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Electrodeposition of Nickel/Montmorillonite Layered Silicate Nanocomposite Thin Films

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In this study, the electrochemical deposition of nickel/montmorillonite nanocomposite films was investigated on stainless steel and copper substrates. Deposition variables that were investigated included electrochemical cell orientation, degree of agitation during deposition, and montmorillonite concentration in the electroplating solution. The resulting films were characterized with scanning electron microscopy, X-ray diffraction, and X-ray fluorescence techniques. By a novel electrochemical cell construction, an orderly deposition of nickel/montmorillonite nanocomposite films was ultimately achieved. Scanning electron microscopy images characterized these films with an ordered surface topography of horizontal montmorillonite platelets held in a nickel media. Profile scanning electron microscopy images further showed a heavily striated stack of aligned montmorillonite layered silicate platelets throughout the profile of the nickel/montmorillonite nanocomposite film. Also, X-ray fluorescence verified the presence of montmorillonite clay within the films, and nanoindentation results showed that the nanocomposite films had higher modulus values than nickel films. The green (unsintered) deposited films showed a 60% increase in hardness over that of pure nickel films. Thus, a successful electrochemical deposition of ordered nickel/montmorillonite nanocomposites has been achieved, and the montmorillonite content of these nanocomposites has been shown to strengthen the films when incorporated in a layered fashion.

Introduction

Recent research has shown that nanocomposites can be synthesized from a smectite mineral,[1] montmorillonite layered silicate, with a variety of polymeric host matrixes.[2−6] Montmorillonite has a 2:1 layered structure with a single layer of aluminum octahedral between two layers of silicon tetrahedral (Figure 1). Montmorillonites refer to hydrous aluminum silicates approximately represented by the formula (Na, Ca)(Al, Mg)$_6$(Si$_4$O$_{10}$)$_3$(OH)$_6$·nH$_2$O. The Al^{3+} or Si^{4+} locations can be replaced by lower valent cations, which cause the montmorillonite structure to have an excess of electrons. This negative charge is satisfied by loosely held cations from the associated water. Sodium montmorillonite refers to the clay mineral in which the loosely held cation is the Na$^+$ ion.[7] The individual montmorillonite platelets exist as coordinated layers that measure 1 nm thick and several microns wide. The layers are periodically spaced apart with a repeating distance in the nanometer range, known as the gallery spacing. Depending on the cation exchange capacity of the clay, the hydration of clay leads to an increase in intergallery spacing (Figure 2). To swell the clay into the more hydrophobic polymer host, the clay is treated to render it more organophilic

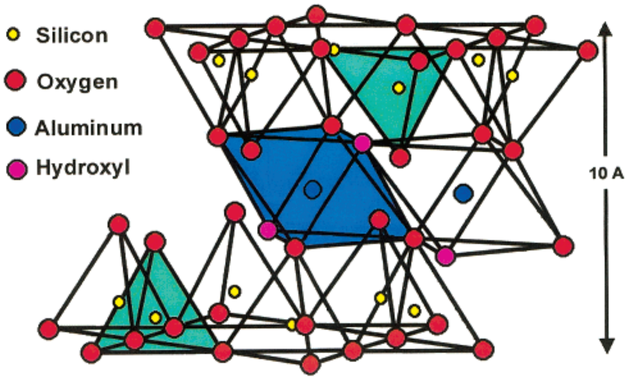

Figure 1. Cross-sectional model of the montmorillonite layered silicate platelet. This arrangement of atoms, called a smectite structure, consists of two inward-facing layers of silicate tetrahedra (light blue) that flank a layer of alumina octahedra (dark blue). The entire platelet is between 7 and 10 Å (about 1 nm) thick, hence the name “nanoclay.”

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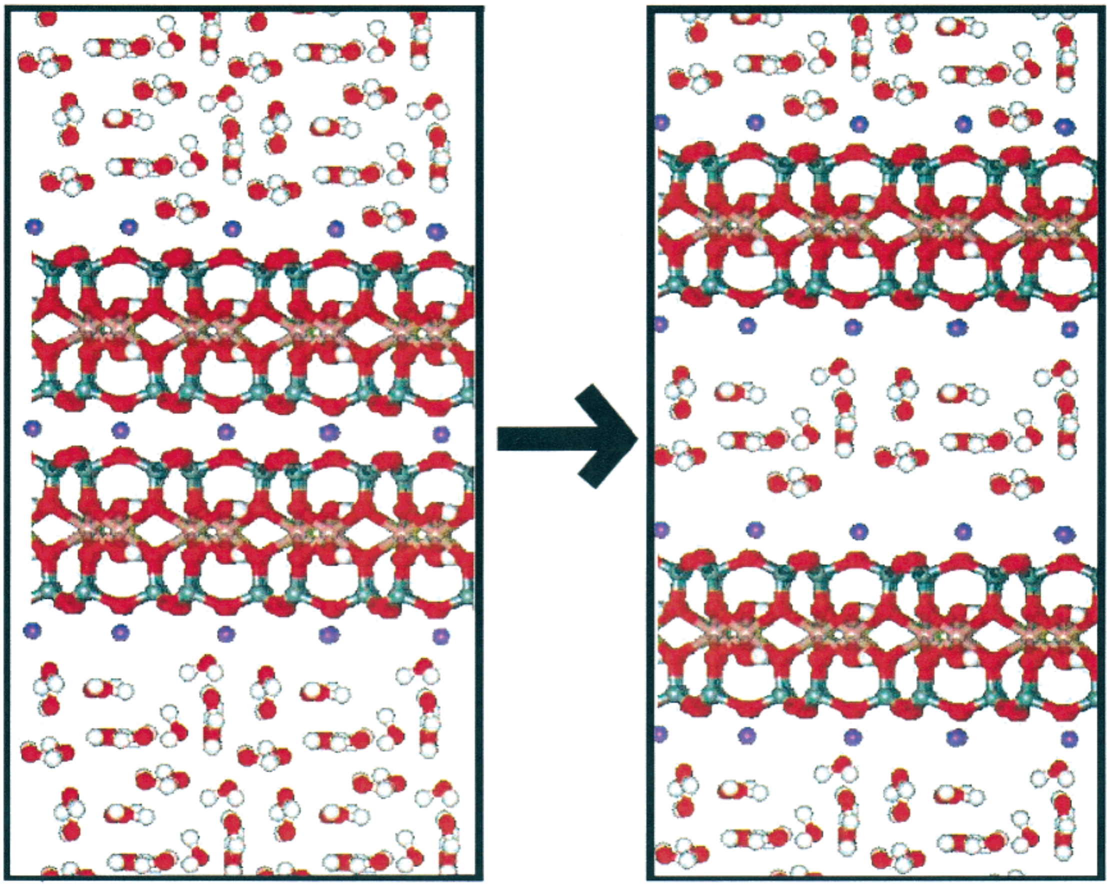

Figure 2. Intercalation scheme of nanoclay mechanics occurring when dissolved platelets (far left) expand their gallery spacing to accommodate intercalants (right). Neutral or cationic species may be intercalated into nanoclay platelets.

through alkylammonium chains. This process of the clay's swelling to incorporate species between its layers is called an intercalated dispersion, and the species that is incorporated is called the intercalant. When a high degree of swelling is accomplished, the van der Waals forces holding the individual layers together are overcome and the individual layers become "exfoliated" or "delaminated".

Structurally, the introduction of a platelet reinforcement with micron dimensions and nanometer thickness results in high aspect ratios—an important parameter in reinforcing materials. These montmorillonite nanoclay platelets are capable of aligning within an epoxy media to form epoxy/nanoclay nanocomposites, which are arrays of elongated molecules linked end-to-end to form strong molecular "chains" that are approximately 1 nm in width. These types of nanocomposites are structurally valuable, as the primary components in advanced plastics, such as those used in dent-resistant car bumpers and ultrastrong epoxies.[5,8]

Development of silicate nanocomposites (composites where at least one dimension of the reinforcement is in the nanometer range) has been done through techniques such as layer-by-layer assembly,[9-11] organometallic substitution and deposition,[12] sintering of powders with mechanical trapping,[13] and the sol–gel method.[14,15] In this paper we investigate another promising mode of synthesis using electrodeposition.

There are several benefits of using an electrochemical process to deposit layered nanocomposites. Montmorillonite, the ceramic nanoclay component of the layered nanocomposites described in this study, does not readily degrade under chemical, pH, or temperature extremes, making it viable under a wide array of electrochemical scenarios and solutions. In solution, the montmorillonite is capable of swelling to incorporate a wide variety of intercalants, which may be neutral or cationic molecules, amphipathic complexes, or organic species. Thus, there is a wide range of electrodepositable species that may be employed in nanocomposite synthesis with montmorillonite; nickel cations were employed in this study to synthesize nickel/montmorillonite nanocomposites. In addition to the benefit of electrochemical diversity, the polar electrochemical deposition environment allows montmorillonite nanoclay platelets to exfoliate in solution and realigned to produce nanocomposite thin films with promising physical properties.

Such electrochemical deposition of montmorillonite nanoclays within a metallic media has been an unex-

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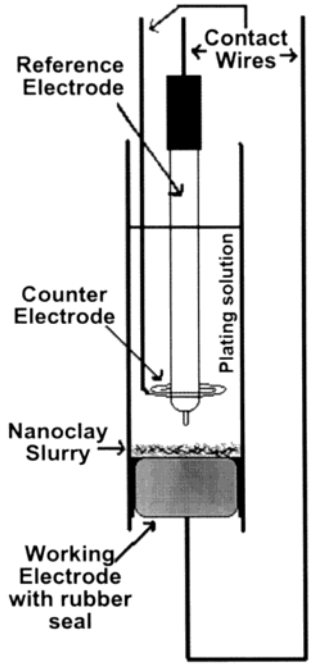

Figure 3. Novel electrochemical cell setup for the electrodeposition of nanocomposites.

plored alternative to the existing methods of nanocomposite deposition. Using basic electrochemical techniques, this study shows that metallic/montmorillonite layered silicate nanocomposite synthesis is achievable within electrochemical environments and is feasible as a synthetic method.

Experimental Details

Electrochemical Cell Construction and Operation. All electrochemical experimentation was performed with an EG&G Princeton Applied Research (PAR Model 273A) potentiostat/galvanostat. All working electrodes (WEs) were constructed from $^{3}/_{4}$-in.-wide, cylindrical epoxy stubs that encased either stainless steel or copper foil connected to a lead wire with conducting silver epoxy. The electrode was then polished until the metal substrate was exposed and flush with the epoxy; all working electrodes were final polished to a mirror finish with 0.05-μm γ-alumina. The counter electrode (CE) was a coiled platinum (Pt) wire or a Pt sheet, and the reference electrode (RE) was a standard saturated calomel reference electrode.

There were three different orientations of the WE, CE, and RE that yielded consecutively improved results. The first orientation was a laboratory-standard, three-electrode method. Operational conditions ranged from −0.9 to −1.1 V (potentiostatic control) at 5−25 mA and were determined by cyclic voltammetry.

The second electrochemical cell orientation involved replacing the platinum wire CE with a small platinum sheet and repositioning the WE to face up in the solution. Because of the new orientation of the WE, the submerged contact wire of the WE was shielded with Nalgene $^{3}/_{16}$-in. tubing to prevent electrochemical plating on the working electrode's contact wire. Operational conditions ranged from −0.9 to −1.1 V (potentiostatic control) at 5−25 mA and were determined by cyclic voltammetry.

The third electrochemical cell orientation was a novel, custom-built columnar cell in which there was no physical agitation of the plating solution. The CE sheet was replaced with a flat spiral wire and RE tip set between the WE and CE. Thus, a static nanoclay slurry formed directly above the surface of the WE (Figure 3). Operational conditions ranged from −0.7 to −0.9 V (potentiostatic control) at 0.1−10 mA and were determined by cyclic voltammetry.

Electrochemical Plating Solution. The nickel electroplating solution consisted of 0.2 M $NiCl_2$, 0.15 M H_3BO_3, and 0.45 M NaCl dissolved in DI H_2O. A predetermined amount of montmorillonite clay was suspended/dissolved into this solution to study its incorporation into the Ni thin films for nanocomposite synthesis. The montmorillonite nanoclay employed was Southern Clay Product's Cloisite NA+, a sodium-doped, supercharged alumina−magnesia silicate that formed an exfoliated suspension in aqueous solutions. The final solution of 0.2 M $NiCl_2$, 0.15 M H_3BO_3, 0.45 M NaCl, and various concentrations of nanoclays is henceforth referred to as the "plating solution".

Analytical Techniques. X-ray diffraction (XRD) was conducted on the nanocomposite samples with a Seimens D500 X-ray diffractometer (Cu Kα wavelength 0.154 056 nm); the filament voltage was 40 kV, and the filament current was 30 mA. X-ray fluorescence results were obtained from a Seimens XRF/4 with a LiF crystal. Scanning electron microscopy (SEM) was conducted with a JEOL JSM-T300 scanning electron microscope at an accelerating voltage of 25 kV and a general working distance of 20 mm. Nanoindentation/wear (NIW) results were compiled from a NANO III nanoindentor (nanodiamond tip) with an attached Nikon optical microscope (up to 800× magnification) that provided optical micrographs.

Results

A unique electrochemical process was employed for the synthesis of nickel/montmorillonite nanocomposite (Ni-MLS) thin films in which nanoclay platelets are doped in situ into a growing nickel thin film. Initially, a standard three-electrode electrochemical cell was used, which yielded unfavorable results. The resultant films were heterogeneous and rarely adhered to the stainless steel substrate of the WE. A copper substrate was later employed, with marginally improved film adherence (due to the lower coefficient of substrate mismatch between the nickel and the copper substrate), but the resultant films were still heterogeneous and difficult to reproduce. During the course of several electrochemical experiments in this standard setup, it was empirically noted that the homogeneity of the deposited thin films was inversely proportional to the stirring rates of the solution; thus, the quicker the solution was stirred, the more heterogeneous the deposited thin films were, and visa versa. It was hypothesized that stirring the solution created abrasive waves of suspended montmorillonite layered silicate (MLS) platelets across the surface of the depositing film on the WE, therefore disrupting the formation of the nanocomposite film. Agitation served to counter sedimentation effects in the suspension. SEM micrographs of films produced at higher stir rates show a few MLS platelets extruding from the surface of the films in a random arrangement (Figure 4). A large number of operational conditions were explored, but the overall results were still unsatisfactory. The XRF results gave 718 counts per second of silicates, with a background of 650 counts per second; thus, there was a low concentration of silicate (nanoclay) mass in the films. Films grown with the stir rate of the solution at an absolute minimum were only quasi-homogeneous and difficult to reproduce, since the MLS suspension in solution tended to settle to the bottom of the electrochemical cell, away from the surface of the WE at the top of the cell (thus removing it from the electrochemical reaction). The resultant films had a powdery appearance, and loosely adhered to the substrates. SEM verified that there was an underlying

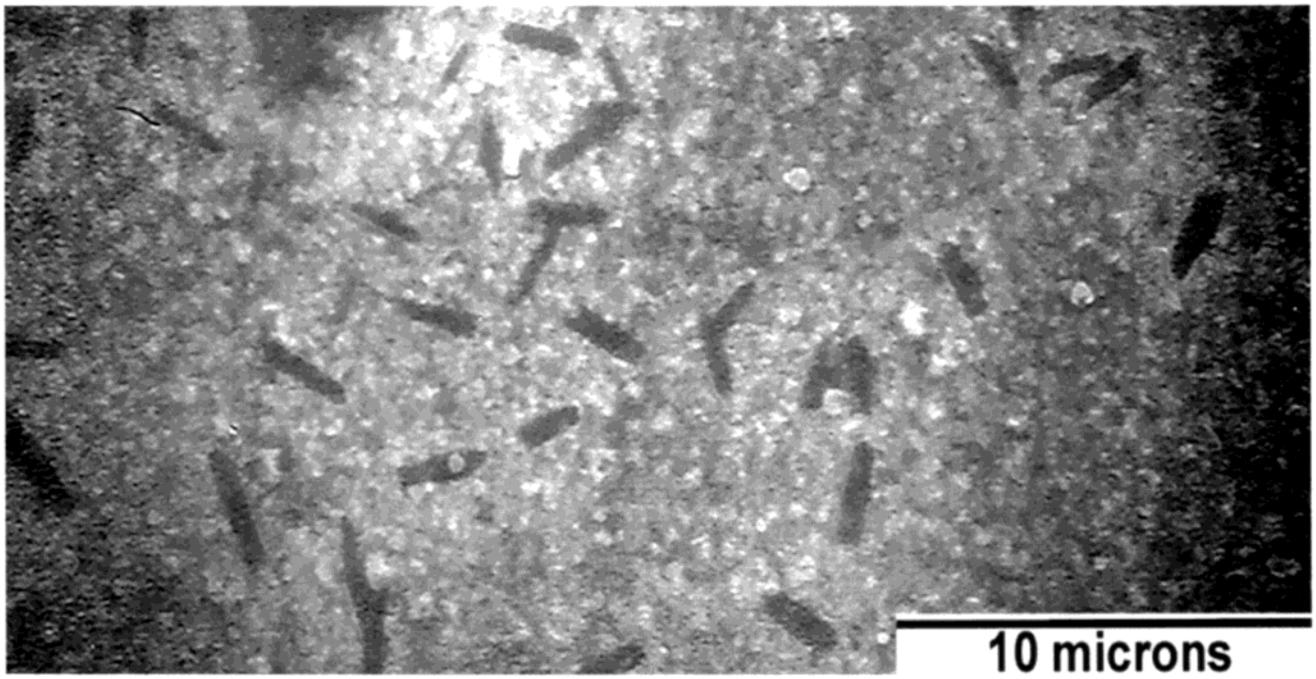

Figure 4. Scanning electron micrograph of a film deposited with a standard electrochemical cell setup at higher stir rates. Montmorillonite layered silicate platelets (dark, rodlike objects) can be seen extruding from the surface of the film.

nickel film with globular nanoclay depositions on the surface.

It is hypothesized that since the surface of the WE was facing downward, the MLS platelets were swept from the surface of the WE and fell to the bottom of the cell. The small concentrations of nanoclays that were incorporated into the growing films merely stuck to the surface of the films, accounting for their heterogeneity and powdery texture.

A second electrochemical cell orientation was established in which a Pt CE sheet was fixed above an upward facing WE. It was anticipated that such an orientation of the WE would capture the powder products noted in the first electrochemical cell orientation and would reduce the abrasive/disruptive physical currents of the solution against the growing film. This second electrochemical cell orientation yielded improved results: all films grown with this cell orientation tightly adhered to the surface of the WE, were smooth and homogeneous, and were easily reproducible. SEM showed MLS incorporation into the electrochemically deposited, homogeneous nickel film. The 001 reflection in the X-ray pattern for nanoclay in the nanocomposite film had completely disappeared, indicating exfoliation of nanoclay platelets within the film. XRF gave 1325 counts per second in the silicate (nanoclay) range, with a background of only 650 counts per seconds; thus, there was a larger concentration of nanoclays in these films than in those grown in the first electrochemical cell setup.

During the course of several more electrochemical platings, it was once again noted that the stir rate of the cell directly affected the growth of the MLS nanocomposite films. Empirically, it was found that the stir rate of the solution dynamically changed the degree of nanoclay incorporation into the nickel thin films—the faster the stir rate, the less the nanoclays were incorporated; and the slower the stir rate, the more the nanoclays were incorporated. Thus, a third electrochemical cell was designed to improve MLS platelet incorporation.

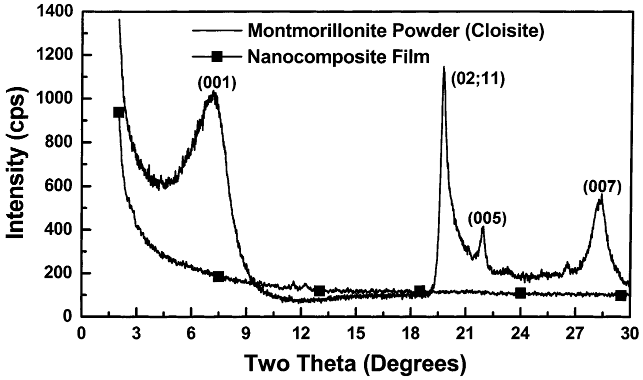

Figure 5. This XRD pattern compares the Ni-MLS film (squares) grown in the third electrochemical cell setup to the pure nanoclay powder (solid line). In the Ni-MLS pattern, the 001 nanoclay peak has disappeared, indicating that the incorporated nanoclay is exfoliated and exists as individual platelets.

The third electrochemical cell setup was a novel, columnar design and was custom built (Figure 3). This new cell was constructed in such a way as to eliminate the need for stirring the plating solution: in previous cell designs, the plating solution was stirred to keep suspended nanoclay platelets in contact with the growing nickel film. However, in this third cell design, the MLS platelets settle out of the suspension into a slurry at the bottom of the cell, in constant, static contact with the working electrode. Thus, on the microscopic level, the MLS platelets were free to settle gently to their lowest potential energy conformation—a conformation that helped aligned the MLS platelets in a face-down orientation parallel to the working electrode. Once the operational voltages and currents of the cell were determined, films were deposited with improved results.

Table 1. Reflections, *d* Spacings, and Intensities for the Nickel Peaks of the Nanocomposite Films Compared with Those of the PDF Card #04-0850 (Synthetic Nickel)

reflection (*hkl*)	obs 2θ (deg)	obs *d* spacing (Å)	obs intensity, I/I_o (%)	JCPDS *d* spacing (Å)	JCPDS intensity, I/I_o (%)
111	44.69	2.027	15	2.0340	100
200	52.07	1.756	8	1.7620	42
220	76.76	1.241	100	1.2460	21
311	93.09	1.061	8	1.0624	20

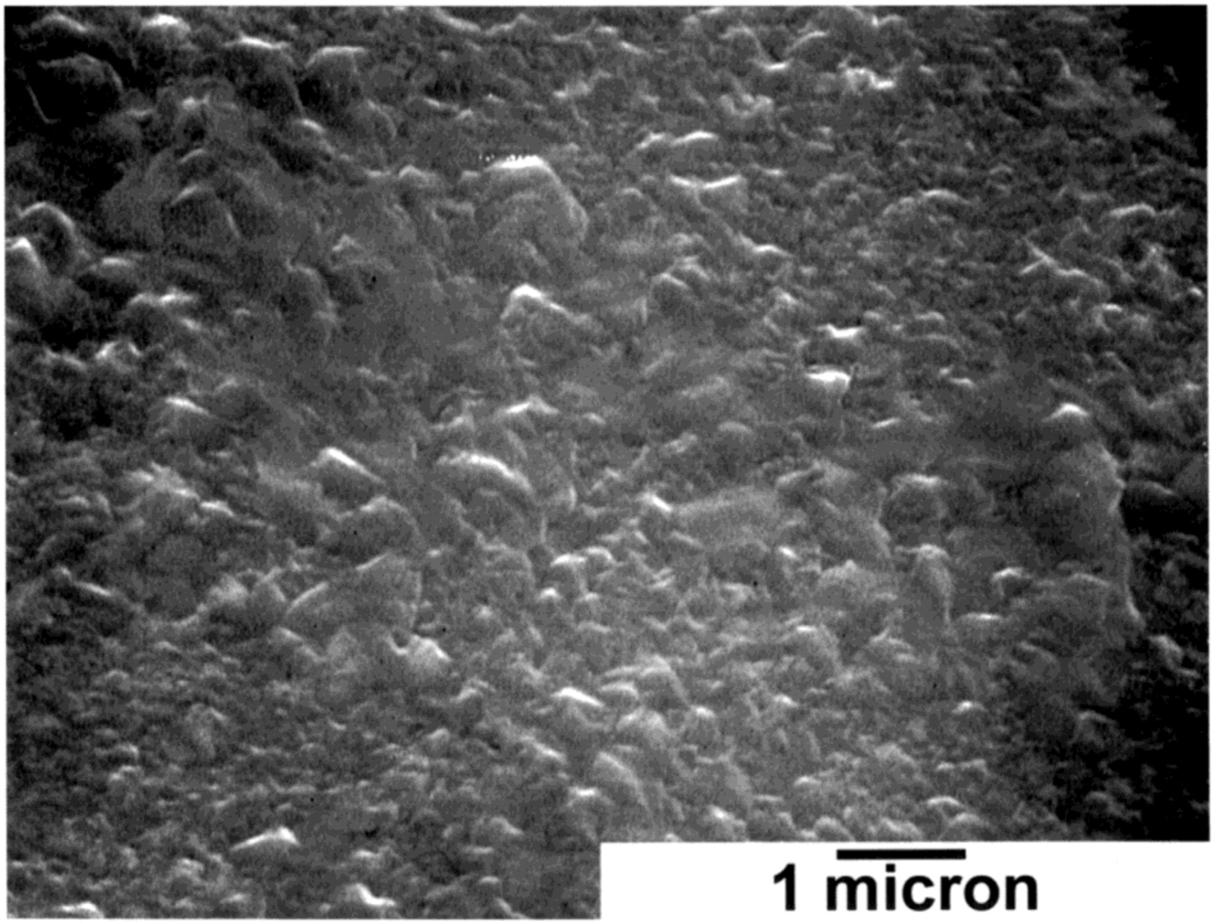

Figure 6. Top-view SEM micrograph of a nickel/montmorillonite layered silicate nanodeposit (Ni-MLS).

With the third electrochemical cell design, nickel/MLS nanocomposite (Ni-MLS) thin films were synthesized for the first time with the silicate platelets aligned in a parallel fashion within the thin films. The XRD pattern of the resulting film grown with the third electrochemical cell design is contrasted with the pure cloisite powder pattern in Figure 5 at lower angles. The 001 reflection for nanoclay in the nanocomposite film has completely disappeared, indicating exfoliation of nanoclay platelets within the film. Also, Table 1 lists the reflections for the nickel metal within the film occurring at higher angles in the XRD pattern. The XRD experimental values are compared to the International Centre for Diffraction Data Powder Diffraction File (ICDD PDF) values for synthetic nickel powder. The top-view SEM micrograph (Figure 6) shows a smooth continuous surface. Figure 7 shows the cross section of the film at a low angle of incidence, in which the nanoclay platelets are aligned horizontally to the substrate in the nickel matrix. XRF values in the silicate (nanoclay) spectrum increased to values in excess of 1550 counts per second (with a background of 650 counts per second), indicating a higher percentage of MLS in the Ni-MLS thin films. Most notably, however, nanoindentation tests of “green” films show a dramatic rise in the hardness of these Ni-MLS films over that of plain nickel thin films (without any nanocomposite formation) (Figure 8). According to existing nanoclay studies,[3,16] crystallized nanoclay masses (such as those in the Ni-MLS films) triple or even quadruple their hardness once annealed; thus, once annealed, the Ni-MLS thin films synthesized via the third electrochemical setup will theoretically have phenomenal hardnesses for their Young’s modulus and lack of brittleness—a topic of continued research.

In addition to their hardness, the Ni-MLS thin films synthesized in this research are characterized from the same nanoindentation experiment as that in Figure 8, with a favorable Young’s modulus, on par with that of stainless steel (Figure 9). Therefore, the thin films have shed the brittleness inherent to ceramic media and adopted a small degree of ductility inherent to nickel. Traditionally, ceramics have been valued for their hardness, yet their brittle properties have plagued them with structural instability, for, as is commonly known, ceramics tend to fracture easily under sudden physical

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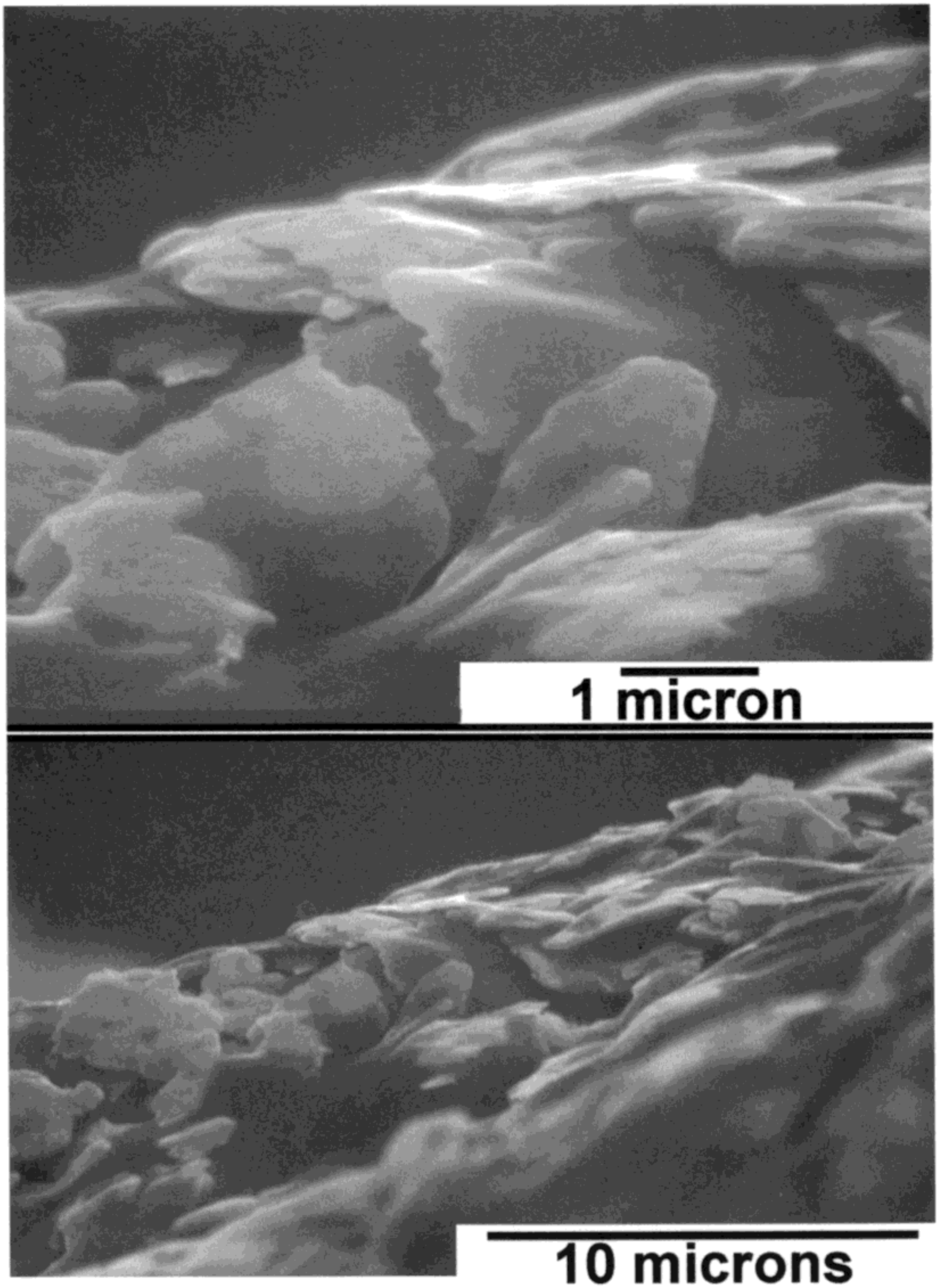

Figure 7. These two scanning electron micrographs show the high degree of MLS platelet alignment along the Ni-MLS thin film. The surface of the film was rippled for contrast, and some of the platelets were pulled apart.

stress. Thus, the Ni-MLS thin films possess two extremely valuable physical properties: stout hardness and a resistance to shattering (shock absorption). Thus, culminating XRD, XRF, and NIW results, it is clear that Ni-MLS film synthesis has been successfully achieved within a unique, electrochemical environment.

Discussion

Montmorillonite Structure.[3,9,17,18] Montmorillonite layered silicates exist as platelets of 2-to-1, layered smectite clays, with a central row of silicate octahedra flanked by two inward-pointing rows of magnesia or alumina tetrahedra (Figure 1). These platelets exist as coordinated layers that measure 1 nm thick by several microns wide. Perhaps the most interesting characteristic of montmorillonites is that there are discrete gallery spacings between each platelet. Additionally, the MLS platelets can be widened to a point at which they become “exfoliated”, and no longer exist as layered platelets in solution (Figure 2). Such an action is useful

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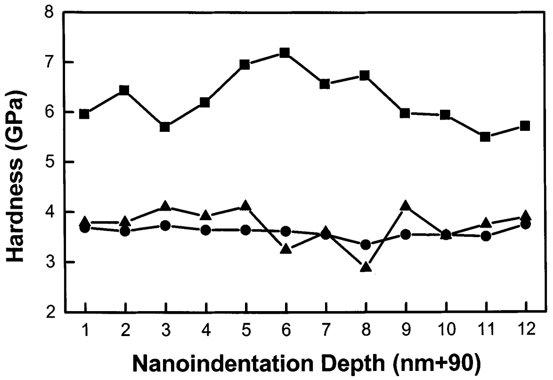

Figure 8. Nanoindentation data of the hardness of a "green" Ni-MLS thin film (squares) deposited on a copper substrate relative to those of the copper substrate (circles) and an electrodeposited nickel thin film (triangles) on a copper substrate.

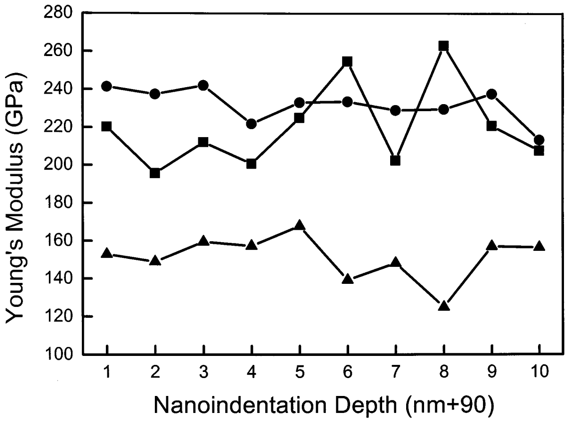

Figure 9. This graph relates the Young's modulus of a Ni-MLS thin film (squares) to an electrodeposited nickel film on copper (triangles) and a stainless steel substrate (circles).

when the precise reassembly of MLS platelets is required, because MLS platelets exist naturally in several large domains, or randomly oriented clumps of platelets. As mentioned earlier, the X-ray diffraction data (Figure 5) of the Ni-MLS films have an absent 001 reflection, indicating that the MLS is exfoliated within the matrix. Even though the MLS platelets are horizontally aligned within the film (as shown by SEM data in Figure 7), the repeat distance between the platelets is not uniform, since the nickel thickness varies between the platelets throughout the film. It is also interesting that the nickel particles within the films have a 220 preferred orientation (Table 1) compared to the random nickel powder pattern. This texture effect is an issue of further study. We hypothesize that the exfoliation occurred when the MLS platelets were suspended into solution. Having been completely broken apart from their pre-existing clusters and disordered domains, the MLS platelets were then free to realign precisely within the growing Ni-MLS thin films via electrochemical incorporation. Since the nanoclay itself is not electroactive, exfoliation of the nanoclay is important in the plating solution. Without exfoliation, the process of inserting individual MLS platelets into the growing metal matrix would not be possible. Thus, the electrochemical environment developed in this research is apparently suitable to the task of successfully synthesizing layered Ni-MLS thin films.

Applications of Ni-MLS Thin Films. Because of the reported physical properties of the thin films synthesized in this research, several mechanical and chemical applications for the films immediately arise. Because of their notable hardness and wear resistance, the Ni-MLS thin films synthesized in this study could be used as protective coatings on components or substrates that are otherwise fragile and require structural reinforcement or surface protection. Also, because of the fact that nickel thin films melt at temperatures in excess of 1450 °C, the Ni-MLS thin films are viable for several high-temperature applications and applications that require wear resistance at high temperatures.

Furthermore, the Ni-MLS thin films synthesized in this research could be used as chemically resistant thin film coatings because of the corrosion-resistant properties of both of the film's components—nickel and montmorillonite layered silicate. Additionally, several other metals may be used in place of nickel in the nanocomposite thin films to tailor the chemically resistant thin film coating to a specific type of environment.

Applications of the New Processing Method Developed in this Study. The electrochemical plating method developed in the third electrochemical cell setup is essentially a new processing method that synthesizes otherwise unattainable Ni-MLS thin films. In short, this processing method is versatile and consequently has several inherent applications. Because of the mechanics of montmorillonites, nearly every weakly (positively) charged or amphipathic species that can be electroplated can be incorporated into this electrochemical methodology. Thus, depositable metals, ceramics, and organometallic species may all structurally benefit from this processing method. Consequently, new ceramic—metallic alloys, organic—ceramic species, and metallic—organic-ceramic combinations of media may be synthesized as nanocomposites and via the electrochemical processing method. And finally, this electrochemical processing method allows research into the incorporation of nonelectroactive species within ceramic or metallic media for producing nanocomposites.

Conclusion

In conclusion, electrochemical MLS incorporation has been achieved within metallic thin films to yield nickel/montmorillonite nanocomposite (Ni-MLS) thin films. Analytical techniques such as XRD, XRF, SEM, and nanoindentation tests reveal that nanoclays have been incorporated to various degrees and orientations in nickel thin films under various electrochemical scenarios. The most successful scenario for nanoclay incorporation proved to be a novel cell design and processing method—a columnar cell in which there was no physical agitation of the plating solution. The lack of agitation in this cell allows for a more ordered incorporation of the MLS platelets into the growing film, and the parallel orientation of the nanoclays above the working electrode can be preserved within the resultant thin film via the Ni-MLS processing method. As shown in this research, electrochemistry has proven to be a viable method of synthesis, as there are fewer processing steps, yielding a simplistic methodology of synthesis with fewer variables of concern. Future research includes implementing the columnar cell design to incorporate nanoclays within electrochemically grown ceramic thin films, and the columnar cell design may be implemented to incorporate nanoclay platelets within a wide variety of electrochemically deposited films, both metallic and ceramic. Thus, it is believed that the new processing method developed in this study will expand the horizons of nanocomposite formation, opening research and industry of the future to novel, ultrastrong materials.

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