Developments in Hard Materials
Introducing the World of Modern Hard Materials

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What is a “hard” material?

• Material harder than carbon- and low alloy steels
• Hardness above ~850 HV / ~65 HRC / ~8 Gpa
Where are hard materials used?

- Wear (resistant) parts
- Cutting & drilling tools
- Chipless forming tools
- Power tool inserts

Diamond tools

Note: This list is not exhaustive
How are components manufactured?

• Different forming methods depending on component size and geometry
• Made from powder, shaped and sintered (example: hardmetals)

Die pressing

Extrusion + grinding

Extrusion or tape casting / high shear compaction

Direct & indirect shaping by green machining / additive manufacturing / slip casting / CIP / HIP / …

Note: Examples of hardmetals
(*) Recent developments in (*) hard materials

• PM Tool Steels (and hard phase reinforced MMCs)
• Hardmetals (cemented carbides and cermets)
• Cutting Tool Ceramics (and new hard composites)
• Coatings (CVD, PVD)
• Polycrystalline Diamond (and polycrystalline cubic boron nitride)
• Monocrystalline Diamond (and cubic boron nitride)
PM tool steels & MMCs

• Greater purity through clean powder production
• Better microstructures and properties
  • fatigue & wear resistance, strength & toughness, ...
• Expanded range of alloy compositions
  • carbon free intermetallic reinforced (maraging) steels
  • very high carbon contents (carbides >25 vol%)
  • mixed hard phases of carbides and borides
  • complex alloy binders
  • special alloys for additive manufacturing
  • ...
PM tool steels have improved performance

- Example: fatigue resistance
  - Gigacycle fatigue testing finds the last remaining defects in such PM tool steels

K390 cold work PM tool steel → Higher homogeneity and purity eliminates most defects, though not all (see above)
- Better fatigue resistance but with greater scatter (predominantly microstructure & surface finish controlled failure)

K110 conventional cast & wrought D2-type cold work tool steel → Lower fatigue resistance but more predictable
- Always a “defect” in the microstructure (eg carbide cluster)
Additive manufacturing of tool steels

• Today, generally lower alloyed, lower C steels, or
• Mixtures of higher-C steels and AM-suitable alloys
Additive manufacturing of tool steels

• Some issues with laser processing of conventional tools steels, but
• AM is developing fast and learning from, e.g., the welding community
Specific AM alloys now being designed

- Example: Ledeburitic and stainless high Cr alloys
PM Metal Matrix Composites

• Containing 25-45 vol.% hard carbide phase (TiC, WC) in an alloy matrix
• Cu-, Ni-, Fe-, Co-based including tool steels, stainless steels & superalloys
AM Metal Matrix Composites

- E.g. containing up to 70 wt.% sintered WC spheres (50 vol.%)
- Metallic matrix of, Ni-, Co-, Inconel 625, NiSiB, ...

Electron beam processed, fully dense
Hardmetals (cemented carbides and cermets)

- Many types of hardmetals
- Hard phases of carbides and carbonitrides
  - Grainsizes from 50 nm to 50 µm
  - Metallic binders of Co, Ni, Fe, Cr, Mo, ...
- Binderless to >40 vol% binder
Hardmetals

• Binder modification by heat treatment
  • E.g. precipitates of $\text{Co}_3\text{W}$ or $\text{M}_{12}\text{C}$ with WC-Co

• Alternative binders as potential substitutes for cobalt
  • e.g. Fe- and Ni-based, High Entropy Alloys (HEA), intermetallics, ...

Dark Blue – WC
Light Blue – Cubic carbide
Red – 5-component HEA
Yellow – Intermetallic phase
Hardmetals

- Surface and bulk gradients
- Gradients in hard phase and/or binder phase, µm to mm in depth

Note: for example only, the modelling is not the same case
Hardmetals

• Advanced characterization and modelling
  • Gaining a greater understanding of hardmetals from atoms to microstructures

Density Functional Theory, cluster expansion, Monte Carlo, CALPHAD, Compound Energy Formalism, DICTRA...

...and many more
AM of hardmetals

- Direct melting methods generally unsuitable for hardmetals
- AM methods for shaping followed by conventional sintering preferred
Cutting tool ceramics

• Combined whisker & particulate reinforced (phase toughened)
• Multi-phase mixed ceramics of oxides, carbides, nitrides, borides, ...
• Multi-layer CVD coatings (TiN, TiCN, Al₂O₃ ...)
Coated hard particles and new hard composites

- CVD coatings of carbides, carbonitrides and metals onto hard particles
- Processing by sintering, HPHT, HVOF or laser metal deposition
Coatings (PVD, CVD)

• Many PVD process variants, mainly based on evaporation and sputtering
  • Electric arc, electron beam, electrical resistance, laser ablation, plasma, ...
  • TiN, TiC, TiCN, TiALN, AlTiN, AlCrN, AlTiCrN, ZrN, CrN, CrTiN, CrTaN, TiB₂, DLC, ...
  • Range of coating architectures: Monoblock, conventional with adhesion layer, triple with top layer, quad structure

• Assisted CVD processes at lower temperatures (microwave, plasma)
  • Deposition of pure metals, carbides, nitrides, carbonitrides, oxides and diamond
Coating stress state design possible

• Example: Comparison of two CVD coatings on WC-6Co
  • 3 µm multi-layer with 0.3 µm TiN adhesion layer between substrate and carbonitride, and Ti(C,O_x) bonding layer between carbonitride and top oxide layer
  • Thermally cycled (Coated-RT-800°C-RT) and stresses measured at RT and 800°C
Polycrystalline Diamond (PCD)

• Wide variety of grades available
Polycrystalline Diamond (PCD)

- Wide variety of shapes and sizes available
  - Stress management (NPI, interlayers) and enhanced thermal stability (leaching)

Ø80 x 8 mm discs
Ø25 x 25 mm cylinders
Polycrystalline Cubic Boron Nitride (PCBN)

- Wide variety of grades available, either solid or carbide backed, plus coated
  - Binders TiC, TiCN, AlWCoB, AlN, borides, metals, ceramics, with cBN content 45-95%
Single Crystal Diamond

- Very large single crystals (up to 10mm) by HPHT and CVD
- Crystallographically oriented for specific properties by application

For cutting tools, grinding wheel dressers, knives, wear parts and wire drawing dies
Single Crystal Diamond (and cBN) Grit

- Tailored morphologies (size and shape)
Single Crystal Diamond Grit

- Tailored properties (strength, toughness, thermal resistance)
- Arranged diamonds in segments
I hope you enjoyed this introduction to the world of hard materials...

- AFM image and the depth profile of a scratch from ReB$_2$, 230 nm deep on diamond surface
- Elemental analysis confirmed a carbon surface free of rhenium

...even though we’ve only just scratched the surface! Thank you for your attention.