

Electroplated diamond tools made with a new matrix of nanocrystalline Ni-Co alloy

This article, by Y. Li, H. Jiang, F. Wu and H. Li, describes the development of a new matrix of nanocrystalline Ni-Co alloy for the production of higher quality diamond tools. Containing about 8.5% Co and possessing colony-like morphology with a grain size of approximately 15 nm, the alloy is pulse plated by adding appropriate amounts of non-organic grain size refiner Co and less amount of organic refiner saccharin to the electrolytic solution which was developed to produce pure nanocrystalline nickel deposit, a potential upgrading substitute for conventional polycrystalline matrix material. Compared with the pure nano-nickel, the Ni-Co deposit has a similar hardness but substantially higher tensile strength, which should be attributed to the remarkably reduced amount of saccharin (also responsible for introduction of sulphur and carbonate into the grain boundaries and reduction of the deposit strength and ductility) needed to produce a nanocrystalline structure. Performance testing of the diamond tools shows that the average service life is 15.5% higher than that for the pure nano-Ni samples.

Electroplating of diamond tools has become an accepted industrial production technique because electroplated composites have very good bonding characteristics [1-6]. The tools are made under normal temperature so that diamond grains suffer no loss from high temperature and can be retained tightly in the matrix. Moreover, the manufacturing technique is rather simple and does not require a great deal of investment in equipment.

As a result, it has been used to produce many different kinds of electroplated diamond tools with complex shapes and high precision including hand and machine files, hones, cut-off discs, dressing tools, grinding wheels and geological drilling bits. These tools are in great demand for processing advanced materials such as grinding and machining superalloys and high-tech ceramics, metalworking hardened steel, bi-metals or metal matrix composites, sawing or drilling stone and concrete from huge quarries, shaping wood and laminates, grinding glass, etc. [1-6].

The industry has strict requirements on matrix materials for use in diamond tool fabrication because of diamond's unique surface properties (e.g., bad wettability), i.e., diamond grains only adhere to the matrix by mechanical interlocking, rather than chemical bonding [4, 7]. They tend to fall off easily, therefore, the matrix must be of not only of high hardness and wear resistance to retain and mechanically impregnate diamond grains, but also be of enough toughness to ensure that the tools are able to bear heavy impact during operation. If the matrix is too brittle, it may break into pieces and drop out of the substrate.

We developed a simple approach to producing better diamond tools at lower cost and with higher productivity by introducing nanocrystalline matrix of nickel deposit pulse-plated from modified Watts-type bath [8]. Indeed, nanocrystalline electrodeposits are chosen as the matrix of diamond tools due to: (1) their unusual wear resistance; (2) no problems caused by low thermal stability of nanocrystalline materials. In fact, because of the low thermal stability of diamond itself, diamond tools can be used only when water serves as a cooling medium.

In spite of its desirable microhardness, the nano-nickel matrix is still not satisfactory in terms of embrittlement that results from the high addition of grain size refiner, i.e. saccharin, which is widely believed to be responsible for the embrittlement of nanocrystalline Ni and nickel alloys deposits [9, 10]. Therefore, non-organic refiner cobalt is introduced in the hope to reduce saccharin addition. This article details the fabrication technique of the new diamond tools and their performance and gives information about the nanocrystalline Ni-Co deposit composition, microstructure, hardness and tensile strength.

Fabrication of diamond tools with the new matrix

Four pieces of grinding samples with the nanocrystalline matrix of Ni-Co electro-deposit were made for evaluation of the new matrix. The electrolytic solution consisted of nickel sulphate (300 g l⁻¹), nickel chloride (40 g l⁻¹), boric acid (40 g l⁻¹), cobalt sulphate (6 g l⁻¹), saccharin (3 g l⁻¹) and sodium laurel sulphate (SLS, 0.05 g l⁻¹).

The advantage of employing a high metal content was that higher current density can be used and a thicker deposit can be produced in a reasonable time. Boric acid was used as a buffer to maintain the bath pH, SLS as a wetting agent to reduce the risk of pitting, and saccharin as an inhibitor to reduce grain size of the deposit. The pH was adjusted to a constant value of 3.0±0.1 by adding nickel carbonate to raise it or hydrochloric-sulphuric acid ratio 1:7 to lower it. Analytical grade chemicals and distilled water were used to prepare the solution.

Diamond grains (100-150 µm, mainly 120-130 µm) were cleaned in a mixed acid (HNO₃:H₂SO₄=1:9) for 8 h, and then rinsed several times and kept in distilled water for later use.

The PVC plastic plating bath (300x100x50 mm³) containing 1 litre solution was immersed in a thermostatically controlled large volume water container kept at 60±1 °C. A high-purity (99.99%) electrolytic nickel sheet contained in a titanium mesh basket was used as the soluble anode. Its surface area was approximately 10 times greater than that of the cathode to ensure that no problems would arise from anode polarisation.

Electrodeposition was carried out galvanostatically using square-wave pulsed current with current cut-off during the interval between the pulses. The plating parameters, i.e., pulse on-time T_{on} (1 ms), pulse off-time T_{off} (15 ms) and peak current density J_p (100 Adm⁻²) were chosen based on literature reviews as well as exploratory deposition experiments.

After being abraded with 600 grit sand paper to a very fine finish, the substrates of the four grinding samples, 1 mm thick low carbon steel rings seen in Fig 1 (a), were stuck to a PVC plastic plate and connected with each other by thin copper foil for power supply purposes so that they were treated as a whole cathode (total area to be coated was 0.06 dm²) during all the production process. The copper foil was covered by acid-resistant organic coating to prevent it from being electroplated as well. The cathode was placed 80 mm away from the nickel anode during the pulse plating period and 300 mm away during direct current plating.

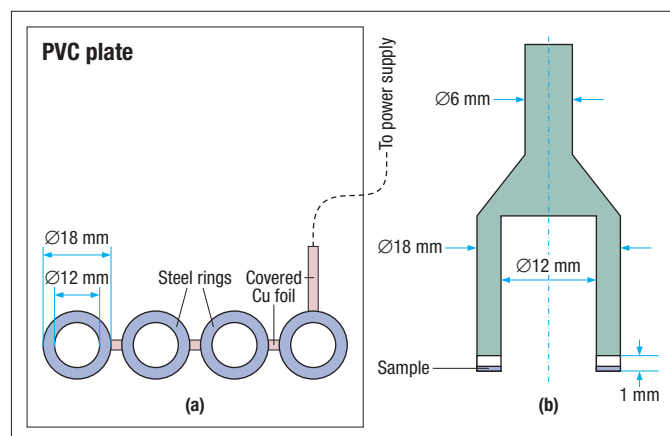


Fig 1 Layout of the four samples to be electroplated (a) and schematic diagram of a drill bit with one of the finished samples (b)

Before being immersed into plating bath, the steel surface was electro-cleaned in an alkaline solution consisting of NaOH (40 g l⁻¹), Na₃PO₄ (40 g l⁻¹), and Na₂CO₃ (40 g l⁻¹) at a temperature of 60-70 °C, then cleaned in 50% HCl, and finally chemically activated in 5% sulphuric acid at room temperature. Pulse plating current was kept at 375±5 mA (i.e. average current density 6.25 Adm⁻², peak current density 100 Adm⁻²).

After 10 minutes of pre-plating, the current was changed to conventional direct current ($T_{off} = 0$ ms, $J = 1.0$ Adm⁻²) and the cathode was put 30 mm away from the anode before being inclined with its submerged end closer to the anode (a slope of approximately 30°). This end was suspended in the solution, no longer touching the bath bottom. After the fixation (about 1 min spent), sand-planting plating began with sprinkling diamond (mixed with water) onto the cathode surface so that the grains covered the surface uniformly, completely, and as thinly as possible. This process took about another 1 min.

After 25 minutes of planting-plating, the cathode was put vertically again so that the stuck diamonds remained on the cathode surface and the unstuck fell off. Then the cathode returned to the position 80 mm away from the anode and the pulse current was restored, keeping J_p at 50 Adm⁻². If the space occupied by diamond grains was deducted, the real current density J_p for metallic ions to deposit was still approximately 100 Adm⁻². The continuous deposition after grain-planting could make the stuck grains tightly embedded in the newly formed Ni-Co matrix. This so-called post-planting process lasted for 1.5-2.5 h.

As the cathode was placed almost horizontally during the planting process, deposit thickness variation should exist. But when comparison between the slight distance difference on the cathode (18 mm at most) and the long anode-cathode distance (300 mm), and another comparison between the thinner deposit plated during sand-planting time and the thicker deposit obtained during the post-planting time were considered, it would become understandable that only slight thickness difference could be found after the fabrication. Japanese authors [5, 6] who reported that the electrodeposited layer on the edge parts of the wheel body was thicker than that in the central part suggested that using long distance between two electrodes (up to 300 mm) would be very effective in improving the uniformity of electrodeposited thickness.

Initially we tried to use pulsed current for the grain-planting process, but eventually failed. Presumably, this is caused by the diamond layer acting as a barrier to transportation of metal ions that are scheduled to pass through the layer and finally reach the cathode surface. That is why the direct current density in conventional grain planting process (normally less than 1.0 Adm⁻²) is lower than those in pre- and post-plating processes.

The failure in grain-planting when using pulse current is believed to result from the instantaneously high current at a current peak. The high current density may lead to supply shortage of metal ions, H₂ evolution, pH increase and Ni(OH)₂ appearance around the cathode. Once Ni(OH)₂ is produced at any time during the grain-planting process, it will never again be possible for the metal to be normally electroplated on to the cathode even after the current is restored to lower level.

Based on above-mentioned experiments and consideration, we chose the direct current grain-planting approach. In fact, this will not affect the tool's quality because the inner layer deposited during grain-planting period is much thinner than

the outer produced in the post-plating process. Also, the outer coating plays a major part in embedding the diamond grains and resisting wear when the finished tool is used.

In order to assess performance of the diamond tools with the new coating, other four pieces of the same-sized grinding samples with pure nanocrystalline Ni matrix were also made by a similar method: the same bath conditions (e.g. pH, T, etc.) and same procedures; similar bath composition with higher saccharin concentration and no cobalt sulphate, i.e., nickel sulphate (300 gl⁻¹), nickel chloride (40 gl⁻¹), boric acid (40 gl⁻¹), saccharin (5 gl⁻¹) and sodium laurel sulfate (SLS, 0.05 gl⁻¹); and similar pulse pattern, i.e., pulse on-time (2 ms), pulse off-time (45 ms) and peak current density (188 Adm⁻²).

Grinding performance and discussion

Comparative grinding tests were carried out under the same working conditions. The finished grinding samples were mechanically stripped off the PVC plastic plate to which they were stuck for the plating process, and then were individually stuck to a drilling bit-shaped steel substrate, shown in Fig 1 (b). During the testing, the bit with the sample was mounted on a drilling machine to drill (with pressing force of approximately 200 N) 30 mm thick blocks of natural granite with a relative hardness of 6.5-7.0. The sample at a rotary velocity of 1000 rpm was cooled by water during the drilling. It was tested until it was worn out and could not be used any longer. The total drilling depth of each sample was regarded as its service life.

The testing result showed that the average service life for the four grinding samples with the nanocrystalline Ni-Co coating was 341 mm, 15.5% higher than 295 mm for the four pure Ni samples. The better performance of the new tools might be the result of tighter impregnation of diamond in the matrix compared with pure nanocrystalline Ni matrix. Presumably, the higher wear-resistance and higher ductility of the nanocrystalline Ni-Co matrix contributes most to the good performance.

when manufacturing diamond composites, hardness and wear resistance of the matrix is essential. If not wear-resistant enough, the matrix would be worn easily and lose its ability to hold the diamond grains tightly, and consequently the diamond grains would fall out prematurely.

Compared with conventional Ni-Co deposits produced by DC plating method (normally containing 20-30% Co and possessing a microhardness of 400-500 kgmm⁻² [4, 11]), the present Ni-Co alloy (containing 8.5% Co) has substantially higher hardness (about 600 kgmm⁻²), which is believed to result from the more satisfactory refinement effect.

Fig 2 shows the surface morphology of the Ni-Co electrodeposit at different magnifications. Apparently, this material possesses colony-like morphology, i.e. consisting of a lot of grain colonies with varying size, and each larger colony could be found to consist of several smaller grain colonies. And this phenomenon could happen at more micro level, clearly seen in Fig 2 (b). As a result, it is hard to identify the grain size through observation from the magnification-limited SEM technique. From an XRD pattern of the deposit, the grain size of approximately 15 nm could be determined.

The refinement to nano-grain is believed to result from the combination of high current densities (during pulse plating) to enhance the over-potential, with inhibitors (i.e. saccharin in this case) to reduce the surface mobility of adions, and Co addition

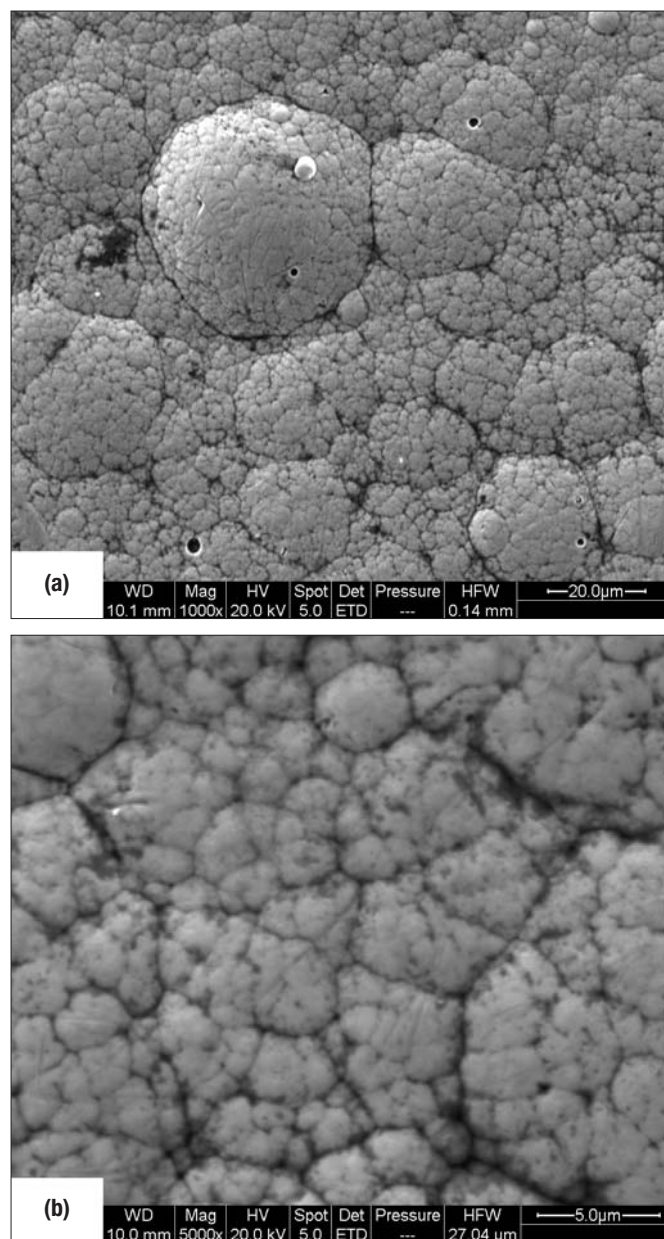


Fig 2 Surface morphology of the nanocrystalline Ni-Co deposit with different magnifications. (a) 1000; (b) 5000

to the electrolyte. El-Sherik et al. [12] reported that the grain size of nickel deposits produced by pulse plating initially decreased rapidly with increasing saccharin additions before levelling off at saccharin concentrations of 5 gl^{-1} and higher. Increasing the saccharin concentration in the bath from 5 gl^{-1} to 10 gl^{-1} had little effect on the grain size reduction. As a result, 5 gl^{-1} saccharin has been widely accepted by many researchers for production of nanocrystalline nickel electrodeposits [8, 9, 12]. In present work, by adding Co ions to the electrolyte, the amount of organic refiner saccharin needed to produce nanocrystalline structure deposit could be reduced remarkably (3 gl^{-1}).

It is interesting to note that there is only a slight difference in hardness between present nanocrystalline Ni-Co alloy and pure nano-nickel we previously produced (also about 600 kgmm^{-2}). This might be because the refinement hardening effect is dominant in nanocrystalline materials and the solution hardening effect is not so important as it is in polycrystalline materials. Sriraman et al. [13] pointed out that the solid solution strengthening effect of W on the Ni-W nanocrystalline deposit was about an order of magnitude smaller than the intrinsic hardness of Ni and much smaller than grain size contribution (grain boundary hardening).

Furthermore, compared with pure nickel nanocrystalline deposit we previously reported (with maximum tensile strength of about 1000 Mpa), the present Ni-Co nanocrystalline deposit has significantly higher tensile strength (about 1200 Mpa). We believe this is because of the higher ductility resulting from less saccharin addition to the electrolytic solution.

El-Sherik et al. [12] reported that with increasing saccharin additions in the plating bath, the sulphur and carbon impurity contents in the deposit increased rapidly before reaching a plateau at higher saccharin levels. Zimmerman et al. [9] reported that pure nanocrystalline Ni produced from a modified Watts bath containing 5 gl^{-1} of saccharin was relatively brittle, possessing little plastic deformation.

Yin et al. [10] reported that nano-nickel produced by an electrodeposition method was contaminated with impurities such as S and C deriving from the additive saccharin. These impurities tended to segregate to grain boundaries. From the tensile tests they conducted on nano-nickel with high concentration of sulphur, the ductility was so poor that all tensile specimens were broken during loading, indicating that the high concentration of interstitials at grain boundaries was very efficient in hindering grain boundaries sliding.

Finally, it should be noted that the better bonding between diamond particles and Ni-Co alloy deposit adopted in this work might also add its contribution. Wang et al. [11] reported that the addition of Co^{2+} in the Ni/diamond plating bath significantly improved the matrix' bonding ability with diamond particles because Co^{2+} was adsorbed on the diamond particles much easier compared with the Ni^{2+} , and Co had better wetting ability with diamond compared to Ni. They concluded that Ni-Co/diamond composites had better anti-wear performance than Ni/diamond composites.

Conclusion

Electroplated diamond tools with a new matrix of nanocrystalline Ni-Co alloy deposit have been fabricated, and the performance testing shows that their average service life is 15.5% higher than that for the pure nano-Ni samples. This better performance might be the result of tighter impregnation of diamond in the matrix which possesses higher wear-resistance (higher tensile strength and higher ductility in spite of the close hardness) and better wetting and bonding abilities with diamond particles. ◆

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