Nanostructured Zn-Ni Alloys by Pulse Electrodeposition

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In the current work, nanostructured Zn-Ni alloys are electrodeposited by direct and pulse current from alkaline sulfate electrolytes in the presence of additives and complexing agents. The ratio of the zinc and nickel was effectively controlled by varying the concentration of the electroactive species and operating parameters. The new electrodeposited Zn-Ni alloy has an increased content of nickel as compared to the conventional Zn-Ni alloy. The increase in the nickel content accounts for the decreased corrosion potential of the Zn-Ni coatings. The corrosion potential of the Zn-Ni alloy is -0.702 V (vs. SCE), which is still electronegative when compared to steel and offers sacrificial protection to steel. The coatings have superior corrosion resistance and barrier properties when compared to conventional Zn-Ni and cadmium coatings. Polarization studies on nanostructured Zn-Ni coatings show a barrier resistance that is higher than the conventional Zn-Ni coatings by an order of magnitude. The compositions of the coatings were analyzed by EDX. The surface morphology of the coatings was studied using SEM (Scanning Electron Microscope). Improved corrosion and hydrogen inhibition properties make it a potential alternative for the cadmium coatings.

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Introduction

Steel substrates are electrodeposited with sacrificial coatings for corrosion protection. Zn, Zn-Ni, Zn-Co and Cadmium alloys are some of the widely used sacrificial coatings [1-8]. Among them cadmium coatings are considered very reliable owing to their superior corrosion and engineering properties [2]. But the cadmium coatings are highly toxic and they are generally prepared from toxic cyanide baths [3]. Also cadmium plating introduces large amount of hydrogen in the underlying substrate and thus increases the susceptibility of the substrate to hydrogen embrittlement [4]. Growing ecological concerns in recent years have led to the search for an alternative coating that can effectively replace cadmium coatings. Zinc deposits exhibit excellent sacrificial behavior. However, a high dissolution rate and poor mechanical properties limit the use of Zn coatings in the automotive industry. Alloying of zinc with noble metals like nickel has proved to increase the corrosion resistance and mechanical properties of zinc coatings. Zn-Ni alloys are considered as a viable alternative to cadmium coatings [6-11]. Zn-Ni alloys containing 15 - 20 wt% of nickel possess four times more corrosion resistance than cadmiumtitanium coatings [12]. Although zinc is less noble than nickel, the electrodeposition of Zn-Ni results in the preferential deposition of the zinc and a higher amount of zinc is observed in the final deposit. Therefore, Brenner classifies Zn-Ni codeposition as anomalous [13]. The mechanism for the preferential deposition of Zn has been discussed extensively in literature [13,14]. Due to the higher percent of zinc in the coating, these alloys are more electronegative than cadmium and hence dissolve rapidly in corrosive environments. Any further increase in nickel composition is based on using a higher than predicted Ni/Zn ratio in the bath [15,16]. Though Zn-Ni alloys have good corrosion resistance in comparison with Zn coating, further development for better coating and corrosion characteristics is of commercial interest. An enhancement in the nickel composition of these alloys would lead to more anodic open circuit potential, which will in turn reduce the driving force for galvanic corrosion. Also the barrier properties of the coating increases with increased nickel content in the deposit. Several attempts have been made earlier to decrease the anomaly and increase the nickel content by either introducing an inert species in the bath or by developing a ternary alloy [17-24]. Nonyl phenyl polyethylene oxide (NPPO) has been used to reduce the Zn-Ni ratio and produce more corrosion resistant deposits. NPPO inhibited zinc electrodeposition and acted as a leveling agent as seen in our earlier studies on the deposition of zinc and galvanostatic pulse and pulse reversal plating of Zn-Ni alloys from sulfate electrolytes[20,21].

Codeposition of phosphorous along with Zn-Ni alloy improves the corrosion resistance [17] and hydrogen permeation [18] characteristics of the deposit. Zhou et al [19] have studied the effect of tin additions on the anomalous deposition behavior of Zn-Ni alloys. The nickel ratio increased from 6 to 8 % with the addition of small amounts of tin. Earlier, we have developed a novel plating process for the electrodeposition of Zn-Ni-Cd coatings [22-24]. It was found that use of small of ternary alloying elements like cadmium can effectively control the Zn-Ni ratio. Cadmium codeposition was observed with a significant decrease in the Zn-Ni ratio. The Zn-Ni ratio [24] was as low as 1.7:1. Also the corrosion resistance of the coating was improved by an order of magnitude when compared to that of commercial Zn-Ni and cadmium coatings. The inclusion of ternary element like cadmium prevented the hydrogen entry in to the substrate as compared to the Zn-Ni alloy and cadmium coatings [23]. However, the use of the cadmium salts in the bath poses ecological concerns.

Autocatalytic reduction of metals and alloys offers an attractive and alternate method of increasing the amount of Ni in the final deposit. In our earlier study [25], we developed Ni-Zn-P composites using electroless method with enhanced Zinc content in the alloy. Such an approach ensured that the coating exhibit sacrificial properties by virtue of its zinc content while the presence of high Ni content provided extended life in corroding media. A similar alkaline bath was developed to deposit NiZn alloys with nickel content as high as 72 % by dc currents. In this study, we tried to develop similar Ni-Zn composites with high Ni content and nanostructured grain size using pulse deposition technique. In a broad sense, the present study is focused on developing nanostructured Ni-Zn coatings with improved mechanical properties that will provide sacrificial protection to steel and have low dissolution rates. The corrosion characteristics of these newly developed nanostructured coatings have been compared to that of cadmium.

Experimental

Sample Preparation:- Plating and subsequent corrosion studies were done on low carbon coldrolled steel foils of thickness 0.5 mm and area 25 x 25 mm. Initially, the steel sample was mechanically polished with successive finer grades of emery paper. The samples were then degreased with alcohol and rinsed with de-ionized water. Next, the samples were treated in 10 % (v/v) H₂SO₄ solution for 1 minute to remove any adherent oxide layer present on the surface. Finally, the samples were again washed in de-ionized water. This procedure was repeated until a clean and smooth surface was obtained.

Electrolyte preparation and deposition:- Ni-Zn composites were prepared from a bath of alkaline sulfate electrolytes similar to the bath used in our electroless process [25]. Complexing agents were used to prevent Ni and Zn from precipitating at an alkaline pH. Steel foil prepared as mentioned above was used as the substrate. Ni-Zn coatings with different amounts of Zn were obtained by varying the pulse parameters and also by varying the amount of ZnSO₄.7H₂O in the bath. The pH was maintained at 10.5 during the deposition by the addition of NaOH. All solutions were prepared with analytical grade reagents (obtained from Sigma-Aldrich) and triply distilled water. The deposition time was changed according to the required thickness of the coating.

Material Characterization:- Energy Dispersive Analysis using X-rays (EDAX) was used to analyze the distribution of the elements in the final deposit. To ensure accuracy of the element

distributions, EDAX analysis was done at several points on the surface of the substrate. The accuracy of the measurements for the equipment used was rated as ± 0.1 -wt%. The surface morphology and the microstructure of the coating were analyzed using Scanning Electron Microscopy with the help of Hitachi S-2500 Delta Scanning Electron microscope. *Electrochemical Characterization:*- A variety of electrochemical techniques including Linear and Tafel polarization were used to evaluate the barrier resistance properties of the coating. Since chemical dissolution of Zn occurs in both acidic and alkaline media, corrosion testing was performed in 0.5 M Na₂SO₄ and 0.5 M H₃BO₃ solution at pH 7.0. The electrochemical characterization was done using an EG&G PAR model 273A potentiostat/galvanostat interfaced with a computer and a three-electrode setup. The steel substrate with the coating was used as the working electrode and a platinum mesh was used as the counter electrode. A standard calomel electrode (SCE) was used as the reference electrode. All potentials in this study are referenced to the SCE.

Results and Discussion

In an electroplating process, metal ions are transferred to the cathode and adatoms are formed by the charge transfer reaction and finally incorporated into the crystal lattice. This phenomenon occurs by building up existing crystals (growth of crystals) or creating new one (nucleation). These two steps are in competition and can be influenced by the surface diffusion rate of adatom and the rate of charge transfer reaction. High surface diffusion rates, low population of adatoms caused by slow charge transfer reaction and low overpotential leads to the growth of crystals, while conversely low surface diffusion rates, high population of adatoms, and high overpotential increases the rate of nucleation [26]. The nucleation rate [27] is given by

$$J = K_1 \exp\left[\frac{-bs\varepsilon^2}{zekT\eta}\right]$$
[1]

where K_I is the rate constant, b is the geometric factor depending on the shape of the 2D cluster (b=P²/4S, where P is the perimeter and S is the surface area), s is the area occupied by one atom on the surface of the nucleus, ε is the edge energy, k is the Boltzmann constant, z is the electronic charge of the ion, e is the charge of the electron, T is the temperature. The overpotential, η , is given by the Tafel expression,

$$\eta = \alpha + \beta \log i \tag{2}$$

where α and β are constants and *i* is the current density. From the above equations it can be seen that as the applied current density increases the overpotential increases, which in turn according to Eq. 1 increases the nucleation rate.

When compared to direct current (D.C) deposition, pulse electrodeposition enables higher cathodic current density to be applied at the electrode interface due to higher concentration of metal ions at the surface of electrode. A simple diffusion model was suggested in literature to interpret theoretically the pulse and D.C. deposition processes [28, 29]. The current wave form of pulse deposition is shown in Fig. 1. Pulse electrodeposition has three independent variables, namely, on time (θ_1), off time (θ_2) and peak current density (i_p). The duty cycle is defined as follows

Duty cycle (%) =
$$\frac{\theta_1}{\theta_1 + \theta_2} \times 100$$
 [3]



Figure 1: Current waveform and pulse deposition parameters.



Figure 2: The ratio of limiting current density between pulse electrodeposition and direct current electrodeposition with respect to pulse period and duty cycle.

The ratio of the limiting current density in pulse electrodeposition $(i_p)_1$ and D.C. plating $(i_{dc})_1$ was determined by Cheh [27] and is given below.

$$\frac{(i_p)_l}{(i_{dc})_l} = \frac{1}{1 - \frac{8}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{(2j-1)^2} \cdot \frac{\left(\exp\left[(2j-1)^2 a\theta_2\right] - 1\right)}{\left(\exp\left[(2j-1)^2 a\theta\right] - 1\right)}}$$
[4]

where $a = \pi^2 D / 4\delta^2$ (sec⁻¹) is the diffusion parameter. This ratio for various values of $a\theta$ (pulse period) and θ_1/θ (duty cycle) are plotted in Fig. 2. The result shows that the limiting current density of pulse electrodeposition is always higher than D.C. electrodeposition. And the electrodeposition can be carried out at a higher current density by decreasing the pulse periods or by decreasing the duty cycle. According to equation 2, the larger the current density, the higher is the overpotential. Thus, the nucleation rate increases resulting in a finer crystal grain.



Figure 3. Composition variation with peak current density (duty cycle 0.1)



Figure 4. FESEM micrograph of NiZn deposit (ip = $300A/dm^2$ peak, duty cycle = 0.1)

Figure 3 shows the effect of peak current density on the composition of Ni-Zn deposition at constant duty cycle. Composition variations show an increase in the weight percent of zinc with increase in the peak current density. Figure 4 shows the FESEM micrograph of Ni-Zn sample at prepared at a peak current density of 300A/dm². FESEM micrograph indicates the presence of dendritic growth on the surface. Also careful analyses of the micrograph show the presence of nanostructured particles underlying the dendritic growth. The decrease in the particle size is due to increase overpotential arising due to higher applied peak current density. However the formation of dendritic growth indicates a depletion of electroactive species at the interface. The increase in the average current density leads to the formation of dendritic growth. Also increase in avg. current density has lead to the increased content of zinc in the deposit which is not desired for the present case.

Figure 5 shows the variation in composition of Ni-Zn deposits with peak current density (avg. current density being constant). Peak current density was increased with decrease in duty cycle. The nickel content in the deposit increases with increase in peak current density. Also the particle size decreases in accordance with the theory stated before. Figure 6 shows the SEM micrograph of a Ni-Zn sample deposited at $300A/dm^2$. The grain size of the deposit is in the order of 70-80nm. These nanostructured deposits produced at high current density have nickel content as high as 50%. The increase in nickel content can be attributed to the increase in t_{off} with decrease in duty cycle. In the rest period of a pulse deposition, deposition of nickel occurs with the dissolution of zinc. This behavior is well known as substitution reaction arising due to the difference in thermodynamic potentials. Thus nanostructured deposits with increased nickel content were obtained at high peak current densities. Efforts to increase the nickel content further and decrease the particle size are being currently pursued. The results will be summarized at AESF SURFIN 04.







Figure 6. FESEM micrograph of NiZn deposit ($ip = 300A/dm^2 peak$, duty cycle =0.01)

Corrosion Characteristics of the Coating:

As the whole endeavor of this work is to develop a sacrificial coating that can replace Cadmium coatings, it is critical to compare the performance of the nanostructured Ni-Zn coating to Cadmium and other sacrificial coatings. The coatings that have been chosen for comparison in this study are Zinc, Zinc-Nickel and Cadmium, for these are the most commonly used sacrificial coatings for protection of steel. The thickness of the various coatings was kept constant at 2 μ m for these comparison studies.

Linear Polarization Studies:

Linear polarization studies were carried out to determine the polarization resistances of the various coatings. Linear polarization studies were carried out on Cd, Zn, conventional Zn-Ni and nanostructured Ni-Zn alloy coatings. The nanostructured Ni-Zn alloy presented for comparison was pulse deposited from alkaline sulfate electrolytes at a peak current density of 300A/dm^2 . The potential was swept linearly from + 10 mV to -10 mV vs. E_{corr} at a scan rate of 0.5 mV/s. The resulting graphs of overpotential vs. current density for Ni-Zn and various Zn-Ni alloy coating are shown in Figure 7. The slope of these lines yields the value of the polarization resistance. The slopes of overpotential vs. current density plots are very high for the Ni-Zn alloys suggesting that they have excellent barrier properties. The low polarization resistance of the Zn and Zn-Ni alloy suggests a high corrosion rates for these coatings in comparison with electrodeposited non-anomalous Ni-Zn alloy. The resistance values in the case of electrodeposited Ni-Zn alloy were five times higher than those of the cadmium coatings.



Figure 7. Linear polarization plots for the various sacrificial coating.

Figure 8 shows the corrosion rates of the various coatings in the form of a bar plot. It can be readily seen from the plot that the corrosion rate for the nanostructured Ni-Zn (28-wt% Zn) coatings is five times lower than Cd coatings. These studies show that the nanostructured Ni-Zn coating possesses superior corrosion characteristics as compared to the other sacrificial coatings.



Figure 8. Comparison of corrosion rates for various alloy coatings

Conclusion

Composite Ni-Zn alloys with different amounts of Zn were prepared by controlling the deposition parameters such as average pulse current density, pH and amount of ZnSO₄ in the bath. Material characterization studies on the resultant coatings showed the co-deposition of Zn and Ni and the coatings were nanostructured. The decreased grain size was achieved by optimizing the pulse plating parameters. The Zn content in the alloy can be controlled by varying the applied pulse current density. Electrochemical characterization studies reveal that composites with 50% Ni have rest potential more electronegative to steel and hence are applicable as a sacrificial coating for the protection of steel. The high Ni content (50-wt%) ensures the superior corrosion resistance of the composite alloy as compared to conventional Zn-based coatings obtained by electrodeposition. Polarization resistance studies reveal a four-time increase in the resistance value for the nanostructured Ni-Zn coating over that of Cd. The low potential difference that exists between the coating and the substrate results in a lower dissolution rate for the deposited alloy as compared to Zn, Zn-Ni and Cd coatings. Owing to its excellent corrosion properties, this new nanostructured Ni-Zn alloy can be considered as an ideal replacement for cadmium coatings.

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Nano-Crystalline Tin Alloy Layers as Corrosion Inhibiting Coatings

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Several tin alloys, including tin-zinc, tin-cobalt and tin-silver, for use as nickel-free corrosion inhibiting coatings, were deposited from organic-additive-free plating baths using pulse reversed plating to produce nanocrystalline metal layers. The influence of plating conditions on the elemental composition of the deposits as well as their influence on the structure is presented. Electron microscopy, with energy-dispersive x-ray spectroscopy, atomic force microscopy and X-Ray diffraction results are shown. The corrosion resistance was determined by both electrochemical methods and salt spray tests.

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Functionalized Metal Layers by the Combination of Pulse Deposition & Incorporating Nano-Particles

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Changing the properties of metal plated surfaces by combining pulse deposition with dispersion coatings offers numerous opportunities in the electronics and automotive fields. This paper covers several possible uses for codeposited nanoparticles within electrodeposited metal layers. Different materials were investigated, including. silicon carbide, zirconia, boron carbide and diamonds in combination with a copper, gold, tin or nickel matrix. The techniques of deposition, especially the influence of the pulse sequence on the particle incorporation, will be discussed as well as the resulting surface properties.

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HVOF Thermal Sprayed Nanoceramic-Reinforced Protective Polymer Coatings with Improved Wear Properties

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Polymers reinforced with nanoscopic ceramic particles exhibit dramatic improvements in the wear properties of protective polymeric barrier coatings. Work with nylon 11/silica materials showed that the high velocity oxy-fuel [HVOF] technique can be used to spray 5-15 vol. % nanoreinforced coatings that exhibit improved scratch resistance, modulus etc., and decreased permeability compared to pure polymer coatings. The properties were found to depend on reinforcement volume fraction, reinforcement type, polymer powder size and crystallinity. Background on thermal spraying of polymers and polymer/nanoceramic composites, as well as important mechanical properties arising from the nanoscopic reinforcement will be reviewed. Recent work on crystallinity development in sprayed, reinforced nylon 11, pure and filled polycarbonate [PC] (an amorphous matrix material) and on multiple scales of ceramic reinforcement will be discussed. Improved properties have again been observed in each case.

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Introduction

The potential of polymer nanocomposites for improved physical properties has attracted a great deal of attention. Mechanical properties, such as modulus or scratch resistance, and barrier properties, such as permeability, can show dramatic improvements over pure polymer or traditional composites [1-11]. For example, Sumita et al. demonstrated that 20 wt. % of 7 nm silica reinforcement in semicrystalline nylon 6 increased the yield stress by 30% and Young's modulus by 170% compared to pure polymers, while micron sized inclusions decreased the yield stress and only marginally increased the modulus [1]. They observed similar effects of nanosized fillers in polypropylene: dynamic storage modulus increased by almost 100% with the addition of 20 wt. % of 7 nm silica particles while upon addition of the same amount of 200 µm glass particles dynamic storage modulus increased only by 20% [2].

An important technical challenge, however, in the practical use of nanocomposite coatings is achieving a uniform dispersion of nanoparticles. Incorporating as much as approximately 5% of nanoceramic generally causes a high melt viscosity [5,6]. Processing higher volume fractions usually requires special measures: large amounts of solvent (20 to 60 vol. %) [5], high processing temperatures, or in-situ polymerization [6]. Filler volume, particle geometry and size all have effects on the viscosity of filled melts that may introduce additional difficulties.

Thermal spray is a solution for overcoming these processing limitations. Previous results have demonstrated that the HVOF combustion spray technique allows solventless processing of ceramic reinforced polymers [7]. In HVOF, a powder is heated, accelerated and propelled by a high temperature jet through a confining nozzle toward a surface. The individual molten or softened droplets impact, spread, usually called "splatting", cool and solidify to form continuous coatings. Particle heating, quenching, consolidation and post-treatment are thus combined into a single step process in which relatively thick coatings, up to several millimeters, can be produced. At each step of HVOF spray, there are decisions affecting structure development. These include co-spraying two materials with potentially different inertias, and matrix melting and restructuring during heating and impact. This paper discusses some of these structure considerations.

Background

Nanocomposites

One explanation for the improvements of nanocomposites above standard micron-scale fillers involves load transfer at the particle/matrix interface. Even in fairly compatible systems with good bonding between the matrix and microscopic particles, the particle interface curvature can lead to loads exceeding the mechanical strength of the interface. Due to the small size of the nanoscopic particles, a small fraction of the load borne by the material is transferred to individual particles, as shown in Figure 1. Thus, each particle bears a smaller part of the load; not enough to overwhelm the interface. In this manner, nanoscopic particles can reinforce the matrix more effectively than microscopic ones do. This is also consistent with prior work that showed that the properties in standard, particulate-reinforced composites improved as the bonding between the matrix and the particles improved, to at least a limited extent.

The mechanical properties show improvement as the size of the reinforcements decrease [8]. Figure 2 shows the results of nylon 11 coating scratch testing, a surface mechanical property important in assessing the durability of protective coatings. Reinforcement with 7 nm particles resulted in coatings with a 40% larger scratch resistance than that of the 100 μ m reinforced coatings, and about 50% relative to pure polymer.



Figure 1. Force is transmitted to the particle from the matrix across the interface.



Figure 2: Scratch depth as a function of reinforcement particle size using a 2 kg load. The matrix is nylon 11, with 10% of silica reinforcement. The dashed line is a trend line included for visualization purposes.

Thermal Spray

Prior results [7-10] have shown that thermally sprayed nanocomposites exhibit improved scratch and wear resistance upon addition of nanosized filler and that these properties depend on optimized filler particle distribution and on the degree of crystallinity of the polymer matrix. Further, evidence also suggests that greater amounts of reinforcing material in the coatings significantly improve the mechanical properties [1,10,11].

HVOF spray uses a thermal jet to soften or melt a particle and accelerate it toward a surface where the drop will impact, spread, cool and solidify to form continuous coatings. Figure 3 shows the major features of an HVOF spray torch. HVOF has been demonstrated to be a method for creating high performance composite coatings. Many polymers have been deposited, including polv(ether ether ketone) (PEEK) and poly(phenylene-sulphide) (PPS) [12]. poly(ethylene terephtalate) (PET) [13] and polycarbonate [14]. There have been reports on spraying composites, mainly micron-sized filled polymers via plasma spray, including Al₂O₃, SiO₂ filled epoxy [15], Al₂O₃ and NiCr filled EMMA



Figure 3. Schematic of the HVOF Thermal Spray Process.

[16], and glass, Al₂O₃, SiO₂ filled nylon 11 [17]. Experiments on nanocomposites [9,10], multiple scales of composite [8], and graded composites where the volume fraction of reinforcement increases with proximity to the surface [18] have demonstrated potential for further improvements. The properties of thermally sprayed coatings depend on numerous processing parameters. The time during which a particle resides in the jet, dwell time, along with the jet velocity and temperature determines the degree of particle heating.

Powders can be fed through the spray torch or introduced to the flame at the nozzle exit. Cospraying two powders, as in the case of composites, can result in inhomogeneities in the coating when the filler and polymer powder are injected separately. Particles of different mass or size have different inertia under acceleration. The difference in density between nanoreinforcements and polymer particles can result in even greater segregation. Further, nanoparticles do not usually flow well through powder feeders. A solution to this is to ball mill the reinforcement with the matrix particles to create a composite feed powder [8-10]. Ball milling embeds the silica into the surface of the polymer particles, as shown in Figure 4. Some optimization of this ball milling is discussed in the research below. Alternatively, the nanoparticles may be preagglomerated to a size similar to the polymer matrix feed powder, for example tungsten carbide nanoparticles in a cobalt matrix, WC-Co, an emerging high hardness, wear-resistant ceramic. In such a case, the two particles can be either milled to form a composite feed powder, or fed separately. This allows a graded coating to be formed by varying the volume fraction of the ceramic feed as layers are deposited.



Figure 4. SEM image of a single nylon 11 /12 nm fumed silica feed particle. The nylon 11 is ball milled with a nominal 5 $\%_{vol}$ of silica. An approximately 4 μ m thick, silicon rich layer forms on the outside of the particle.

The particle velocities achieved in the HVOF process, around 1,000 m/s depending on the particle density and size, are significantly higher than in conventional flame spray, 50-100 m/s, or plasma spraying, up to 800 m/s [19]. This results in large deformation of the particles on impact at the substrate, even if the particles are still relatively viscous, producing denser coatings. Thus, polymers can be processed below their degradation temperatures. Impacting, heated particles become flattened, disc-like structures called splats, which spread over the substrate surface and fill underlying interstices. The characteristic "layered" splat structure can be observed across the cross-section of the thermal spray coatings. Splat structure is indicative of the degree of particle melting achieved during flight. Figure 5 shows predicted temperatures based on thermal modeling for 30 µm nylon 11 particles as a function of travel rate and distance [19]. Particle velocities are important since higher particle velocities imply higher particle impact energy. This leads to better splatting, resulting in better coating adhesion and higher deposit densities. Higher particle velocities also result in shorter dwell times, leaving less time for particle heating. Higher particle velocities and lower jet temperatures result in well-densified coatings, good adhesion to the substrate and more uniformly dispersed coating structures. The coating distribution is further described below.



Figure 5. Calculated increases in reduced radial temperature profile as a function of reduced radius for an idealized 30 μ m nylon 11 particle at velocity $v_p = 1410$ m s⁻¹ and at travel distances of: 1) 0.28 m, 2) 0.14 m and 3) 0.08 m. T_d is the degradation temperature, T_m is the melting temperature.

Property	Nylon 11	PC	PMMA	HDPE
Compressive Yield Strength [psi]	7,300	10,000	16,000	3,250
CTE [-]	100 x 10 ⁻⁶	68 x 10 ⁻⁶	70 x 10-6	84 x 10-6
Flexural Modulus [ksi]	110	330	600	185
Shrinkage [in/in]	0.012	0.006	1.7	0.028

Table 1: Some Properties of Some Sprayable Polymers

The temperature profile leads to the suspicion that only a portion of the particle is in the thermal processing window, due to the low thermal conductivity of the polymer. While this also allows the polymer to be processed by HVOF without significant degradation, there can be structural implications on the coatings. Partial melting may lead to lower deposit densities, more particle "blow by", and a higher percentage of unmelted or partially melted particles included in the coating. However, even viscous polymer particles can be well splatted on the surface due to the high kinetic energy of the supersonic gas. A critical diameter exists above which complete melting of the particle will not occur [19]. A typical thermal spray powder size ranges from 45 to 90 μ m for most metals and polymers, and from 10 to 45 μ m for higher melting materials. The partially molten polymer can be quenched as it strikes the surface. This can lead to reduction of the coating crystallinity or to the formation of meta-stable structures. Metastable states have been identified in HVOF sprayed coatings, as described below.

Methods

Materials

Choice of matrix material for HVOF sprayed coatings is driven first by bulk properties. Table 1 shows properties of some polymers that have been thermally sprayed [20]. Table 1 shows that both amorphous and single crystalline polymers have been sprayed. This paper focuses on: 1) Nylon 11, a semicrystalline thermoplastic, 2) polycarbonate, an amorphous polymer with some liquid crystallinity, and 3) a thermosetting polyimide.



Figure 6. Two crystal structures of nylon 11: a) the stable, triclinic aunit phase and b) the metastable γ unit phase. In a), the hydrogen bonding is regular, whereas in b) the bonding is random

Nylon 11 is an aliphatic, semicrystalline polyamide with two crystal forms, as shown in Figure 6 [21]. Nylon 11 ("French Natural ES", Atofina) powder with a nominal particle size of 60 μ m was used as the matrix for the composite materials. Nylon 11 is an industrially important material which exhibits high chemical resistance and a wide processing window - melting at ~183°C and degrading at much higher temperatures (~360-550°C). Examples of applications include printing rollers and splined drive shafts, airport luggage trolleys, outdoor furniture, and

marine hardware such as boat ladders and diving tanks. Polycarbonate (PC), on the other hand, is a common, amorphous engineering polymer material with some evidence of liquid crystalline structure, shown in Figure 7 [20]. Polycarbonate was chosen for direct comparison with the nylon 11 because of its amorphous structure and hetero-atom backbone. A Selective Laser Sintering (SLS) quality of Polycarbonate (PC) powder donated by DTM Corporation, Austin, TX, was used for processing. The particle size range was broad, at $175 \pm 30 \mu m$. Finally, polyimide is an aromatic, heterocyclic, high-temperature polymer that is being used for the construction, automotive and aerospace industries [20]. The properties come from strong intermolecular forces between the polymer chains formed during cross-linking. The powder is received in the B-stage courtesy of NASA. The secondary cross-linking reaction is initiated at 300 °C, generally achieved by a combination of substrate heating in the thermal jet and by direct substrate heating. The polyimide is considered here as a cross-linked comparison material.



Figure 7. X-ray analysis of the structures formed by polycarbonate. PC cooled at normal conditions allows rearrangement of the chains to form an amorphous solid with an amorphous halo centered about 2Θ of 18° . With quenching, peaks at 8° and 45° are observed due to spontaneous alignment of the relatively stiff chains in the liquid phase. The peak at 18° was present in the quenched material, but with sufficient time to cool, this peak becomes the dominant feature.

Three classes of reinforcement have been explored: 1) dispersed, 2) high aspect ratio, and 3) agglomerated. Silica, found in products ranging from paints and printing inks, tires, polymer composite materials used in aircraft and computers, to personal items such as protective helmets and utensils, was selected as a typical spherical nanoreinforcement. Various types of silica from the Aerosil and Sipernat line produced by Degussa Corporation were used to evaluate particle size and surface compatibility issues. By comparison, traditional composites are often reinforced with fibers. The effect of creating composite feedstocks with high-aspect ratio reinforcement (IM-6, Hercules) consisted of fibers with a nominal 7 μ m diameter. These were cut to 1-3 cm length. Two forms of nanotubes, with and without non-graphitic coatings were used. Pyrograf PR-19-PS nanotubes (Applied Sciences, Inc., Cedarville, OH) consist of graphite cores with turbostratic carbon overcoats. These nanotubes were 150 nm diameter, 1.95 g/cc specific gravity, and surface area of 15-25 m²/g. Pyrograf PR-24-PS nanotubes had no carbon overcoating, a nominal 60 nm

diameter, 1.5 g/cc specific gravity, and 50-55 m^2/gm surface area. Finally, incorporating agglomerated particles was explored using 88/12 WC-Co feedstock powders (Stellite Coatings, Inc. JK-112).

These particles had nominal particle size ranges of $(-150, +102 \ \mu\text{m})$ and $(-44, +22.5 \ \mu\text{m})$, respectively. Composite coatings were sprayed using nominal 50:50 and 90:10 Vol. % polyimide/WC-Co blends of the two materials.

Spray Conditions

A Stellite Coatings Jet Kote II[®] HVOF combustion spray gun with internal powder injection and a 0.076 m long and 0.008 m \emptyset nozzle, was used to spray the composite powders. Typical processing parameters, are listed in Table 2.

Ball Milling

Samples of polymer and hydrophobic silica particles of various types were mixed for ball milling. In addition to the various feed powders for structure analysis, mixtures ranging from 10 - 50 $%_{vol}$ silica with particle sizes ranging from 7 nm to 10 μ m were milled to explore the rate of incorporation. Mixtures were milled using an Amoco 115 Volt ball mill for up to 48 hours. Materials were milled with about 500g of Al₂O₃ balls at a speed of 60 rpm, or an equivalent process. Samples were removed and analyzed for silica content by ashing in a flame and microscopic analysis.

Structure analysis

Coating microstructure was evaluated using optical microscopy. Coated substrates were sectioned, mounted in a slow curing epoxy and polished using a series of SiC papers on an automated polishing ma-chine. The materials were then examined using Olympus inverted metallographic microscope, or sputter coated with gold-palladium and examined in an FEI/Philips CROSS-LINK-30 Field Emission Environmental Scanning Electron Microscope. Coatings were also re-moved from the substrates and evaluated using a Siemens model D-500 X-ray Diffraktometer. The diffraction pattern was obtained for 2θ scans ranging from 5° to 70°.

Parameter	Nylon 11	Polycarbonate	Polyimide
Powder Feed Rate	0.25 g/s	0.25 g/s	0.05 g/s
Powder Carrier Gas	Nitrogen	Nitrogen	Nitrogen
Powder Carrier Gas Flow	$0.5 x 10^{-4} m^3/s$	$0.5 \times 10^{-4} \text{ m}^3/\text{s}$	$0.5 \text{ x } 10^{-4} \text{ m}^3 \text{s}^{-1}$
Gun Surface Speed	0.23 m/s	0.23 m/s	0.11 ms ⁻¹
Spray Distance	0.2 m	0.18 m	0.15 m
Oxygen Flow	0.66 m ³ /s	0.47 - 0.62	$0.6 - 0.7 \text{ m}^3/\text{s}$
Hydrogen Flow	0.28 - 0.31 m ³ /s	0.28 - 0.31 m ³ /s	$0.3 \text{ m}^3/\text{s}$
Hydrogen/Oxygen Ratio	0.63 - 0.65	0.5 - 0.6	
Substrate Temperature	≈ 15 - 20 °C	No control	300 −340 °C
Powder Feed	Internal	Internal	External

Table 2:	Sprav	parameters	for th	he denositio	on of Nvi	lon 11	with silica	reinforcement
1 4010 2.	Spray	parameters	joi in	ie aepositie	$m O j \perp i y i$		with stice	

of the ball miller	i sumples.			
Silica	Size	%vol	Ball Mill	Percent
			Time (hrs)	Incorporated
Aerosil 300	7 nm	10%	0.5	15.2 <u>+</u> 1.5%
			1	13.5 <u>+</u> 1.6%
			2	13.7 <u>+</u> 1.3%
			4	12.1 <u>+</u> 1.8%
			8	15.8 <u>+</u> 1.0%
Aerosil 300	7 nm	30%	0.5	32.2 <u>+</u> 2.7%
			1	28.4 <u>+</u> 1.4%
			2	29.0 <u>+</u> 2.6%
			4	32.6 <u>+</u> 3.8%
			8	29.6 <u>+</u> 0.5%
Aerosil 300	7 nm	50%	0.5	54.4 <u>+</u> 4.7%
			1	53.8 <u>+</u> 1.2%
			2	52.5 <u>+</u> 1.7%
			4	51.8 <u>+</u> 1.4%
			8	53.1 <u>+</u> 0.8%
Aerosil 200	12 nm	50%	0.5	47.3 <u>+</u> 3.3%
			1	48.1 <u>+</u> 1.9%
			2	47.7 <u>+</u> 0.5%
			4	49.3 <u>+</u> 3.4%
			8	47.6 <u>+</u> 6.4%
Aerosil R972	16 nm	50%	0.5	59.7 <u>+</u> 2.9%
			1	56.9 <u>+</u> 0.8%
			2	57.7 <u>+</u> 1.6%
			4	57.0 <u>+</u> 1.6%
			8	59.7 <u>+</u> 2.1%
Aerosil	40 nm	50%	0.5	58.6 <u>+</u> 2.9%
OX50			1	56.5 <u>+</u> 2.3%
			2	57.7 <u>+</u> 1.5%
			4	55.6 <u>+</u> 0.5%
			8	56.8 <u>+</u> 2.0%
			16	55.7 <u>+</u> 1.3%
			32	57.5 <u>+</u> 4.5%
Sipernat 50S	10 µm	20%	24	26.8 <u>+</u> 1.8%
			48	26.8 <u>+</u> 2.1%

Table 3: Volume percentage of silica found by ashing for each of the ball milled samples.

Results

Incorporation During Ball Milling

Ashing was performed to find the volume percentage of silica in mixtures of varying particle size and ceramic volume loading levels. The weight of ash remaining after heating each sample was converted to volume. The values obtained for each powder and ball mill time are summarized in Table 3. There was no significant change observed in the volume percentage of silica incorporated beyond thirty minutes.

Ash testing indicated that no significant changes occurred in the quantity of embedded silica after the first thirty minutes of ball milling. One finding was that the amount of silica obtained by ashing was occasionally slightly higher than that added to the original mixture. The error is larger for larger silica particles and for lesser fractions of silica. There are several possible explanations for this effect. First, the silica forms a capsule around the nylon. For the large particles, on the order of the size of the nylon, if two particles of silica bind to one nylon particle, and since the silica is the denser phase, an abnormally dense composite particle will be observed. Also, if some of the nylon particles are coated with silica to the point of inhibiting oxygen transport to the burning polymer, some graphitization may result, increasing the net weight of ash. Finally, the volume conversion uses ideal densities, which may introduce a systematic error.

Scanning electron microscopy led to different conclusions than ashing. The particle crosssections indicated thicker coatings had formed on the nylon particle surfaces with extended ball milling times. Surface images of the particles also showed thicker and denser coatings on the particles that had been ball milled the longest. SEM indicated that the optimum milling time for maximum incorporation is between 16 and 32 hrs, regardless of particle size or volume loading.

Changes in the appearance of the powders offered other indications of the physical changes occurring during ball milling. The presence of airborne silica indicated that silica had not been embedded. The amount of airborne silica decreased as ball milling time increased, which indicated that more material was continuously being embedded. Decreases in the milling volume indicated that the composite particles were being continuously compacted by ball milling. Both physical changes were clearest up until four hours of ball milling had been completed.

Results with high aspect ratio fibers

The film formed from a hand-mixed nylon/graphite fiber combination was marble-patterned, as shown in Figure 8. Regions of white indicated pure Nylon 11, areas with black contained graphite fibers. This mixture would be unlikely to exhibit good spray parameters, due to the mismatch in both shape and mass that would be expected to result in material segregation during spray.



Figure 8. Pattern formed by hand-mixed 90% nylon 11 powder and 10% 7 µm carbon fiber materials by compression molding.



Figure 9: Ball-milled mixture of 90% nylon 11 powder and 10% 7 µm graphite fiber exhibiting clumping.



Figure 10. The relative sizes of a) 60 μ m nylon 11 particles, b) and c) 7 μ m graphite fibers, and d) 150 nm carbon nanotubes.



Figure 11. Test plaque made from ballmilled 90% nylon 11 powder and 10% 7 µm carbon fiber.



Figure 12. Plaques made from 90% nylon 11 powder and 10% a) PR-19-PS and b) PR-24-PS nanotubes.

During ball milling, the fibers seemed to be broken down, forming a gray composite powder. The powder contained some large clumps, shown in Figure 9. The clumps are the combined function of the size and shape relationship between the graphite fibers and the nylon 11 particles, as illustrated in Figure 10. The nominally 60 μ m nylon particles are nearly 10× the diameter of the graphite fibers. This allows multiple fibers to adhere to a single nylon particle. The carbon fiber, at around 10,000 μ m in length, can in turn bind more than one nylon particle. The chances of two carbon fibers bound by one nylon particle binding to a second nylon particle is nearly twice as large as the chances for one fiber; the chances for one of two nylon particles attached to the same fiber binding a second carbon fiber is twice as large in turn as a single nylon particle. In this manner, each clumping step increases the chances that the clump will grow in favor of creating singlet nylon/fiber pairs. This interaction should be experimentally verified by changing



Figure 13. SEM mage of a 7.5% vol. PC/Silica coating: The light, thin regions, which are silica rich boundaries between polymer particles (confirmed by EDS dot mapping, shown in Figure 7).



Figure 14. Spectroscopy (EDS) dot-map shows that the silica nanoparticles remain localized on the surface of the polymer particles.

the initial lengths of the carbon fiber. Further, through rational application of statistics based on the available surface area, there may be a way to calculate length and diameter ratios that should eliminate or limit the

quantity of clumping. The resulting plaque formed had a visually more uniform distribution, shown in Figure 11.

The ball milled mixtures of nylon and nanotubes did not exhibit the clumping observed for standard fibers, due in large part to the much shorter fiber lengths. The plaques made from these powders were visually uniform. These powders show promise as a source of thermal spray powders. Plaques yielded by compression molding were visually uniform, as shown in Figures 12 a and b.

Spraying Polycarbonate

Figures 13 and 14 show the distribution of silica in HVOF sprayed PC. The silica, originally ball-milled onto the surface of the polymer particles, remains in a silica-rich boundary layer between the lamellae formed by the polymer particles. This has been observed in previous work with Nylon 11 [9,19]. The distribution of PC nanocomposites was observed to be more uniform with conditions leading to increased splatting. HVOF tends to form a coating with a lamellar structure [14].

Spraying Polyimide/WCCo

HVOF sprayed 90/10 polyimide/WC-Co coatings, with the polyimide fed internally and the WC-Co fed externally, are shown in Figure 15. The coatings showed uniform distributions of the WC-Co phase [bright areas] within the polyimide matrix, together with moderate levels of porosity, although some of the larger pores were likely due to "pull-out" during polishing. The B-stage curing was carried out both by allowing the flame to provide sufficient heat and by heating the substrate.



Figure 15. Optical micrographs of 90 % polyimide/10 % WC-Co composite coatings on steel. There appears to be some loss of the WC-Co during the spray process and perhaps through particle pull out during sample preparation.



Figure 16: X-ray diffraction of the sprayed composite coatings. [---] 7 nm, [---] 20 nm, [---] 10 μ m, [---] 100 μ m.

7000 6000 PC coating 5000 PC powder Intensity 4000 3000 2000 1000 0 0 20 40 60 80 20 [degrees]

Figure 17. X-Ray of the as-received PC powder and an HVOF sprayed coating. There is a slight increase in the size of the liquid backbone alignment at 8° and 45° peaks in the sprayed coatings.

Spraying Nylon 11

Figure 16 shows x-ray patterns for sprayed coatings with 4 nm, 20 nm, 10 μ m, and 100 μ m silica particles. All four coatings exhibit significantly different profiles from the pure (sprayed) nylon coating and from each other, as well. X-ray diffraction curves of nylon 11 exhibit characteristic peaks at the 21° and 23.4° positions of 2 Θ , reflections (100) and (010), respectively, as expected for nylon 11 [22]. The presence of these well-resolved peaks is typical for crystalline nylon with the triclinic α -form of the crystal structure. A shift in the (010) peak to a lower angle corresponded to larger spacing between hydrogen-bonded sheets of nylon chains, indicating a decreasing crystalline perfection and transition to the pseudo-hexagonal γ phase of the matrix [22]. For all composite coatings, fusing of the two peaks was also observed, which was especially pronounced for the 7 and 20 nm reinforced coatings. In addition, the 7 nm reinforced coatings exhibit a lower angle peak which may be further characteristic of the metastable γ phase. The implications of the x-ray patterns are still under consideration.

Spraying Polycarbonate

In Figure 17, x-ray analysis of the as received polycarbonate powder and a thermally sprayed coating, shows that the 8° and 45° peaks indicating a quenched, metastable aligned structure were nearly completely suppressed for the as-received powder. After HVOF spray, the sprayed coatings showed reassertion of these peaks, and these melt structures were "frozen in" during the splat deposition. These changes did not show correlation with the presence or absence of silica reinforcement, and so appear to be a feature of the semi-molten processing of the HVOF technique.

Conclusions

Thermal spray provides an alternative technique for depositing thick coatings of amorphous, semicrystalline or even cross-linked polymers reinforced with large volume fractions of nanoreinforcements.

The composite spraying powder approach is suitable for spherical and high aspect ratio nanoparticles. Optimization studies show that up to 50% by volume of spherical particles can be incorporated in between 16 and 32 hours. The silica was loosely incorporated very quickly, within about 30 min, but further milling was required to densify the coating sufficiently to survive the spraying process. Milling carbon fibers indicated that clumps are readily formed, but milling carbon nanofibers proved successful in creating a sprayable powder.

Composite coatings can result in a lamellar structure with reinforcement rich zones in the final coating. Spray parameters and material choice may be useful in minimizing this effect. Under circumstances where the polymer and ceramic powders are of similar size, both powders can be fed separately to obtain a well-dispersed coating.

Modeling and coating distribution indicate that polymer powders are only partially melted while transiting the jet. Since fully dense coatings are obtained, it is believed that the high velocity provides the remainder of the energy for deposition. Splatting on a cold substrate with high thermal conductivity, such as a metal, can result in quenching. The combination of partial melting, large deformation during impact, and quenching can result in metastable states with a potential for changes in mechanical and barrier properties.

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