Surface Modification by High Speed Macroscopic Particle Impact

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Abstract

Several new surface modification processes are introduced and described. All employ kinetic energy to form new surfaces exclusively through high speed particle impact – thermal energy is not introduced. These processes represent a previously underutilized regime of particle-substrate interaction that falls between conventional powder based processes and microscopic particle (eg., ion) based processes. Surface interactions are proposed and experimental results correlated to theory. Kinetic Energy Metallization–KEM™ and Kinetic Energy Polymerization–KEP™ produce coatings through plastic deformation and creation of free surface. These coatings comprise unique microstructural and mechanical properties. Kinetic Energy Implantation–KEI™ modifies surfaces through implantation of rigid particles into malleable substrates. Kinetic Energy Ablation-KEA™ removes material through the fracture of the substrate. Each of these processes employs a unique debris recovery system that renders them compliant with the most strict environmental regulations. They are frugal in the use of energy and raw materials.
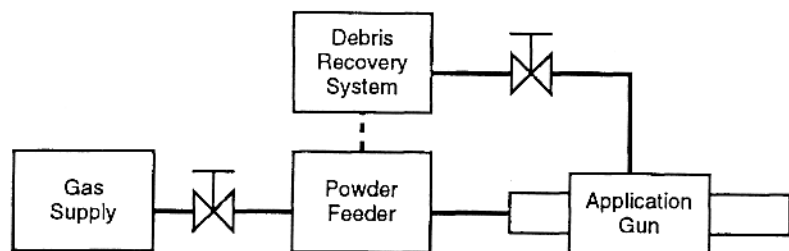
Figure 1:   Block diagram of kinetic energy surface modification apparatus.

1.0 Introduction

Kinetic energy surface modification is based on material interaction induced by the high speed impact of fine particles (1-250 μm) without combustion of fuel. These include material deposition and removal techniques. Other variations produce mechanical treatment of metals.

All interactions occur essentially in the solid state – bulk melting does not occur. Thus, surface modification may be performed on materials that will not tolerate melting or near melting conditions. Coatings may be applied to, or made from, highly metastable materials, such as rapidly solidified alloys and mechanically alloyed metals. The absence of bulk melting also allows for the application of multiple layers of functionally graded material (FGM) without thermal degradation or chemical interaction between layers. Polymers and other low melting point materials may also be applied from the solid state, without recourse to solvents.

Kinetic energy material removal process rates are very high and high spatial resolution is achievable. These properties allow for such diverse applications as, the thinning of single-crystal silicon wafers and for bulk removal of minerals. As these are entirely solid state reactions, the potential for the release of pollutants into the environment is limited to the production of dust and debris; these are captured with a fluid-coupled debris recovery system.

1.1 Process Description

Figure 1 contains a block diagram of the equipment required to perform kinetic energy processes. The following is a brief description of how the processes are accomplished:

*   Fine particles are entrained in a noncombustible carrier gas
*   The gas/particle suspension is accelerated through a special converging-diverging nozzle

Table 1. Comparison of Kinetic Energy and Conventional Processes

Process	Surface Modification	Material	Particle Size, µm	Speed m s^{-1}	Kinetic Energy Density, J kg^{-1}
KEM	coating	Al	10	700	245,000
FTS	coating	Al	125	200	20,000
KEA	preparation	Al_2O_3	50	500	125,000
GB	preparation	Al_2O_3	200	50	1,250

- The outlet of the nozzle is directed to the substrate
- Surfaces are modified through the impact of particles on the substrate
- Particle kinetic energy is partitioned into deformation energy, work of adhesion (both chemical and mechanical), and heat
- A debris recovery system removes excess particles and debris from the substrate

The principal difference between kinetic energy processes and conventional (macroscopic particle) surface modification processes is the kinetic energy density (energy per unit mass, J kg^{-1}), which is directly proportional to the square of the particle speed. Conventional processes deliver large particles to the substrate at relatively low speeds and therefore low kinetic energy density. Kinetic energy processes deliver small particles to the substrate at high speed, thereby providing a high kinetic energy density. Particle sizes range from the submicron level to 30 µm (metals), 100-250 µm (polymers), and 50-250 µm (abrasives). Particle speeds range from a few hundred to 1,600 m s^{-1}.

Kinetic energy processes employ small particles. Because the expanded gas density and the length of the nozzle duct are limited, larger particles are difficult to accelerate to the required speeds in a gas stream. This limitation is due to the need to maintain supersonic, shock free flow throughout the nozzle.

Table 1 illustrates the implications of these factors and compares kinetic energy processes to conventional ones (where: FTS is flame thermal spray and GB is grit blasting). Note that the energy densities (energy per unit mass) are at least an order of magnitude larger for kinetic energy processes than for conventional processes due to the speed differences.

Preliminary flow calculations indicated that particles below about 1 micron in diameter could not be induced to collide with the substrate. Instead, it was postulated that, due to insufficient momentum, these particles would turn with the gas phase at the substrate. However, for most materials, as
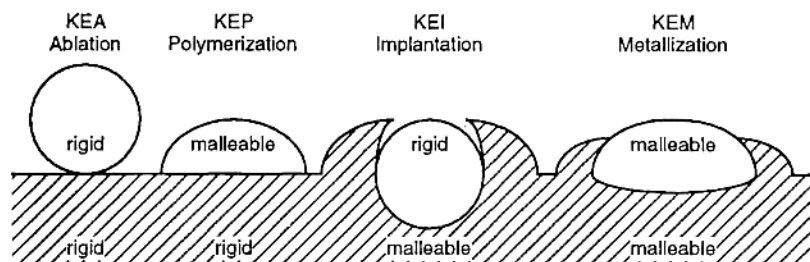
Figure 2: Graphic representation of kinetic energy processes.

particle size is reduced to the submicron level, electrostatic forces tend to agglomerate the particles into 1-3 μm clumps. These clumps can be used in these processes. Thus, it is likely that kinetic energy processes can be used to apply nanomaterials, and may be the only practical way to use these materials.

In a first approximation, kinetic energy processes are defined by the relative rigidity of the particle and substrate. This relationship is best described in Figure 2. Of course, ductility and toughness influence the process; and, for KEP, KEI, and KEM, the collision process is inelastic, while for KEA it is elastic.

1.2 Background

While collisions are used in many forms of surface modification, the use of high speed interaction in the solid state is a recent development. The KEM phenomenon was first identified in 1986 during high speed particle impact ignition studies performed at the NASA, White Sands Test Facility in Las Cruces, New Mexico.[1] In these tests, metal particles injected into a supersonic flow of oxygen at up to 700 K and up to 6.9 MPa produced metal coatings on glass and metal test apparatus components.

Of course, it has long been noted that under certain conditions turbomachinery is subject to material buildup from high speed particle impact. In fact, Russian workers attempting to produce coatings by explosive impact of powder on substrates at KEM like speeds reported coatings formed in the solid state in 1983 and 1986.[2,3] In 1990 another Russian group reported coatings formed from gas entrained particles.[4] In 1992 Browning reported coatings produced with high velocity oxygen-fuel (HVOF) and high velocity air-fuel (HVAF) equipment that exhibited metallurgical bonding.[5]

Over the last three years a great deal of work has been done on the fundamental fluid dynamics of these process and on the design of nozzles to achieve the particle speeds and manage the debris recovery flow. Predictably, work was required to extend the life of the converging-diverging nozzle

which otherwise wore out quickly. Most of the work described in this paper was done with nozzles made from ceramic materials which provide long life and improved performance. These fluid dynamic and nozzle design issues are outside of the focus area for this paper, and will therefore be described in other technical publications.

2.0 Kinetic Energy Processes

2.1 Kinetic Energy Metallization (KEM)

KEM is a unique means of applying metal coatings at low bulk temperature. Feedstock composed of fine metal particles is forced to collide with the substrate at high speed. During impact the particles undergo very high linear strain (up to 80%) at a very high strain rate (up to $10^{10}\,s^{-1}$). The oxide covering the particles cannot achieve strains of this order and must fracture. Thus, large oxide free surfaces are created. When these extremely active surfaces encounter one another, true metallurgical bonding occurs. The deformation process is essentially adiabatic and high local temperature may exist. For some materials formation of cracks may be part of the formation of new surface.

Surface preparation is not required since coatings will not form until the substrate is essentially clean. Initially the metal particles act to remove oxide, previously applied coatings, and other contaminants from the substrate. Of course, when coating a surface with large quantities of mill scale, corrosion products, or previously applied coatings, the use of a cleaning abrasive is an economical alternative to cleaning the surface with metal powder (see section 2.3).

KEM coatings exhibit very fine grain size. Figures 3 contains a micrograph of a zinc KEM coating that illustrates this. Note that the average grain size is smaller than the 7 μm particles used to produce this coating. The large, predominantly white regions in the micrograph represent areas where melting and resolidification occurred. These are particularly evident at higher magnification, Figure 4. The density of these regions will affect the mechanical and physical properties of the coating and can be controlled by altering the particle speed. The secondary electron image, Figure 5, shows evidence of finer melted-resolidified layers within the fine grained structure.

KEM coatings have very low porosity. This is evident in Figure 6, which contains a micrograph of an unetched copper KEM coatings with 3 μm particles. One would expect that the oxide concentration of KEM coatings would be extremely low too, especially when compared to thermal spray coatings; but this remains to be confirmed by X-ray mapping.

KEM has many potential applications, especially for substrates or particles that do not tolerate high temperature. Intriguing possibilities include:
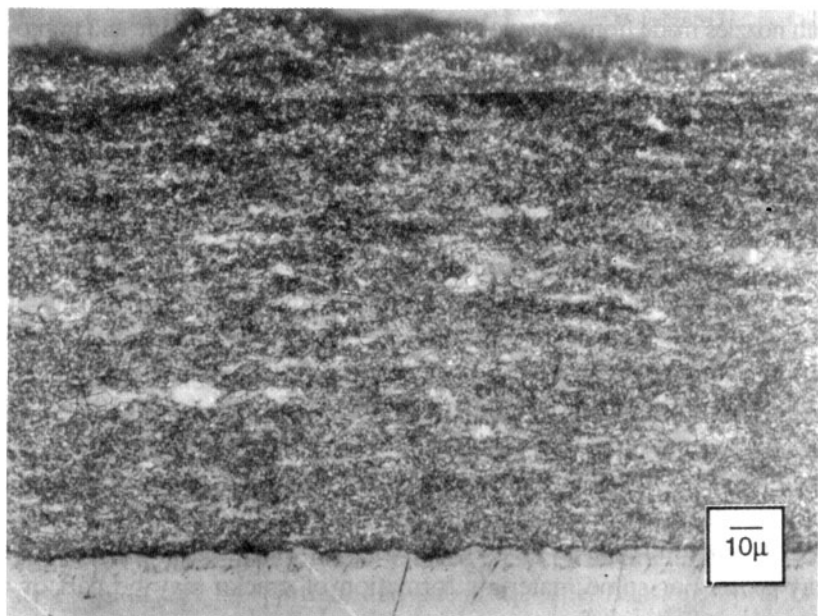
Figure 3:   Zn KEM coating on brass substrate, etched 1% nitric acid, original
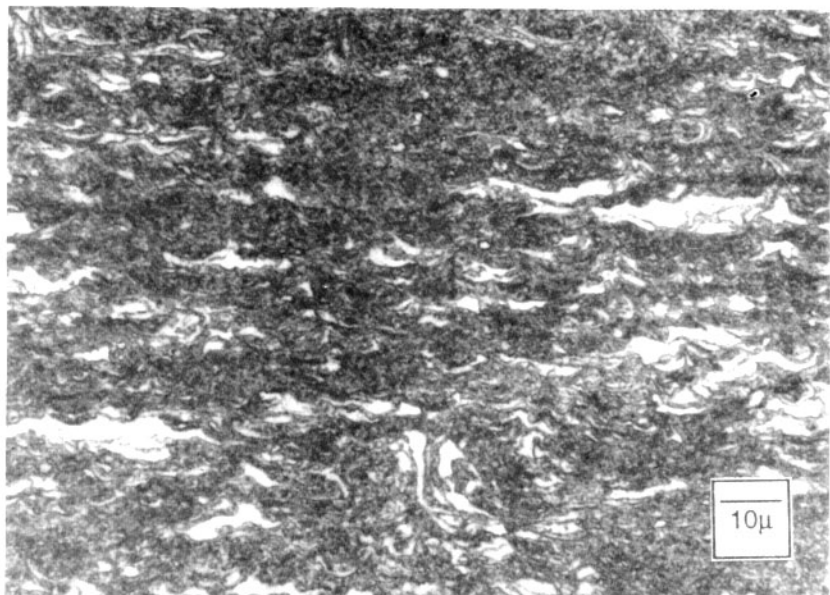   magnification 400x.

Figure 4:   Zn KEM coating on brass substrate, etched 1% nitric acid, original
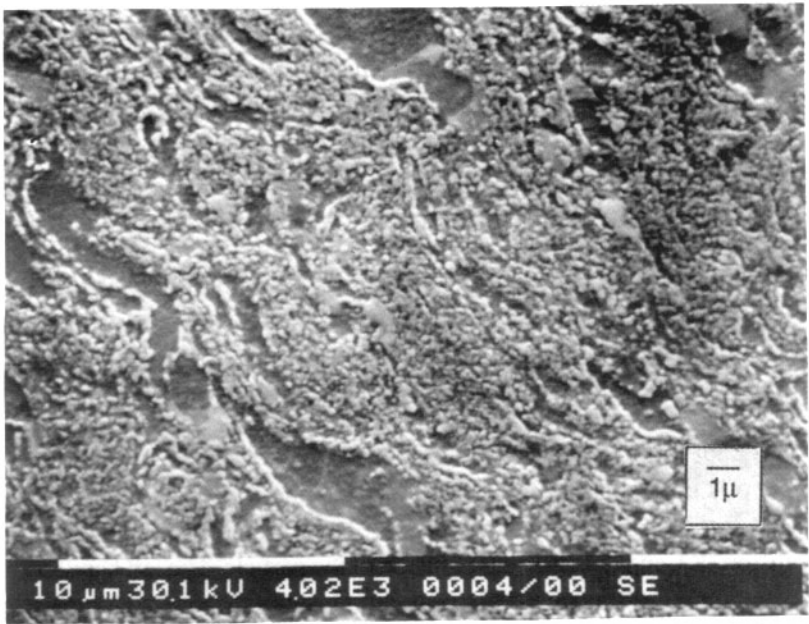   magnification 800x.

Figure 5: Zn KEM coating on brass substrate, etched 1% nitric acid, secondary electron image, original magnification 4,000x.
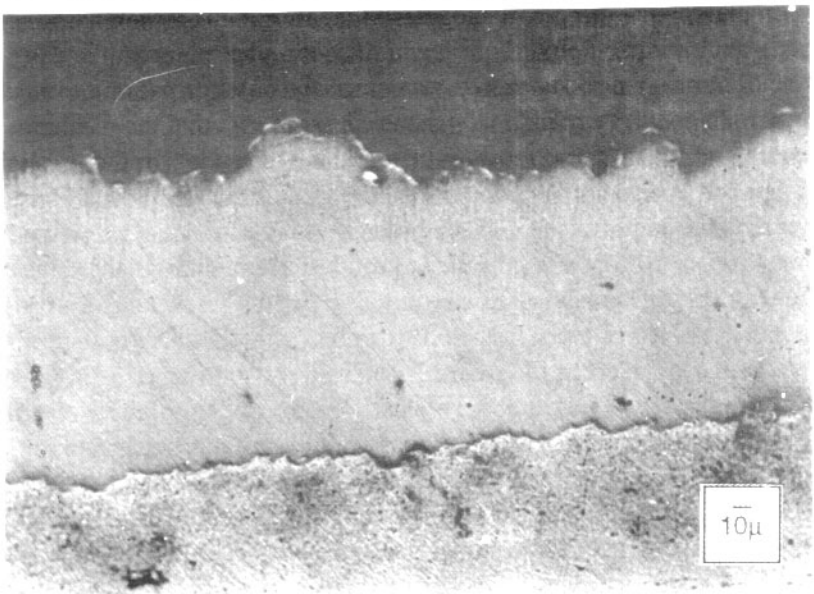

Figure 6: Cu KEM coating on Al substrate, unetched, original magnification 220x.

application of high melting point, oxidation resistant materials on intermetallic compounds and abradable coatings on ceramic and ceramic matrix composites. Also, KEM coatings can be used to produce high melting point ceramic-ceramic and ceramic-metal bonds through the application of partial transient liquid-phase joining materials. These comprise a layer of a low melting point material followed by a layer of a refractory metal.

2.1.1 Mechanism

Initially we assumed that the cohesive mechanism for KEM involved melting. In fact, empirical results indicated that kinetic energy on the order of that required to melt the particle was necessary to produce coatings. Such a model, for self-coating, is mathematically described in Equation 1.

$$\frac{1}{2}\rho V v^2 = \rho V [c_p(T_{mp} - T_0) + H_f] \tag{1}$$

Where: ρ is the density, V is the volume, v is the speed, c_p is the specific heat, T_{mp} is the melting temperature (K), T_0 is the ambient temperature prior to collision (K), and H_f is the heat of fusion of the particle. The left hand side of this equation is the kinetic energy of a particle and the right side the energy required to raise the particle to the melting point and the energy necessary to convert the particle from solid to liquid. Since ρV appears on both sides of the equation, a simple expression for the coating speed may be derived.

However, this relationship overstated the minimum coating speed for some metals. For example, it suggested that aluminum, which has a very large heat-capacity, should require a high coating speed, and this was not the case. Intuition also suggested that, since the transformation of kinetic energy to heat energy requires the material to deform, that the mechanical properties of the material must be included in the model. In fact, a slight modification based on the bulk modulus of the material alters the relationship above to fit the empirical data. This is presented in Equation 2, which includes a dimensionless factor formed by the ratio of the bulk modulus of the material, B_m to that of tungsten, B_w.

$$\frac{1}{2}\rho V v^2 = \rho V \left[C_p(T_{mp} - T_o) + H_f \right] \frac{B_m}{B_w} \tag{2}$$

The melting speeds predicted by Equation 2 permit a relative ranking of metals particles in agreement with the experimentally observed self-coating KEM data. For example, solving Equation 2 for particle speed yields the following results: zinc 350 m s⁻¹, aluminum 700 m s⁻¹, copper 750 m s⁻¹, and iron 1,020 m s⁻¹.

However, as indicated in the micrographs (Figures 3-5), bulk melting does not occur in KEM coatings. Thus, while Equation 2 is empirically
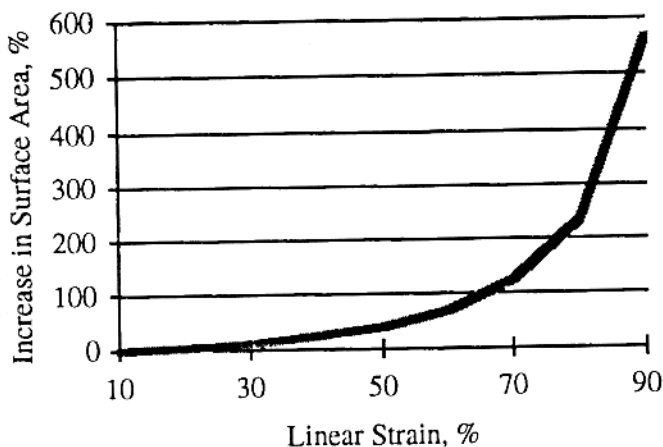
Figure 7: Relationship between surface area and linear strain for a spherical particle.

correct, it is not mechanistically revealing. Evidence for a more correct model is available from the micrographs. Here one can clearly see that tremendous amounts of strain have occurred in individual particles. In fact, the deformation is so great, and the boundary between original particles so obscured, that our first concern was the explanation of how this magnitude of strain can occur.

The explanation comes to us from studies of the deformation during impact of ordinance projectiles. At high strain rate, strain of the magnitude suggested by the micrographs (superplastic deformation) is well documented in the literature.[6,7] Dynamic recovery and possibly dynamic recrystallization must occur, but a detailed explanation of the deformation process is not fully understood.

Because of the high strain rate, the deformation process is largely adiabatic and particle temperature could be high, especially at the particle substrate interface (where frictional heating adds to heat generated by deformation). Additionally, certain metal-metal and ceramic-metal reactions are highly exothermic. It is also possible that, for some metals, fracture has a role in the deformation process. In these cases, (oxide free) fracture surfaces will contribute to the fusion bonding process, provided the fractured segments of the particle remain in contact with the substrate.

Figure 7 illustrates the relationship between linear strain and surface area for a spherical metal particle after impact on a rigid substrate. As the particle departs from spherical geometry and flattens, surface area rapidly increases, especially above 50% linear strain. For example, at 65% strain the surface area doubles (increases 100%).
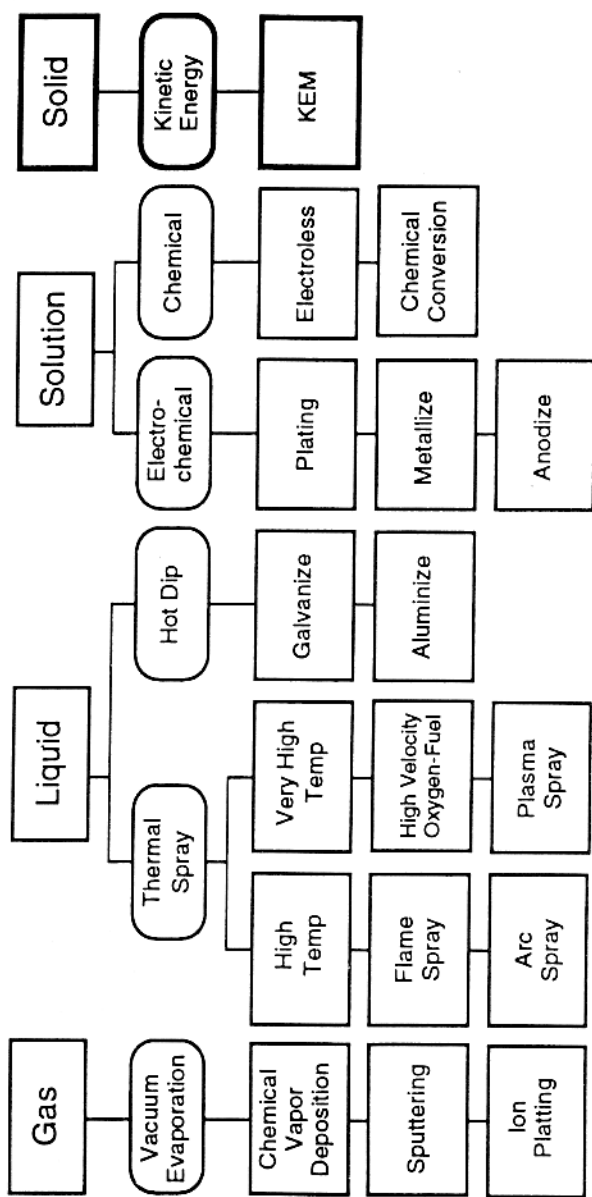
Figure 8:   The relationship between various metal coating processes.

To attain strains of this magnitude, the particles must be subjected to very high strain rate as indicated above. While KEM particle speeds are very high, it is important to note that strain rate is not limited to the speed of the particle, but to the speed of sound in the metal (eg., 5,000 to 6,000 m s^{-1}). Thus, KEM coatings are formed when clean (unreacted) metal surfaces come into contact. These surfaces are formed due to the large magnitude of strain that the particles undergo in the collision process. It is possible to overdrive this process by accelerating the particles beyond the necessary coating speed. Early indications of this are illustrated by the melted regions in the Figures 3-5.

2.1.2 Relationship With Other Metal Coating Processes

KEM differs from other metal coating processes because it is essentially a solid state process. Other processes are gas, liquid, or solution based, Figure 8. Although these processes are capable of depositing metal coatings on a variety of substrates, all have severe drawbacks. The gas phase processes require expensive vacuum systems, offer low deposition rates, and require complicated designs to produce uniform deposition over large area. The liquid phase processes place large heat loads into the substrate and deliver coatings that are contaminated with oxide and are not metallurgically bonded. The solution based processes employ chemicals that are not only expensive, but also environmentally objectionable.

While all of these processes produce metal coatings, thermal spray coating is most closely related to KEM. The following section compares these two technologies.

2.1.3 Relationship with Thermal Spray Coating Processes

Thermal spray coating processes resemble KEM in that metal particles (albeit in the liquid state) are sprayed at the substrate at high speed to produce coatings. In fact, the demand for low porosity, highly adherent coatings composed of exotic materials has generated a trend to higher speed thermal spray processes.[8] These processes rely on the input of large quantities of thermal energy to rapidly expand the carrier gas and thereby propel molten particles to the substrate.

KEM is a low temperature process and uses only high speed to provide energy to produce coatings. The kinetic energy density of KEM is many times larger than that of thermal spray coating processes. (Although thermal spray coating processes have low kinetic energy density, they do have high total energy density because the particles are melted in the gun.) The KEM process converts high kinetic energy density into sufficiently high total energy density to induce deformation and fusion bonding. While KEM is related to thermal spray coating processes, it is more correctly a departure from that

Table 2. Comparison of KEM with Thermal Spray Coating Processes

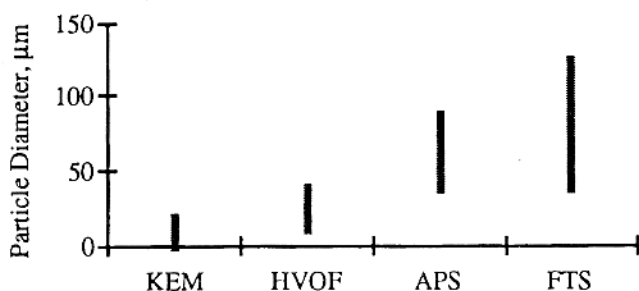|		KEM	HVOF	APS	FTS
Diameter,	Min.	1	10	37	37
μm	Max.	30	40	88	125
Speed,	Min.	500	600	450	50
m s^{-1}	Max.	1,600	800	750	150
Temperature,	Min.	300	4,200	4,700	2,700
K	Max.	500	7,300	16,400	5,800

Figure 9:   Particle diameters of KEM and TSC processes.

technology. This is best illustrated in Table 2 and Figures 9, 10, and 11 (where HVOF is high velocity oxygen-fuel, APS is air plasma spray, and FTS is flame thermal spray). Note that for KEM, particle size is small, particle speed is high, and particle temperature is low compared to the thermal spray processes.

2.2 Kinetic Energy Implantation (KEI)

Kinetic Energy Implantation is a means of forming surface through the impact of a rigid particles on a malleable substrate. The ensuing collisions predominately deforms the substrate. For polymer substrates, the substrate material is softened and forms a sheath around the particles. For metal substrates, the particles extend upward from the surface and are implanted only at the base.

KEI coatings do not increase in thickness (build-up) with increased coating time. It is not a cohesive process, it acts only on the surface of the substrate. However, this surface layer can serve as a base for additional
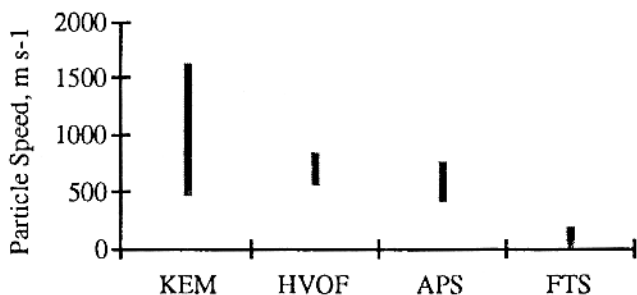
Figure 10:   Particle speeds of KEM and TSC processes.

layers of conventional coatings. The mechanistic treatment noted above for KEM is applicable to KEI except that the particles do not deform – only the substrate does. Again the high kinetic energy density of the particles renders this surface interaction possible. Of course, for materials with low thermal stability, such as polymers, degradation may occur instead of coating. For these reasons relatively low speed, large size particles are used on polymer substrates. Also, for polymers, indication of chemical interaction between the particles and substrate have been noted.

Some very useful surfaces may be formed with this process. For example, metal implanted into polymers form surfaces solderable with conventional lead-tin alloys. These surfaces may also have important wear resistant applications, as do metal surfaces implanted with diamond or cubic boron nitride. Polymers implanted with abrasives or semiconductors form another group of important new materials.

Above a critical kinetic energy density implantation ceases to occur, the collision process becomes destructive and the substrate material is removed. This process is described below.

2.3 Kinetic Energy Ablation (KEA)

Kinetic Energy Ablation is a means of removing substrate material through high speed collision with relatively rigid particles. Mechanistically it is quite similar to grit blasting. Rigid particles are impacted on rigid substrate materials and subsequent fracture of the substrate results in removal of material. For lower melting point or chemically active substrates, surface removal is aided by mechanical and chemical degradation.

KEA differs from conventional grit blasting in that the particle size is smaller and speeds much higher. For example, a typical KEA process uses 20 μm SiC particles accelerated to 350 m s^{-1}. This results in an impact pressure of 5,100 MPa which is sufficiently high to cause fracture and ablation of hard, brittle substrates. The combination of small particles at
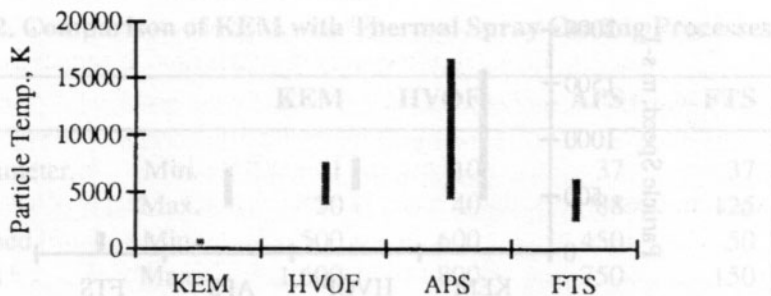
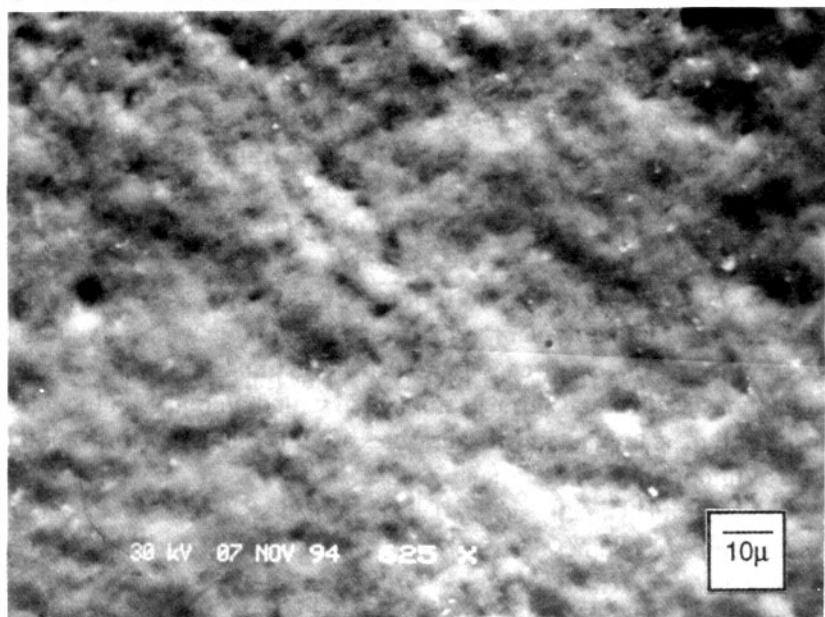Figure 11:   Particle temperatures of KEM and TSC processes.

Figure 12:   KEA of electronic grade Si wafer abraded to 50% original thickness with 50 μm silicon carbide particles, secondary electron image, original magnification 625x.

high speeds facilitates the rapid removal of surface material without damage to the underlying material.

KEA allows for the very rapid removal of substrate material at high spatial resolution. An example of this is the removal of silicon, Figure 12. This wafer was thinned, without damage to the underlying material, from 500 to 100 μm in thickness in less than one second. KEA works on many brittle materials such as glass, concrete, and slate. Material removal rates

are high and the debris recovery system eliminates dust generation. As for the KEM case, the KEA debris recovery system is fluid dynamically coupled to the high speed particle bearing flow. This coupling, which is the result of a carefully optimized design, enables nearly 100% of the abrasive material and ablated material to be captured. This system differs from conventional vacuum-blast process that essentially remove particles after they have settled.

KEA can be combined with KEM simply with the addition of a second powder feeder filled with abrasive material. This allows for the low cost removal of previously applied coatings or oxide film, and eliminates setup costs associated with grit blasting. Other combinations of the two processes include rapid prototyping. Here KEA/KEM make possible the generation of complex three dimensional shapes.

2.4 Kinetic Energy Polymerization (KEP)

Kinetic energy polymerization is a means of depositing malleable materials on rigid substrates. It is not limited to polymer coatings, but has been most frequently used to apply polymers to metals. These coatings reach a critical thickness, related to the initial particle size, above which further build-up will not occur.

Typical speed for polymers is in the 500 m s^{-1} range. Low density polyethylene (100 µm) and tetrafluroethylene homopolymer (8-15 µm) particles were used to produce thin coatings on aluminum substrates. Pyrolysis occurred in some of the TFE coatings, which indicates that a larger particle size or lower speed would be desirable. KEP coatings may be used to manufacture thin polymer sheets and to generate conformal coatings for electronics applications.

These KEP results are quite recent and have not yet been subjected to extensive microscopic evaluation, but preliminary bond strength measurements are encouraging.

Metal coatings can be applied to rigid substrates with this process. For example, copper, chromium, nickel, aluminum, and titanium have been deposited on Al_2O_3 and AlN substrates and zinc, aluminum and copper on silicon wafers.

These metal coatings on ceramics are an important enabling technology for new ceramic joining techniques (e.g., partial transient liquid-phase bonding). Metal coatings on silicon wafers offer a new technique for back side metallization. Also for semiconductor application, the deposit of metals on silicon (both single and polycrystal) and on ceramic substrates is envisioned for multi chip module (MCM) applications.

KE processes are especially suited to MCM applications because the scale of the MCM substrates, coatings, and surface features are in

line with the macroscopic nature of the KE processes. The KE processes are capable of rapid and uniform deposition and removal rates. No microscopic, vacuum based technology (such as those intended for semiconductor manufacturing) can produce similar rates.

3.0 Conclusions

Several new surface modification processes (patent pending) are introduced that employ a heretofore ignored regime of particle surface interaction. These modifications are achieved through the conversion of kinetic energy provided to the substrate at very high density. These environmentally benign processes should prove useful in several industrial applications.

4.0 References

1. F.J. BENZ, ET AL.: 'Ignition of Metals by High-Velocity Particles,' *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Second Volume, ASTM STP 910*, M. A. Benning, ed., American Society for Testing and Materials, Philadelphia, 1986, 16-37.

2. A.M. KAUNOV and A.V. SHAMREI: 'Application of powders to metallic surfaces with the aid of condensed explosives,' *Fizica i Khimiya Obrabotki Materialov, **2***, 1983, 25-30.

3. A.M. KAUNOV, ET AL.: 'Formation of the Structure of Power-Metallurgy Coatings Obtained by the Impact Wave Method,' *Soviet Powder Metallurgy and Metal Ceramics, **25**(5)*, May 1986, 402-405.

4. A.P. ALKHIMOV, ET AL.: 'A Method of Cold Gas-dynamic Deposition,' *Soviet Physics Doklady, **36**(12)*, December, 1990, 1047-1049.

5. J.A. BROWNING: 'Hypervelocity Impact Fusion – A Technical Note,' *Journal of Thermal Spray Technology, **1**(4)*, December 1992, 289-292.

6. L. ZERNOW, ET AL.: 'Experimental and analytical study of early time material processing, in a collapsing shaped - charge liner, using 'softly - recovered' partially - collapsed copper liners,' *International Journal of Impact Engineering, **14**(1-4)*, 1993, 863-875.

7. M.E. KASSNER, ET AL.: 'Effects of temperature and strain rate on extended ductility of aluminum,' *Materials Science & Engineering A*: Structural Materials Properties, Microstructure and Processing, **A132**(1-2),

February 1991, 97-105.

8. M.L. THORPE: 'Thermal Spray Industry in Transition,' *Advanced Materials & Processes,* **5**, May 1993, 50-61.