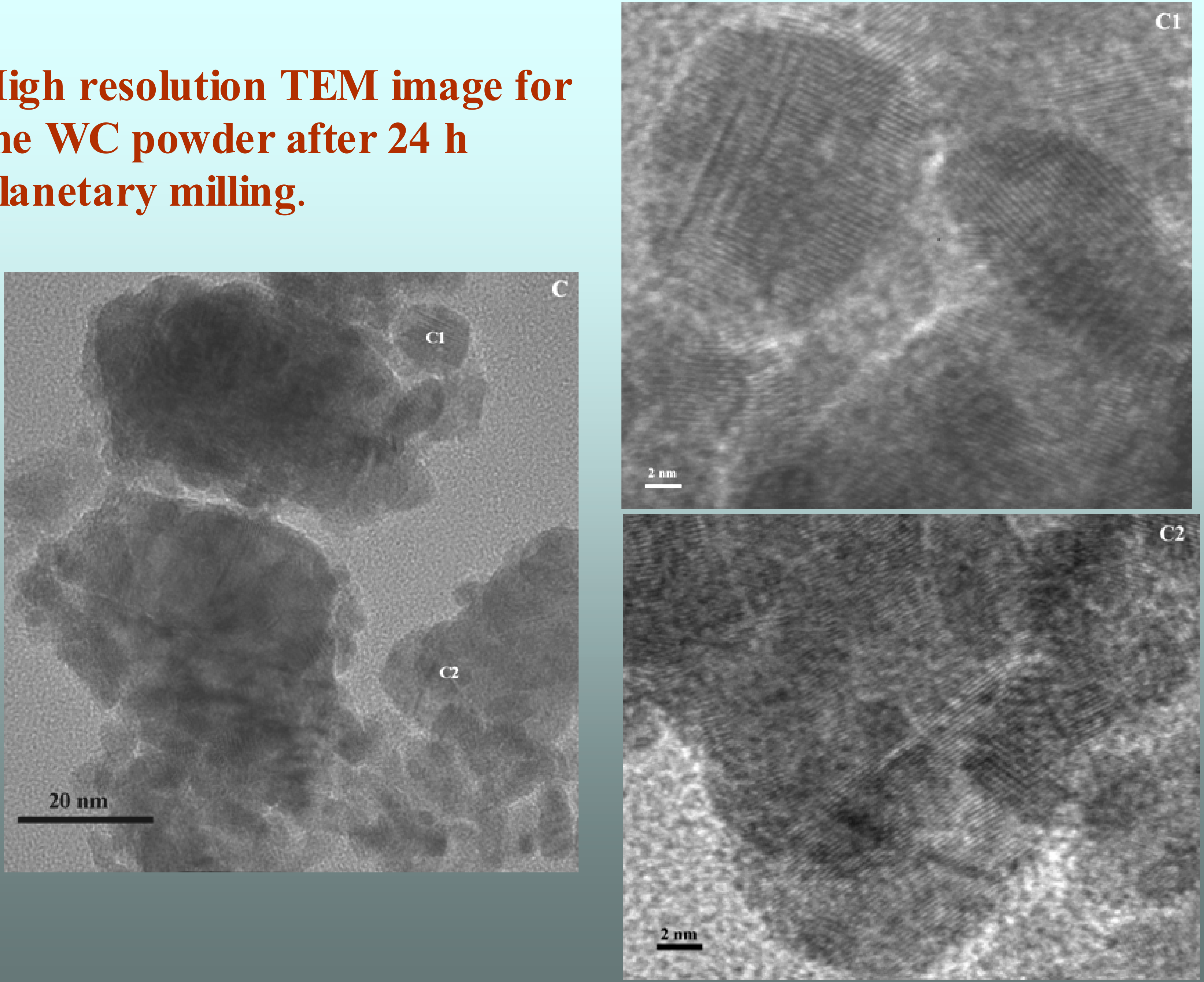
XRD patterns of WC after differernt milling time



Grain size Vs Milling time



High resolution TEM image for the WC powder after 24 h planetary milling.



Major Milestones to date

2. Ultrahigh pressure rapid hot consolidation press system (UPRC)

   Ultrahigh pressure cell

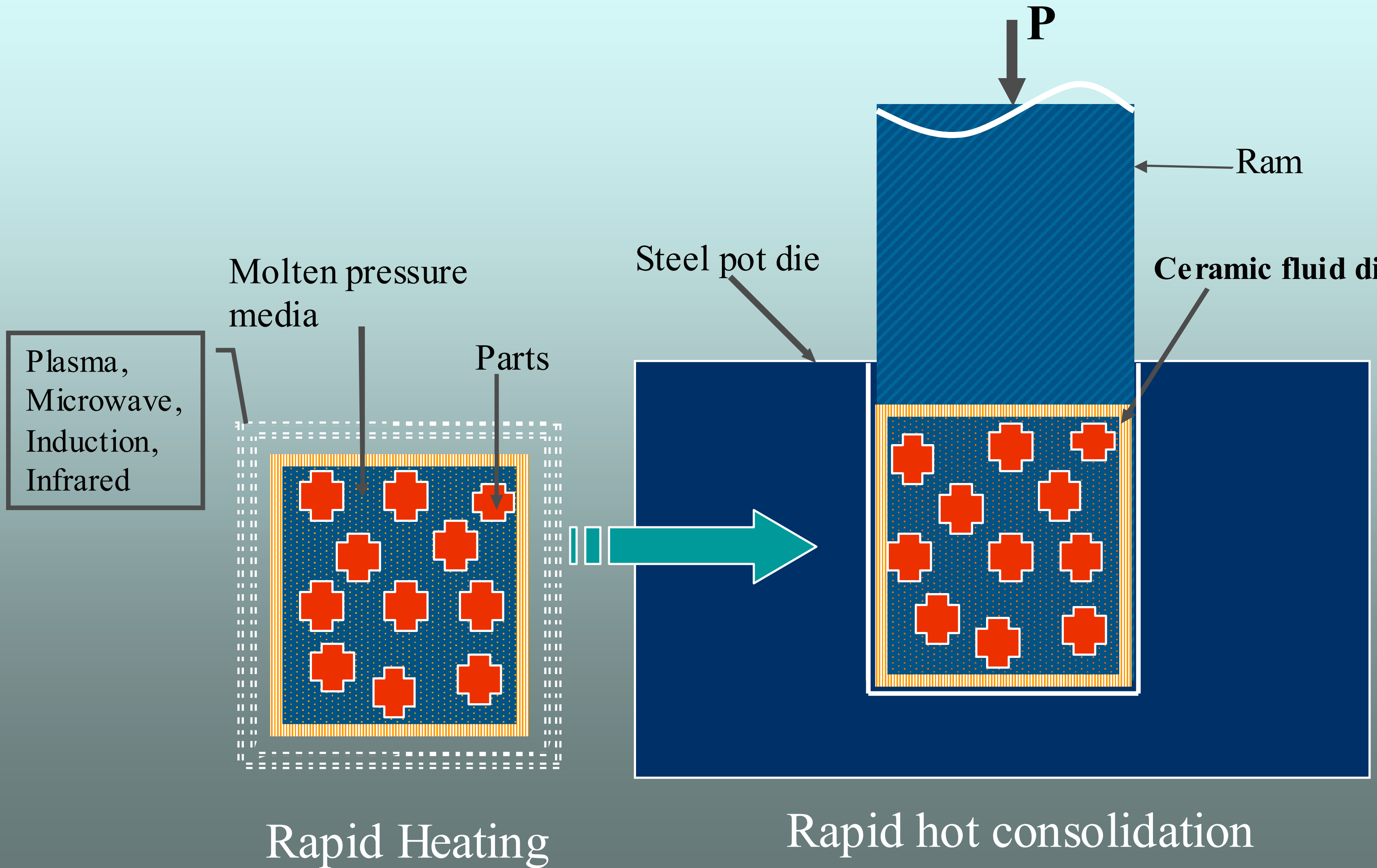
   Rapid plasma heating

Status:

All major system components have been built.

The system is ready for making specimens.

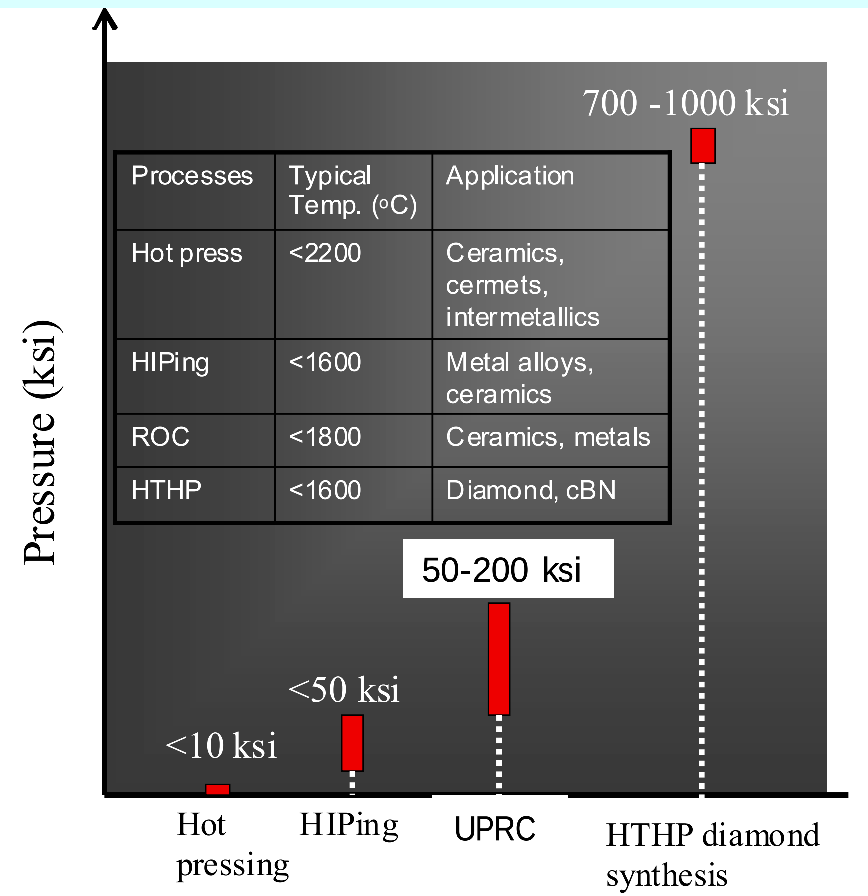
Ultrahigh pressure rapid hot consolidation



Ultrahigh Pressure Rapid Heating and Hot Consolidation

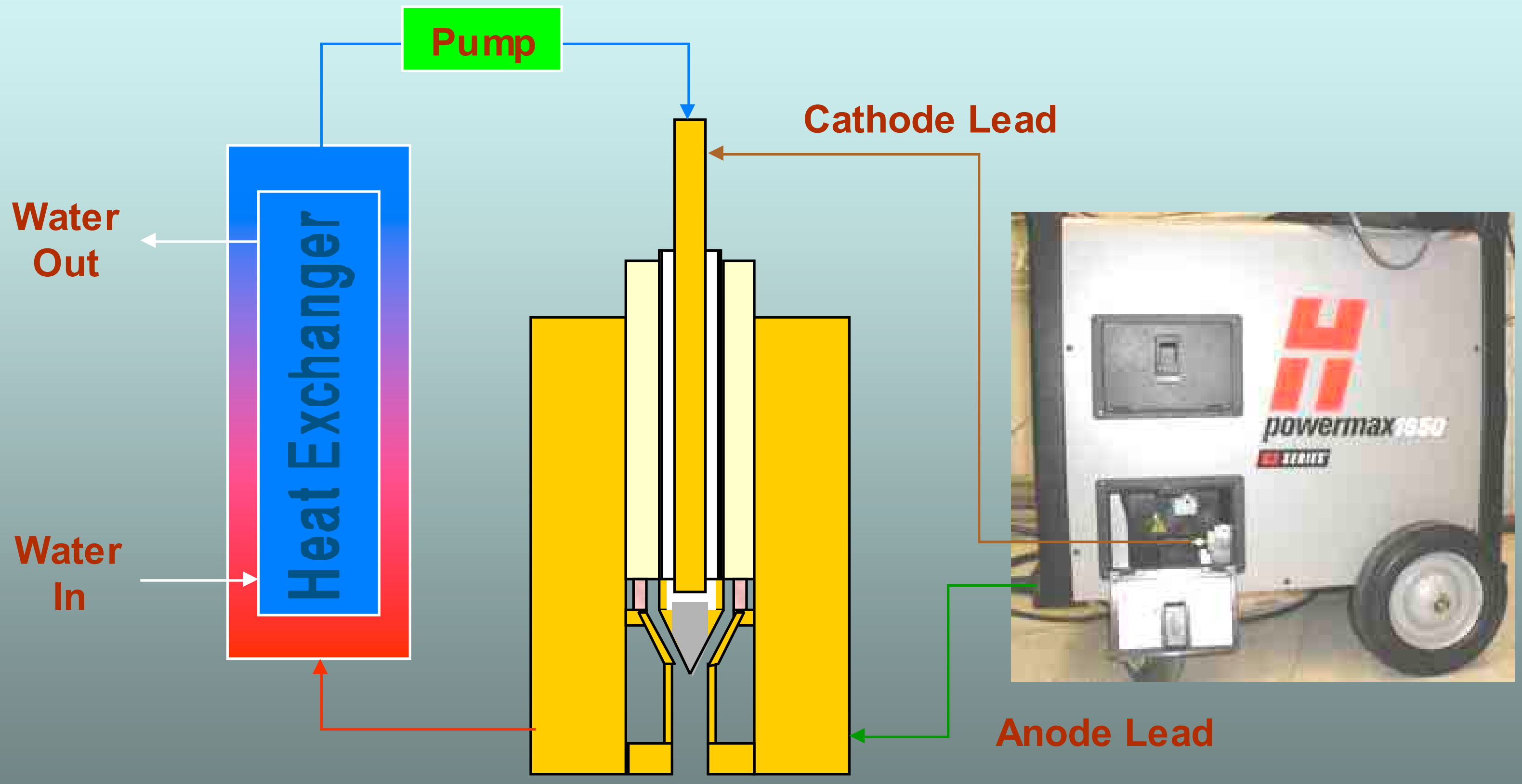
Plasma rapid heating unit

- Rapid and energy efficient process.
- A batch process - commercially viable high pressure technology.



Processes	Typical Temp. (°C)	Application
Hot press	<2200	Ceramics, cermets, intermetallics
HIPing	<1600	Metal alloys, ceramics
ROC	<1800	Ceramics, metals
HTHP	<1600	Diamond, cBN

Plasma Heating System



Major Milestones to date

3. Understanding densification and grain growth

Goals of Sintering

- Achieve 100% densification while retaining nanocrystalline grain size
- First step: bulk WC-Co with grain size <100 nm
- Second step: bulk WC-Co with grain sizes <50 nm
- Final goal: bulk WC-Co with grain sizes <30 nm

Major Milestones to date

3. Understanding densification and grain growth of nano powders

Some critical lessons:

- Grain growth and densification most rapidly during heat-up
- Grain growth by becoming faceted and coalescence of grains within aggregate particles

Focus:

Grain growth during heat-up must be controlled if one is to obtain nanoscaled grain sizes in bulk state.

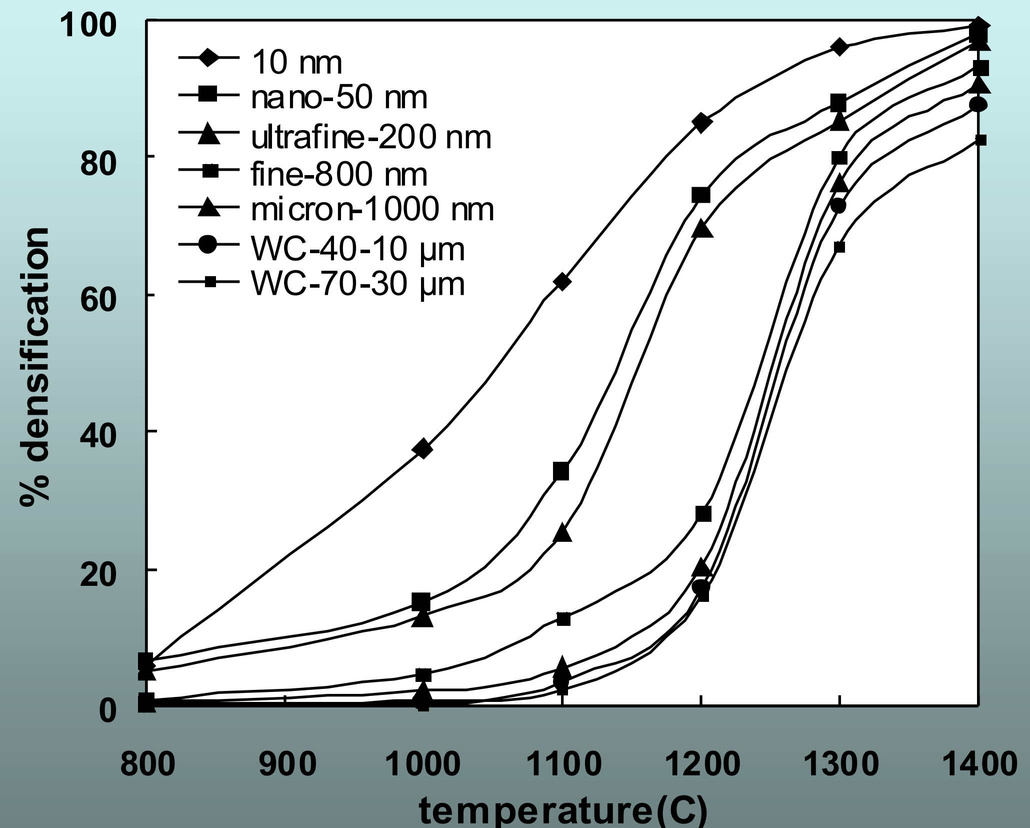
Extensive and detailed studies were carried out using:

- HRSEM
- TEM
- EBSD (OIM)
- DSC
- XRD

Densification and grain growth as functions of temperature during heat-up

Densifications during heat-up:

- Rapid densification at solid state
- Large amount of densification before liquid forms.
- Particle size dependence.



$$\%densification = \frac{\rho_s - \rho_g}{\rho_T - \rho_g}$$

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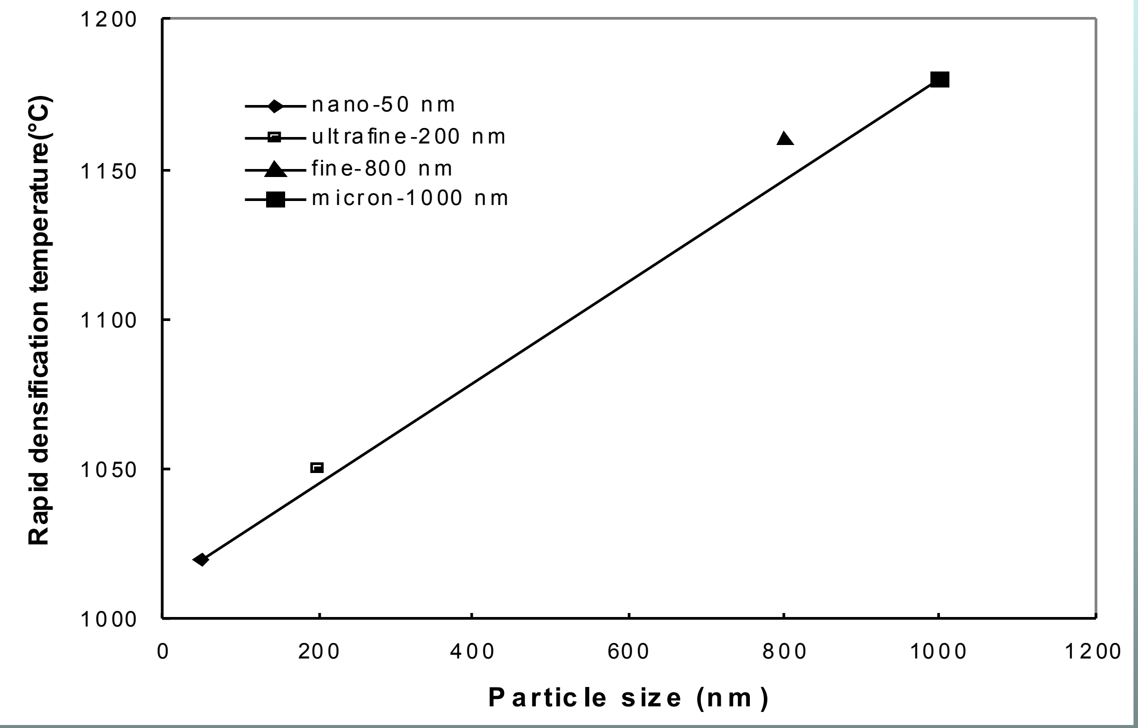
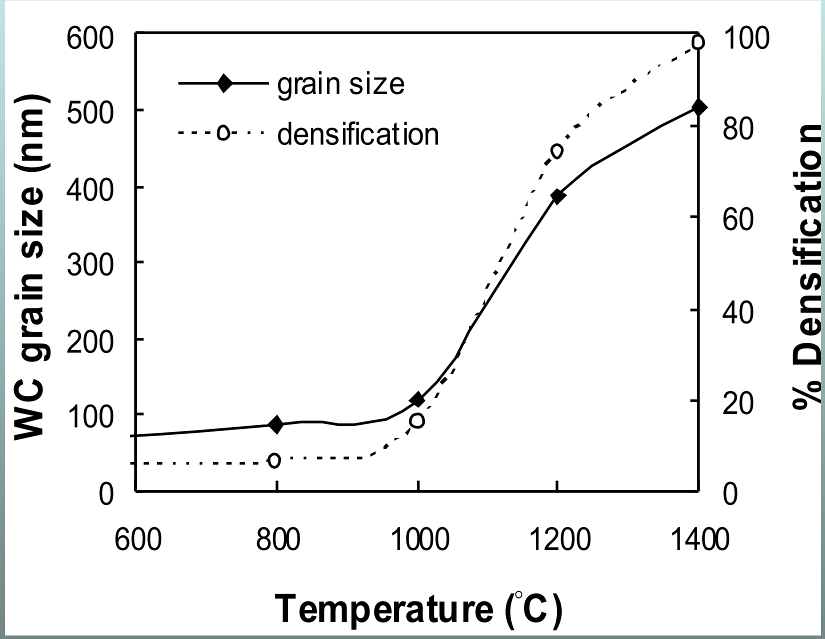


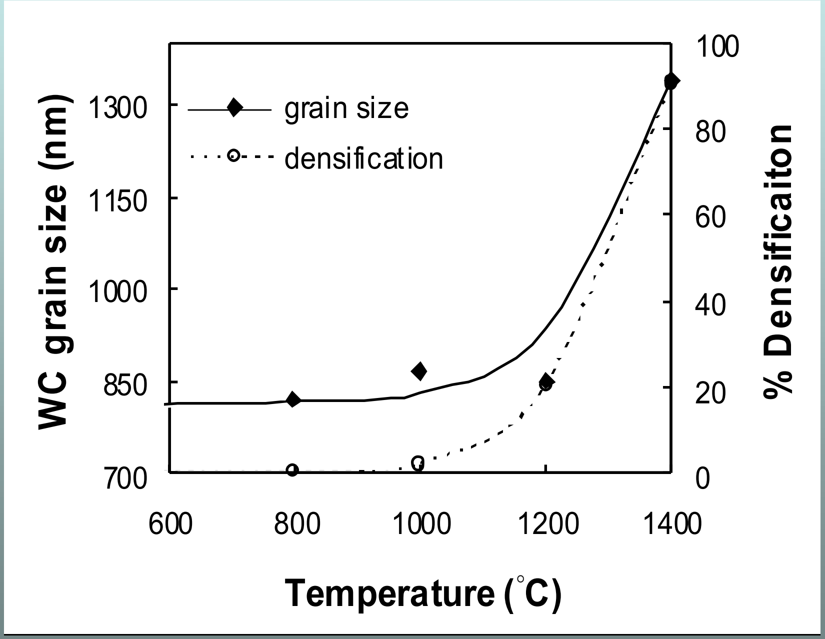
Onset temperature of rapid densification stage during sintering of WC-Co as a function of initial gain sizes.

Densification and grain growth as functions of temperature during heat-up

Grain growth vs. T follow that of densification vs. T



(a)

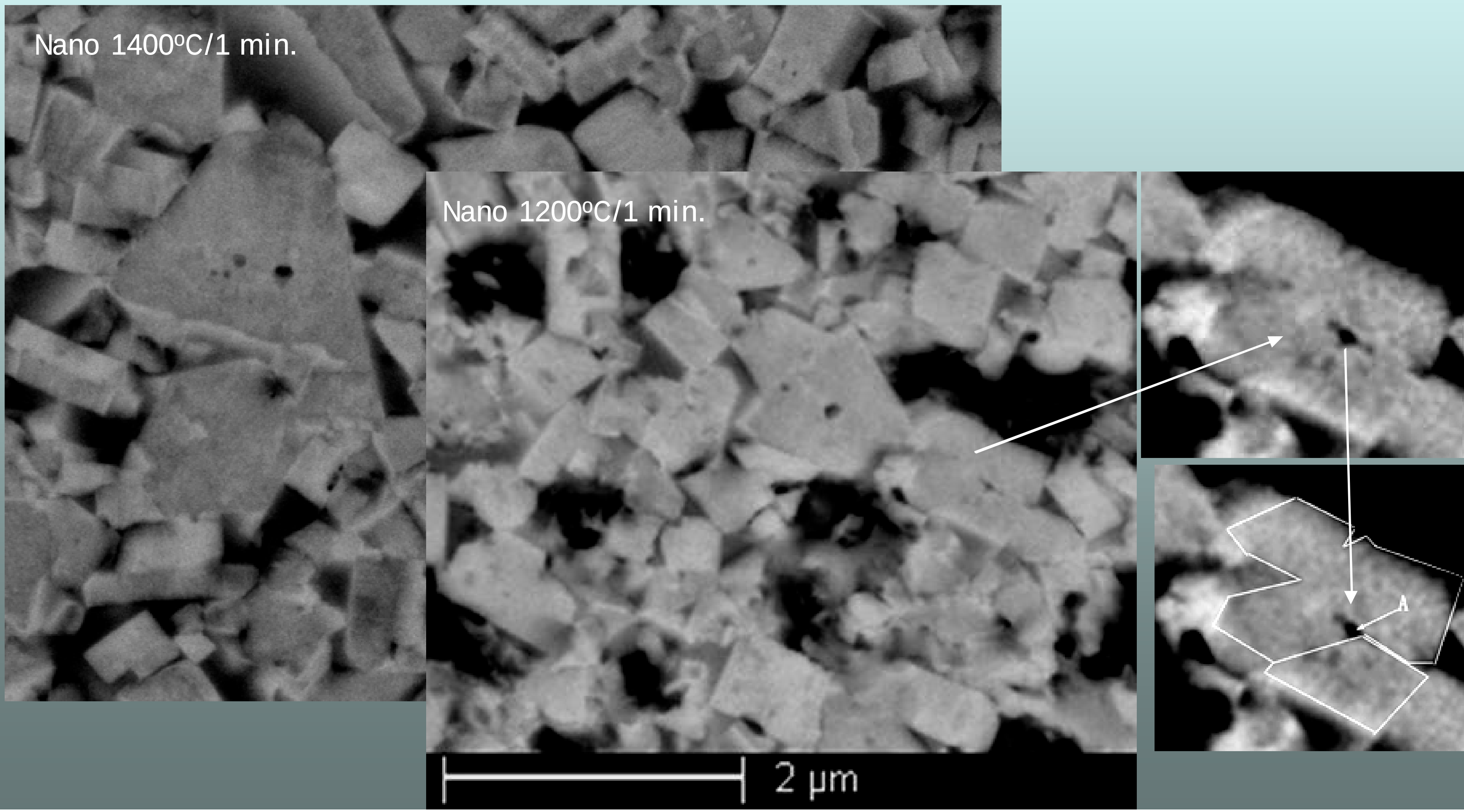


(b)

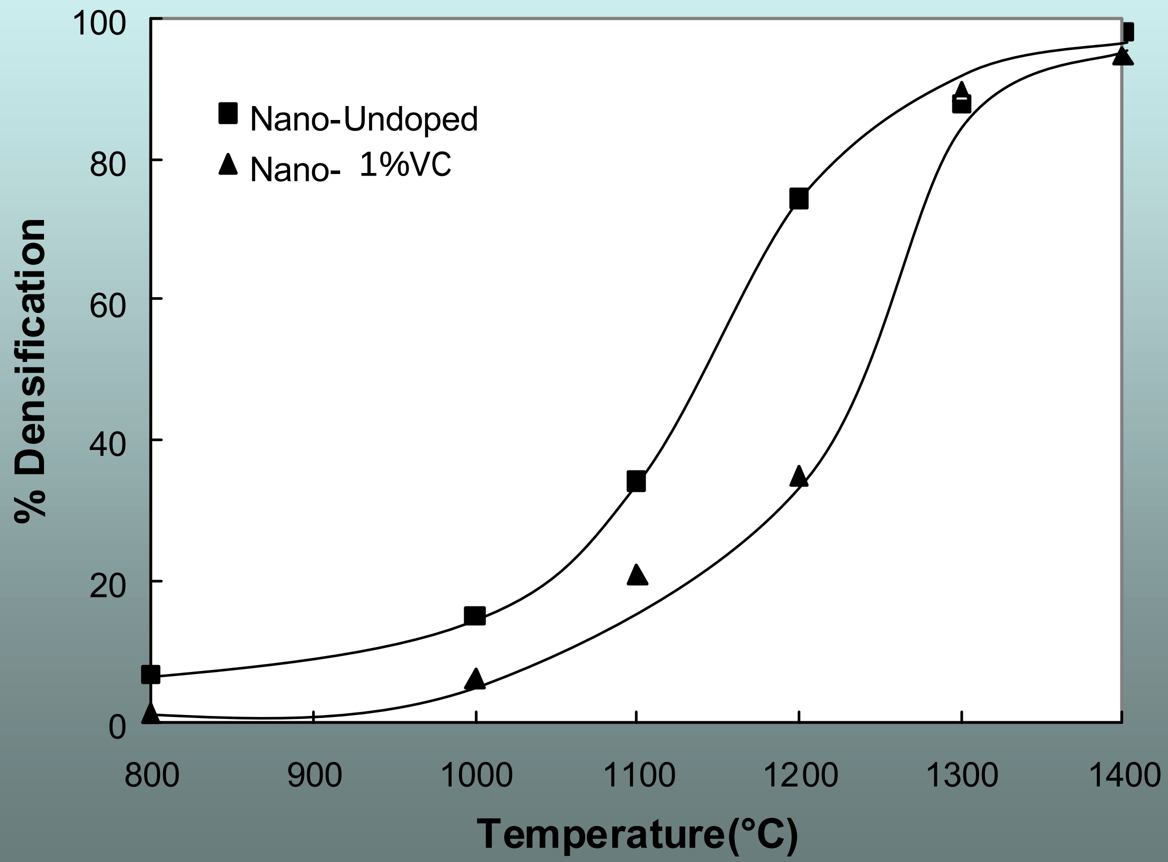
(a) Nanocrystalline (50 nm) - Rapid grain growth at low T.
(b) Micron-sized (1 μm) powder - Grains grow near liquid T.

Evidence of coalescence

Pores observed inside faceted grains seemed to have been trapped during coalescence

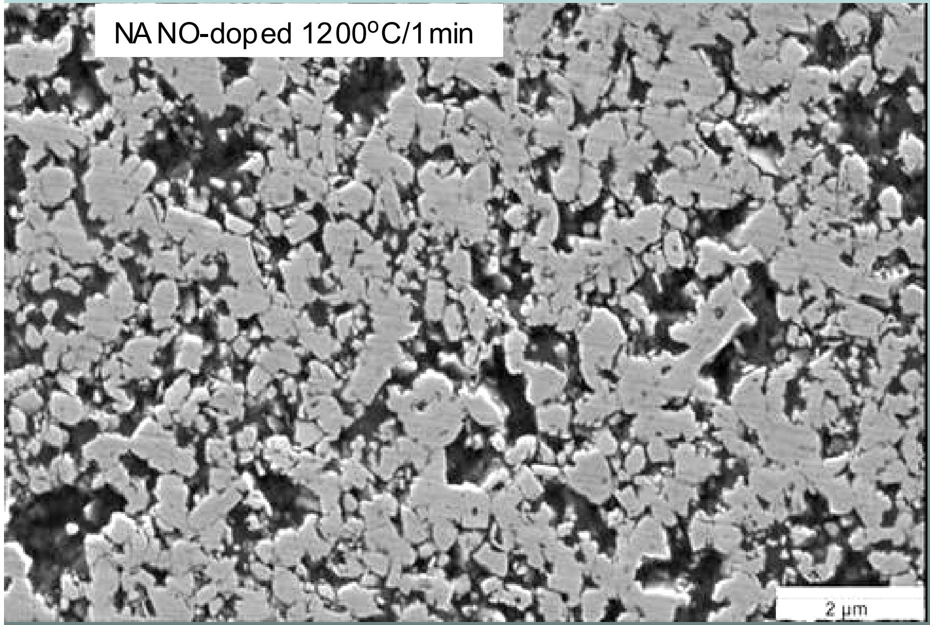


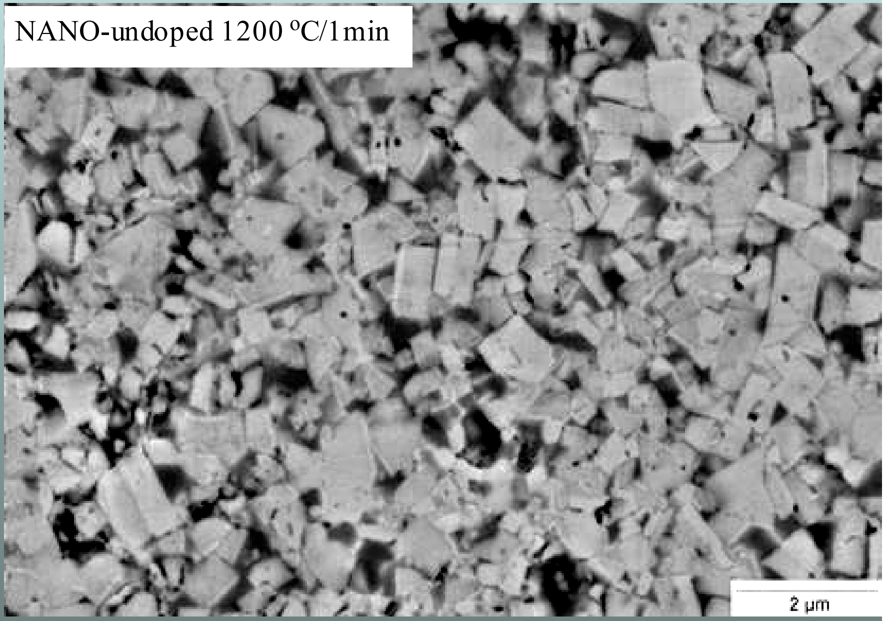
Effect of VC on the densification of nanocrystalline WC-Co as a function of temperature during heat-up.



Effects of VC

Effect of VC on the changes of grain size and crystal morphology during heat-up.



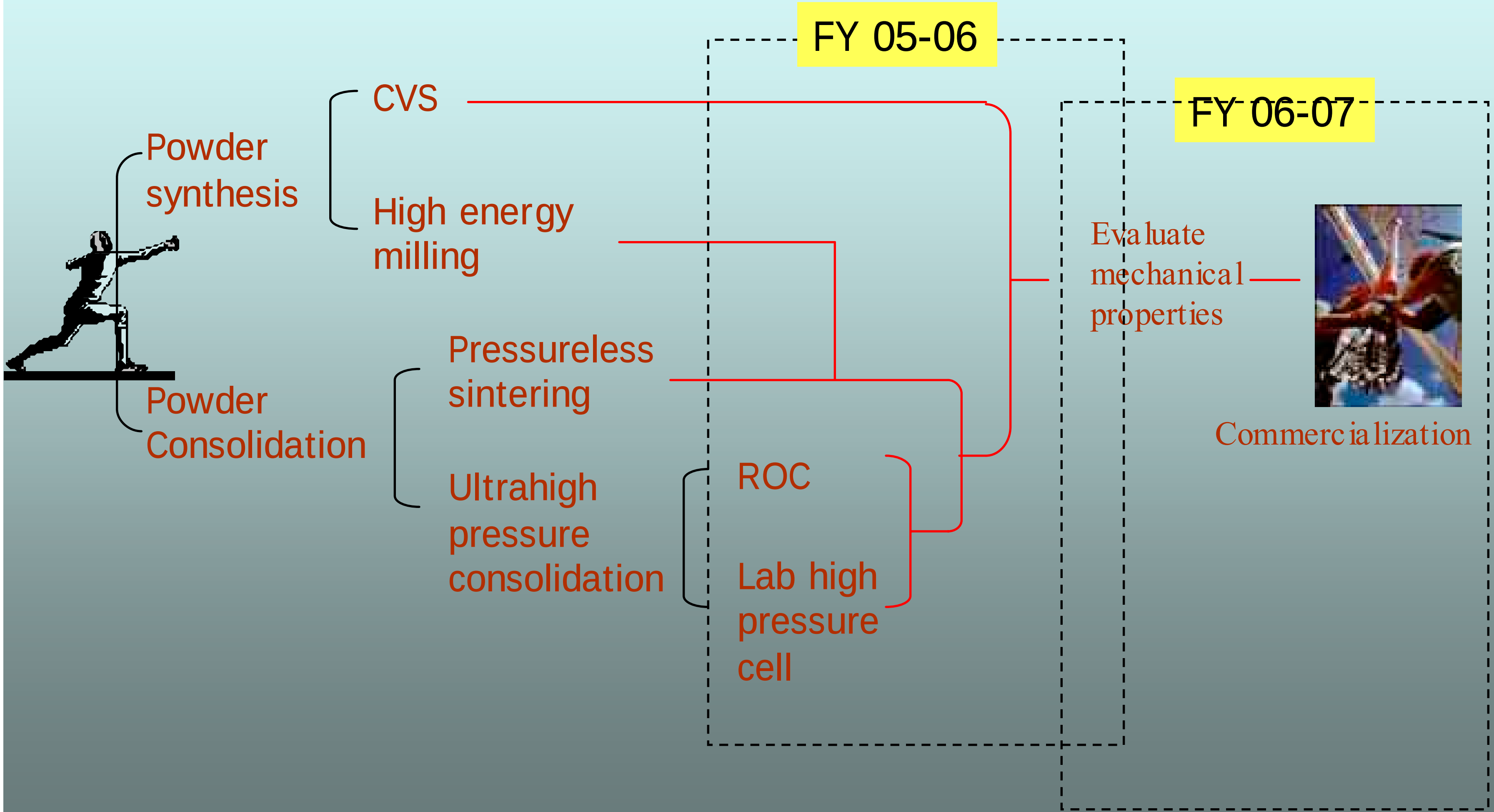


Bottom line:

Critical issues for consolidating nano powders with minimum grain growth:

- Control grain growth during sintering within aggregate particles
- Control coalescence during heat-up / early stage
- Rapid heating – bypass early stage coalescence
- Modify surface energy using doping elements
- Use high pressure – increase driving force for densification, but not grain growth

Future Plan – *continue on the pathway*



Future Plan *– continue on the pathway*

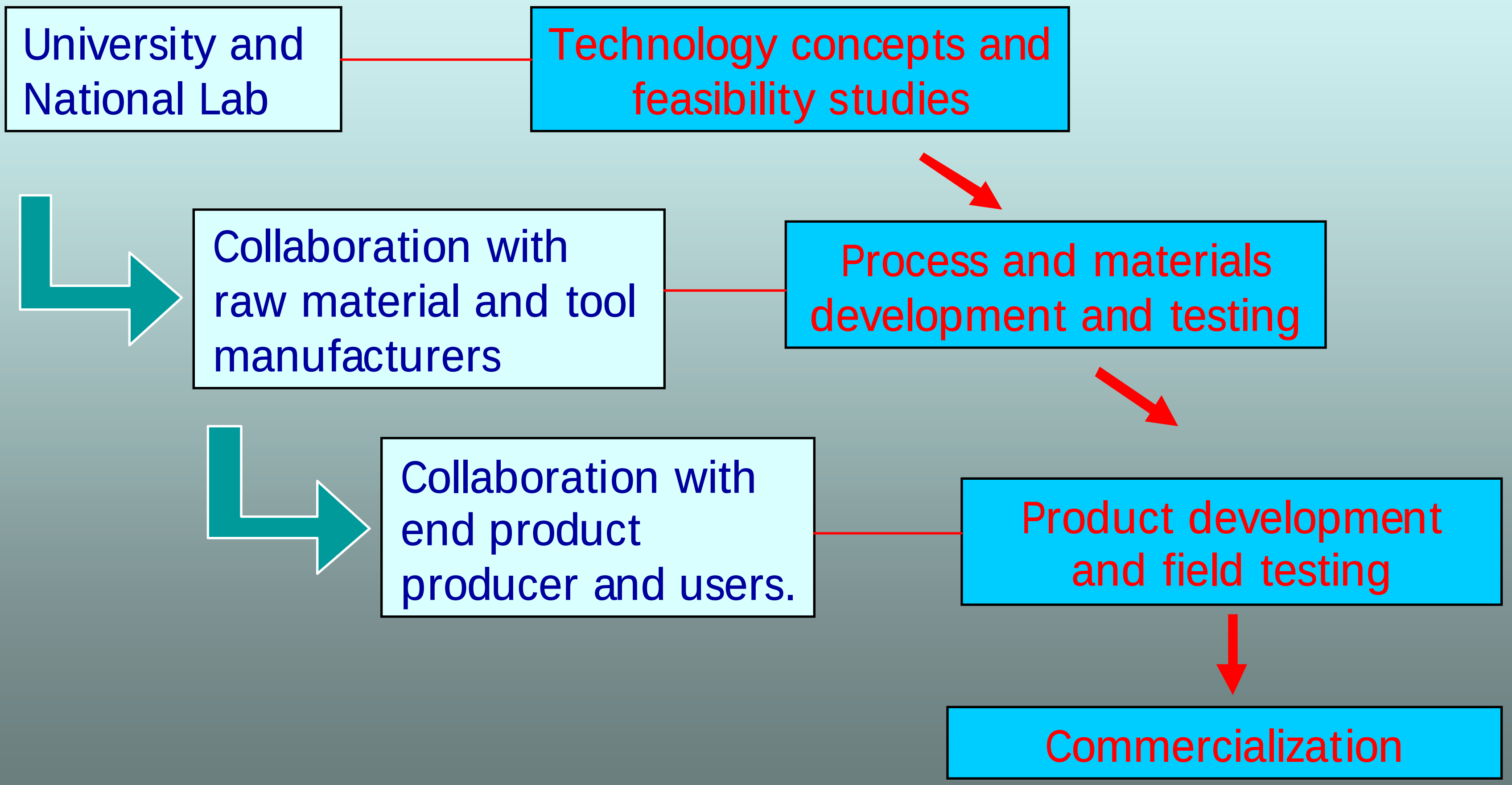
FY 05-06

- Optimize CVS process (thermal, flame, and plasma reactor)
- Optimize UPRC process and produce specimens
- Characterize mechanical properties

FY 06-07

- Produce Kg quantity of powders
- Manufacture selected engineering components
- Lab functional tests
- Field tests

Commercialization pathway



Marketing Strategy

- Leverage collaboration with industrial partners, both OEM and end users
- Initial market penetration through the partners.
- Start-up to manufacture specialty cutting edge products.
- A field-of-use based licensing strategy

Thank You!

Guidance for Presentations at Materials Project Review

May 31 – June 3, 2005

1. Summary slide (see example slide, please update information from last year)
   - Goal, Challenge, Benefits, Potential End-User Applications, FY06 Activities, and Partners (specifically discuss which parties are involved in which activities)
2. Barrier-Pathway-Metrics slide (see example slide, please update from last year)
   - Summarize barrier, pathway, metrics, and potential benefits
3. Discuss major milestones to date (emphasis on most recent)
4. Discuss future plans (emphasis on coming year: schedule, go/no-go decision points, milestones)
5. Discuss commercialization plans, pathways, and risks

Please Note:

- All presentations are restricted to 20 minutes maximum, with 20 minutes of Q&A with reviewers. 20-25 slides are likely to be appropriate.
- Contact Gareth Williams, Energetics at 410.953.6209 or gwilliams@energetics.com with questions.