传统材料研究体会

主要内容

- 文献阅读
- 实验开展
- 结果总结
- 思路设计

1 文献阅读

➢传统材料领域

- “There is nothing new under the sun！”
- 较成熟完善的理论体系
- 材料性能提出了更高要求

创新难度大
挑战难度高

扎实的理论基础

➢基础积累

研究课题

XX工艺制备XX背景应用的具有XX性能的XX材料（工艺流程、材料设计、性能表征、理论研究）

泛读——掌握相关背景

- 师兄师姐毕业论文、领域优秀硕博论文绪论部分；
- 经典教材、网上学习、交流了解某些难以理解的概念
- 综述论文，掌握该领域研究现状、发展历程
- 快速掌握工艺流程原理、材料属性、需求背景、性能要求和领域难点等

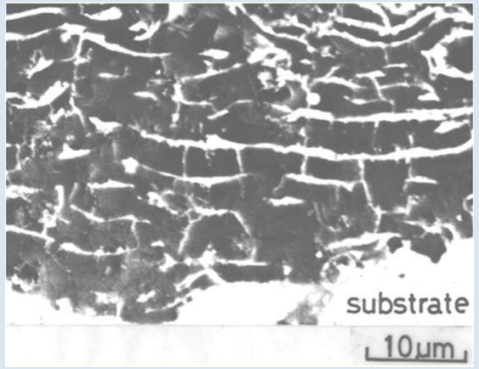
精读

- 明确具体的研究问题，追踪相关的权威期刊、课题组论文，掌握目前存在的研究研究方案及优缺点；
- 明确”别人做了什么，没有做什么，还有什么东西可以做”;
- “借鉴别人方法/方案来研究自己问题“
- 结合实验中具体问题追述经典书籍、权威文献来解决具体问题，阐明相关原理；

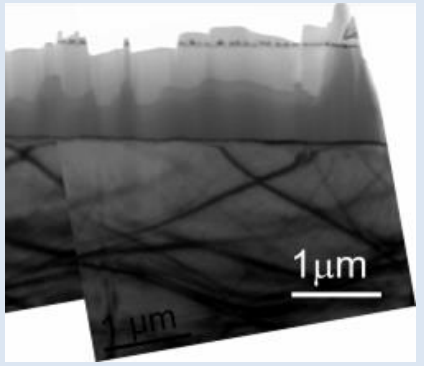
1 文献阅读

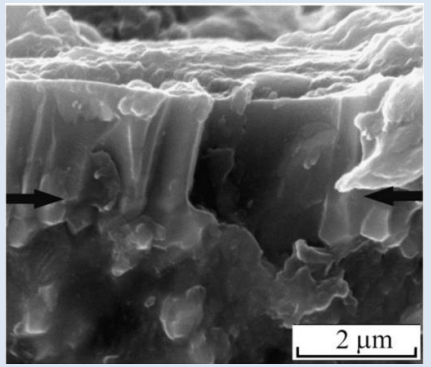
➢研究问题：

热喷涂陶瓷涂层粒子层间存在大量未结合界面，最近研究发现等离子喷涂Al_2O_3、YSZ扁平粒子存在临界结合温度，沉积温度高于这一温度界面产生良好结合，研究临界结合温度和什么有关以及界面结合原理。



氧化铝陶瓷涂层断面组织结构





氧化铝、YSZ扁平粒子断面结构：临界结合温度300℃、600℃

➢基础积累

热喷涂、等离子喷涂？
扁平粒子？
沉积温度？界面结合？
…

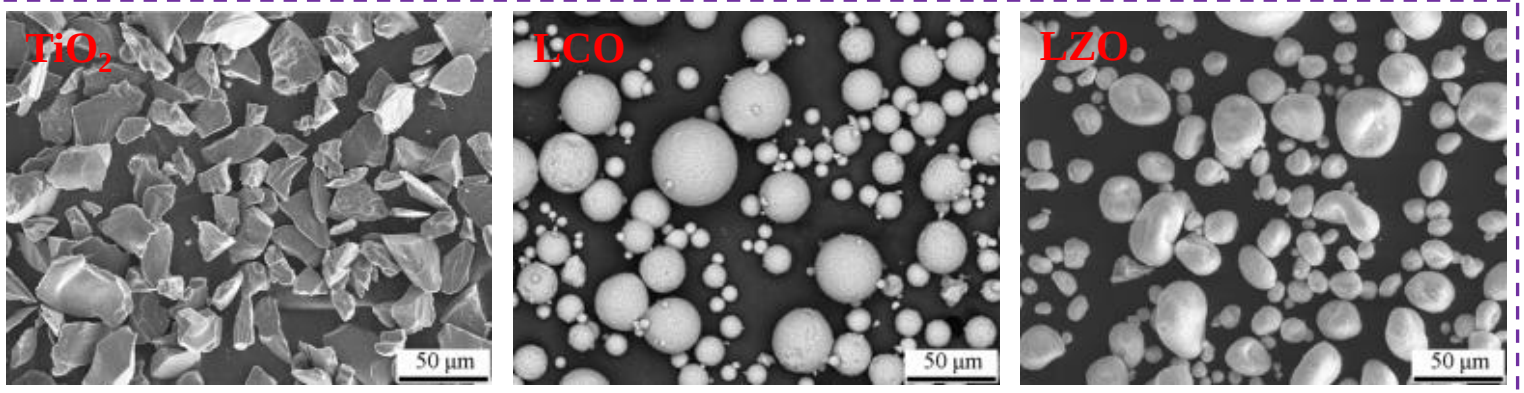
泛读——掌握相关背景

- 材料工程大典 16卷 第五篇（徐滨士李长久）
- 王卫泽．等离子喷涂涂层结构的定量表征及涂层结构与性能之间的关系[D] 2004
- 郝顺．沉积温度对大气等离子喷涂氧化铝涂层结合特性及性能影响的研究[D] 2010
- 邢亚哲．等离子喷涂氧化钇稳定氧化锆涂层中晶粒跨扁平粒子界面连续生长规律的研究[D] 2008
- 杨二娟．等离子喷涂陶瓷涂层晶体结构及组织形成的研究［D］2014.
- Li CJ, Yang GJ, Li CX. Development of particle interface bonding in thermal spray coatings: A review[J]. J Therm Spray Technol, 2013, 22(2-3): 192-206.
- 快速大量阅读对相关课题研究背景有基本了解（①工艺种类、特征、物理原理；涂层种类、性能、应用；②涂层形成过程、粒子沉积特性；涂层组织结构、粒子层间结合的影响因素及现有形成机制；③课题研究的基本历程和本课题组的研究特色）

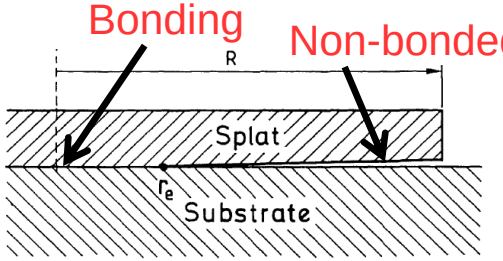
1 文献阅读

根据具体问题不断最终权威文献精读分析

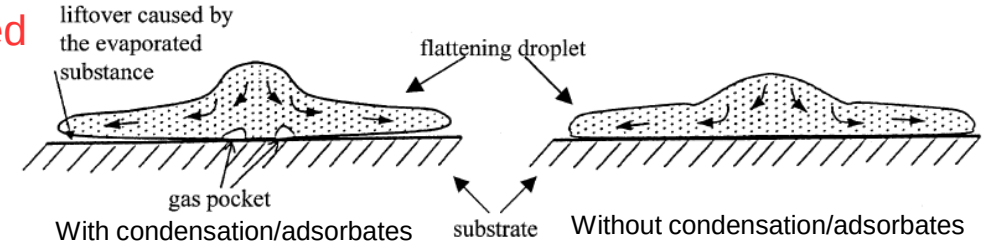
- **沉积温度vs界面结合**
  - 影响规律明确、临界结合温度概念课题组已提出（别人做了）
  - 临界结合温度的普适性，和材料属性的关系（没有做）
  - 明确陶瓷材料（可以做）
- **层间结合形成机理**
  - 结合方式：机械结合、物理结合、化学/冶金结合（明确我们研究的是化学结合）
  - 结合机制：已提出四种结合机制，都有部分结果可以佐证（别人做了），但每个机制都有难以解释的实验现象，尤其解释不了沉积温度与界面结合的影响（没有做）
  - 扁平沉积特性决定了无法通过实验研究其沉积行为，粒子快速冷却凝固数值模拟为研究这个过程提供了可能，但没有将冷却凝固过程与结合联系起来。（可以做、有可能行）
- **数值计算（针对具体问题不断扩展阅读）**
  - 数值模拟建模方法、传热学、凝固理论→快速凝固条件下热物性参数拟合模型



陶瓷喷涂粉末形貌



$P_{碰撞} \geq P_{毛细}$，界面结合



碰撞时基体表面吸附物快速气化阻碍界面结合

界面结合形成机制

自主学习、批判阅读，通过不断扩展阅读理清实验中的问题

2 实验开展

➢细心阅读师兄师姐论文、虚心向其请教有利于前期快速开展实验

扁平粒子制备方法

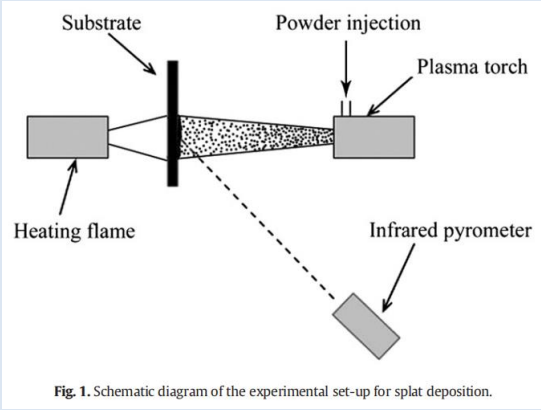
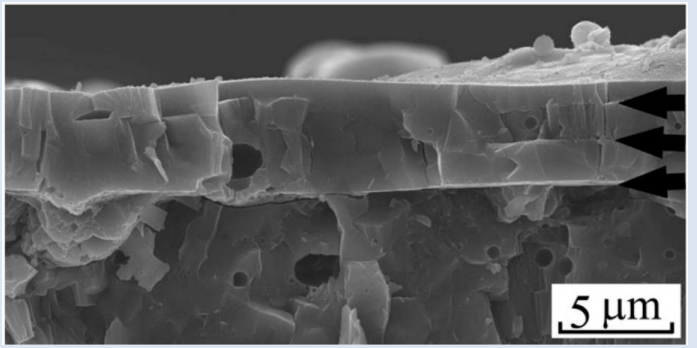


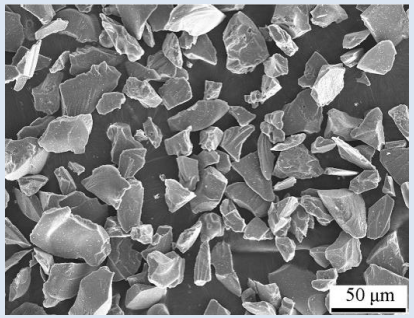
Fig. 1. Schematic diagram of the experimental set-up for splat deposition.

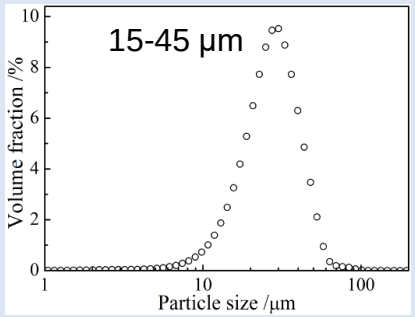
界面结合表征方法

The splat bonding state was examined by the cross-sectional morphology of the fractured samples using scanning electron microscopy.

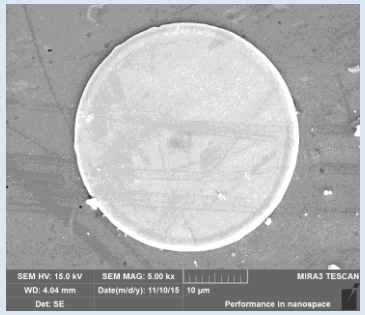


➢实验不仅仅是简单的表征结果堆积，而应紧密结合相应的研究目的

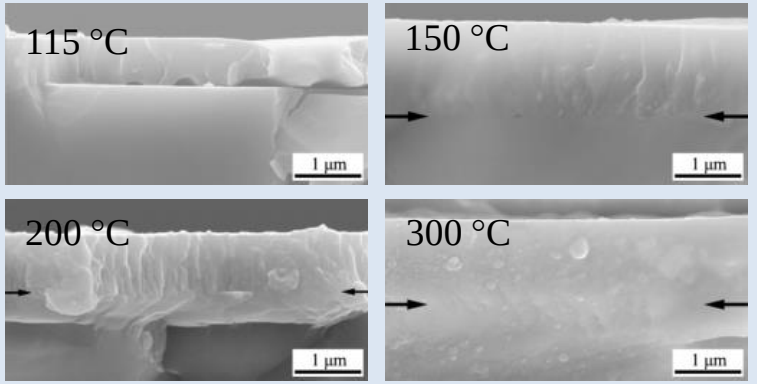




TiO_2粉末颗粒形貌及粒度
（影响粒子形貌结合状态）



TiO_2扁平粒子表面形貌
（影响粒子结合状态）



TiO_2扁平粒子断面结构

2 实验开展

➢没有研究是一帆风顺的，遇到困难多尝试，多思考，多请教，不断积累

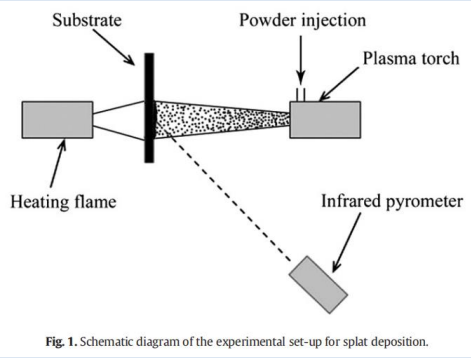
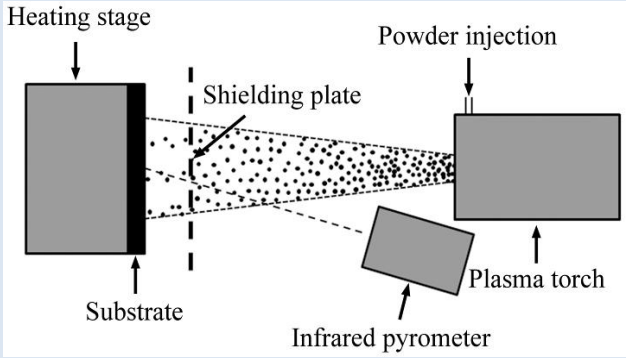
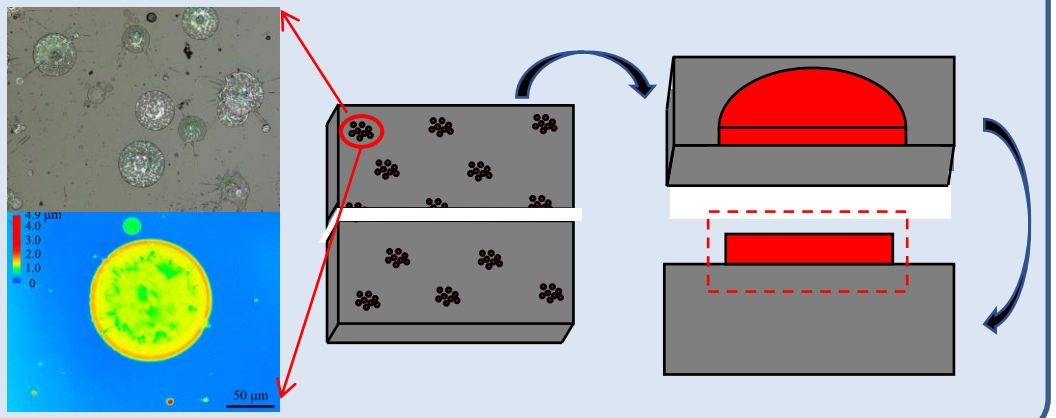
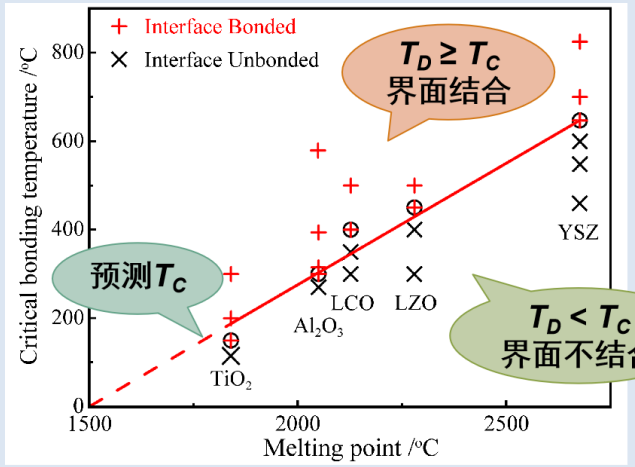


Fig. 1. Schematic diagram of the experimental set-up for splat deposition.

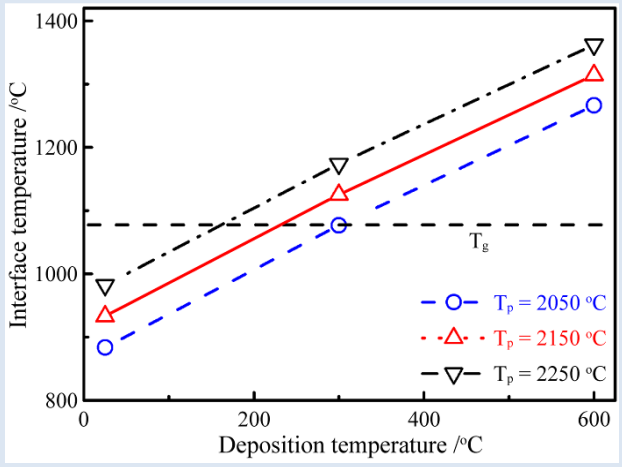


原方案温度偏差百度以上，粒子相互干扰，新方案温度偏差<10℃，相互干扰少





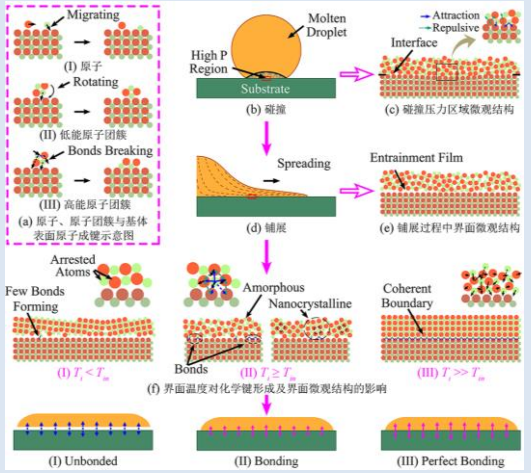
临界结合温度vs材料熔点



粒子温度、基体温度vs界面温度

2014~2016

提出多种解释模型

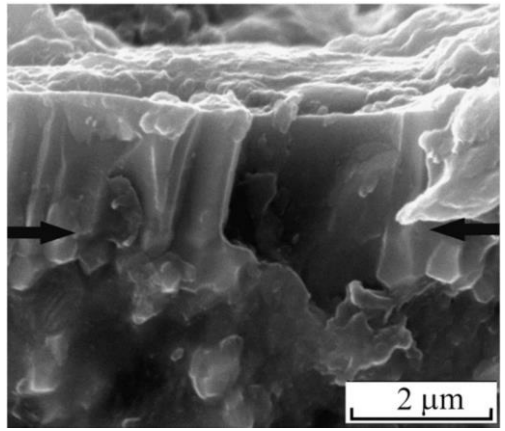


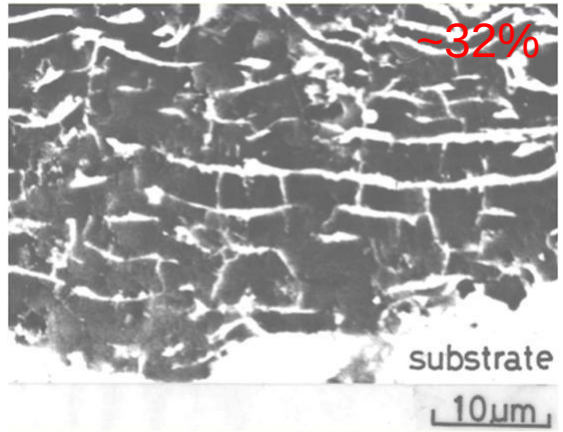
陶瓷扁平粒子界面结合形成机制

3 结果总结

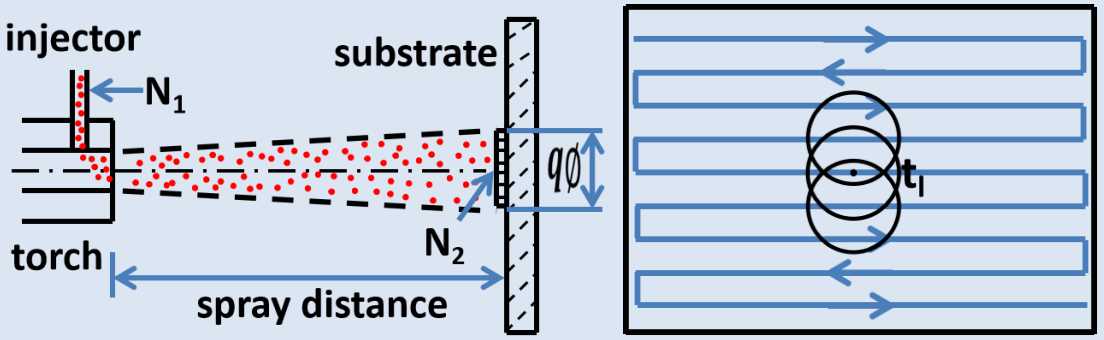
➢结果总结比实验更总要！

- 科研：我要往哪里走，我现在在什么地方，我怎样才能从“这里”到“那里”
- 基于具体小目标，条理清楚的呈现客观结果
- 便于讨论，导师等人指出问题指明方向
- 培养科研思路、表达能力、发现新现象
- 急迫感、推动力



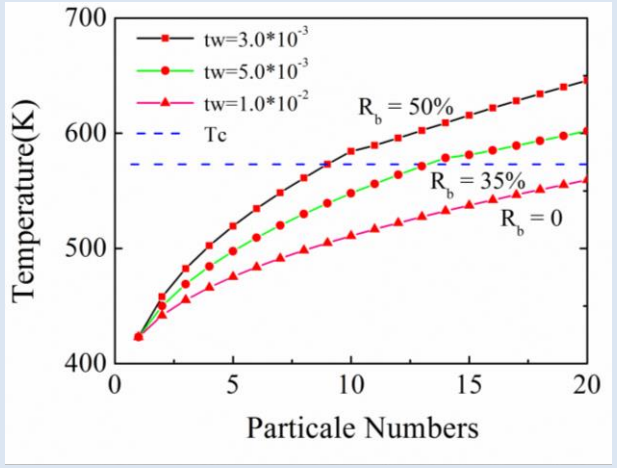


氧化铝扁平粒子临界结合温度300℃，为何室温沉积涂层存在32%结合？

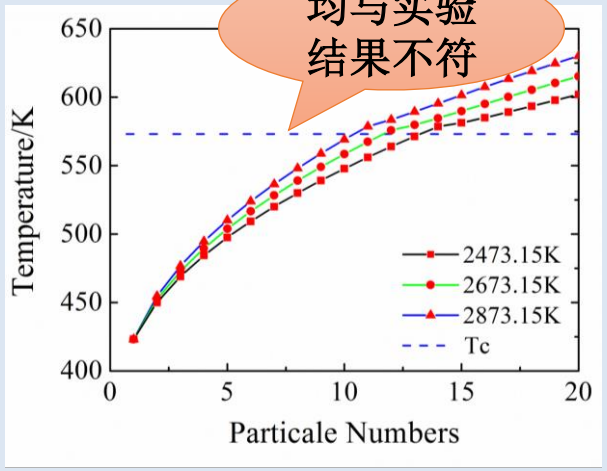


热喷涂工艺中局部温度差异、粒子沉积过程中基体表面热量堆积

粒子沉积间隔时间、基体厚度物性参数、融滴温度等等因素

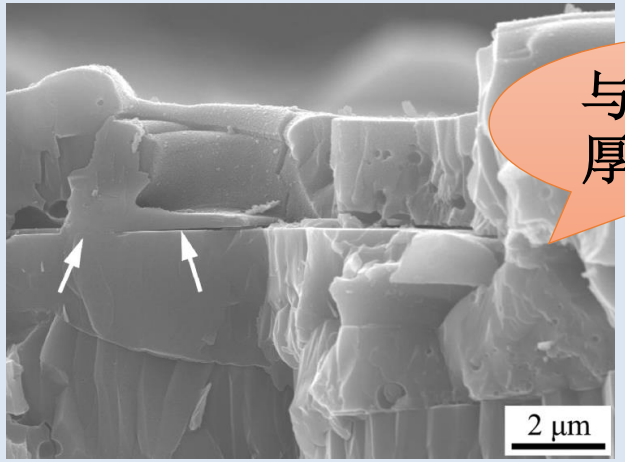


等待时间vs涂层结合率



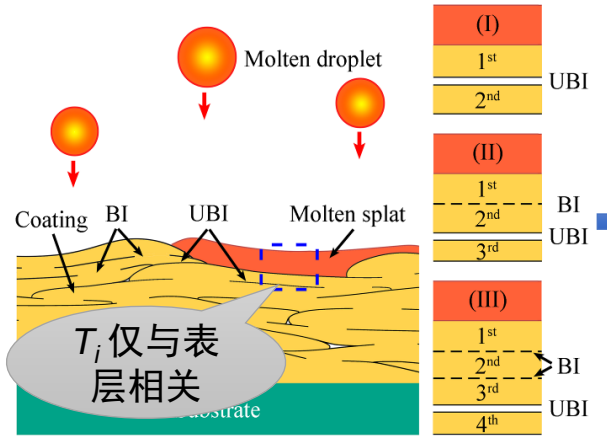
熔滴温度vs涂层结合率

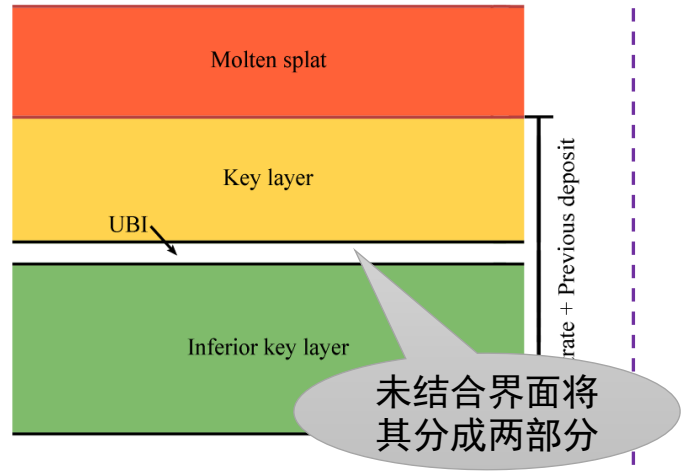
3 结果总结

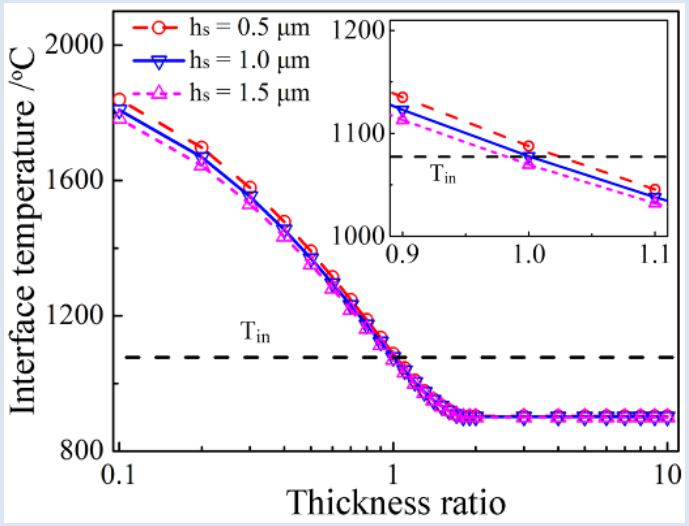


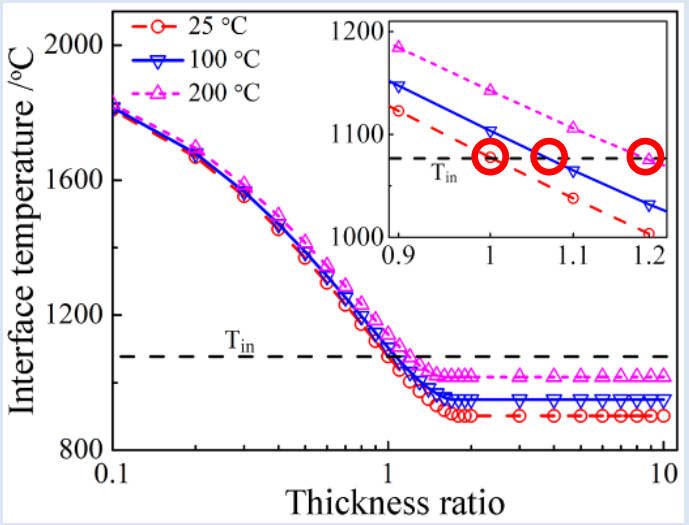
与扁平粒子厚度有关？

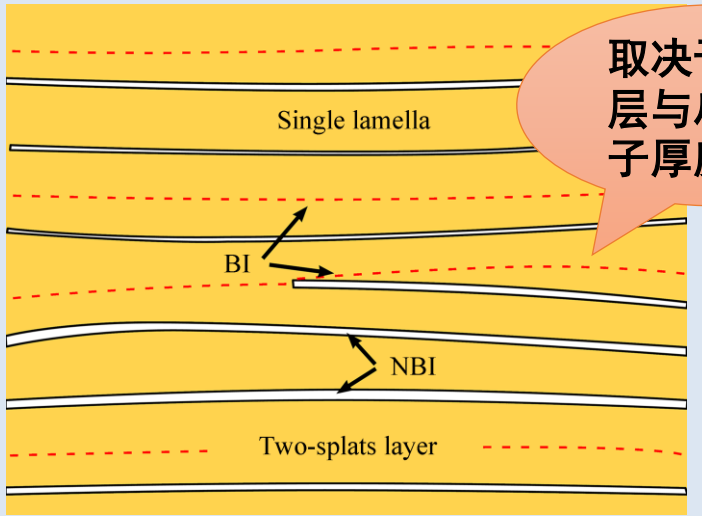
270 °C 沉积Al_2O_3 扁平粒子







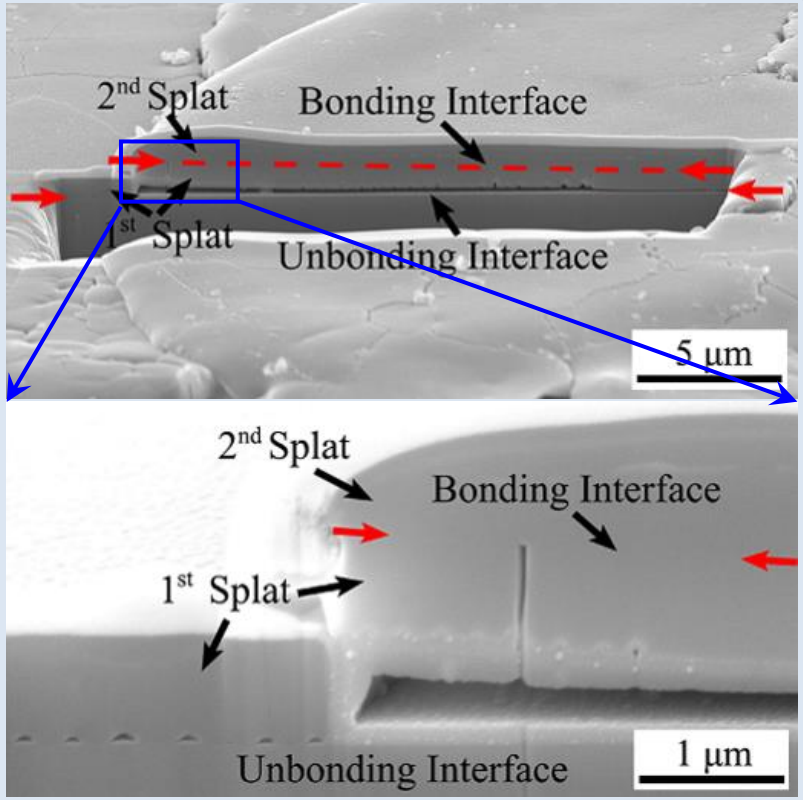


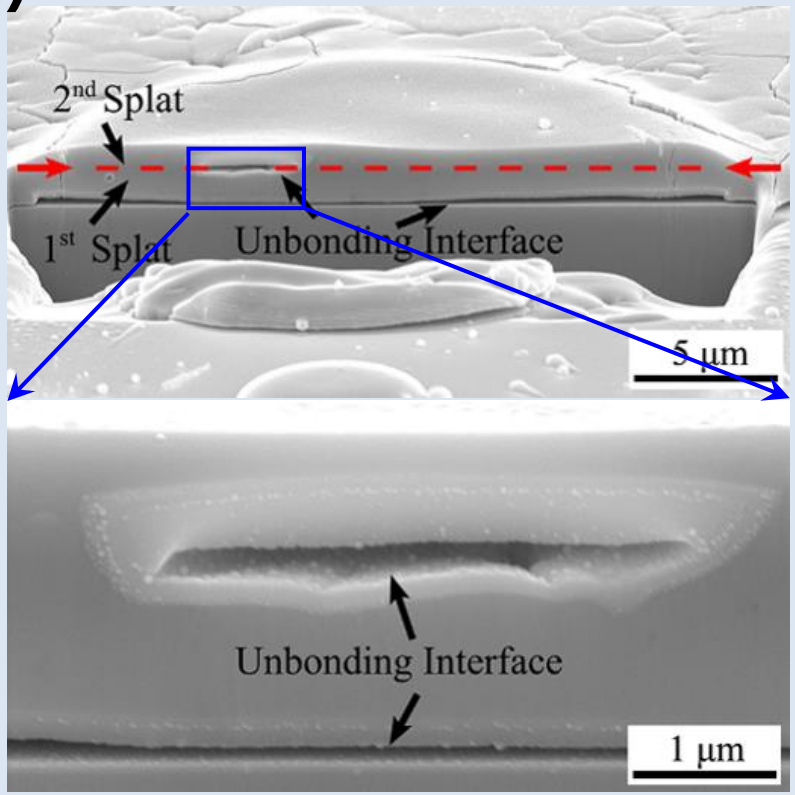


取决于关键层与扁平粒子厚度之比

3 结果总结

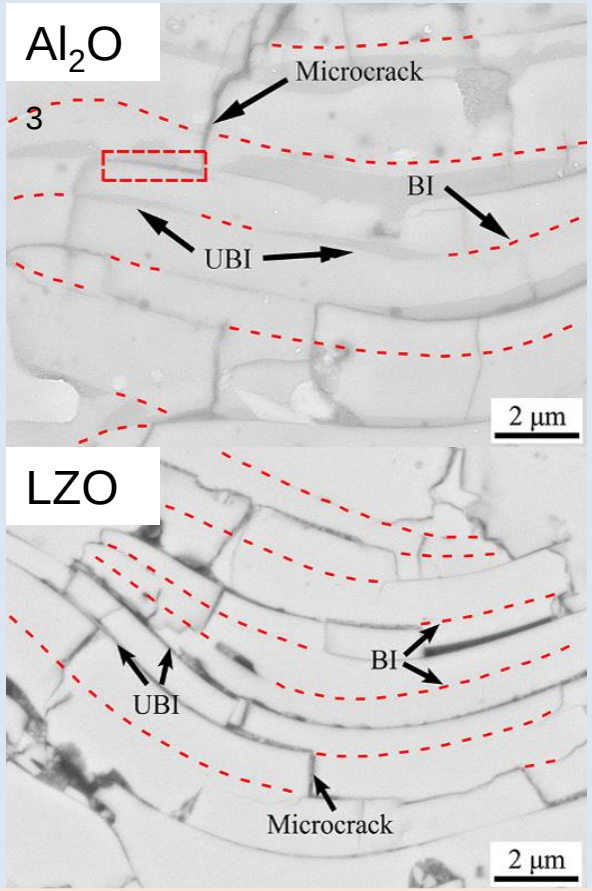
Al_2O_3扁平粒子界面结合状态 (200 ºC)





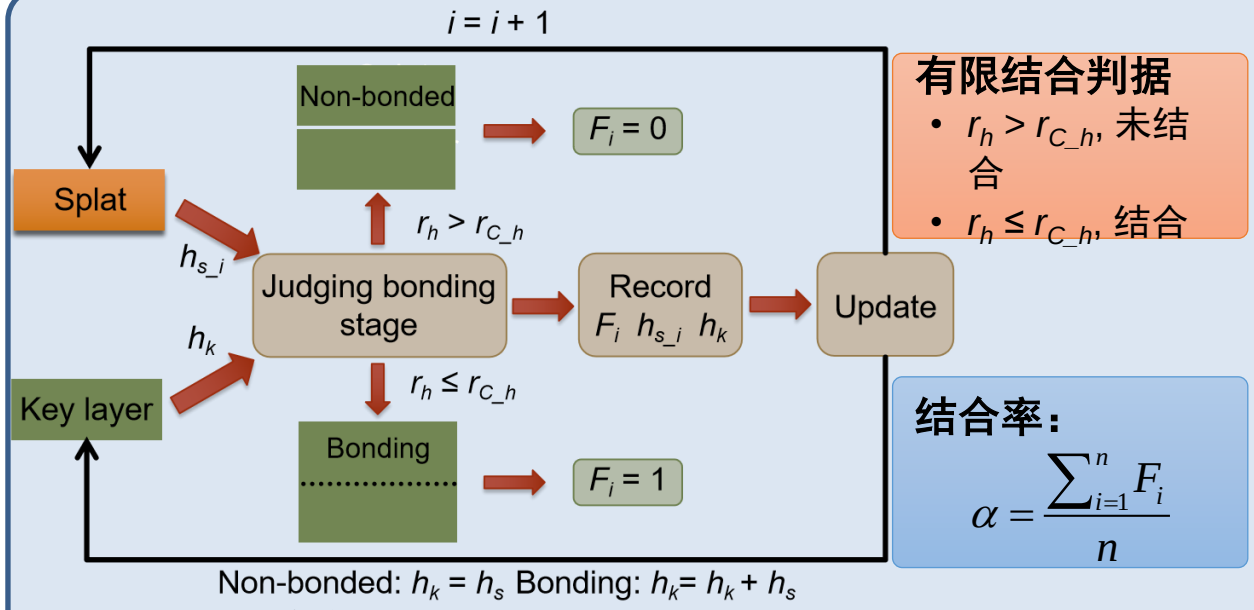
- 第一层扁平粒子与同质基体不结合
- 大粒子/小粒子界面良好结合
- 小粒子/大粒子存在不结合区域

涂层断面结构 (室温)



涂层粒子层间有限结合特征与非等厚模型预测结果相符

3 结果总结



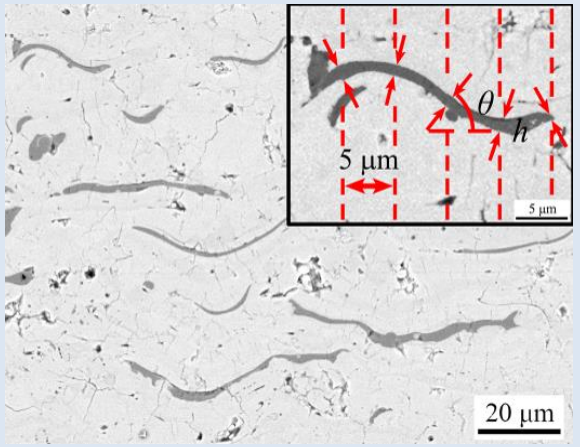
陶瓷涂层层间结合率预测模型

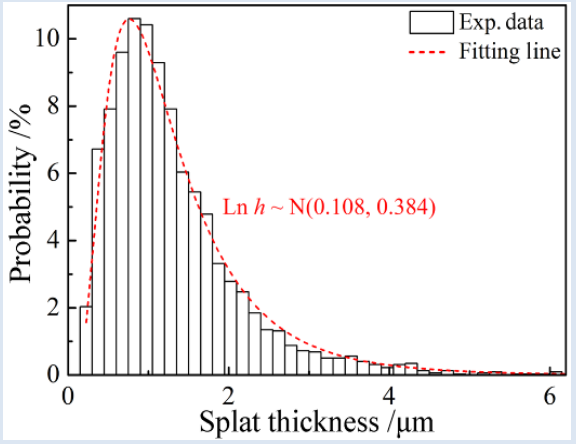
有限结合判据

- $r_h > r_{C_h}$, 未结合
- $r_h \le r_{C_h}$, 结合

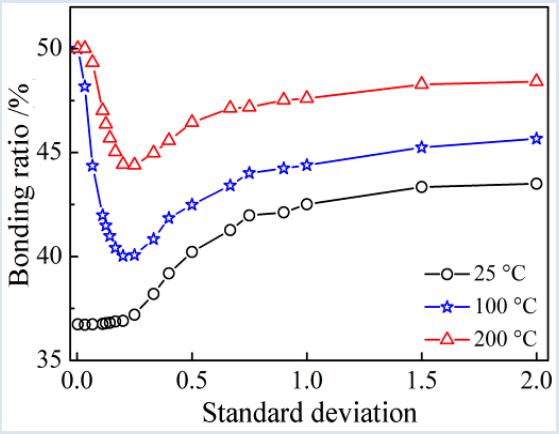
结合率：

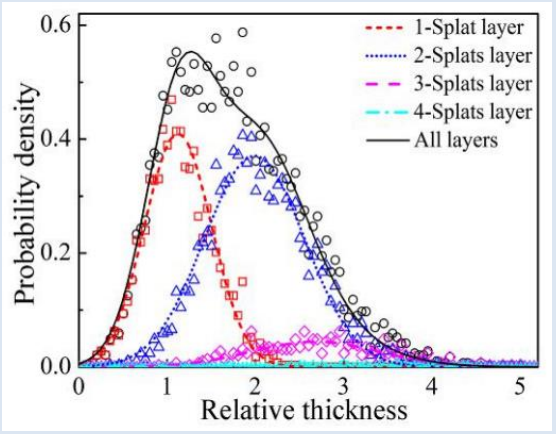
$$\alpha = \frac{\sum_{i=1}^{n} F_i}{n}$$



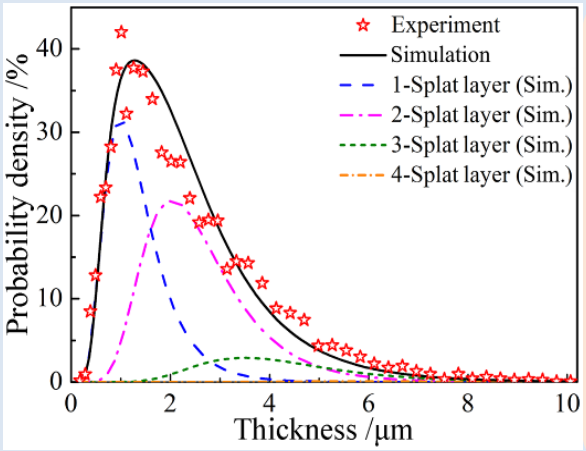


- Al_2O_3粒子厚度服从对数正态分布





陶瓷涂层结合率与扁平粒子厚度分布有关



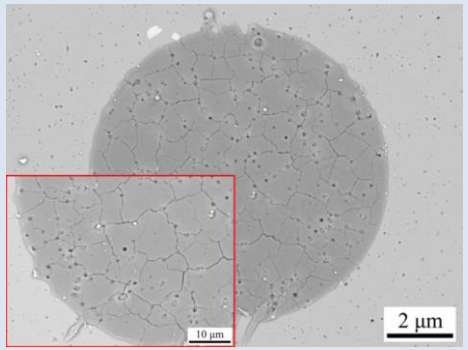
- 基于Al_2O_3粒子厚度涂层理论结合率：41%
- Al_2O_3涂层中多层扁平粒子层厚度分布与计算结果一致

4 思路设计

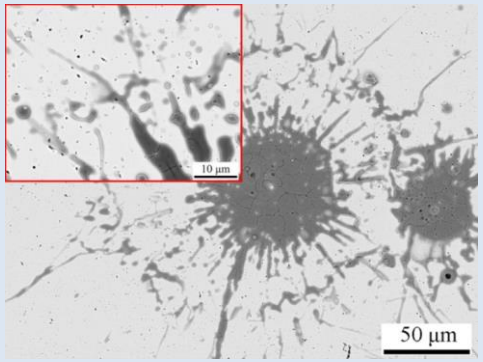
➢研究中另一至关重要环节！

- 没有哪一个课题是研究初期能完全规划好的
- 思路设计应是明确目标和现有状态条件，实现目标的具体可行方案
- 好的方案设计建立在文献积累和实验结果准确把握基础之上
- 切忌思路太活，东打一枪西打一枪
- 切忌仅执行，不思考

扁平粒子表面形貌



Al_2O_3/TiO_2 125 ºC



Al_2O_3/YSZ 125 ºC

液滴碰撞

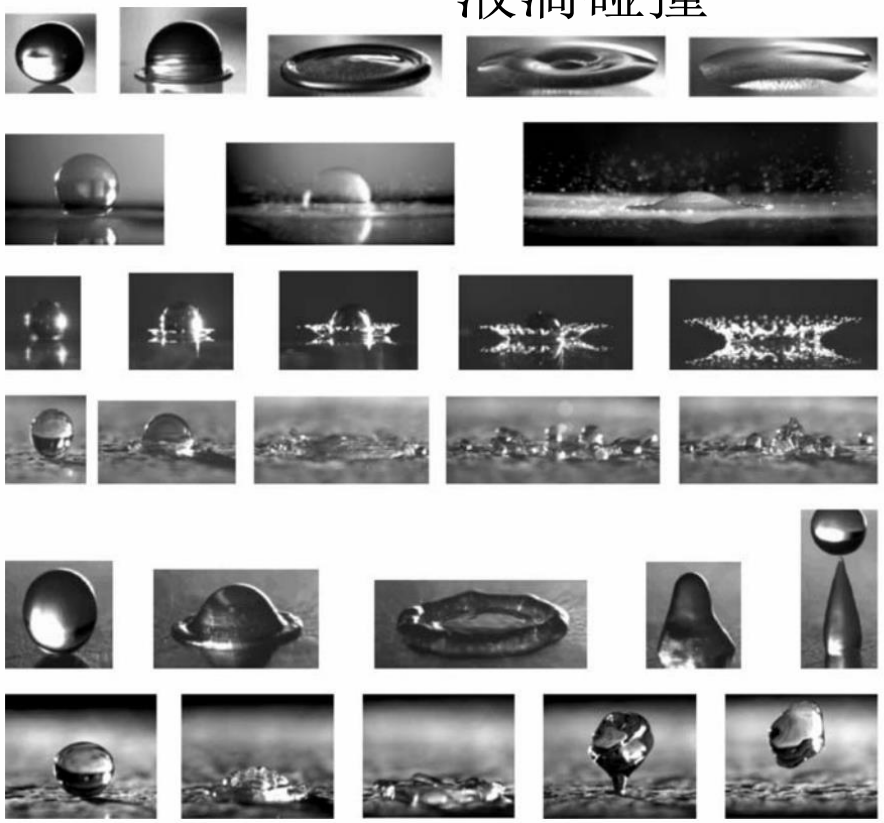


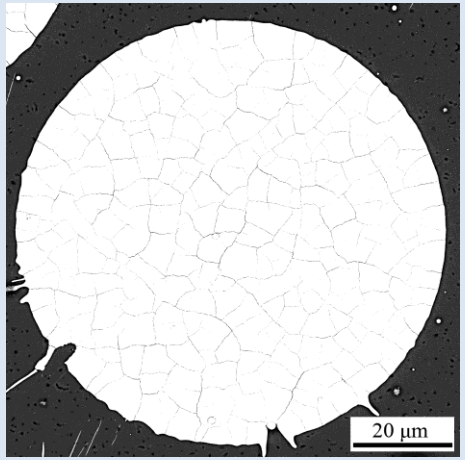
Table 3 Summary of the Influences of Each Parameter on Each of the Six Outcomes

An increase of	Deposition	Prompt splash	Receding breakup	Complete rebound	Corona splash	Partial rebound
V	↓	↑	↑		↑	↑
D	↓	↑				
σ		↓	↑	↑	↓	↑
μ	↑	↓	↓		↓	
R_a	↓	↑			↓	
R_ω		↓				
$\theta_{rec.}$			↑	↑		↑

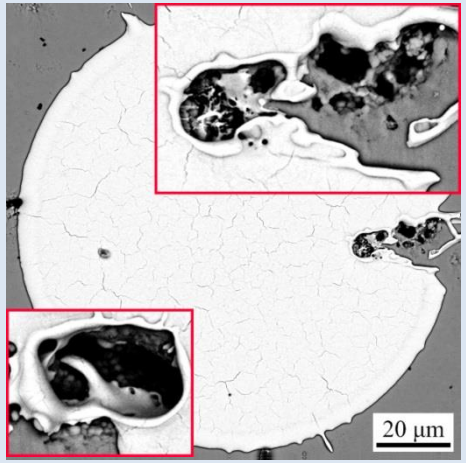
4 思路设计

扁平粒子表面形貌

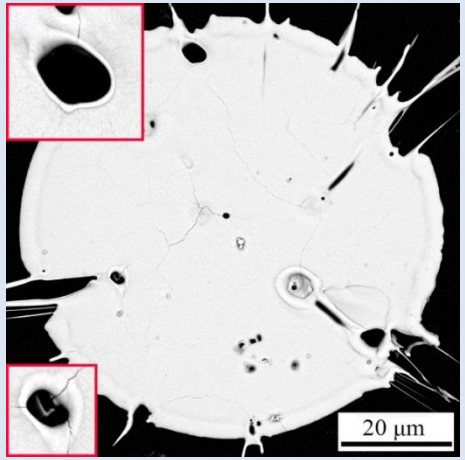
LCO/TiO_2 150 ºC



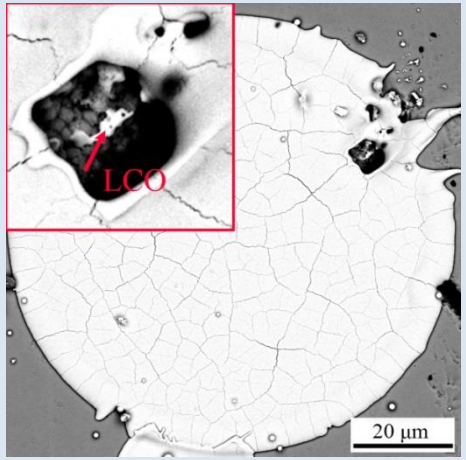
LCO/YSZ 300 ºC



LCO/TiO_2 300 ºC

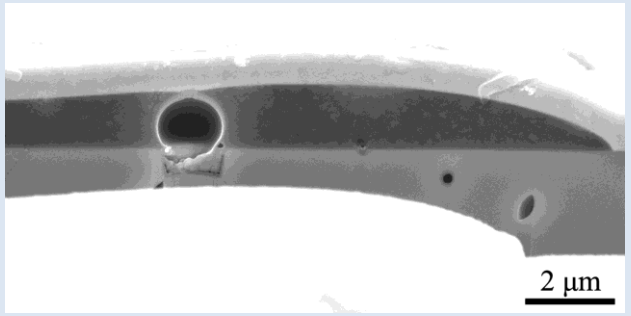


LCO/YSZ 400 ºC

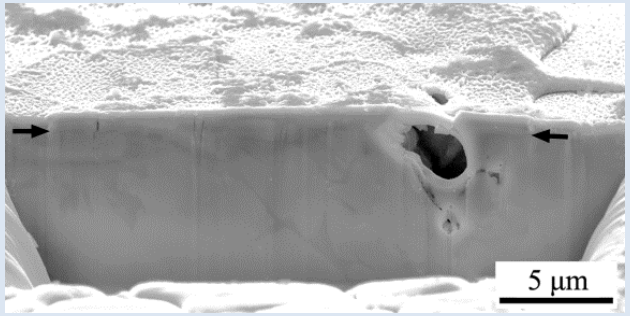


扁平粒子断面形貌

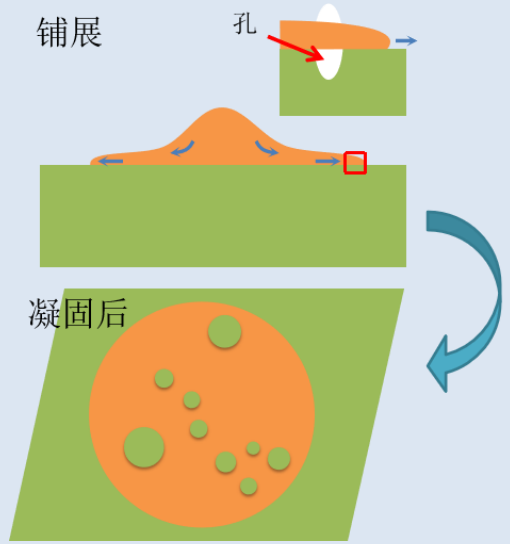
Al_2O_3/YSZ 125 ºC

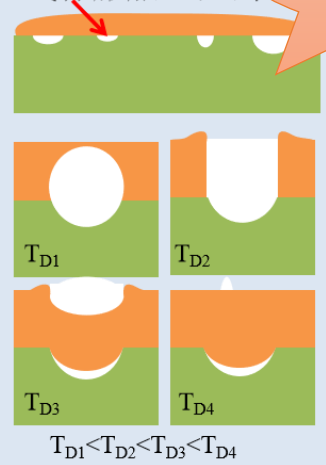


LZO/LZO 450 ºC



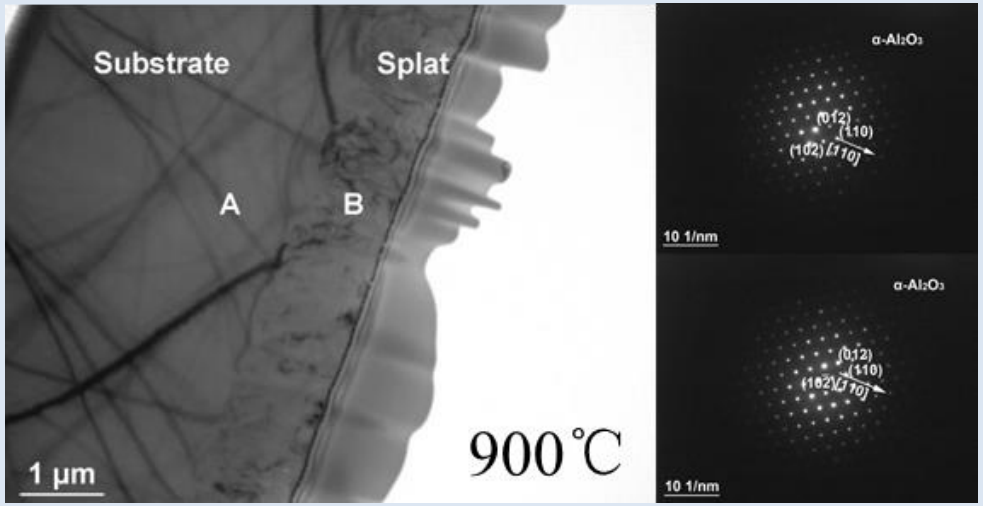
孔洞演变过程分析

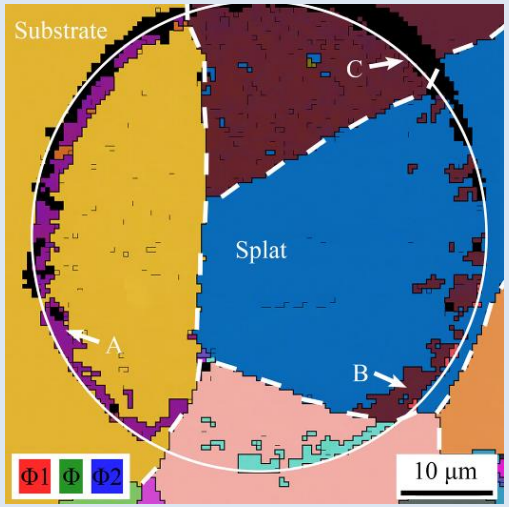




偏离目标！
知识储备不足！

4 思路设计

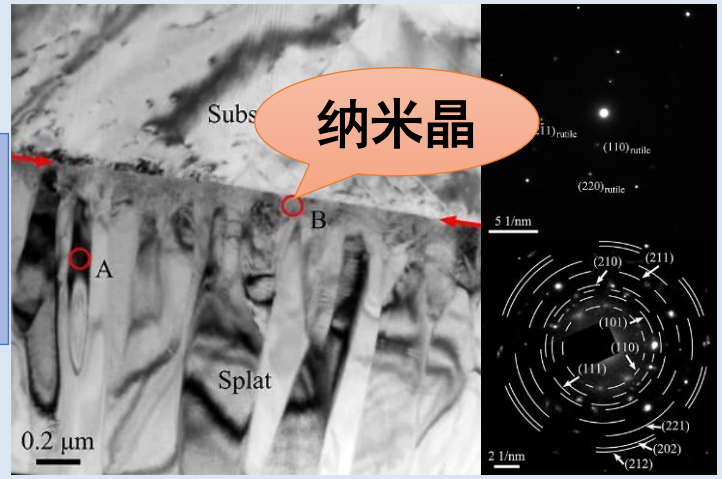




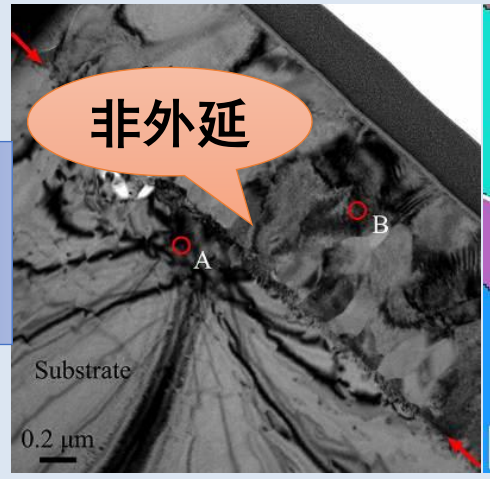
- 极少研究报道热喷涂陶瓷扁平粒子存在外延生长现象，机制无研究
- 实验中发现一种更为便利的表征方法
- 外延生长有助于认知界面结合行为，促进界面结合，组织调控

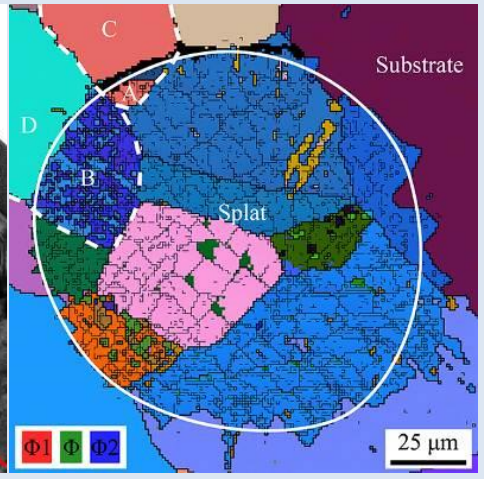
沉积温度vs外延生长

150 °C

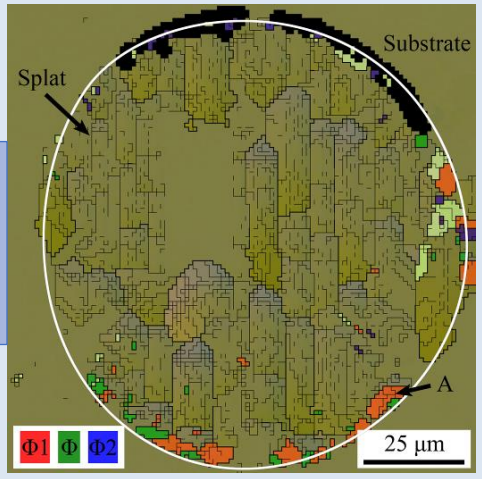


300 °C





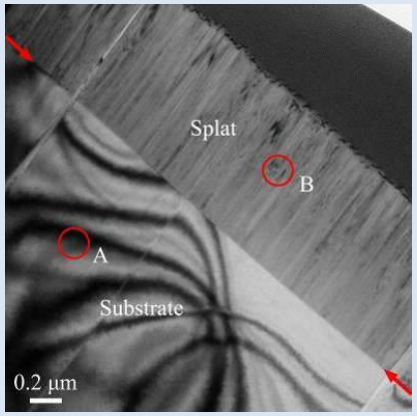
500 °C

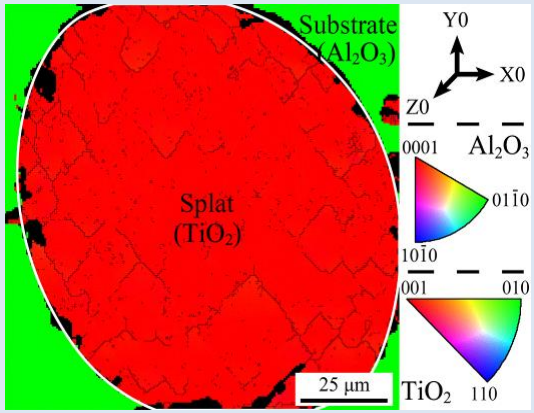


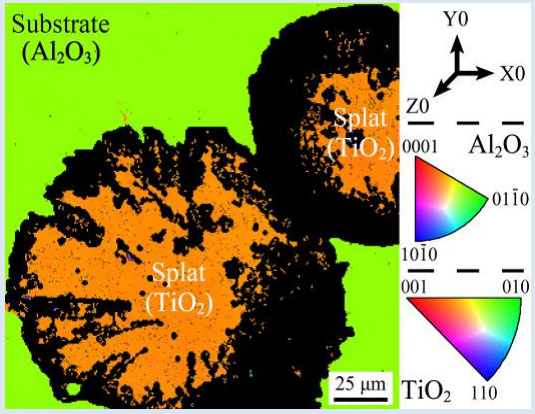
4 思路设计

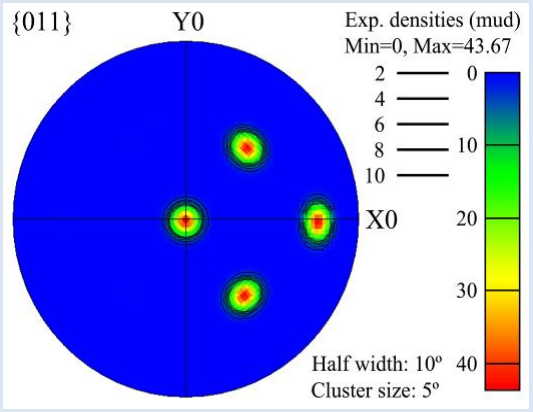
沉积温度500 °C

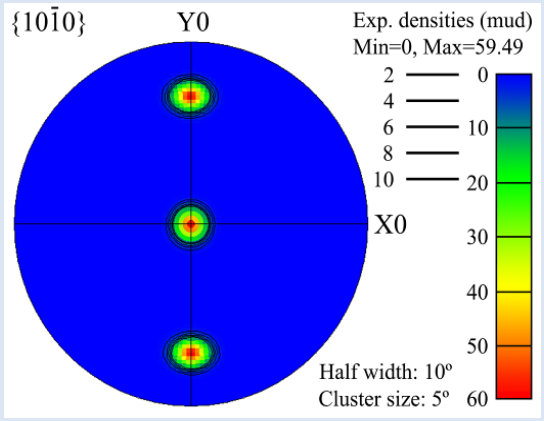
α-Al_2O_3 $(10\bar{1}0)$晶面沉积TiO_2扁平粒子显微组织

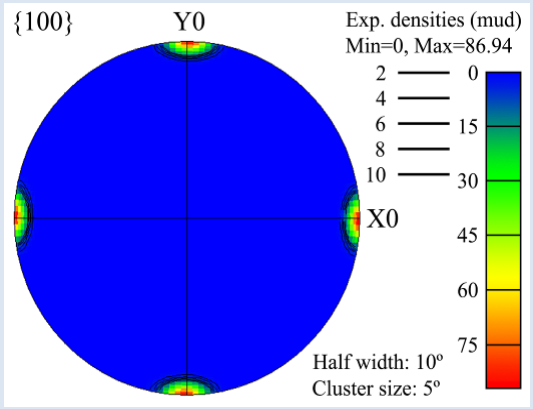


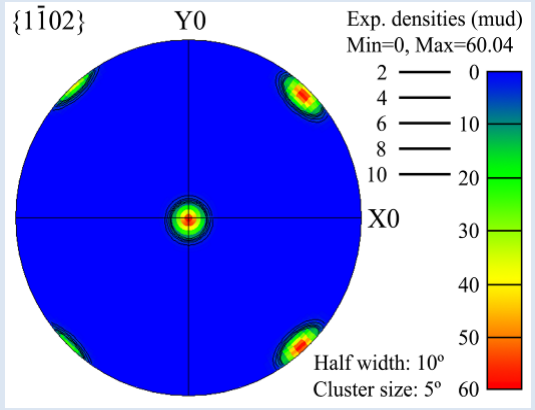












500 °C TiO_2扁平粒子外延生长

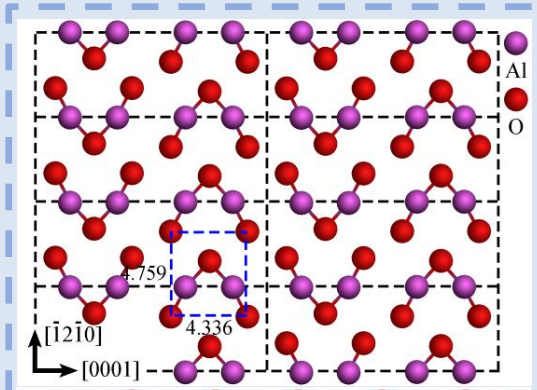
取向关系$(001)[100]_{rutile}//(10\bar{1}0)[0001]_{sapphire}$

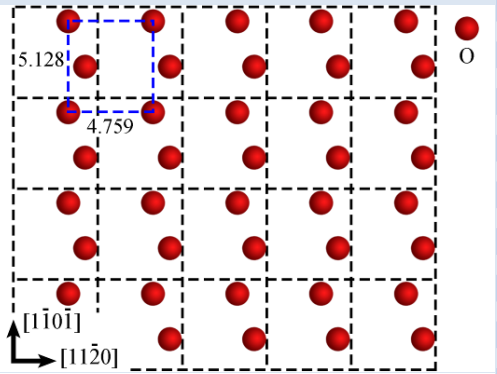
500 °C 扁平粒子外延生长

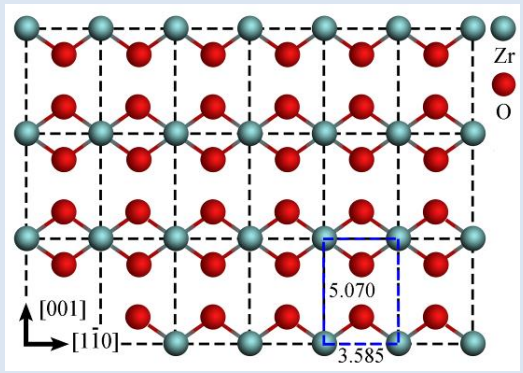
取向关系:$(011)[100]rutile//(1\bar{1}02)[11\bar{2}0]sapphire$

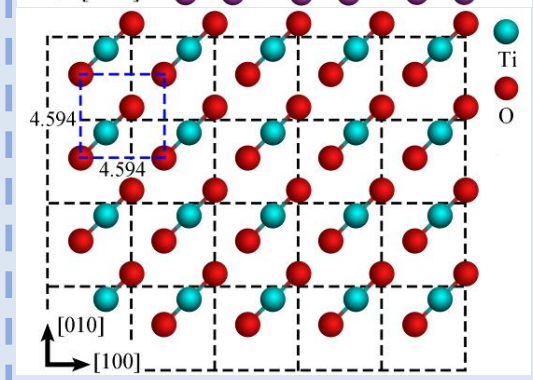
4 思路设计

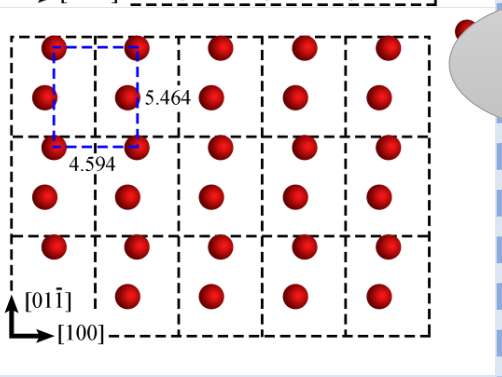
晶格匹配性对TiO_2扁平粒子异质外延生长影响



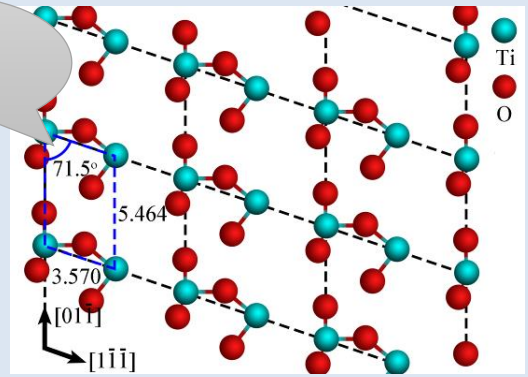








夹角不同



α-Al_2O_3 (10$\bar{1}$0)
错配度：X 5.95%

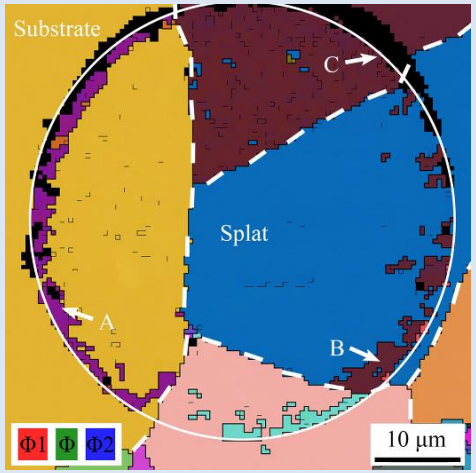
α-Al_2O_3 (1$\bar{1}$02)
错配度：X -3.47%

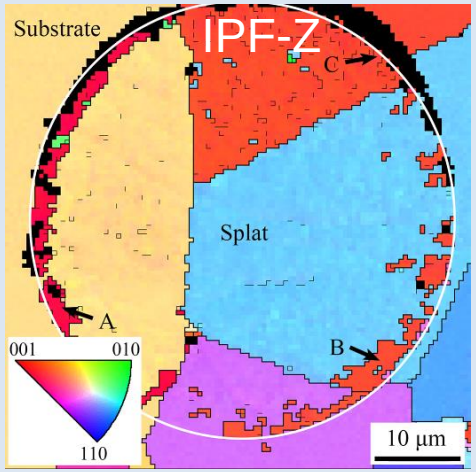
ZrO_2 (110)
<011>$_r$/<001>: 7.77%
0.42%

能否发生异质外延生长还取决于基体晶面与TiO_2晶体某一晶面二维点阵结构的匹配性

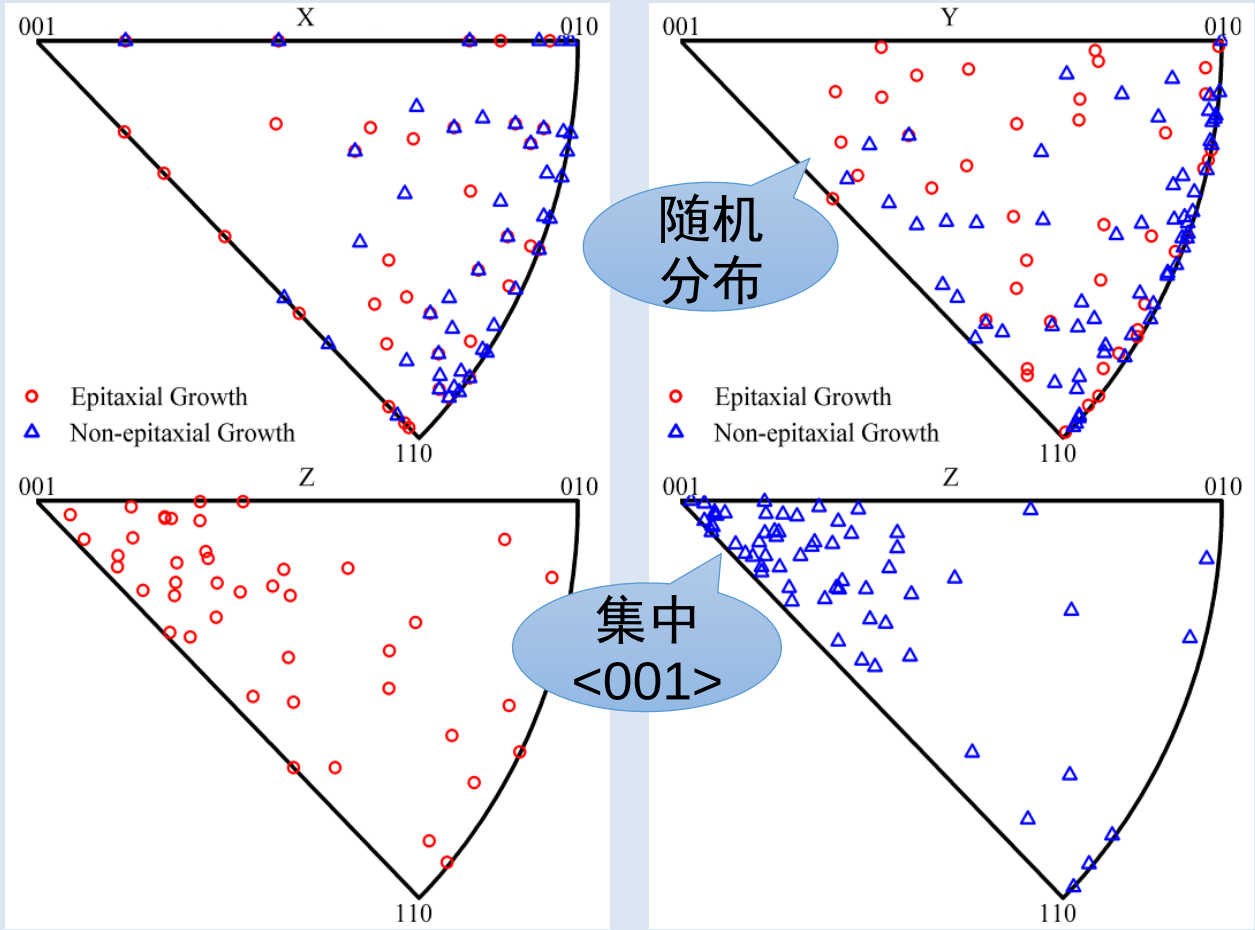
4 思路设计

晶体取向对TiO_2扁平粒子外延生长行为的影响





取向影响外延生长

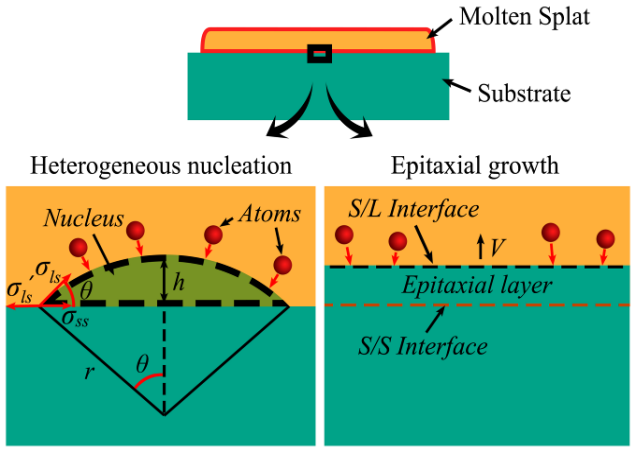


- 沿<001>生长的外延晶粒容易生成
- 非外延晶粒呈现<001>择优生长

4 思路设计

TiO_2扁平粒子外延生长行为数值分析

TiO_2扁平粒子快速凝固过程中存在异质形核和外延生长两种竞争方式



晶核数目：$N=\int_{t_m}^{t} I(t)\,dt$

外延厚度：$h_e=\int_{t_m}^{t} V_{hkl}(t)\,dt$

球冠高度：

$$h_c=\frac{2\sigma_{ls}T_m}{\rho_l\Delta H_m\Delta T}(1-\cos\theta)$$

非稳态瞬态形核

$$I=I_s\exp(-\frac{\tau}{t})$$

孕育时间

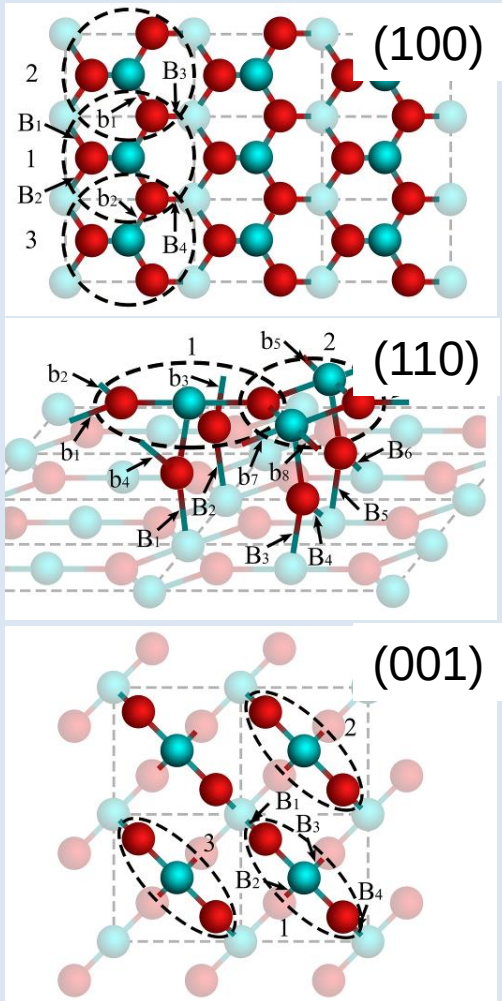
$$\tau=\frac{7.2Rf(\theta)}{1-\cos\theta}\cdot\frac{\lambda^4}{d_a^2}\cdot\frac{T_r}{D\Delta S_m\Delta T_r^2}$$

晶体生长速度

$$V=\frac{D}{a_0}[1-\exp(\frac{\Delta H_m\cdot\Delta T}{RT\cdot T_m})]$$

不同晶面生长速度：

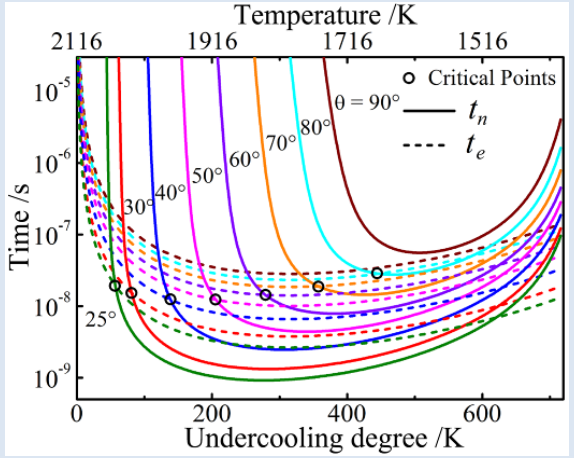
$$\beta_{hkl}=\frac{\Delta E_{hkl}}{(1+n_{hkl})}\qquad V_{hkl}=\frac{\beta_{hkl}}{\overline{\beta}}V$$



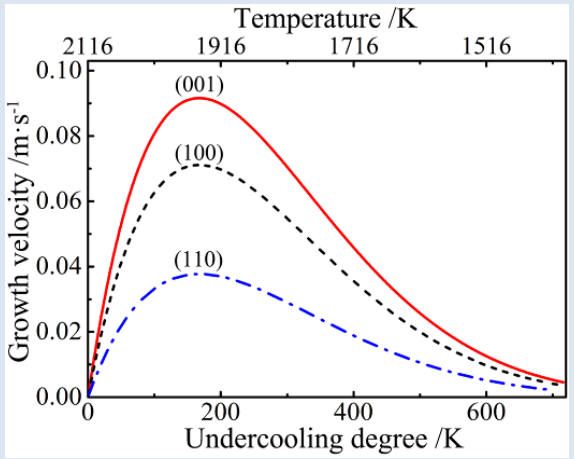
不同晶面晶体生长

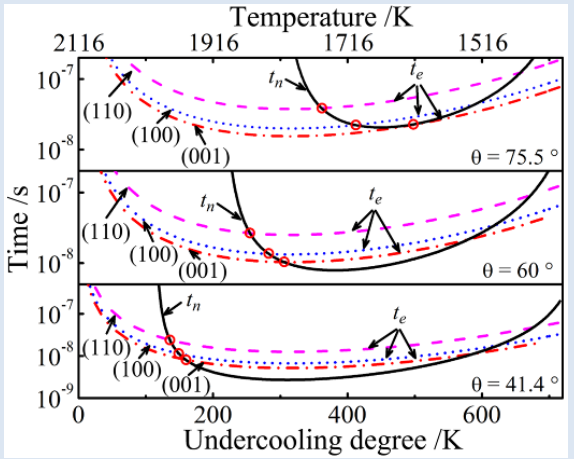
4 思路设计

沉积温度对扁平粒子外延生长的影响机制



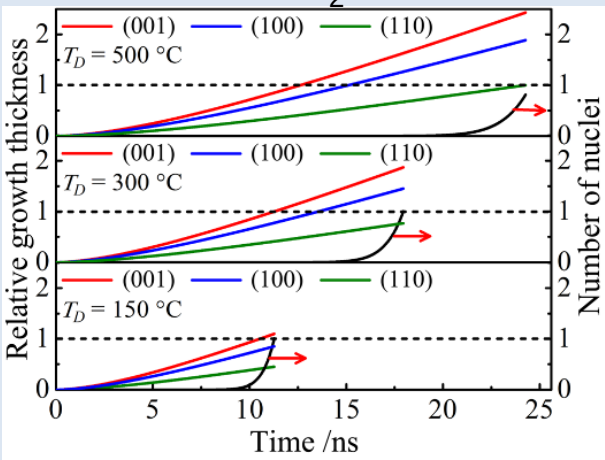
- 过冷度小于临界值发生外延生长
- 接触角减小临界过冷度降低，促进异质形核



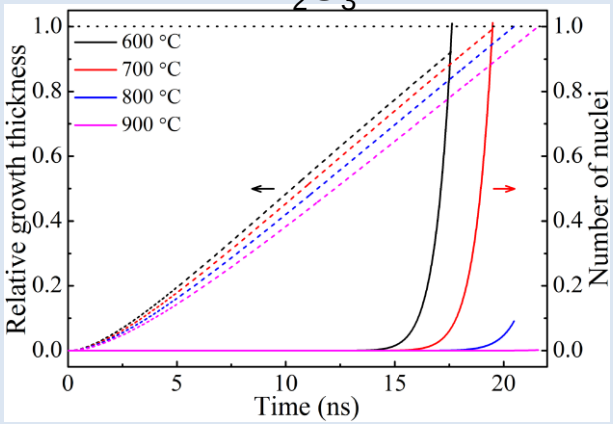


(001)晶面生长速度最高促进扁平粒子外延生长

TiO_2



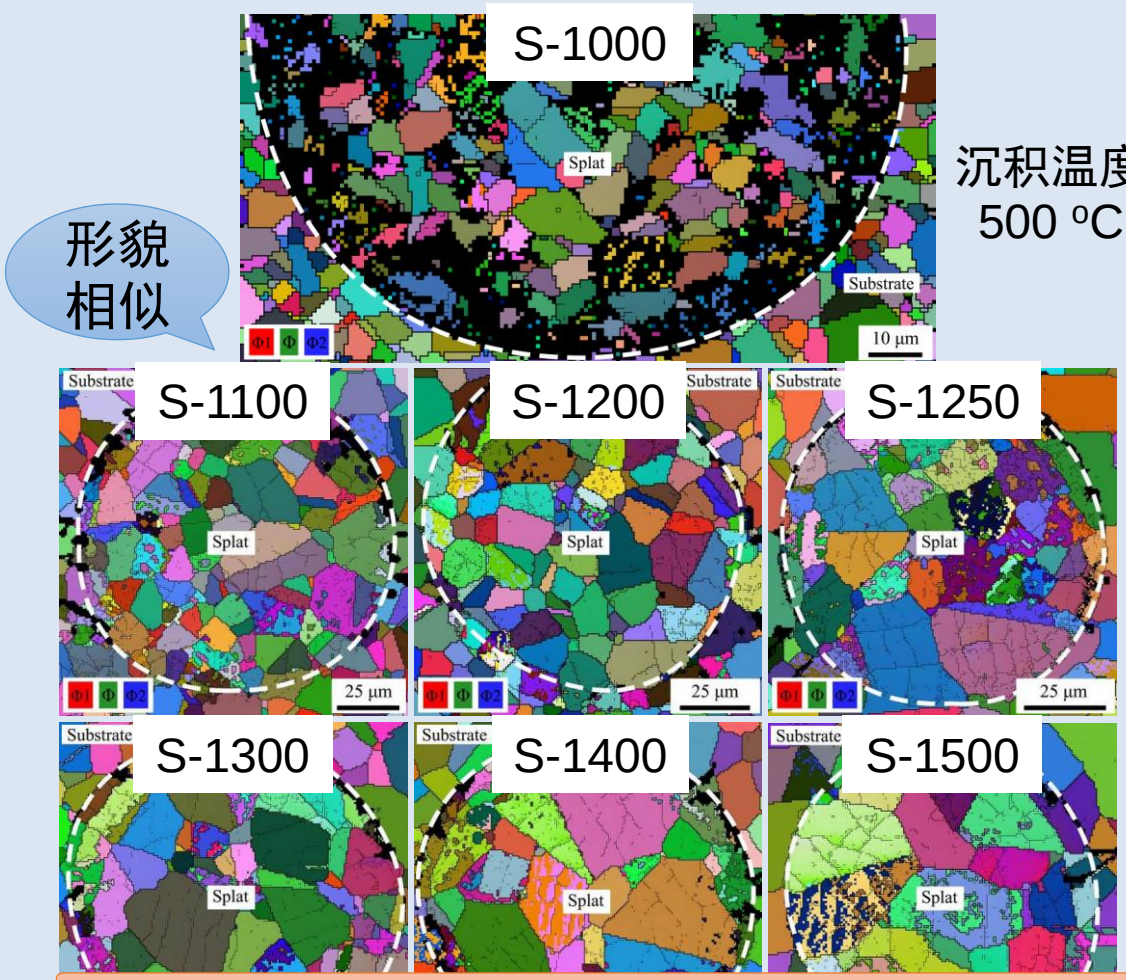
Al_2O_3

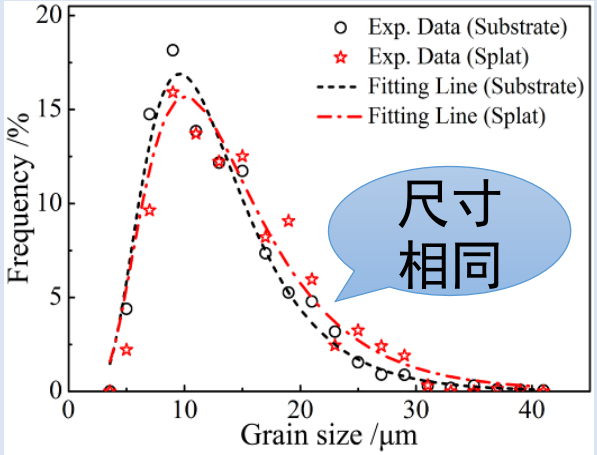


T_D↑异质形核→外延生长

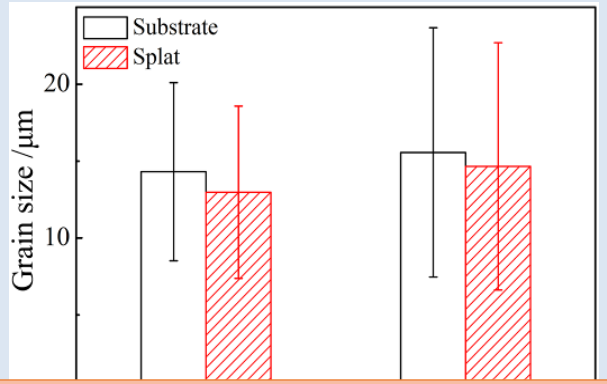
4 思路设计

TiO_2烧结基体上沉积TiO_2扁平粒子组织结构



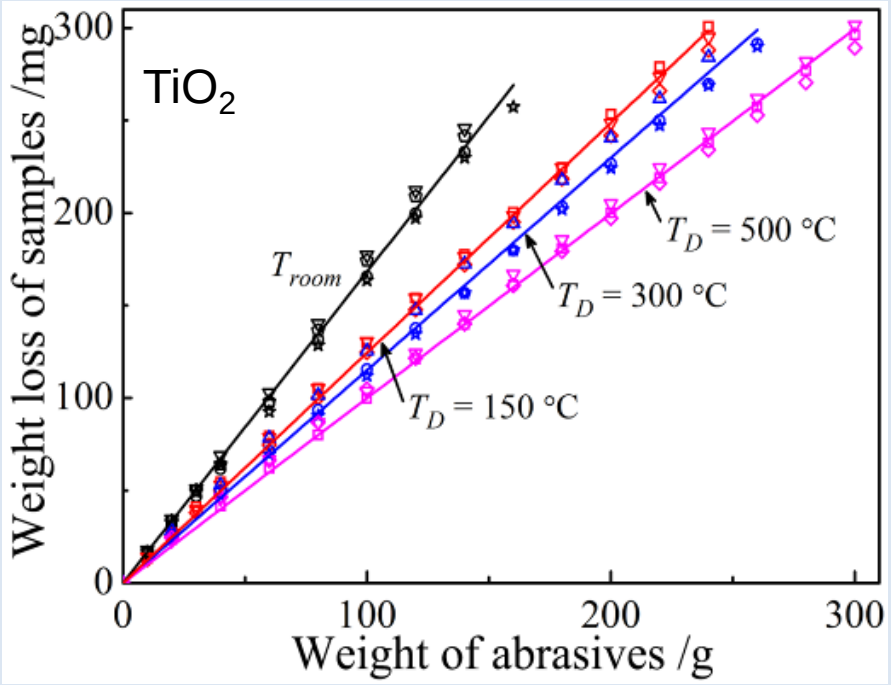


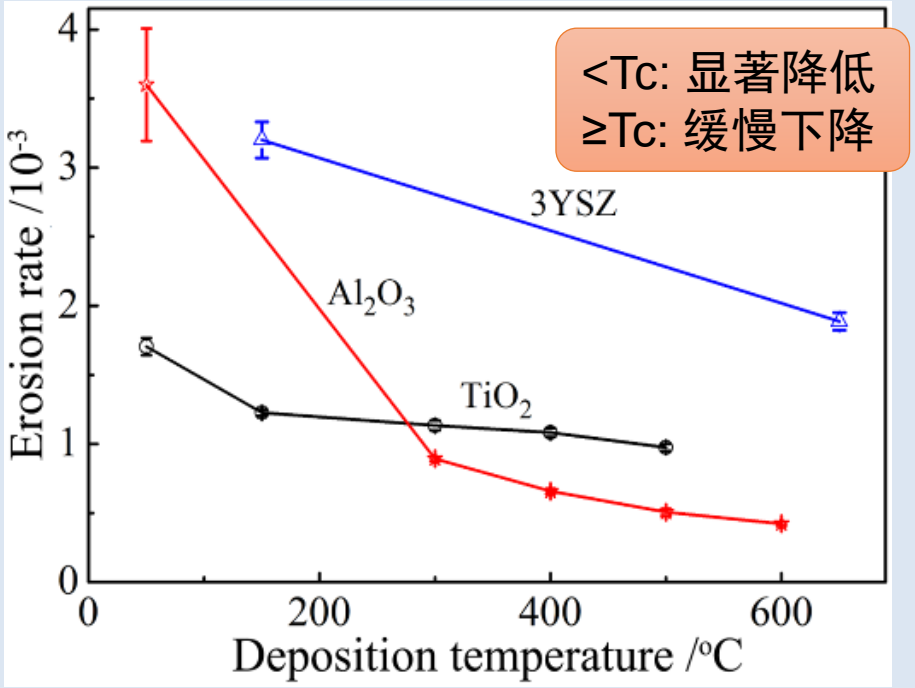
S-1100沉积粒子晶粒尺寸分布



基于外延生长特性，调节基体组织可实现TiO_2粒子组织调控

陶瓷涂层抗冲蚀性能


TiO2
Weight loss of samples /mg
Weight of abrasives /g
T_room
T_D = 500 °C
T_D = 300 °C
T_D = 150 °C
0
100
200
300


<Tc: 显著降低
≥Tc: 缓慢下降
Erosion rate /10-3
Deposition temperature /°C
3YSZ
Al2O3
TiO2
0
1
2
3
4
200
400
600

祝大家：
科研顺利，硕果累累