How New Paradigm Properties Are Possible With TCHPs

A. Concept Feasibility

In TCHP, toughness of the article or thermally-applied coating as a whole is based on the strength of the building-block particles. The outer surface of an article (or particle) bears most of its mechanical load. It is well known that a tube with a wall thickness only 5% of its diameter will sustain 90% of the load of a solid rod of the same diameter. A structure of bonded tough hollow spherical shells would transmit an even greater load percentage. Filling the hollow rod or sphere with an incompressible material such as a ceramic returns the hollow rod or sphere to full strength. Thus, the brittle core particles are essentially bypassed as strength factors. EternAloy™ technical feasibility is further aided by these facts:

1. Refractory CVD coatings on tungsten carbide substrates are well known. We are just bonding the same materials in *reverse*: ductile WC coatings on refractory core particles. Other particle coating applications have been known for over 20 years.
2. The performance characteristics of many TCHP core particle candidate materials are well known.
3. Instead of using many complex precursor chemicals to apply several hard layers on tough substrates, TCHPs require the reverse, coating primarily *one* tough material and *one* binder.
4. The consolidation process will see WC-Co coated core particles that sinter much as WC-Co powders have been sintered over the past 70 years.

Titanium nitride (TiN) and alumina (Al_2O_3) were chosen as the first core materials because their very low solubility into iron-based workpieces at operating temperatures from 100°C to 1100°C makes them effective diffusion wear extenders on *coated* tools. The small-wire drawing and mining industries have not been able to exploit this important benefit because external coatings are impractical in these applications.

WC was chosen as the first tough coating. WC-Co has the highest fracture toughness of all transition metal carbides and iron group binders because the interface energy between WC and Co is very low. Therefore, the fracture path has to proceed through the tough Co binder phase rather than along the WC-Co phase. WC also has one of the highest Young's moduli, enabling the WC-Co structure (rather than the core particles) to carry most of the mechanical load. Co has lower stacking fault energy than Ni, imparting a much higher toughness to the TCHP/WC-binder matrix.

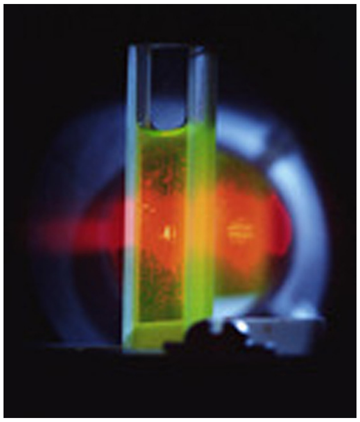
B. TCHP Technology Advantages

To provide a new paradigm combination of properties (hardness + wear resistance + toughness + light weight), the TCHP technology intimately "combines" thermodynamically incompatible materials in all-in-one "building block" designer particles. This cannot be done if the materials are able to reach their natural phase equilibria by allowing them to alloy with themselves as is inherent with mixing or milling operations or porous coatings. The TCHP core and coating separation structure is constrained and preserved during coating *and* sintering of the TCHP particles. The nanoencapsulated contiguous coatings serve to protect certain of the core particle material choices (*e.g.*, TiN or ZrN) from attack, property-robbing metallurgical reactions, or dissolution by the binder metal phase (*e.g.*, cobalt) by uniformly and preferentially exposing the outer layer (*e.g.*, WC) to this wetting and dissolution. This creates a harmonious mutually-protective symbiosis between the tough coating and hard particles that has *eleven advantageous purposes*.

1. Novel Combination of Properties

After 3000 years of metallurgical development and 800 years of lamination development, it appears that few "new paradigm" tool materials combining high fracture toughness and wear resistance will result using classical metallurgical or coating principles. Except for TCHPs, the physical, chemical, and mechanical properties of new materials will be determined mainly by chemical composition and chemical equilibria, microstructure, the rule of mixtures, and deformation- or thermal-treatments.

Using novel TCHP technology, nanoencapsulating fine particles having one set of desirable properties with grain boundary modifiers having other properties allows us to unite and intimately combine heretofore thermodynamically uncombinable material-property combinations. For the first time, TCHPs allow design engineers to create a homogeneous "core-rim" cellular structure of evenly distributed *hard* core particles of the most *wear resistant* refractory core materials known in a tungsten carbide (WC) (or other) tough coating matrix support structure with *toughness* and *strength* comparable to WC-Co substrates. Thus, TCHPs promise the elusive combination of properties that state-of-the-art rule-of-mixtures and solubility limit-, diffusion coefficient-, and physical/chemical constituent property compatibility-constrained materials cannot.



2. Engineering Control of Properties

Nanoencapsulation (*e.g.,* with WC) allows the utilization, not only of alumina (Al_2O_3), but also of more than 30 other core particle materials includingTiN, TiC, TiCN, TiB_2, TiAlN, ZrN, ZrC, ZrB_2, HfC, HfN, HfB_2, VN, VC, VB_2, NbC, NbB_2, TaC, TaN, TaB_2, Cr_3C_2, CrB_2, AlN, $AlMgB_{14}$, B_4C, cBN, SiC, Si_3N_4, SiB_6, SiAlCB, MoB_2, WB(alpha), W_2B_5, and diamond (*plus* their combinations and permutations). Allomet's novel and universal concept provides a nanoencapsulated "*building block*" TCHP particle in and of itself containing the essential elements of hardness + wear resistance + toughness + binder metal. This gives the design engineer thousands of new material grades with engineered properties.

TCHP as a material family has broad and universal aspects. The "*genetic code*" of the whole sintered or coated composition is determined by the separate properties of the TCHP building block particle variants, but the properties will not be determined by the rule of mixtures, *a significant new material departure*. TCHPs will enable engineers to economically and commercially design and produce materials and structures with near-atomic level control. Combining nanoengineered particulates with net-shape parts manufacturing technologies will, for the first time, offer engineers opportunities to simultaneously optimize structures at the nano-, micro-, macro- and functional level.

3. Wear Resistance Increase

Thin wear-resistant tool coating thicknesses are only between 1/30 and 1/5 the diameter of a human hair. TCHP can place the wear resistance of diamond, cBN, alumina, and titanium diboride simultaneously *throughout the entire structure* at the cutting edges and working surfaces of a tool or mechanical component. For those applications where only a coating is required, TCHP can be thermally clad to many millimeters thick onto almost any metallic object.

4. Matrix Toughness via Alloy Avoidance

During sintering, most of the TCHP coating remains as undissolved solidus. This protects many core powder material choices (*e.g.*, Ti-, Zr-, or Hf-rich) from dissolution by the binder. Mutual dissolution forms brittle matrix alloys and stimulates random grain growth that would reduce the toughness of the structure to that of a ceramic or cermet. TCHP technology enables thousands of new material and property combinations and structures that up to now could not be achieved by any other technology.

5. Optimal Matrix Toughness via Preserved Coating Stoichiometry

The protection of core particles of the nitrides of the transition metals by the WC coating prevents dissolution by the binder metal, preventing offgassing of N_2 during heating. This in turn reduces carbon depletion that would cause formation of Co_3W_3C (eta phase), which consumes free cobalt binder phase and *embrittles* the structure just as with conventional WC hardmetals. There is insufficient TCHP experience to know how the transition metal borides or other materials such as B_4C will interact with the binder metals.

6. Optimal Matrix Toughness via Chemical Homogeneity

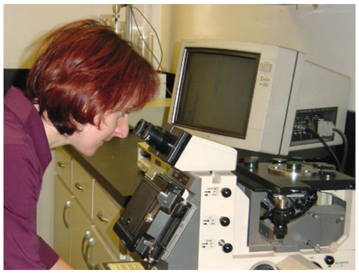
The reprecipitation and “core-rim” nucleation of cubic ceramic (Ti,Mo,W)(C,N) carbonitride particles embedded in a metal binder matrix in cermets is known to be unpredictable and non-homogeneous. The carbonitride particles usually have a characteristic “core-rim” type of structure arising from the widely differing solubilities of the components TiC, TiN, Mo_2C, and WC in the binder melt at sintering temperature. Mo- and W-rich and N-poor phases tend to *randomly* precipitate in “rims” around hard Ti- and N-rich and Mo-, W-, and C-poor “cores” of (Ti)(C,N,CN). The rims become thinner with increasing nitrogen content. Cermet grain sizes are *considerably larger and more irregular* than in WC-Co structures.

Preventing this random binder dissolution of core particles by the protective TCHP tough coatings therefore gives the engineer more control over the chemical structure.

7. Optimal Matrix Toughness via Mechanical Homogeneity

The uniform thickness of the CVD coatings acts as a *gage* to establish and equalize the hard phase interparticulate distances. According to Penn State’s Dr. R.M. German, “the weak link in all engineering materials, especially for brittle phases, is the nonuniform microstructure. Failure cracks like to pass along weak links, so a homogeneous microstructure is very helpful to maximizing the mechanical properties. This can be controlled [with] powder coating uniformity. With a CVD coated powder such as TCHP, the microstructure must be more uniform than with any possible mixed or milled powder. Once the coating thickness is set and the particle size is selected, then particle separation are fixed... With TCHP you can achieve nearly theoretical property levels since the coatings are controlled and uniform. Thus, there will be no agglomerates in the microstructure, leading to essentially identical crack propagation attributes for all regions. This eliminates the weak links, giving a novel route to maximized properties.…This is the old weak link situation, but on a nano to micro particle scale.…Consequently, toughness will be maximized for any composition."

8. Optimal Matrix Toughness via Increased Cobalt Content and Sintering Temperatures



TCHPs do not use WC as the wear-resistant material, relying instead on their orders-of-magnitude more wear-resistant core particles. In addition, the ideal distribution of cobalt on the surface of every TCHP particle virtually eliminates grain growth. These two advantages increase TCHP fracture toughness in three ways: (a) strength-robbing Ostwald grain growth is eliminated, (b) increased cobalt contents become feasible, and (c) increased liquid phase during sintering allows fuller densification.

9. Optimal Matrix Toughness via Nanoproperties

Nanoscale strength stems from opposing image stress fields that stop the progress of cracks at grain boundaries at the near-atomic scale. It is known that, depending upon the cobalt content, sintering aids, and sintering parameters, nanoscale powders (1-200 nm) can produce a finer structure with increased strength and shock-resistance. But such ultrafine nanoscale powders tend to agglomerate (clump) easily, oxidize easily, have pyrophoric reactions more easily, and densify with greater difficulty. As an added benefit, many times larger micron-sized TCHP cores with nanoscale coatings do not require such difficult-to-handle nanoparticles as core powders. *Nano coatings* will leverage nanoscale benefits on larger, easier to handle, and more chemically and pyrophorically stable core powders.

10. Core Particle Wear Resistance Properties Maintained

The tough intermediate TCHP coating maintains the high wear resistance of certain of these core particle materials (*e.g.*, TiN or ZrN). If these materials were unprotected, their dissolution by the binder would form carbonitrides, which are hard but less chemically wear-resistant to iron-based workpieces.

11. Retention of Tough Ligament Structure after Sintering

It has been shown that, even with core particle choices not readily susceptible to dissolution by the binder during sintering, having a mechanical and chemical bond of a contiguous tough coating (*e.g.*, as by CVD) to the core particle provides an important advantage. As temperature increases during sintering, the increasing solubility of the coating (*e.g.*, of WC) in the binder preferentially dissolves the coating from the *outside surfaces toward the core,* leaving an undissolved thin layer of the coating on the core particle surface. Upon *cooling,* this undissolved thin layer acts as a preferential surface site for the WC or TaC solute phase to reprecipitate, nucleate, and recrystallize, onto the remaining coating, increasing the tough WC or TaC ligament layer structure as its solubility by the binder again decreases.