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INFLUENCE OF PHOSPHORUS CONTENT AND HEAT TREATMENT ON THE MACHINABILITY OF ELECTROLESS NICKEL DEPOSITS

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ABSTRACT

Diamond turning is the use of a single point diamond tool on a precision lathe under very precisely controlled machine and environmental conditions to fabricate finished components. Coatings offer significant advantages for diamond turning applications inasmuch as they can be applied to light weight substrates such as aluminum or beryllium, or unusual substrates such as molybdenum or glass. One of the most used frequently employed coatings for diamond turning applications is electroless nickel. On occasions, electroless nickel deposits are not diamond turnable, e.g., tool life is shortened. This could be a function of phosphorus content, age of the solution, stress in the deposit, additives in the solution, heat treat coditions, etc. Efforts reported in this paper include machinability studies on electroless nickel deposits varying in composition from 1.8 - 13% phosphorus in the as-deposited condition, and after heating at 200, 400 and 600°C.

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INTRODUCTION

A. Precision Machining

Precision machining (also termed single point diamond turning o diamond turning) has become very attractive, and in some cases the preferred method for producing certain classes of optical surfaces. those not acquainted with this technology, precision machining is d as the combination of the very hard and sharp edges obtained from c crystalline (usually diamond) tools with extremely precise machine (equipped with either liquid or gas bearings) operating under close controlled environmental conditions to produce finished or nearly f optical surfaces[1]. Overall part or figure accuracy tolerances are least 10 microinches (0.25 micron) or approximately one-half the wa of visible light. This technology removes some of the difficultie encountered when conventional grinding and polishing are used in fo optical surfaces. Precision machining restricts the cutting proce thin shear plane with a minimum of contact stress or friction. Th is a process that minimizes material deformation and hence results the specular finish required for optical surfaces and a contour tha exact copy of the tool path.

The principal advantage of precision machining is that the fami shapes that can be manufactured are limited only by the size of the machine, workpiece, workspace, the machine symmetries (generally rotational), and tool accessibility. It is possible to include the machining of integral precision mounts and references during set assure extremely accurate references and eliminate the need of seve complicating stages in the subsequent alignment processes. Finally process is both predictable and repeatable to within the machine ac which allows for reliable numerical control. Table 1 lists the fin and contours obtainable from polishing and precision machining.

Table 1. Best and average finish and contour obtainable from polishing and precision machining*

		Finish	Conto
Optical Polishing	Best	~ 3A rms	~ 50A p
	Average	20 to 50A rms	~ 250A p
Precision Machining	Best	~ 10A rms	~ 1000A p
	Average	100 to 250A rms	~ 3000A p

*See reference 2

1. Diamond Turnable Materials

Diamond turning can be successfully applied to face-centered cubic metals and some crystals and polymers. Aluminum and copper are among the more common diamond turned materials. It is important to note, however, that not all materials are machinable by diamond tools[1]. For example, materials that generally react with carbon are not considered diamond turnable. Metals on the list of non-diamond turnable materials include ferrous alloys, nickel, cobalt, maganese, nickel-beryllium, chromium, tungsten, tantalum, titanium and zirconium. Since the number of materials machinable by diamond tools is not large, materials which cannot be diamond turned are sometimes coated with a diamond turnable material after rough machining to near-net shape and then diamond machined. Electroless nickel is presently the most popular coating for diamond turning applications and it has been applied to ferrous metals, aluminum, beryllium and glass.

Under a recent U.S. Army Command Contract (No. DAAK-40-79-C-0255), a survey of machined optics requirements was carried out for the Army and other DOD applications. Data were acquired from a number of government and civilian organizations for compiling requirements in the military IR laser optics market. Projections from this study indicated that from Sept. 1980 to Sept. 1990, some 1.2 million components will be required of various geometries including flats, polygon scanners, spherical components and aspherical components. Sanger reported that the annual market for coating these substrates would be approximately $2.7 million per year[3]. A high proportion of the coating would be electroless nickel. To give you a feel for the total size of the electroless nickel market, Kuczma[4] suggested it was about $75 million in 1981.

C. Comments on Electroless Nickel and This Research

Electroless nickel is an interesting material from a precision and optical engineering viewpoint:

- It can be diamond turned to an excellent finish, e.g., recent measurements by Church and Takacs[5] resulted in a "gold medal" finish of 9.6A rms for a diamond machined electroless nickel sample.

- It can be heat treated to a high hardness which provides improved damage handling resistance and excellent polishing characteristics without loss of figure. This is an important requirement for short wavelength optics.

- It can be deposited on many different substrates.

From a materials science viewpoint, it offers the following attractions:

- Wide range of phosphorus compositions.

- o Range of microstructure from crystalline to amorphous.
- o Range of hardness via heat treatment.

Diamond tool wear behavior has been examined carefully but only from the viewpoint of chemical reactivity between the tool and the work materials. Thus, it is not well understood how the metallurgical variables such as microstructure, chemical composition, hardness, and strength affect the surface finish, surface chemistry, and subsurface stresses and deformation of the work materials and diamond tool wear behavior. In an effort to understand which factors influence diamond machinability, we have embarked on a fairly extensive program to study this issue on a systematic basis. Our approach was to select a material of reasonable diamond machinability whose material properties could be varied widely yet closely controlled. The material choice was electroless nickel because it meets the requirements we discussed above.

Another reason for evaluating electroless nickel is that we do not know which are the important material parameters affecting turnability. The best diamond turning results to date have been obtained with deposits produced in acid solutions containing hypophosphite as the reducing agent. Deposits produced in alkaline electroless nickel solutions have also been diamond turned but results have been erraticc. Some of these deposits turned with fair results while others broke down the tool edge immediately[6]. With hypophosphite solutions, studies by Arnold, et al.[7], revealed fast tool wear on in-house electroless nickel coatings while much less tool wear was obtained on coatings produced by an outside vendor. Chemical analysis revealed that the in-house specimens ranged from 8.5 to 10.9% phosphorus while the vendor coating contained 10.7% phosphorus. Microhardness tests showed that the sample surfaces that had given the best diamond turning results were relatively hard (450 - 500 Knoop) while the samples that machined poorly were soft (200 - 250 Knoop), but it was never determined if this hardness difference was the culprit. We have had occasional experiences at LLNL with electroless nickel that performed poorly when single point turned and do not know the cause for the poor performance[8].

D. Experimental Details

1. Sample Preparation and Characterization

The electroless nickel plating process and subsequent heat treatment were adjusted so that samples with six different phosphorus contents (1.8, 7.3, 8.8, 10.8, 11.6 and 13.0 wt percent); therefore, different microstructures and hardnesses were obtained. The deposits, ranging in thickness from 3 to 5 mils were produced on 2 inch diameter copper discs in hypophosphite solutions by two different vendors. Specimens were machined in the as-deposited condition and after heat treating at 200, 400 and 600°C for two hours. These four conditions for each of the six compositions gave 24 combinations. All samples were analyzed before and after machining for hardness, surface finish, surface chemistry of impurity elements and their bonding states. Microstructure and surface chemistry information was obtained via appropriate analytical measurement instruments such as Auger electron spectroscopy, x-ray diffraction and scanning electron microscopy. A Talystep profilometer with the capability of height magnification up to one million times was used to measure roughness of the machined surfaces.

2. Machining

Machining was done on the Precision Engineering Research Lathe (PERL) located at Lawrence Livermore National Laboratory's Large Optics Diamond Turning Machine (LODTM) facility. Details on PERL can be found in reference 9. The machining procedure was chosen primarily to determine the influence of depth of cut. Therefore, the crossfeed rate was held constant at 0.1 in/min and the spindle speed was set to 1000 rpm. For each piece, DIALLA-AX (Shell Oil Co.) was used as a cutting fluid. Diamond tools with a nose radius of approximately 30 mils were employed with about a 0° rake angle and 7° clearance angle. To separate the effects of tool wear from material properties, the tools were rotated laterally so that a different portion of the cutting edge was employed for each part. For the depths of cut employed in this study, 7 non-overlapping cutting regions were available per tool. Four of these regions were used to cut the samples described above, requiring 6 tools. The remaining three regions (center and two extremes) were used as controls, each cutting on an as-plated 13% phosphorus sample from a common batch. The intent of the control scheme was to detect variations among the six diamond tools.

The cutting sequence consisted of 6 facing passes per sample with varying depths of cut. Each pass began at the outside diameter of the sample and the feed was toward the center. Initially, two 400 microinch passes were made where the feed was from the 2 inch outer diameter to a 0.45 inch inner diameter. The inner region was left unmachined both for comparison purposes as well as to reduce the risk of tool failure when machining near the center. Following this were two passes with 200 microinch and 100 microinch depths of cut, respectively, both to an inner diameter of 1 inch. The remaining two passes had depths of cut of 50 microinch and 25 microinch, respectively, and proceeded to an inner diameter of 1.5 inches. The finished specimens then comprised a series of concentric stepped surfaces such that the final surface represented finishing depths of cut of 400, 100, and 25 microinches plus an uncut central zone. The width of each zone was chosen to provide an adequate area for subsequent diagnostics, e.g., x-ray diffraction, etc.

3. Measurement of Cutting Faces

It was desired to measure the cutting forces present on the tool for correlation with depth of cut and material properties. The instrument used for this was a Kistler** Piezoelectric 3-component dynamometer in conjunction with a Kistler 3-channel charge amplifier and a Soltec*** 6-channel strip chart recorder. For this study, only the static tool forces were desired and due to the charge decay characteristic of the instrument, only the engagement and disengagement forces were measured. The dynamometer was designed for maximum cutting forces in excess of 500 Kg but the forces experienced during this study were typically between 0.5 g and 100 g. This resulted in the force signal output of amplifiers being of comparable magnitude to signals generated by random charge and drift properties of the instrument. Although it was possible to discern signals due to the change in force levels on the dynamometer, the employment of the instrument for such a low range of magnitudes contributed a significant experimental error to the results. The magnitude of the errors encountered are currently being analyzed, however, the order of magnitude of the forces as well as the trends in the results are felt to be correct.

4. Diamond Tool Characterization

The diamond tools were inspected and characterized via optical and scanning electron microscopy and a tool nose radius gage before and after each machining operation to determine the cutting edge roundness, sharpness, wear behavior and failure modes when failure occurred.

5. Results and Discussion

Machined specimens and diamond tools used in this study are still being analyzed; therefore, this report contains only our preliminary results.

a. Microhardness

Vickers hardness (50 g load) of the specimens measured prior to machining were plotted on contours of dashed lines over the matrix of the phosphorus content and heat treatment temperature as shown in Figure 1. Each digit associated with the contour lines represents the level of Vickers hardness as specified by the legends. This hardness contour plot shows clearly that for a given phosphorus content, the hardness increases from a low level in the as-deposited condition to a maximum value at an intermediate temperature and then to another low level at the higher heat treatment temperature as has been frequently reported in the

**Kistler Instrument Corp., Amherst, NY
***Soltec Corp., Sun Valley, CA

literature[10]. In the as-deposited condition, the hardness increased as the phosphorus content decreased and this is also in general agreement with the general trend reported in the literature[10]. However, for heat treatments performed at elevated temperature, hardness peaked at an intermediate phosphorus content, and the heat treatment temperature of a maximum hardness shifted to a lower temperature as the phosphorus content decreased. We believe this behavior is controlled by the kinetics of the phase transformation from the as-deposited amorphous state to crystalline phases as shown by the results of the x-ray diffraction analysis.

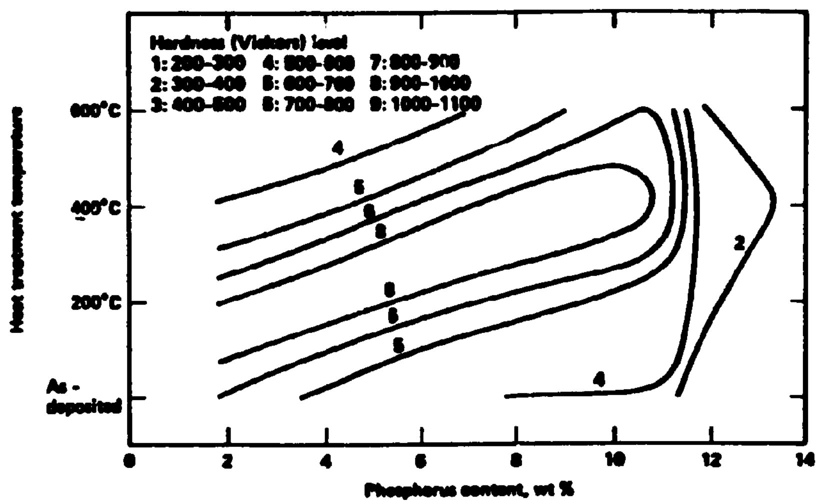

Figure 1: Influence of Phosphorus Content and Heat Treatment Condition on Hardness

b. X-ray Diffraction Analysis

Results of the x-ray diffraction runs performed on the samples before machining were plotted in Figure 2. Specimens in the region marked "amorphous" to the right of the lower solid line were completely amorphous even with heat treatment at 200°C when the phosphorus content was about 9% and greater. Specimens falling in the "transition" region showed slight signs of crystallization of Ni and Ni_3P phases. Specimens belonging to the "crystalline" zone seemed to have experienced complete crystallization and substantial grain growth. Superposition of Figure 1 on Figure 2 reveals that the solid line dividing the "crystalline" and "transition" zones is parallel to and perhaps coincides with the ridge of maximum hardness contour for phosphorus contents less than 10 wt %. Probably the maximum hardness level might have been achieved on the completion of nucleation of Ni and Ni_3P phases when the heat treatment temperatures corresponding to the solid line was adopted. When the heat treatment was done above the temperature represented by the solid line, then an excessive grain growth could reduce the hardness since the contribution to the hardness by the grain boundary was now reduced.

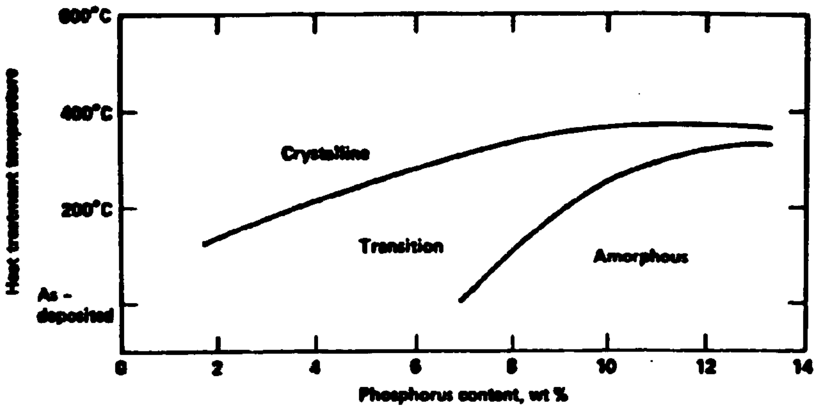

Figure 2: Influence of Phosphorus Content and Heat Treatment Condition on Structure

c. Diamond Tool Wear

The accurate measurement of diamond tool wear due to the machining is still in progress. As a preliminary tool wear analysis, the machining damage on the rake face of the diamond tools was examined via optical microscopy. The degree of the rake face wear of each cutting edge was graded from 0 to 15 depending on the extent of the wear zone. Such grading of the rake face wear provided a semi-quantitative measure of the tool wear; hence, the result was plotted in solid line contours on the matrix of heat treatment temperature and phosphorus content as shown in Figure 3. Samples with phosphorus content correspondng to the right hand side of the contour marked "A" did not render any detectable damage to the diamond tool. Samples with phosphorus content and heat treatment corresponding to the region between the contours "B" and "C" suffered noticeable damage, while those samples to the left hand side of the contour "C" experienced very heavy damage including edge chipping. This general increasing tendency of rake face wear seems correlated to decreasing phosphorus content. As P content decreases, Ni content as crystalline nickel increases, especially when the samples are heat treated and crystalline nickel is known to wear and damage diamond tools very rapidly[1]. An interesting observation was that crystalline specimens of the higher hardness level provided lower tool wear as indicated by the noses in contours "B" and "C". This reduction of tool wear upon hardness increase, if it can be substantiated by further analysis, seems related to reduced cutting forces as observed in conventional cutting operations.

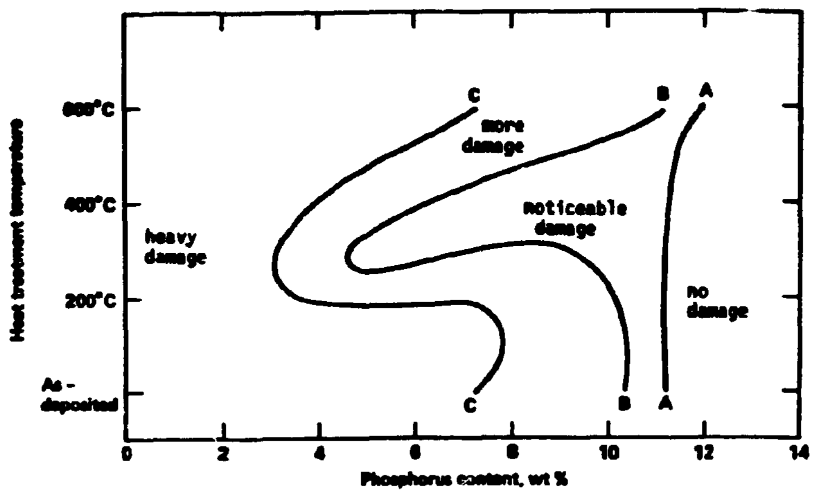

Figure 3: Influence of Phosphorus Content and Heat Treatment Condition on Diamond Tool Wear

d. Surface Finish

Only the peak-to-valley surface finish basically determined by the feed rate was measured in this analysis. We did not include long range waviness. Figure 4 shows that the best finish (finer than 0.1 microinch) was achieved with samples containing greater than 11 % P and heat treated for stress relief but no microstructural change (200°C for 2 hours). Superposition of Figures 2, 3 and 4 show that the best finish was obtained with the samples of phosphorus content greater than 11% and a stress-relieved amorphous structure. However, if the surface finish was relaxed to 1 microinch peak-to-valley, then samples of wider range of phosphorus and heat treatment could be machined with tolerable tool wear.

It was difficult to develop a correlation between surface finish and hardness. The only conclusion that could be extracted from this preliminary analysis was that for a good finish, samples should contain substantial phosphorus and could be heat treated to various hardness levels as already stated above.

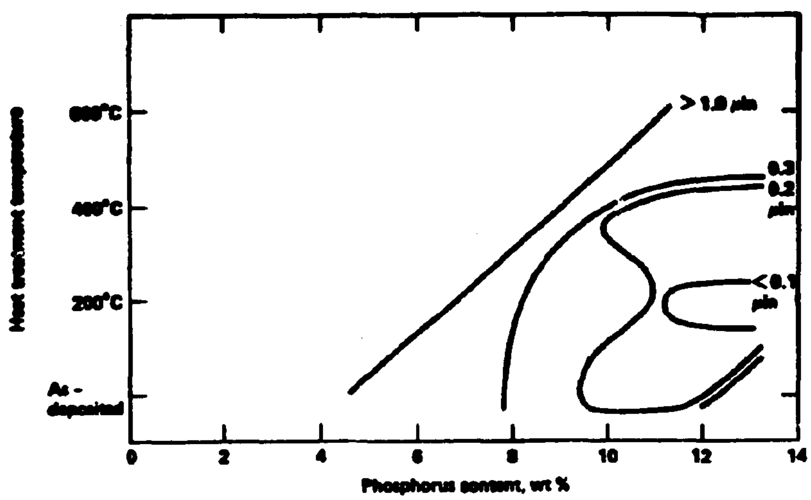

Figure 4: Influence of Phosphorus Content and Heat Treatment Condition on Surface Finish After Diamond Turning

e. Cutting Forces

The measured three components of force correspond to: a) F_x, the cutting force in the direction of feed; b) F_z, the normal force in the direction of the spindle axis, and c) F_y, the cutting force which is positive downward for a typical horizontal-axis spindle. Typical results of the measurements are presented in Figure 5 which is a plot of the arithmetic mean of the engagement and disengagement forces versus heat treatment conditions for the 7.3% phosphorus series specimens. These forces correspond to the 200 microinch depth of cut pass which was felt to provide the most reliable results. Aside from the normal force measurement for specimen 7D, the other conditions demonstrated a good trend correspondence between engagement and disengagement. The shape of the curve demonstrates little change in forces between specimens 7A and 7B but a large increase in force between specimens 7B and 7D, where 7A, 7B, 7C and 7D represent specimens containing 7.3 wt % phosphorus and A = as-deposited, B = 200°C, C = 400°C, and D = 600°C; all for 2 hours at temperature. Preliminary analysis of specimens of other phosphorus levels verify these trends and also suggest the possibility of a force decrease with low temperature heat treating. Although the analysis of these trends is still tentative, this does suggest a large influence of stress relieving for the 200°C heat treatment but that recrystallization is a dominant influence for the higher temperatures.

It is not known why the wear of diamond tools is reduced when nickel contains phosphorus. One speculation is that the reduced wear may be due to the formation of a protective layer of phosphorus on the diamond[12]. Another item worth considering is the fact that as the phosphorus content decreases the tendency for inhomogeneous distribution of Ni and P increases. This increases the frequency of crystalline Ni islands available to degrade the diamond tool.

Another possibility relates to the fact that the behavior of nickel is noticeably changed by the presence of phosphorus. In general, deposits containing phosphorus in excess of 8% are non-magnetic. It has been suggested that perhaps the phosphorus reduces the chemical reactivity of the 3d electron levels responsible for the strong interactions between ferrous metals and diamond. An increase in d-level binding energy and a decrease in density of d-level states has been found in alloys of nickel with a number of metals[13]. It would be of interest to investigate the charge states of nickel containing varying amounts of phosphorus to see if they correlate with changes in wear rates.

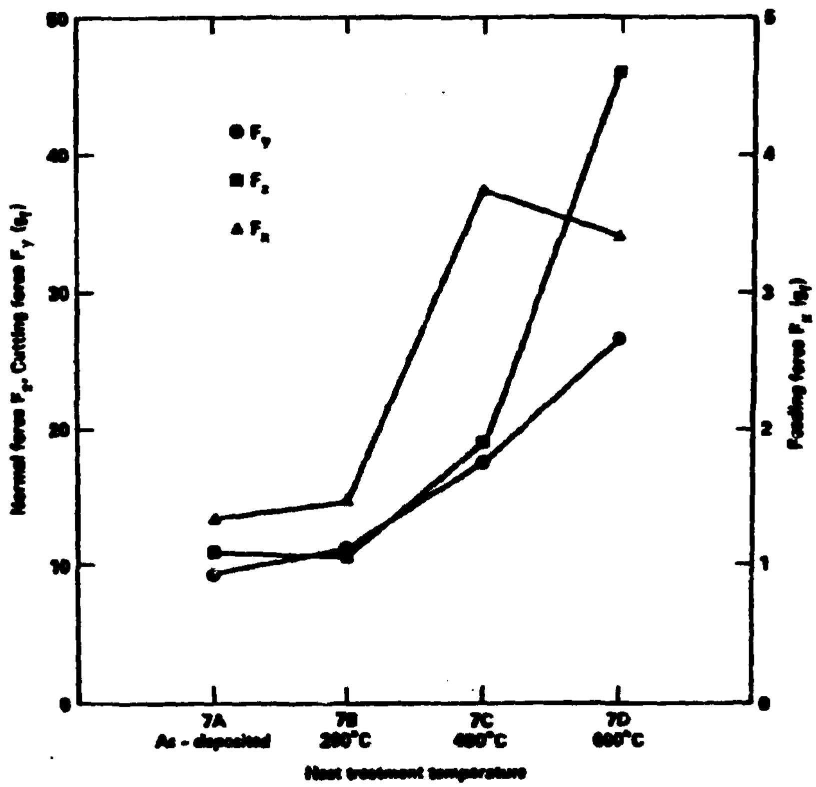

Figure 5: Cutting Force as a Function of Heat Treatment Condition for Electroless Nickel Containing 7.3% Phosphorus

E. SUMMARY

The conclusion drawn from this work is that electroless nickel deposits for single point diamond turning should contain at least 11% phosphorus to minimize tool damage. A stress relief treatment at 200°C for 2 hours appeared to even further enhance the cutting characteristics of deposits containing greater than 11% phosphorus. It was also determined that a significant increase in cutting force was generally noted for samples heated at 400 and 600°C.

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