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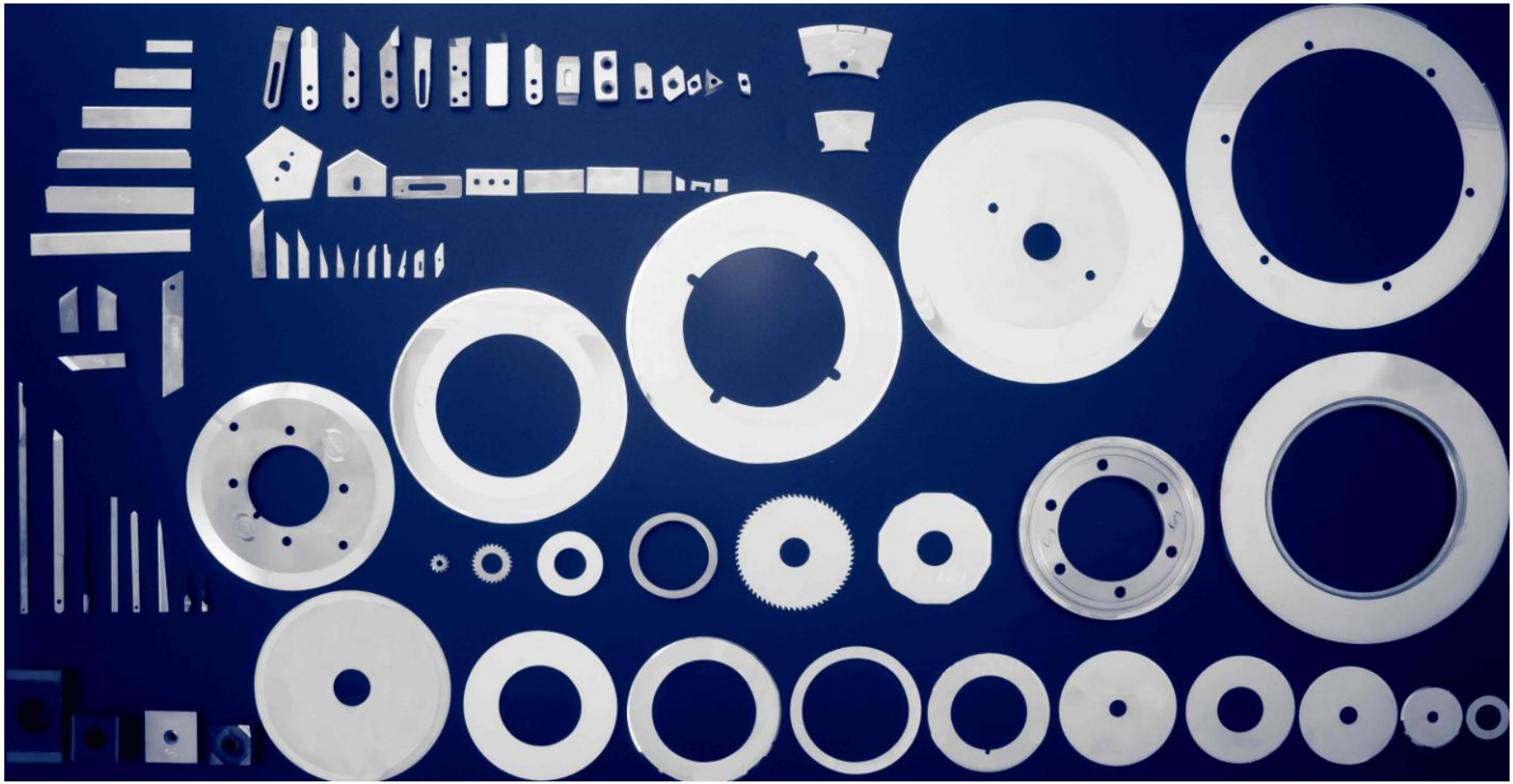
What is 硬質合金?
什么是硬质合金

CEMENTED CARBIDES?... 硬质合金？



我们了解它们吗？

...What do we know about them?

Agenda:
内容提要

What is a cemented carbide?
什么是硬质合金？

Why do we use cemented carbide in PM?
为什么我要使用粉末冶金里的硬质合金

What advancements have been made for PM tooling applications in:
粉末冶金制成的工具在以下这些领域里有哪些发展提升？

-carbide processing and manufacturing?
硬质合金的生产和加工

-carbide failure analysis
硬质合金缺陷分析

What is Cemented Carbide?

什么是硬质合金？

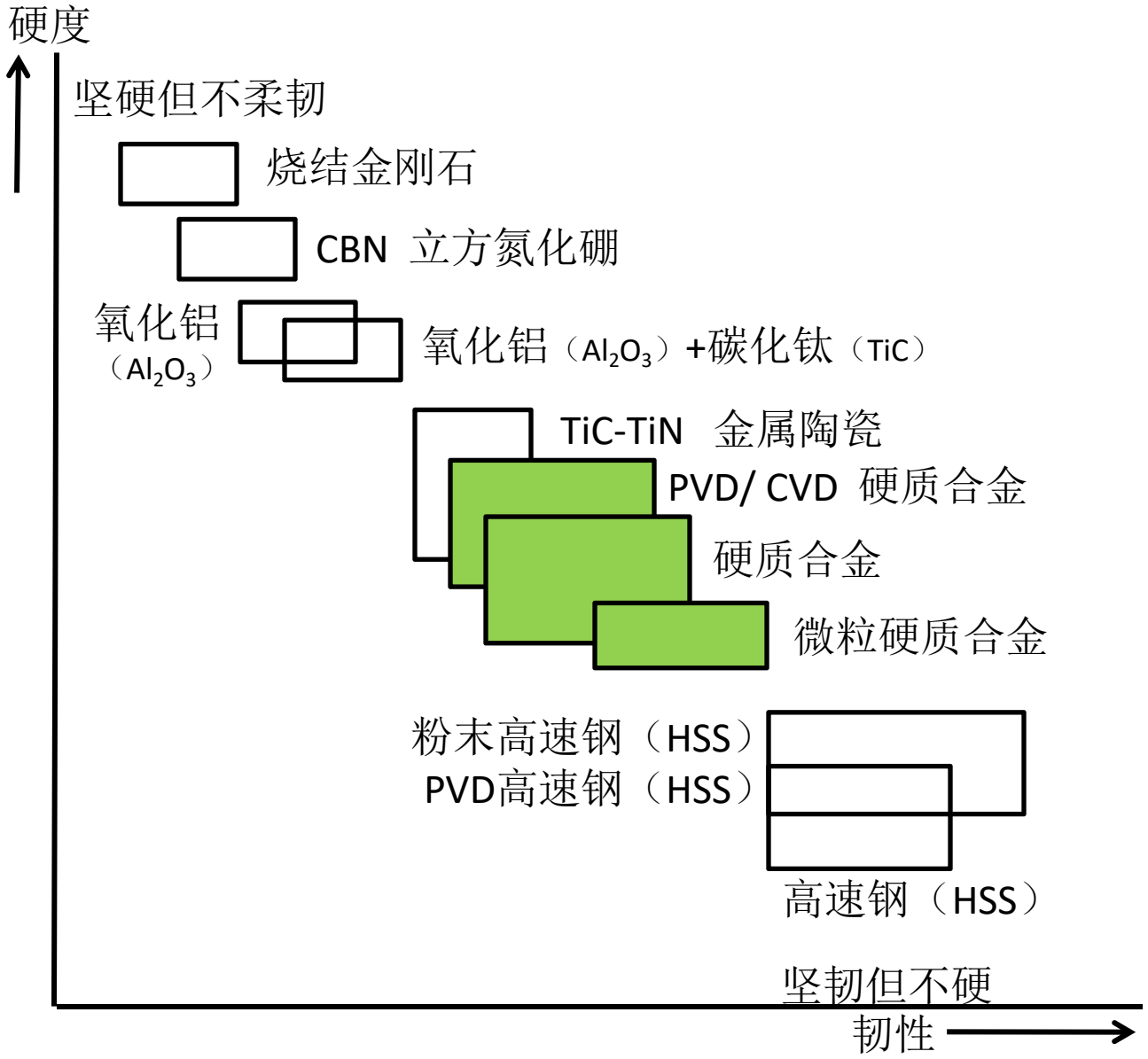
Definition:

定义：

Cemented Carbide is a composite material of a soft binder metal usually either Cobalt (Co) or Nickel (Ni) or Iron (Fe) or a mixture thereof and hard carbides like WC (Tungsten Carbide), Mo2C (Molybdenum Carbide), **TaC (Tantalum Carbide), Cr3C2 (Chromium Carbide), VC (Vanadium** Carbide), **TiC (Titanium Carbide), etc. or their** mixes.

硬质合金是一种复合材料，通常由相对较软的**粘结材料**（例如钴，镍，铁或以上几种的材料的混合物）加上**硬质材料**（例如碳化钨，碳化钼，碳化钽，碳化铬，碳化钒，碳化钛或它们的混合物等）制成。

各类材料的硬度与韧性关系图



硬質合金　国際ISO規格: ISO-4499-2-2016〔最新版〕

ISO:4499-2:2016	microns 微米
Nano 纳米粒	<0.2
Ultrafine 超微粒	0.2-0.5
Submicron 微粒	0.5-0.8
Fine 細粒	0.8-1.3
Medium 中粒	1.3-2.5
Coarse 粗粒	2.5-6.0
Extracoarse 超粗粒	>6.0
Cermet 金瓷	

=結晶径

等級	被切削材料	化学組成	#	钴(Co)重量%	強靭性	耐摩耗性
P級	Steel 钢	碳化钨(WC)＋钴(Co) ＋碳化钛(TiC)＋碳化钽(TaC)	P01			増
			P10	6wt%		
			P20			
			P30			
			P40		↓	
			P50	↓	増	
M級	Stainless Steel 不锈钢	碳化钨(WC)＋钴(Co) ＋碳化钛(TiC)	M10	6wt%		増
			M20			
			M30		↓	
			M40	↓	増	
K級	Cast Iron 铸铁	碳化钨(WC)＋钴(Co)	K01			増
			K10	6wt%		
			K20		↓	
			K30	↓	増	

Carbides: Selected Mechanical Properties

Carbide Formula	Vickers (HV) Hardness @ Various Temperatures, °C (°F)		Rockwell Hardness @ Room Temperature, HRa	Ultimate Compressive Strength, MPa (ksi)	Transverse Rupture Strength, MPa (ksi)	Modulus of Elasticity, GPa (10^6 ksi)
	20 °C (78 °F)	730 °C (1350 °F)				
TiC*	2930	640	93	1330-3900 (193-522)	280-400 (40.6-58.0)	370 (52.9)
HfC*	2860	-	84	-	-	-
VC*	2800	250	83	620 (89.9)	70 (10.1)	360 (51.4)
NbC	2400	350	83	1400 (203)	-	270 (38.5)
TaC*	1570	800	82	-	-	470 (68,2)
Cr_3C_2*	-	-	81	100 (14.5)	170-380 ((24.7-55.1)	280 (40.0)
Mo_2C*	-	-	74	2700 (392)	50 (7.3)	375 (53.6)
WC*	2400	280	81	2700-3600 (392-522)	530-560 (76.9-81.2)	665 (95)

*NOTE: TiC-Titanium Carbide; HfC-Hafnium Carbide; VC-Vanadium Carbide; NbC-Niobium Carbide; TaC-Tantalum Carbide; Cr_3C_2 - Chromium Carbide; Mo_2C - Molybdenum Carbide; WC-Tungsten Carbide.

Why Do We Need and Use Cemented Carbide?
为什么我们需要并且使用硬质合金？

… because of its unique combination of superior physical and mechanical properties including:

因为硬质合金其独特的物理和机械性能结合，如下：

-***Wear Resistance: Cemented carbide can outlast high-speed steel grades by a*** factor up to **100 to 1**

*耐磨性：相较于高速钢，硬质合金的耐磨性甚至在某些情况下可以高出**100**倍。*

-***Deflection Resistance: Cemented Carbide has a Modulus of Elasticity three times*** that of steel which translates into one third of deflection when compared to the steel bars of the same geometry and loading

弯曲强度：硬质合金有三倍于钢材的弹性模量，也就是说在同样的荷载下，同样地硬质合金棒的弯曲只有钢材的三分之一

-***Tensile Strength: Tensile Strength is varied from 1,100 to 2,100 MPa***

*拉伸强度：硬质合金范围从**1100到2100 MPa***

-***Compressive Strength: Compressive Strength is over 4,150 MPa***

*抗压强度：硬质合金的抗压强度高于**4150 MPa***

-***High Temperature Wear Resistance: Good wear resistance up to 540℃.***

*高温工况下的耐磨性：硬质合金可以在高达**540°C**的高温下保持高耐磨性*

…thus, Cemented Carbide is often the best material choice for particularly tough applications providing the most cost-effective solution to a challenging problem…

因此，硬质合金通常是复杂工况下的一种很好的材料选择，为具有挑战性的问题提供最具成本效益的解决方案。

Karl Schroter Patents
卡尔施罗德专利

1925

- **Comp压制. – WC + 3 -10 Co, WC (4 –10 %C)**
- **Sinter烧结 - 1500 – 1600oC**
- **Atmosphere烧结气氛 – H_2, N_2, A, CH_4, CO or Mixture**
- **Binder粘接剂 – Co, Ni, Fe**

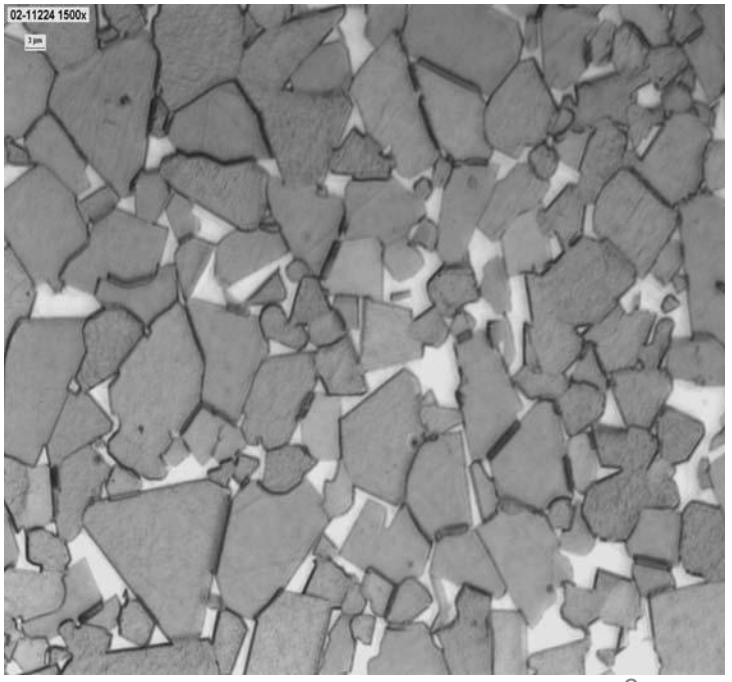
1929

- **Comp压制. 10 -20%**
- **CH_4 Carburized W Powder (Closer to 6.13%C)**
- **Sinter烧结 - < 1400^{o}C with 10 – 20 % Binder**

Just like Almond Chocolate!
合金就像花生馅巧克力一样

1930 – with Hans Wolff – Krupp克虏伯

- **Manufacture of Complex Shapes**
  复杂形状生产
- **Press – presinter – machine – sinter**
  压制-预烧-机加工-烧结
- **With or without binders**
  添加/不添加 粘接剂



Patent Acquisitions专利申请:

- **Krupp (Germany) 1925 – Widia**
  克虏伯（德国）**1925**年-碳化钨硬质合金
- **GE (United States) 1925 – Carboloy**
  美国通用 **1925**年-碳化钨硬质合金
- **Thomson-Houston (UK) 1925 – Ardoloy**
  汤姆森-休斯顿（英国）**1925**年-Ardoloy合金

PROPERTIES OF SOME SELECTED **WC-Co CEMENTED** CARBIDE GRADES

一些钨钴硬质合金的性能

Composition 成分组成 wt.%	Hardness 洛氏硬度 HRa	Abrasion Resistance 抗磨性 1/vol.loss cm^3	Transverse Rupture Strength 抗弯强度 MPa	Ultimate Compression Strength 极限抗压强度 MPa	Ultimate Tensile Strength 极限拉伸强度 MPa	Modulus Of Elasticity 弹性模量 Ton/cm^2	Thermal Expansion @75oC-400oC 热膨胀性 Cal/(s*oC*cm)
WC-6%Co	92.8	35-60	2310	5930	1100	6470	2.9
WC-9%Co	89.5	10-13	2930	4550	-	3120	2.7
WC-13%Co	88.2	4-8	3450	4140	-	5695	3.0
Other Materials (for comparison & consideration) 其他一些材料的相关性能（供参考和对比）							
Tool Steel (T8)工具钢	85 (66HRc)	2	3970	4140	-	2390	6.5
Carbon Steel (AISI1095) 碳钢	79 (66HRc)	1	-	-	2070	2110	-
Cast Iron铸铁	-	2	725	-	-	1055-2110	9.2

Room & Hot Hardness of WC-Co Cemented Carbide vs. High Speed Tool Steel
钨钴硬质合金和高速钢在室温&高温下的硬度对比

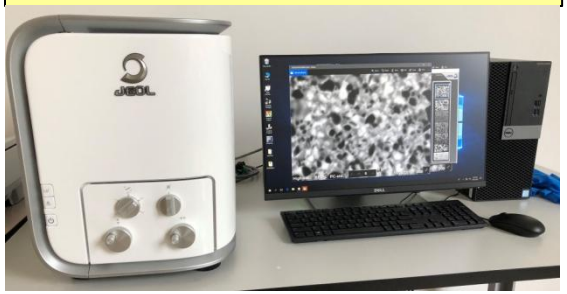
Properties 性能 / Materials 材料	Hardness (HRc) @Various Working Temperatures 在不同工作温度下的洛氏硬度 HRc		
	@20°C (78°F)	@760°C (1400°F)	@1093°C (2000°F)
Cemented Carbide 硬质合金 [WC+6%Co]	77-79	27-29	21-23
High Speed Steel AISI T4 Grade 高速钢 AISI T4牌号 [0.8%C+18%W+4%Cr+1%V+5%Co]	63-65	17-19	N/A 无

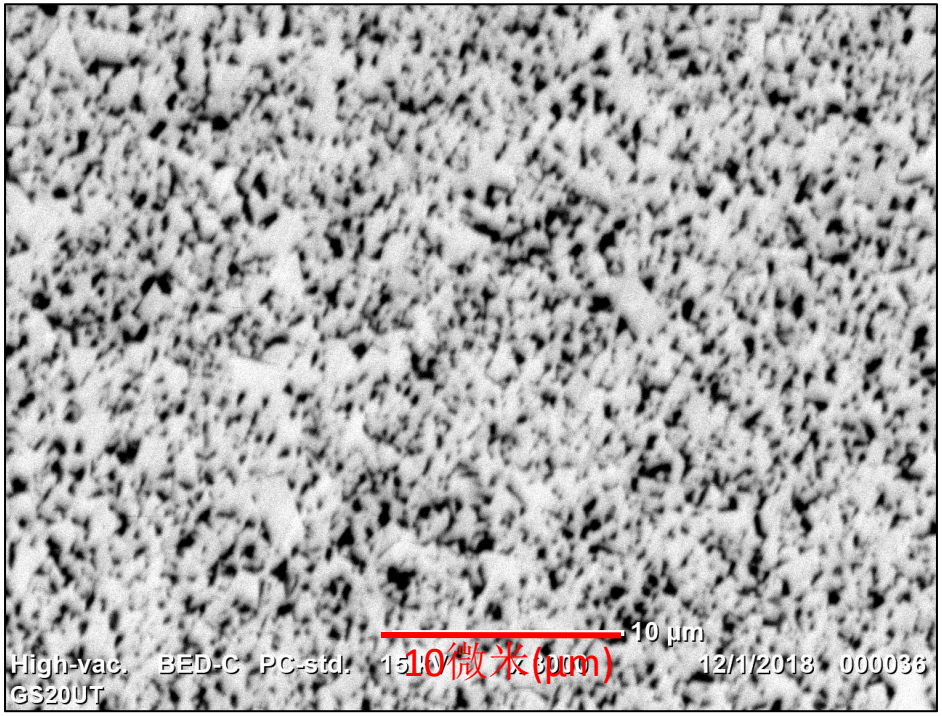
台式扫描电子显微镜 3000倍

白色：碳化钨（WC）

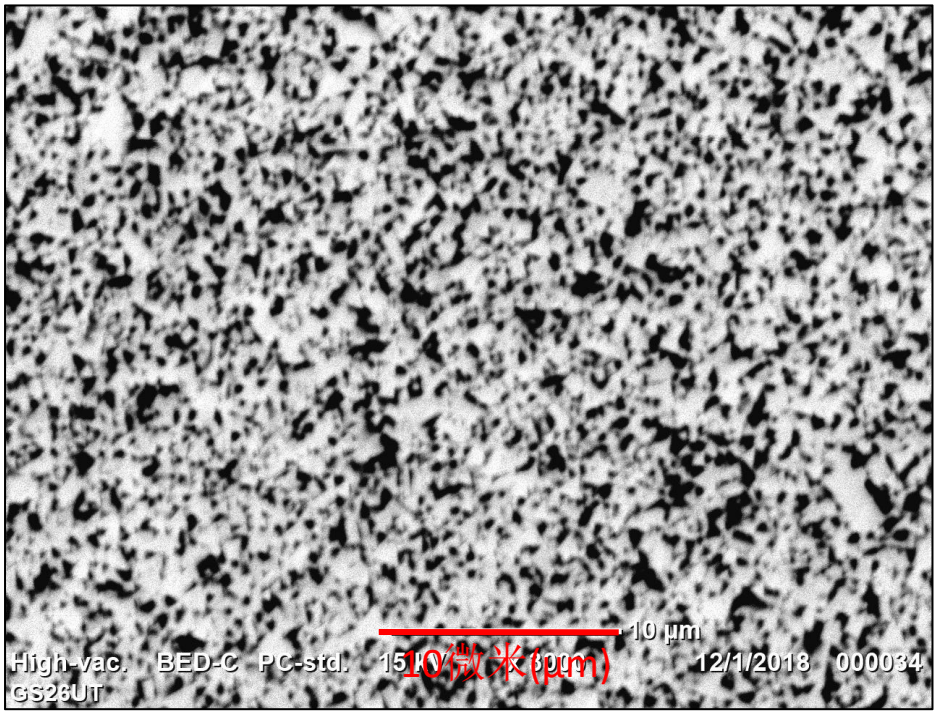
黑色：钴（Co)

Scanning Electron Microscope
扫描电子显微镜





GS20U (Co=10%)



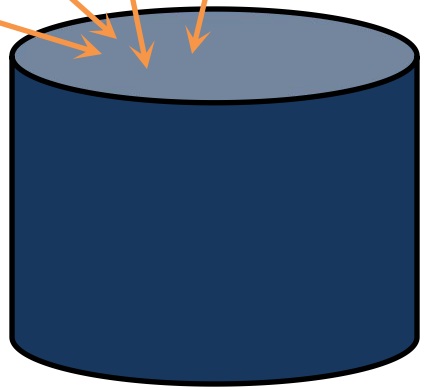
GS26U (Co=13%)

Manufacturing Process of Cemented Carbides
硬质合金的生产工序

① Raw Virgin Materials
(WC, Co, VC, Cr_3C_2, etc.)
原生原料（碳化钨粉，钴粉，碳化钒粉，碳化铬粉等）

80-95 重量%

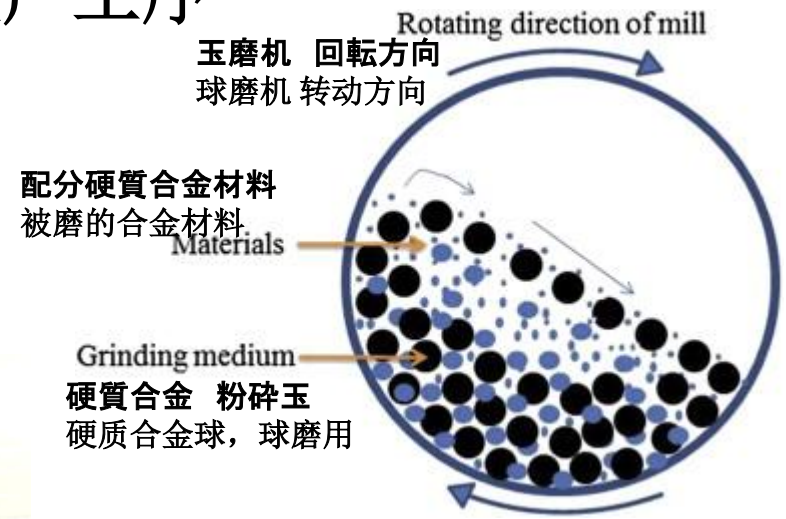
5-20 重量%



② Weigh Each Raw Virgin Materials According to Recipe Sheet
按照配方表称重每种原料

Manufacturing Process of Cemented Carbides
硬质合金的生产工序

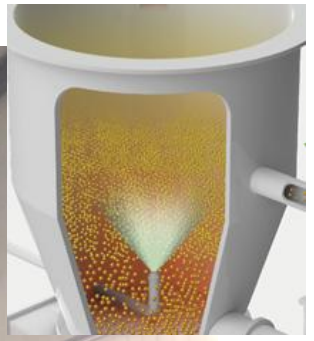
③ Ball-Mill All Raw Virgin Materials
40-70 Hours
Add Paraffin Wax
球磨各种原料40-70个小时，其中加石蜡



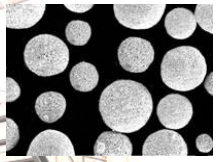
Ball-Milling Machines
球磨机

Manufacturing Process of Cemented Carbides
硬质合金生产工序

④ Agglomeration
Spray Dryer or Heat Batch
团聚造粒
喷雾或者手掺料



Agglomeration
造粒



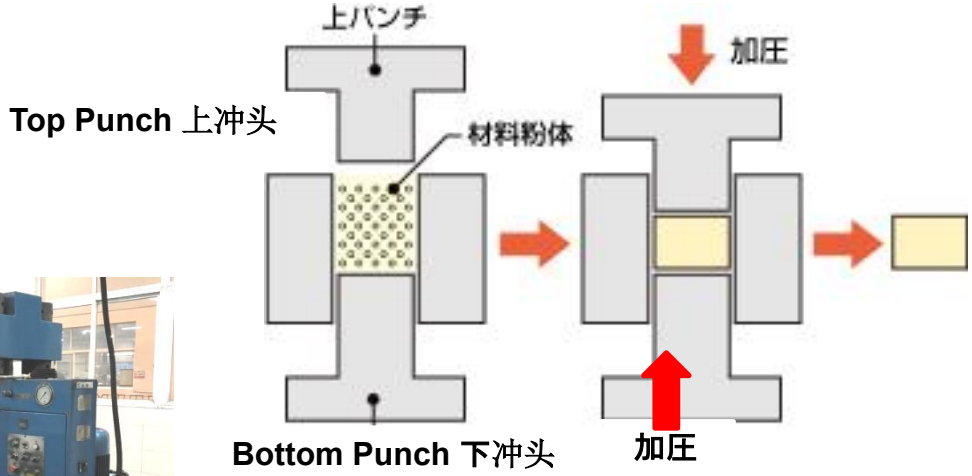
Conventional Heat Batch Dry Machine 传统手掺料烘干机

Spray Drying Machine喷雾塔

⑤ Grade Powder
(RTP, Ready to Press Powder)
混合料（待压制牌号料）

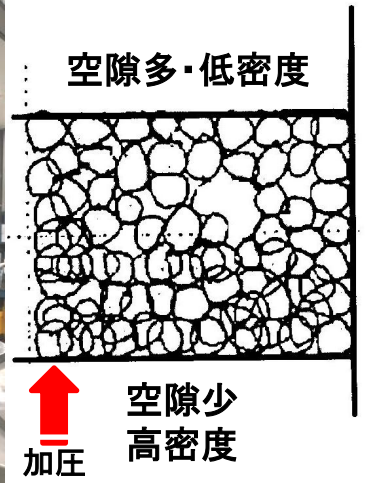
Manufacturing Process of Cemented Carbides
硬质合金生产工序

⑥ Forming成型



Mechanical Press Machine
自动机械压机

Hydraulic Press Machine
液压机

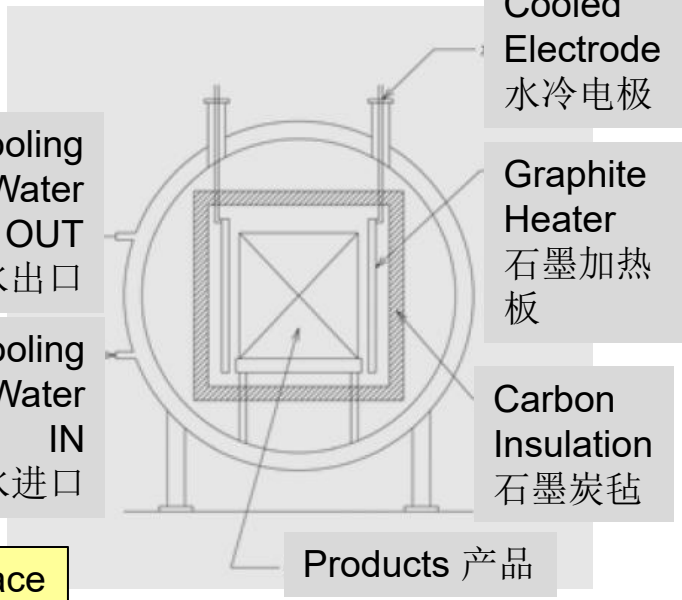


Cold Isostatic Press Machine冷等静压机

Manufacturing Process of Cemented Carbides
硬质合金生产工序

⑦ Sintering (+Dewaxing)
烧结（包含脱蜡）

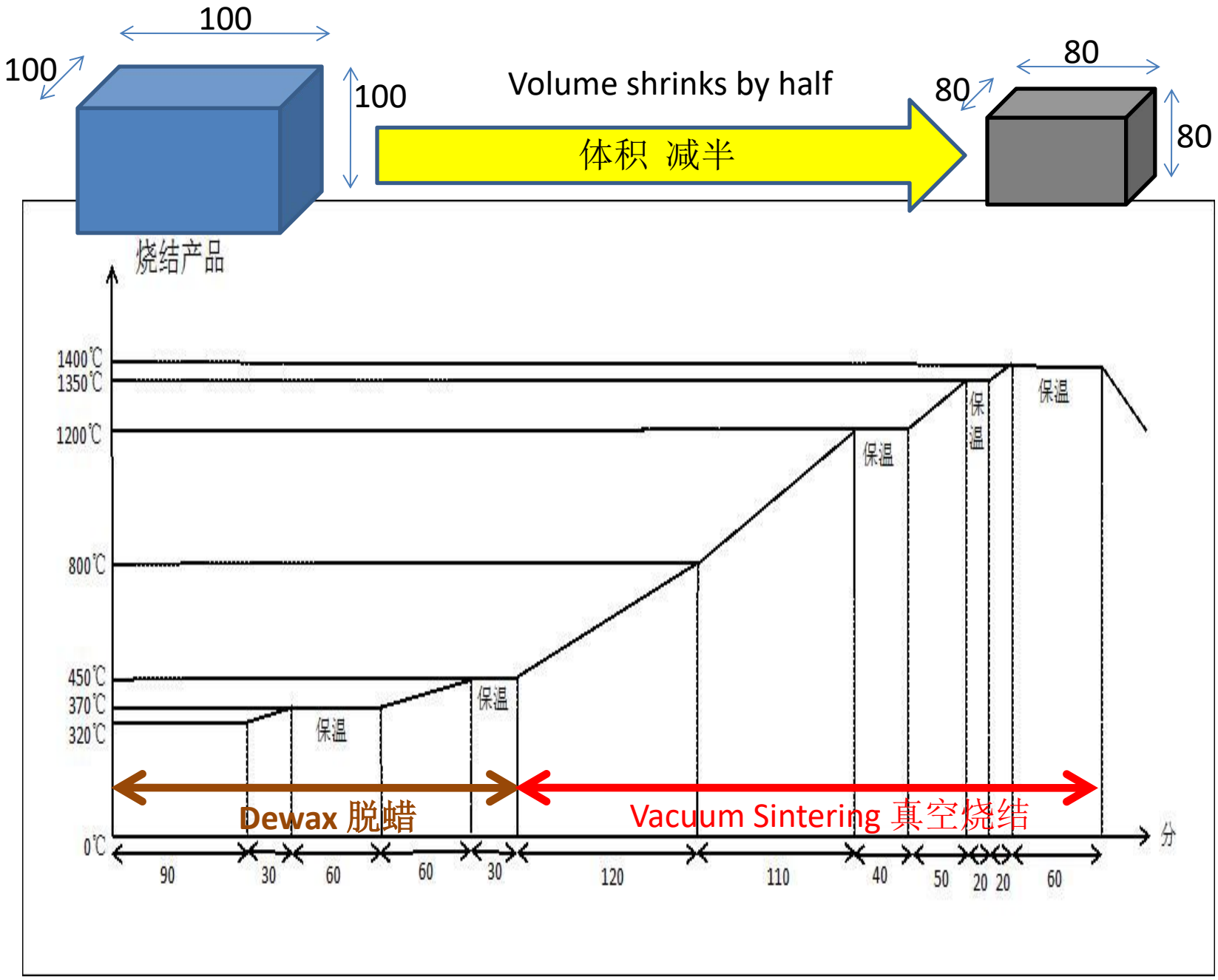
Vacuum Sintering Furnace
真空烧结炉



Sinter-HIP Advantage:
Sinter-HIP processing combines both Sintering and HIP into ONE single processing operation at the last consolidation stage while the whole operation is performed in one furnace.

加压烧结炉优势：
在烧结最后的固相扩散阶段，
将加压和加热合并到一起在炉内进行

Sinter-HIP Furnace
加压烧结炉

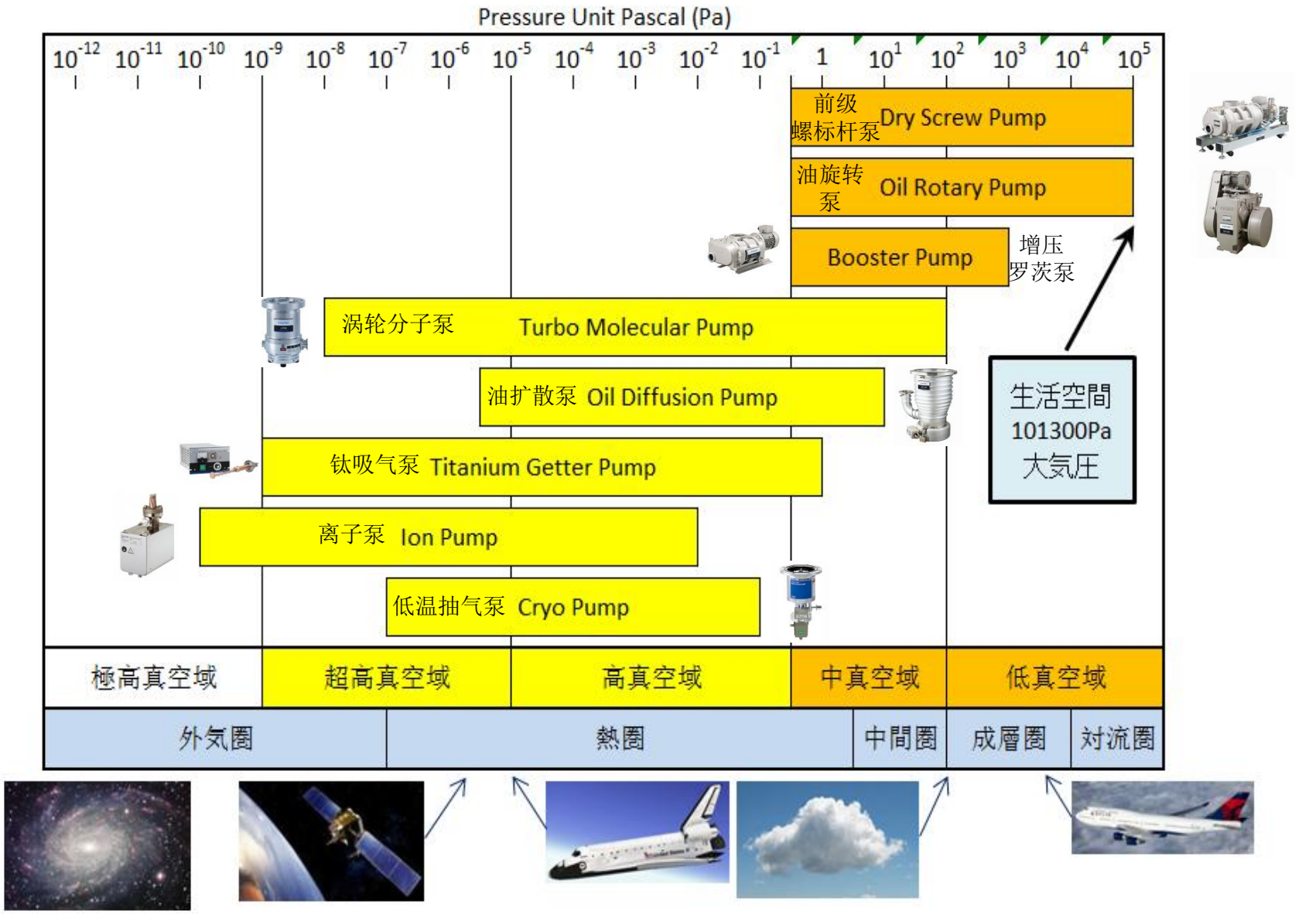

100
100
100
Volume shrinks by half
体积 减半
80
80
80
烧结产品
1400℃
1350℃
1200℃
800℃
450℃
370℃
320℃
0℃
保温
保温
保温
保温
保温
保温
Dewax 脱蜡
Vacuum Sintering 真空烧结
分
90
30
60
60
30
120
110
40
50
20
20
60

What is Vacuum? 什么是真空？

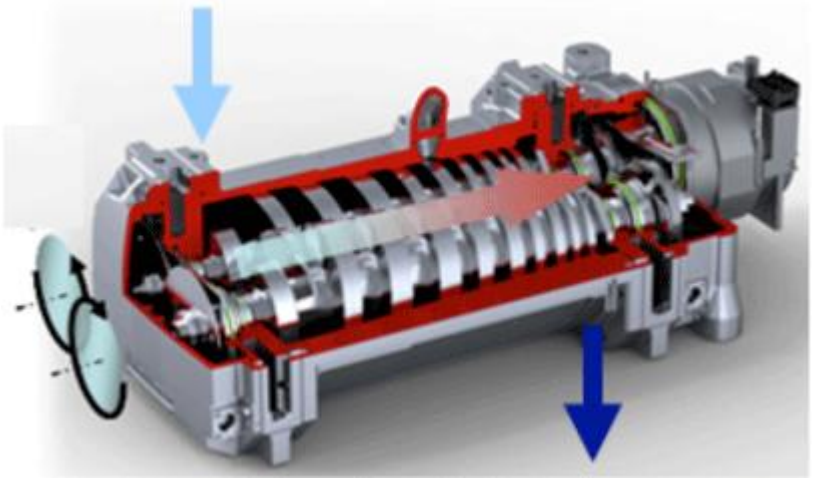
An approximation to such vacuum is a region with a gaseous pressure much less than atmospheric pressure.
Physicists often discuss ideal test results that would occur in a *perfect* vacuum, which they sometimes simply call "vacuum" or free space,
and use the term partial vacuum to refer to an actual imperfect vacuum as one might have in a laboratory or in space.
In engineering and applied physics on the other hand,
vacuum refers to any space in which
the pressure is lower than atmospheric pressure.

近似于这样的真空，是一种比大气压小很多的，有气体压力的区域。
物理学家们经常讨论在绝对真空状态下出现的理想测试结果，
他们有时简单地把这种“绝对真空”称之为“真空”或“自由空间”；
然后用“部分真空”来表示实际情况下在实验室或太空中的不完全真空。
另一方面，在工程技术和应用物理中，
我们所指的**真空**是**任何气压比大气压低的空间。**

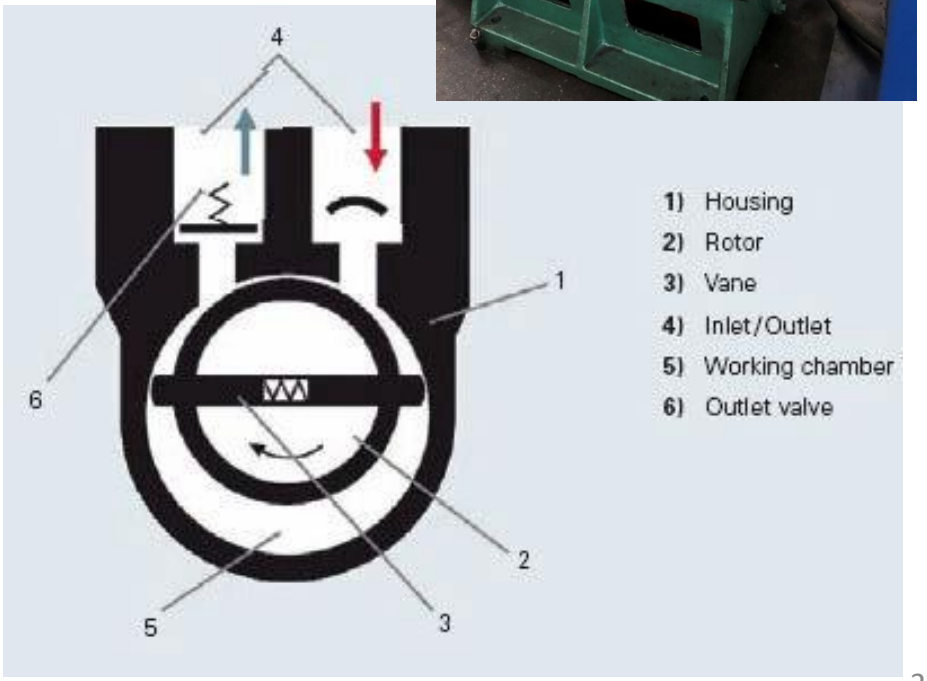
What is Vacuum? 什么是真空？



Dry Screw Pump



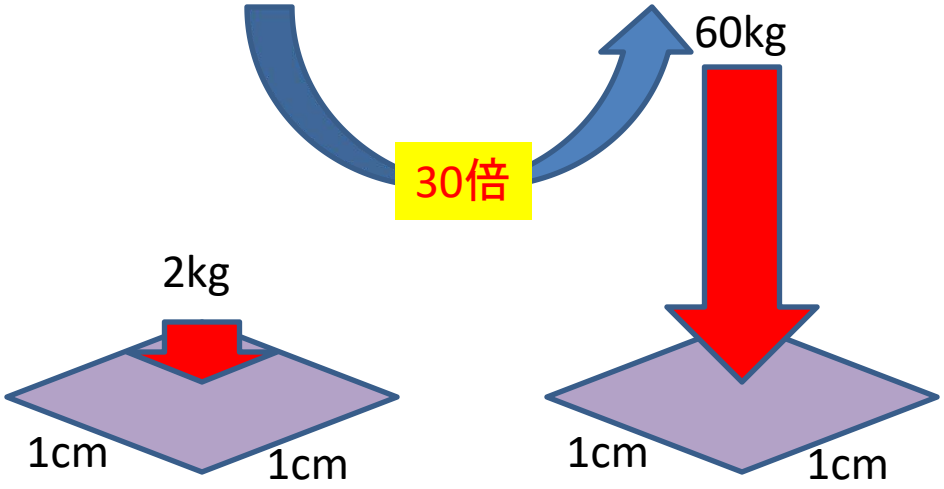
Oil Rotary Pump



How big is 6.0 Mega Pascal?

洗手: 0.2 MPa

加压(6.0MPa)烧结炉



600 m

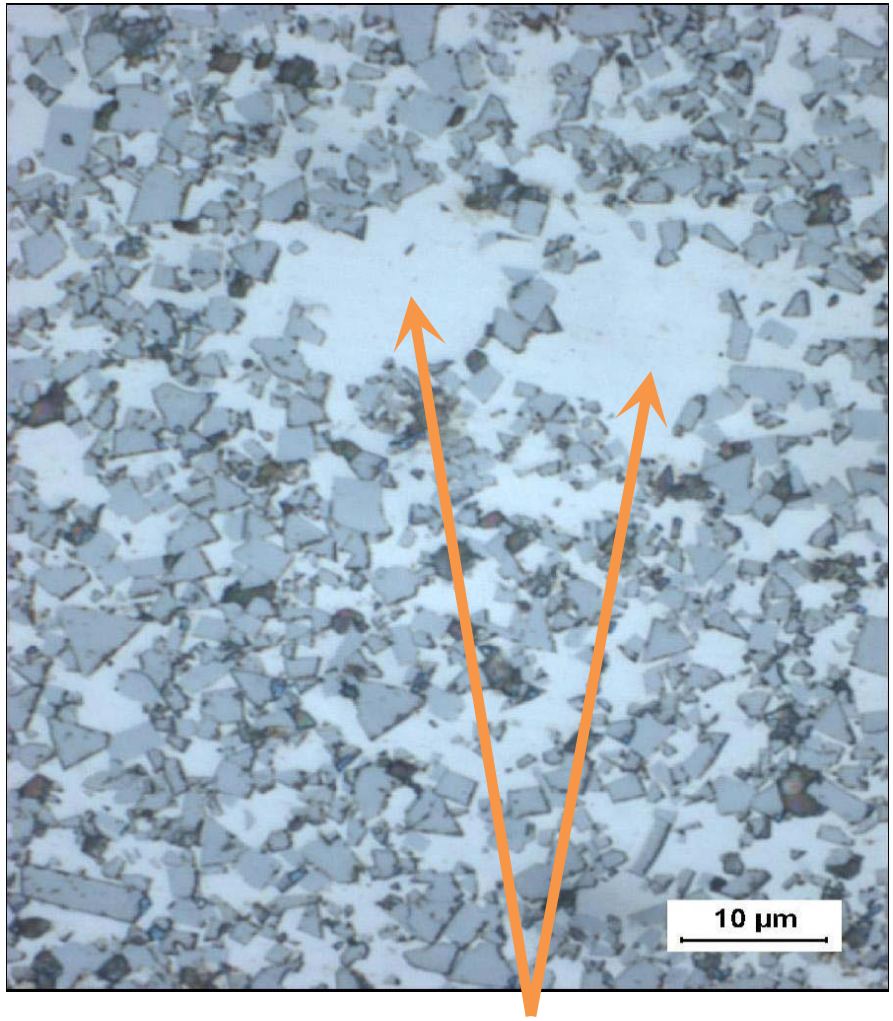
6.0MPa
水压

“Cobalt-Lake” defects that can be found in the process of routine Vacuum Sintering:

在真空烧结时会出现的钴池缺陷

During routine sintering of WC-Co cemented carbides, Cobalt (Co) or Co-based liquid eutectic substances frequently generate a defect of the structure known as a “Cobalt Pool” or “Cobalt Lake”. It is a condition where Co is squeezed into a macrovoid that might occur within the material at the liquid stage of the sintering operation.

在碳化钨-钴硬质合金烧结过程中，钴或者钴的液态共晶体经常会导致一种叫钴池的缺陷。这种缺陷是在烧结进入到液相变化时，钴被挤压进入到一个微孔（微空间）导致的。



“Cobalt Lake” defects钴池缺陷

"Cobalt Lake" Defects and Techniques to Eliminate Them:
钴池缺陷及其解决方案

- **Once a "Co-Lake" defect occurs, it is very difficult to get any amount of WC particles into the affected areas.**
  一旦钴池缺陷出现，碳化钨颗粒变很难再进入到受钴池影响的区域。

- **Sinter-HIP techniques have been developed and applied to achieve better homogeneity of the cemented carbide structure, thereby improving mechanical properties.**
  加压烧结技术已经发展出，并被应用到烧结出更均匀组织的硬质合金技术中来。
  以此来改善合金的机械性能。

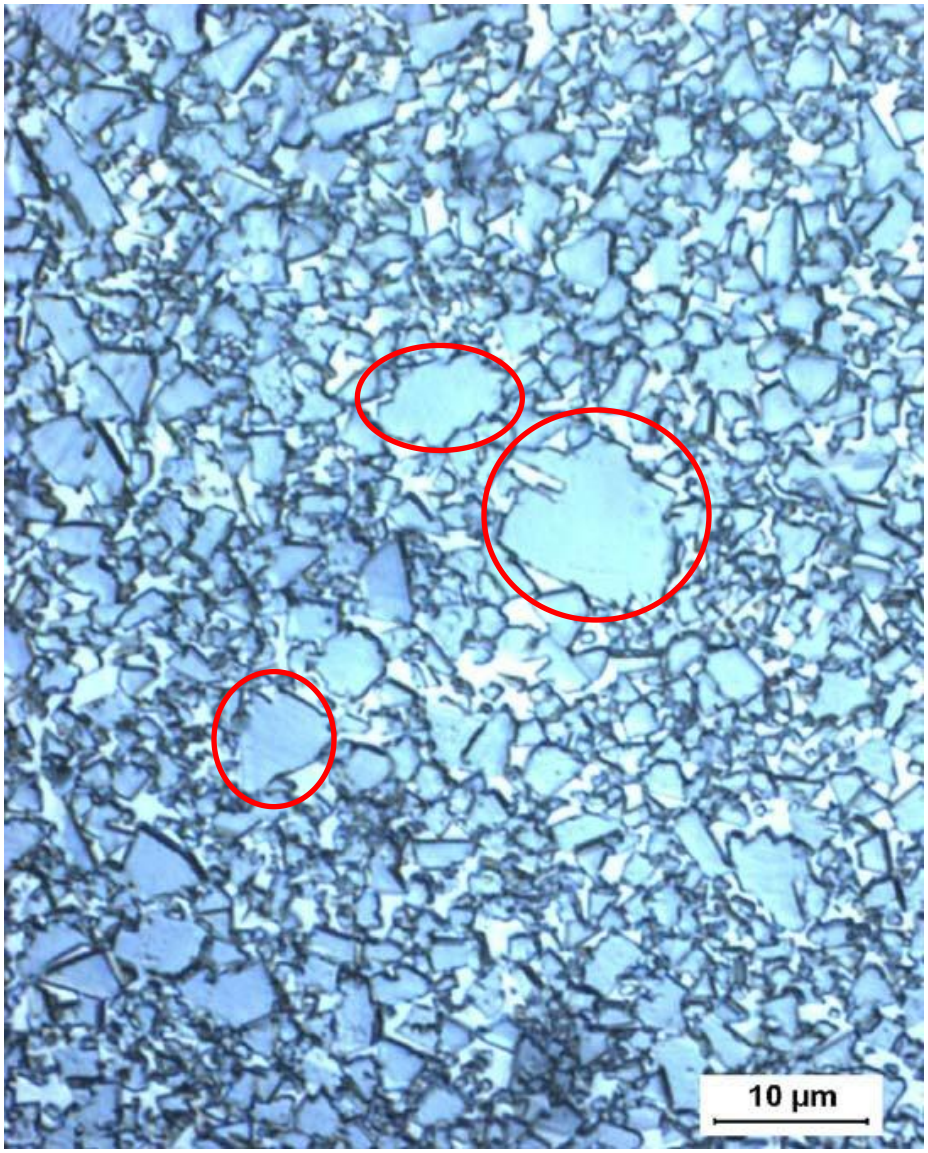
- **Both processes are performed in special pressure-tight vessels through the simultaneous application of heat and pressure for a pre-determined time.**
  在一段预先设定好的时间段里，
  加压和加热两种工序在特殊制造的耐压密闭烧结空间同时进行。

Potential for Defects from Sintering

烧结阶段可能产生的其他缺陷

Due to the fact, that Sintering process is performed *at the solid phase diffusion temperature, there* is a risk of *intensive grain growth Of* ***WC- particles within the sintered*** body that could affect the mechanical properties of the final product.

事实上，在烧结工序的固相扩散温度时，有一种碳化钨颗粒会在烧结体内异常长大的风险，这种风险会影响最终成品的机械性能。



Diversified QC &Test Equipment (Powder Characteristics)
各种各样的质量控制及检测设备（粉末特性）

Powder Distribution Device 粉末粒度分布仪

Water Contents Tester 水分仪

Slurry Viscosity Tester 粘度检测

Powder Flow Tester 粉末流动性检测

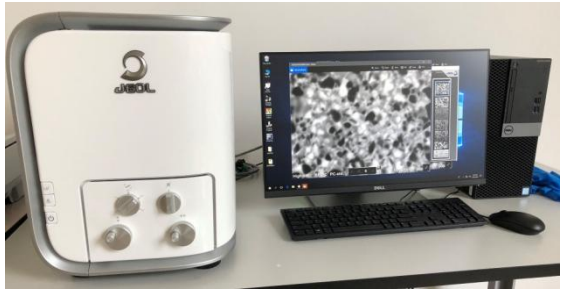
Bulk Density Tester 松装密度检测

Diversified QC &Test Equipment (Sintered Physical Characteristics)
各种各样的质量控制及检测设备（烧结毛坯物理特性）

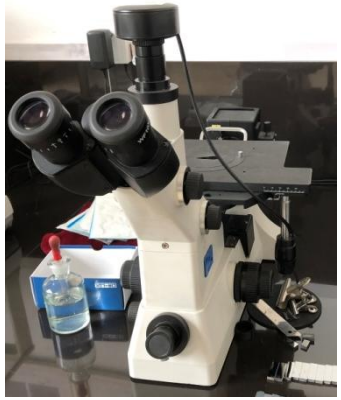
Magnetic Saturation Device
磁饱和检测仪器

Coercive Force Device
矫顽磁力检测

Scanning Electron Microscope
扫描电子显微镜



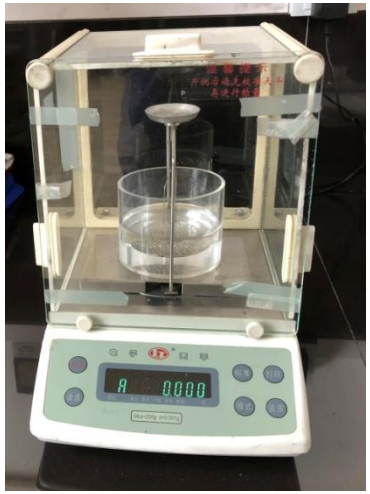
Metallurgical Microscope 金相显微镜



Rockwell Hardness Tester 洛氏硬度

Vickers Hardness Tester维氏硬度检测

Density Tester 密度仪



Transverse Rupture Strength Tester 抗弯强度检测

Typical Defects and Failures of Cemented Carbide Products / Applications
硬质合金产品/生产中典型的缺陷/事故

By its origin, most frequently encountered defects/failures of cemented carbide products can be divided into 4 main groups:

*追根溯源，大部分常见的硬质合金产品/生产的缺陷/事故可以分为 **4**大类：*

- **Processing defects (Eta-Phase occurrence, large grain cluster formations, powder shaping cracks);**

成型缺陷（**ETA**相出现，大颗粒群形成，粉末压制裂纹）

- **Fabrication defects (braze cracks, thermal cracks);**

加工缺陷（焊接裂纹，热裂纹）

- **Environmental failures from corrosion, erosion, etc.;**

环境事故（腐蚀，侵蚀缺陷等）

- **Mechanical failures caused by brittle fracturing, wear, fatigue, etc.**

机械事故：例如脆性碰撞，磨损，疲劳损坏等。

Observed Processing Defects that can occur in Cemented Carbide 在合金里可以观察到的成型缺陷

POROSITY @ 500x

孔洞 500倍放大

CARBON @ 500x

渗碳 500倍放大

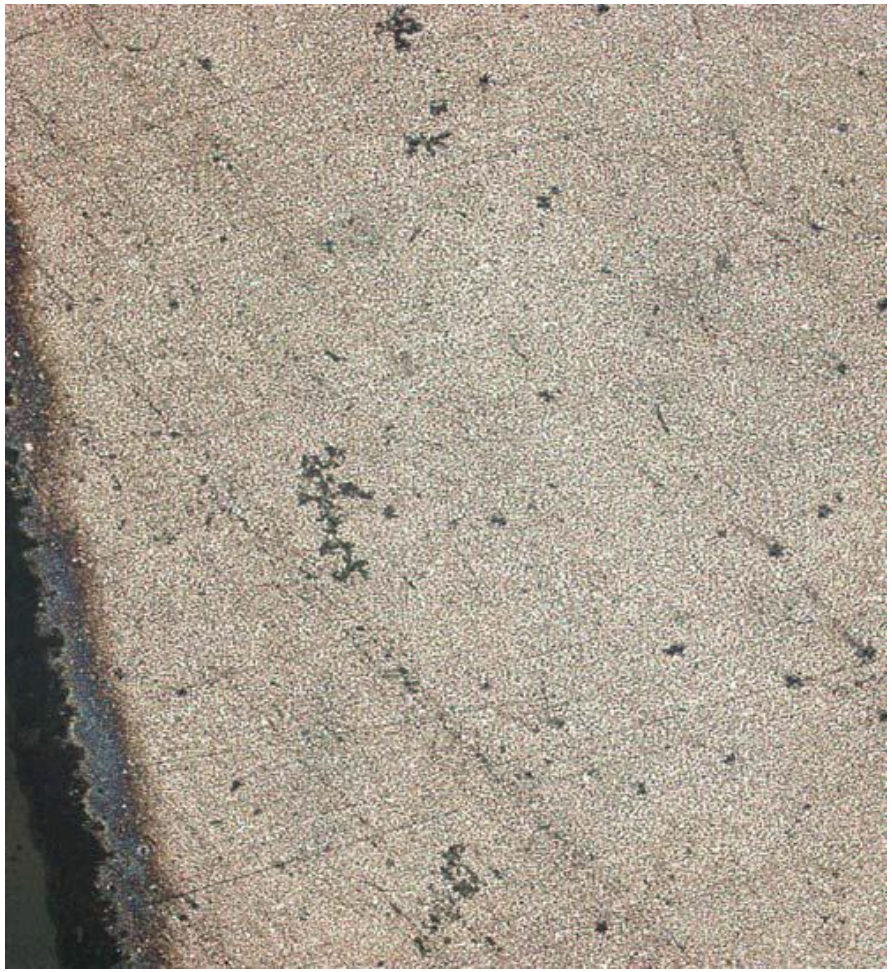
BURNOUT @ 100x

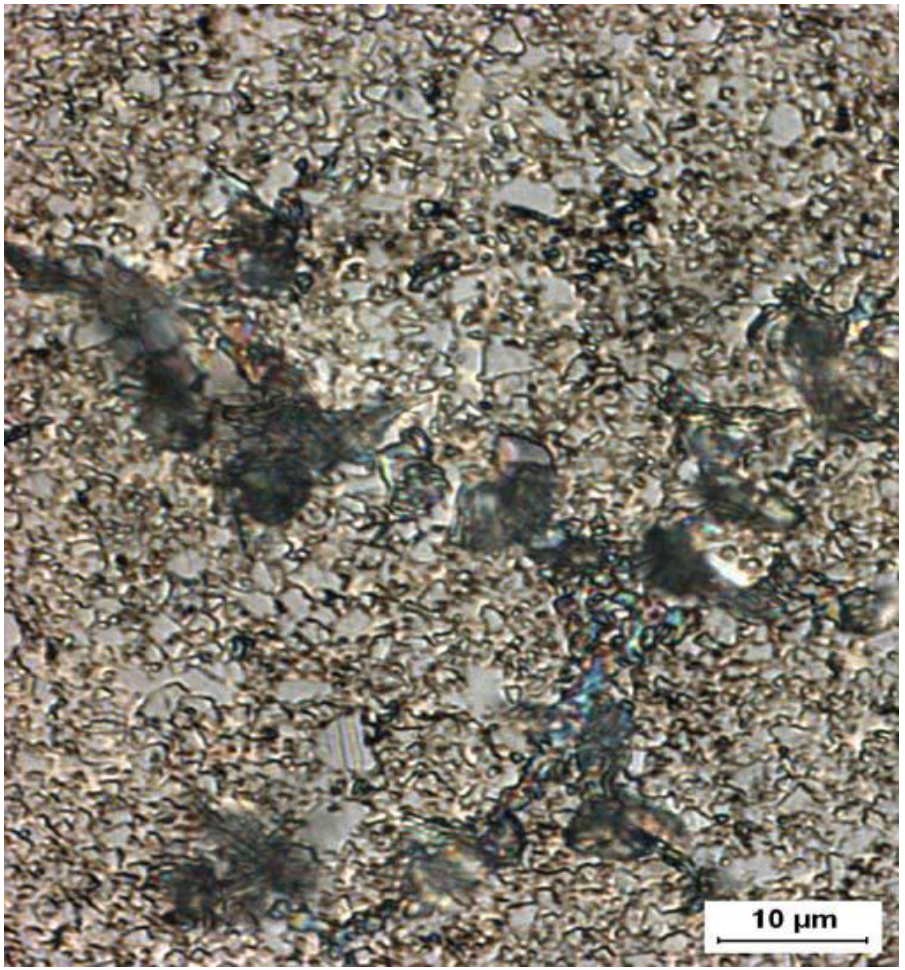
过烧 100倍放大

POOLING @ 1500X

池化 1500倍放大

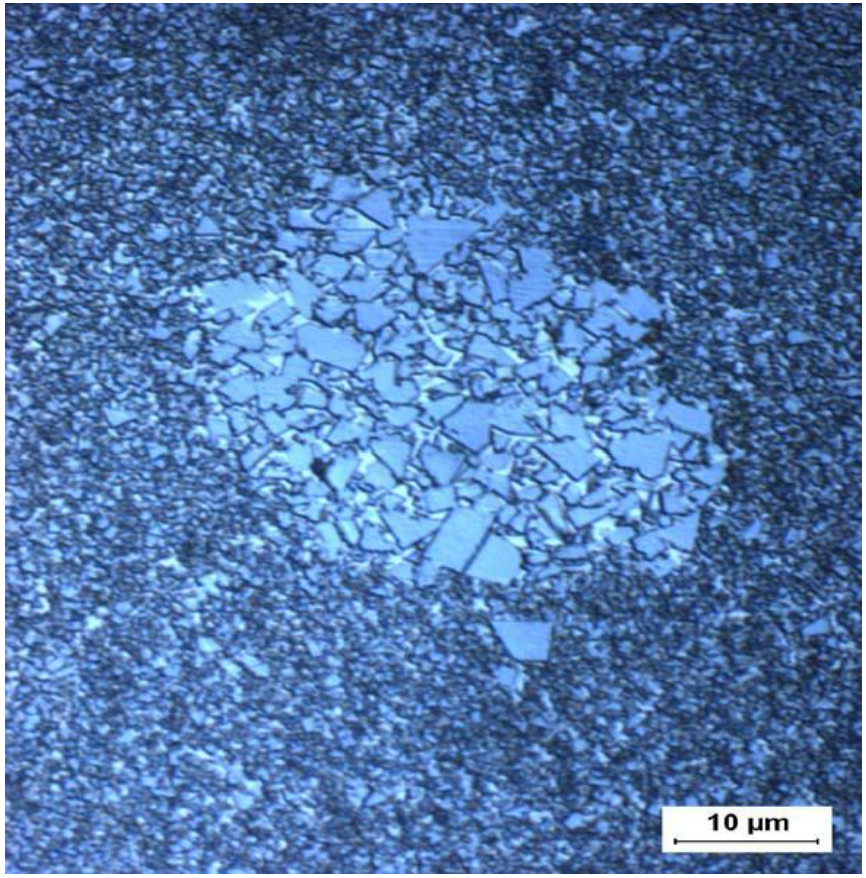
Possible Defect seen in Carbide Processing
合金可能出现的成型缺陷



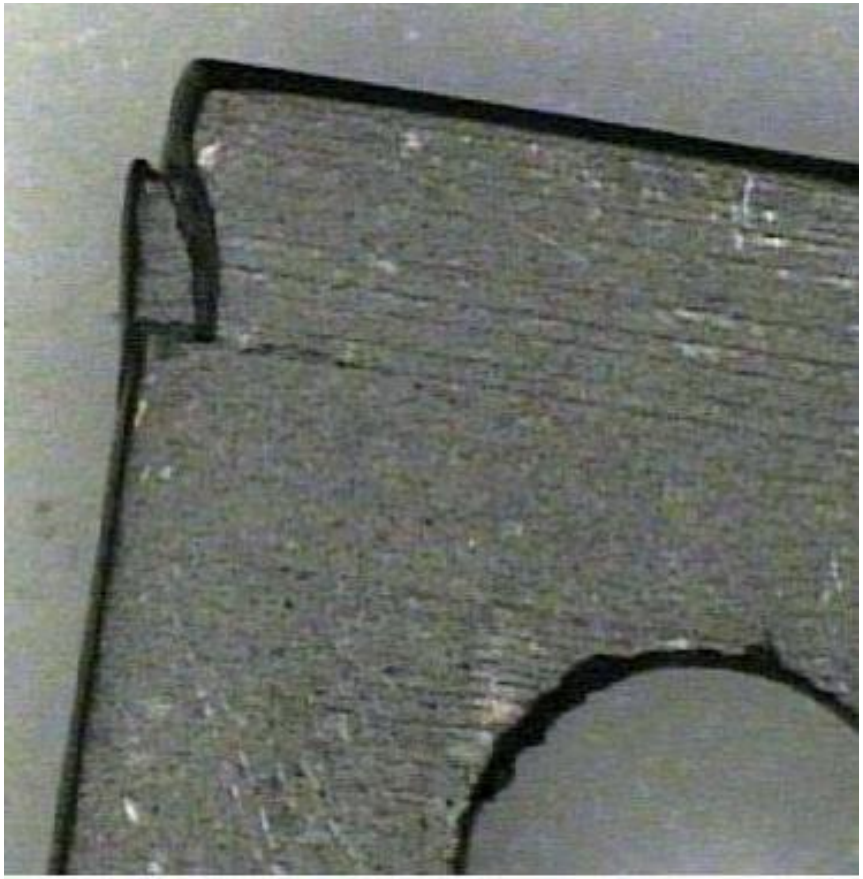


Eta-Phase in Cemented Carbide Materials
硬质合金里的ETA相

Possible Processing Defects seen in Carbide Products Chipping
从合金破碎剥落中观察到可能出现的成型缺陷



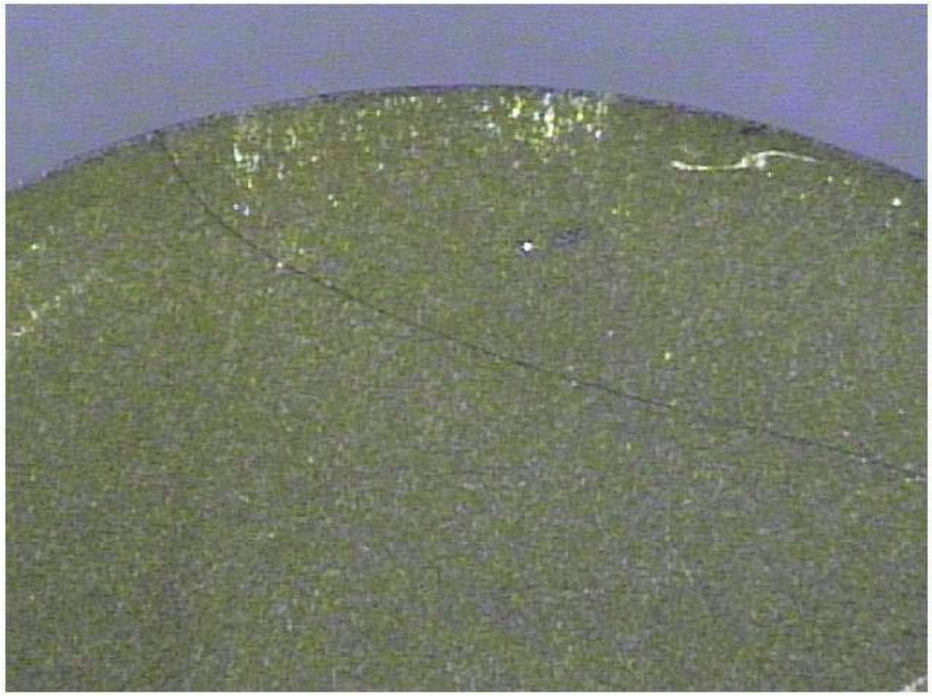
Large Carbide grains cluster formation
异常碳化钨大颗粒群形成



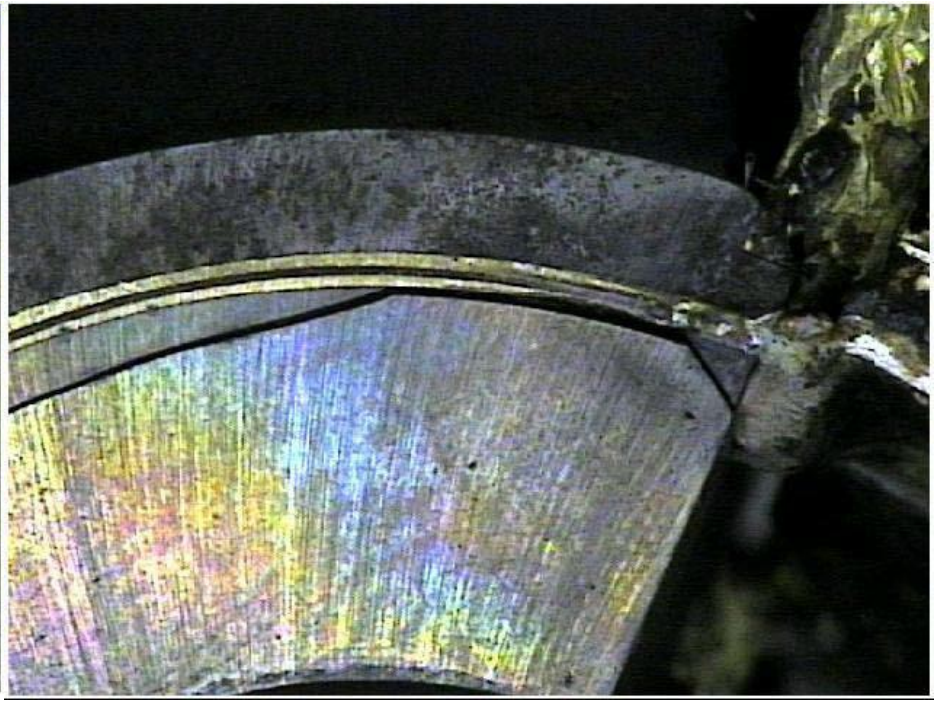
Chipping crack resulting from green carbide shaping operation
压制过程中导致的合金碎裂剥落

Fabrication Defects 加工缺陷

EDM Crack 线切割裂纹

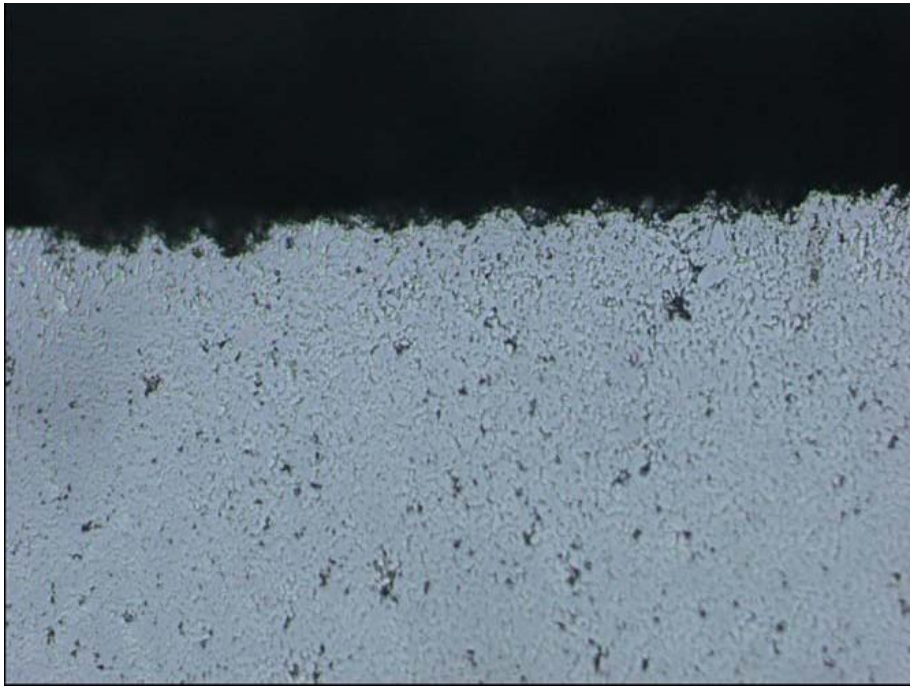


Brazing Crack 焊接裂纹



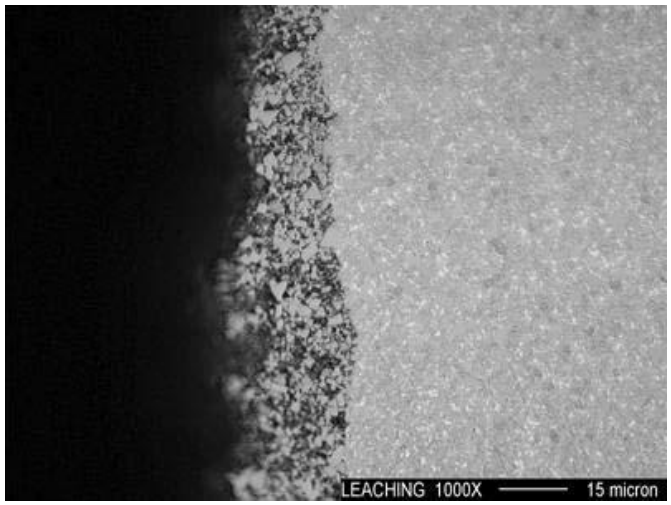
Environmental Corrosion & Pitting Defects
环境事故：腐蚀和凹坑缺陷

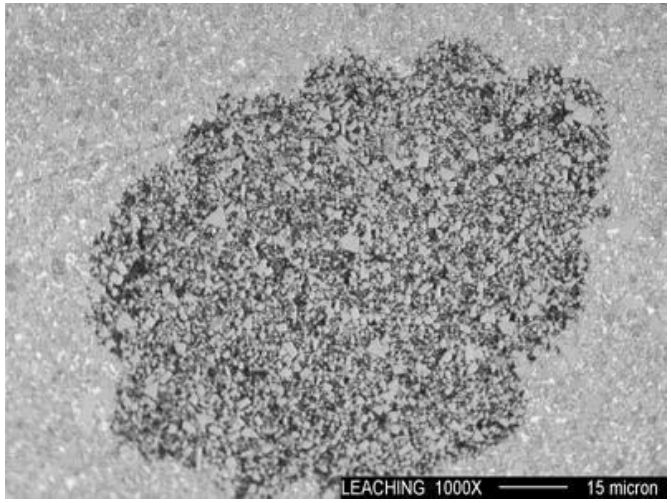
Observable Pitting
可观察到的凹陷



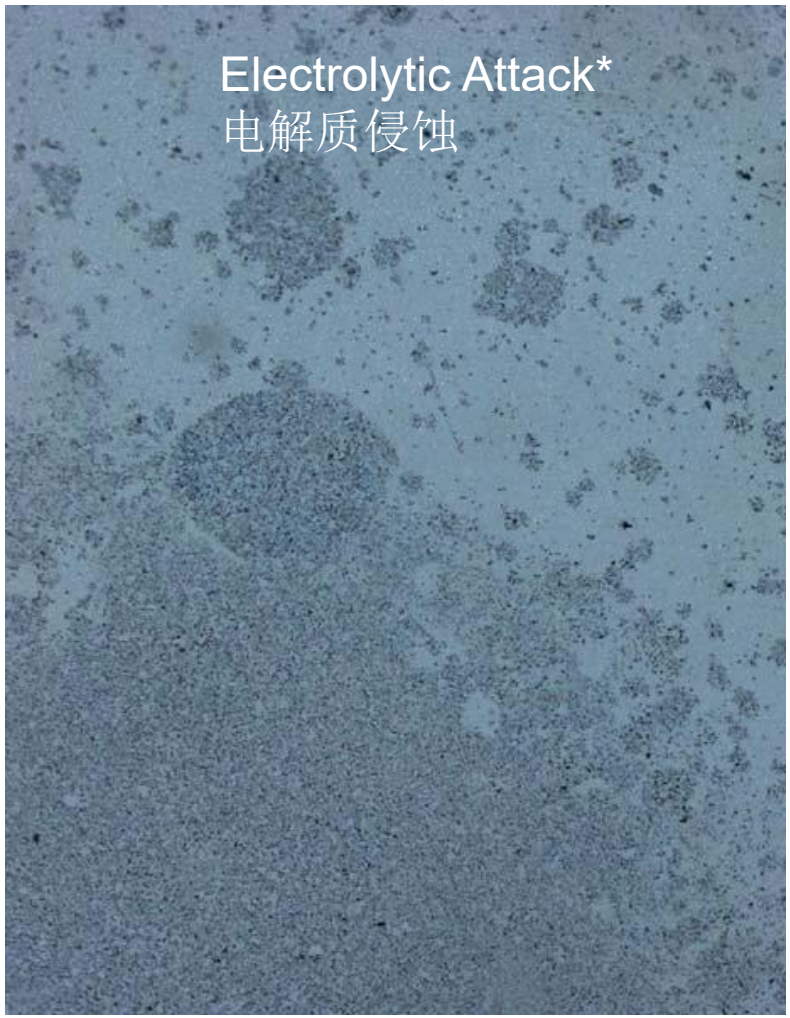
Corrosive attack on binder material
粘接材料被腐蚀

Environmental Failures 环境事故





The selective dissolution (“leaching”) of the binder from the cemented carbide microstructure
从硬质合金里析出粘接材料（浸析）



*Test conducted in wire EDM tank for 100 hours.
合金在线切割池里放置100个小时