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Application of Ceramic Dry Coating Technology to Steel Material Production Tools

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Abstract

To control environmental problems and improve costs in steel material production, extensive research and development is being conducted with the aim of realizing higher functions and longer service life of steel material production tools by using ceramic dry coating technology. This report introduces the case of formation of a diamond-like carbon film (DLC) with high hardness and high adhesive strength on the surface of a work roll by using the plasma CVD process. The result of trial cold rolling of nickel foil confirmed that the adhesion of the rolled material component to a work roll surface was suppressed, and nickel foil excellent in surface quality was obtained.

1. Introduction

Representative examples of steel material production tools are cutting tools, forging tools and work rolls for rolling, the base material of which is tool steel such as hard metal alloy of the tungsten carbide family, die steel and high-speed steel. For any of such tools, high strength and others, high corrosion-resistance is required, and various surface property modification methods are applied to the surface of the tool base materials to secure the abrasion resistance, brittleness fracture resistance and the smoothness against heat generated in processing. Methods for surface property modification include: for super alloys, hard film formation treatment based on various film forming methods; for tool steel, carburizing treatment and nitriding treatment in addition to the hard film forming treatment; and shot-peening treatment etc. Research and development have been extensively conducted as high function surface property modification methods to date.[1, 2)]

As the needs for high corrosion resistance and high accuracy finishing, etc. are increasing, requirements for further improvements on the part of tools are also intensifying. However, there are cases in which sufficient tool performance cannot be obtained with the conventional surface property modification methods. To deal with these technical issues, we have focused on ceramic dry coating technology that provides a wide range of surface property modifying compositions and high freedom of heat treatment conditions, and are promoting the application of the hard film forming treatment to a wider range. This article introduces an example of research on surface property modification conducted to determine the applicability of the technology to the coating of a tool having a length relatively larger than those of conventional tools. A cold rolling mill was selected as the subject coated test body, with the aim of establishing a guideline on solutions for basic problems pertaining to tool surface that cause roll wear, adhesion of rolled material component to rolls and or surface defects on rolled materials.

2. Method of Experiment

2.1 Shape and chemical compositions of work roll equipped for coating test for surface property modification

Figure 1 shows the shape and the basic dimensions of the work roll equipped for coating. The dry coating test requires a large and heavy-weight body, having an entire width exceeding one meter with the shank sections included and a weight exceeding 20kg. The specified work roll is also used for the rolling of special steel materials such as nickel foil in addition to stainless steel. The coating is applied to the entire area of the sliding part in rolling exclusive of

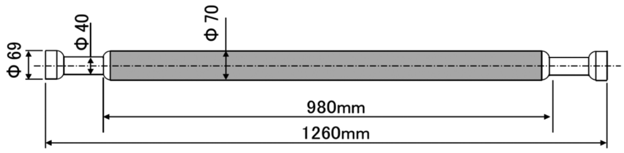

Fig. 1 Shape of the work roll for DLC film deposition

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Table 1 Chemical compositions of the work roll

mass%

Fe	C	Si	V	Cr	Mn	Co	Ni	Mo	W	Cu
Bal.	0.97	0.55	0.02	3.14	0.40	0.03	0.28	0.26	0.02	0.07

the shank parts at both ends. The surface hardness of the sliding part in rolling is specified as a Vickers Hardness of 800 or above and the arithmetic average roughness is controlled to below 0.06.

Table 1 shows the chemical compositions of the work roll equipped for coating. It is a forged steel consisting mainly of the refined martensite phase wherein hard high alloy carbides are dispersed uniformly after specified quenching and annealing treatments.

2.2 Method of selection of ceramic dry coating film for coating work roll

Applying ceramic dry coating to a cold rolling mill suppresses the work roll wear developed in sliding, in rolling and adhesion of the component of the rolled material. With the effectuation of both, improvements in the work roll service life and the finished surface quality of the rolled material are expected. To suppress the work roll wear, the hardness of the film formed on the roll surface must be higher than that of the work roll base material; to suppress the adhesion of the component of the rolled material, the subject film needs to be incompatible in nature to the rolled material. To lower the frictional force in rolling, the friction coefficient of the smallest target film possible was considered as effective. As ceramic dry coating film that satisfies these physical properties, we studied the applicability of diamond like carbon (hereinafter referred to as DLC).

DLC is characterized by hardness that is as high as that of sintered hard metal alloy body and a friction coefficient smaller than that of the coating film of an oxidized metal such as alumina. The main constituent is carbon and contains several metal elements intentionally added as strengthening particles in addition to the very small amount of hydrogen derived from material gas. DLC has an amorphous structure consisting of diamond (sp^3 bond) and graphite (sp^2 bond).[3] With the development of film forming equipment technology, in addition to the ultra-high hardness film having a high diamond structure composition ratio, hard films that take chromium and or silicon into their carbon bond matrixes have recently been put into practical use and consequently, the wear resistance and or the seizure resistance of the various sliding parts of steel materials have been remarkably improved, producing significant results in the entire manufacturing field.[4, 5]

Figure 2(a) shows the ternary phase diagram of the diamond/graphite/hydrogen family.[3] The abovementioned DLC properties are mostly determined by the diamond and graphite structure ratios and additionally by the ratio of hydrogen composition derived from material gas. However, in many cases, the DLC film is designed in accordance with the objective of the application and or the utilization independently. Considering the primary objective of designing is to obtain high hardness and low frictional coefficient, we selected DLC from the region called hydrogenated tetrahedral amorphous carbon (ta-C: H type). Figure 2(b) shows the schematic expression of the DLC film structure containing hydrogen.

2.3 Film forming method of ta-C: H type DLC

As the DLC film forming condition, in view of the annealing condition, shape and dimensions of the work roll to be coated, a low temperature type CVD equipment was used. **Figure 3** shows the outline of the CVD equipment used for the DLC film forming is shown.[6, 7] The surface of the work roll was wet-cleansed with both end shank parts being masked, and the work roll was fixed on the rotating stage in the furnace in an upright-standing posture. Then, the inside of the furnace was brought to a high-vacuum state and film forming was started. The film forming was conducted by the following three processes.

(1) Process of removing the work roll surface scale layer by reducing gas (argon and hydrogen)
(2) Process of forming a metal carbide intermediate layer to be arranged between the DLC film and the work roll base material
(3) Process of forming DLC film using acetylene gas as material

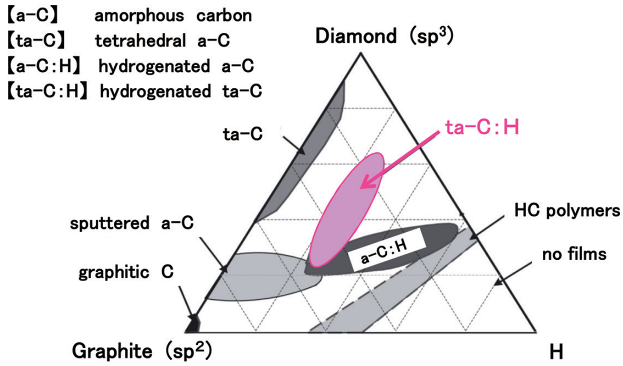


Fig. 2(a) Ternary phase diagram of amorphous carbon

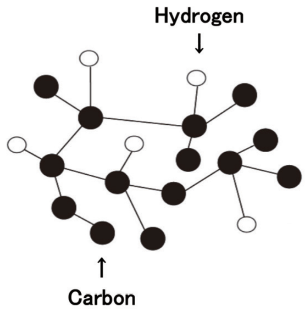


Fig. 2(b) Structure of diamond-like carbon (DLC) films (mixture of diamond structure and graphite structure)

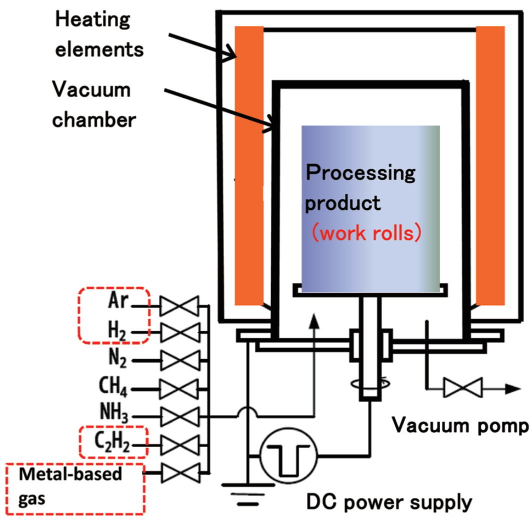


Fig. 3 CVD equipment for DLC film deposition

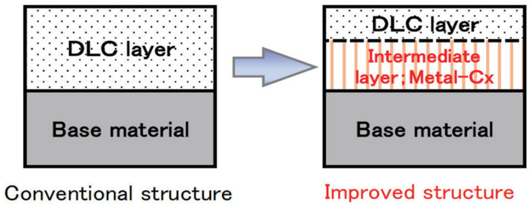


Fig. 4 Film formation structure of the work roll surface

The film-forming temperature inside of the furnace was controlled to below 200°C and the above three processes were completed within about 6 hours, covering the time for mounting the work roll and dismounting the film-formed work roll.

Figure 4 shows the schematic graphical comparison between the structure of the DLC film formed directly on the surface of the work roll base material and that of the DLC film formed when an intermediate layer is arranged on the work roll base material for the DLC film. Generally, the adhesive strength of DLC film to the boundary surface of the base material is weak compared with those of conventional type metal nitride films and metal carbide nitride films, and the film peels off easily when excessive stress is exerted onto the formed film layer.[8] In this test, as a way of increasing the adhesive strength of the DLC film at the boundary surface of the base material, a metal carbide film having chemical affinity to both the DLC film and the base material has been arranged as an intermediate layer. Since the intermediate layer is not intended to assume the tool hard film function, the film thickness is maintained at 100 nanometers at the maximum.

3. Result of Experiment and Examination

3.1 Effect of intermediate metal carbide film layer on the adhesive strength of the DLC film to boundary surface of the work roll

As a result of the arrangement of the metal carbide intermediate layer on the adhesion surface of the work roll base material and the DLC film, remarkable improvement in adhesive strength is recognized. **Figure 5** shows the effect of the thickness of the metal carbide intermediate layer on the adhesive strength. The adhesive strength was measured according to the scratch test method,[9] and the adhesive strength was defined as the load at which point the formed DLC film layer was peeled off the work roll base material wholly or in part, and the exposure of the surface layer of the base material was confirmed. Without the intermediate layer, the adhesive strength remains at 30N and the DLC film might be unable to exert its full function as a hard film. However, with the increase in the thickness of the intermediate layer, the adhesive strength increases, and in the case that the intermediate film layer thickness is 100 nanometers, the adhesive strength is improved to 48N. The adhesive strength reaches a level that does not produce any concerns about sliding. The total thickness of the hard film of the intermediate film layer and the DLC film was controlled to about 1.5 micrometers.

Next, to determine the chemical contribution of the metal carbide film intermediate layer, the carbon 1s photoelectron spectrum was measured by X-ray photoelectron spectroscopy (XPS). **Figure 6** shows the result of the analysis in the depth-wise direction of the test sample that exhibited the highest adhesive strength, namely the test sample with the intermediate film layer thickness of 100 nanometers. In the region of 285 eV, the intensity is derived from carbon and the carbon bond and the DLC layer strength corresponds to this

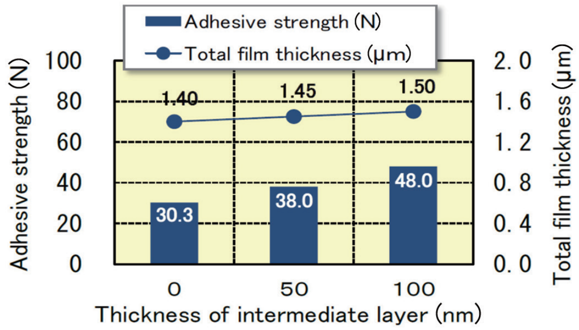


Fig. 5 Improvement effect of the adhesive strength by intermediate layer

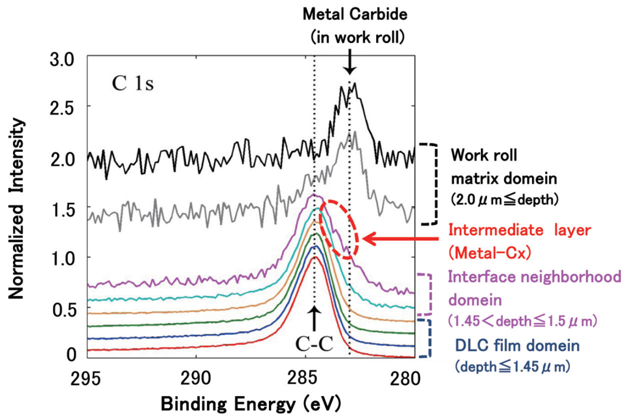


Fig. 6 Carbon 1s orbital energy analysis result of the depth direction by XPS

value. However, in the region of 283 eV, the intensity is derived from the metal carbides, and in this test sample, the strength of the precipitated particles of the metal carbides contained in the metal carbide film intermediate layer and the work roll corresponds to this value. In the region of 1.45 micrometers to 1.50 micrometers below the depth-wise direction where the metal carbide intermediate film layer exists, approximately 283 eV and 285 eV that correspond to the gap difference between the structures of the DLC layer and the metal carbide, a change in intensity derived from the difference of the two compound layers is recognized. This behavior is attributed to the metal carbide film intermediate layer having chemical bonds both with the DLC layer and the work roll base material. These chemical bonds yielded the anchoring effect on the adhesive interface between the DLC layer and the work roll base material, and consequently, adhesive strength was improved.

3.2 Result of DLC film forming on work roll

After the optimization of designing of the metal carbide film intermediate layer described in the previous section, a DLC film was formed on the surface of the work roll equipped for a cold rolling test. **Figure 7** shows a scanning electron microscope (SEM) micrograph of the work roll sectional structure after film forming is shown. The DLC film is shown in the middle of the micrograph. The film is formed uniformly and homogeneously on the surface of the work roll and adhesiveness to the work roll in the entire adhesion region appears to be excellent.

Figure 8 shows the appearances of the work rolls after DLC film forming. A DLC gloss layer in grey is formed on the entire region of the sliding part in rolling, and through visual inspection, no particular surface defects were detected. As the shank parts at both ends were masked when forming the film, the said parts have not been film-forming-treated. **Table 2** summarizes the characteristics of the DLC film formed on the surface of the work roll. The film thickness is 1.5 micrometers, which is sufficient for a tool protecting hard film. The arithmetic average roughness and friction coefficient are sufficiently small, and satisfy the required physical properties of DLC. The adhesion strength is shown as 48N, and was confirmed as having mechanical strength durable to high rolling load in the test rolling. The mechanical strength of the inside of the DLC film layer was measured by the nanoindentation method.[10] The nanoindentation hardness and Young's modulus at the position 1 micrometer from the film surface in the depth-wise direction were measured and as a result thereof, it was confirmed that a sufficient hard film function is secured.

3.3 Result of cold rolling test using DLC film-formed work roll

A cold rolling test using the work roll with the DLC film formed as a hard film was conducted. The six-high precision cold rolling mill in the Naoetsu Works of Nippon Steel & Sumitomo Metal Corporation was used and a pure nickel foil was rolled for the test. In **Fig. 9**(a), the appearance of the cold rolling mill and in Fig. 9(b), the construction of the rolling rolls inside the cold rolling mill are shown, respectively. A pure nickel material 0.193 mm in thickness x 610 mm in width was prepared and rolled to a thickness of 0.1 mm at the rolling speed of 20 m per minute under the target rolling load of 100 tons.

Figure 10 shows the amount of sheet thickness change and the profile of rolling load in cold rolling the pure nickel foil to a rolled length of 300 meters. The entry side thickness was rolled to the exit side thickness with a reduction ratio as high as nearly 50%. However, in the test rolling, it was verified that the material was rolled to the predetermined thickness with one pass. **Figure 11** shows the appearances of the work roll after the test rolling and the surface of the nickel foil. In the case of a similar test rolling using the conventional work rolls with no surface improvement treatment, accumulation of an obvious adhesion layer in the sliding part of the work roll is recognized. However, on the work roll improved with the DLC film forming, no noticeable surface change was observed after the test rolling. The rolled pure nickel foil was free of quality problems such as those of shape and surface quality, and accordingly, it is judged

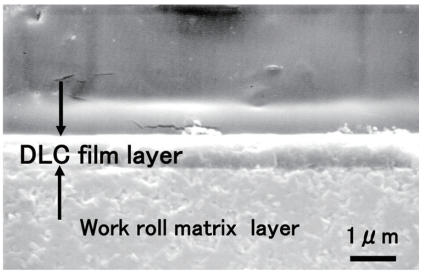


Fig. 7 SEM microphotograph of the work roll sectional structure

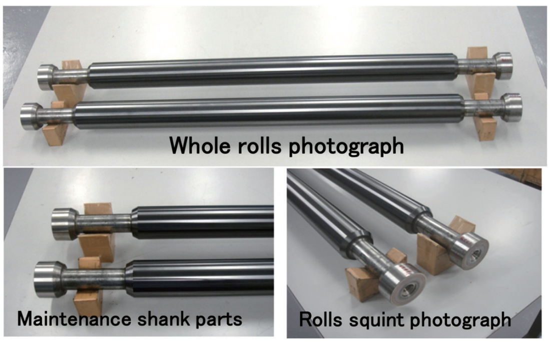
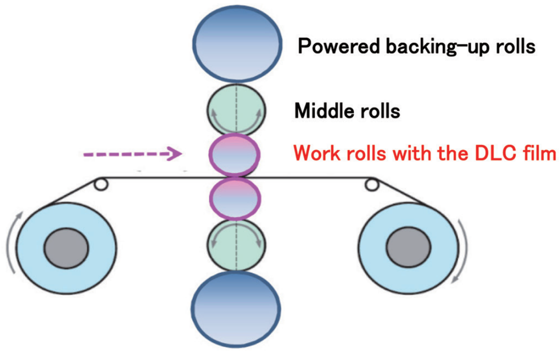


Fig. 8 Work rolls appearance photograph after the DLC film deposition

(a) Precision cold rolling mill for finish rolling of thin steel sheets



(b) Rolls constitution of the precision cold rolling mill

Fig. 9 Cold rolling mill used for a rolling examination

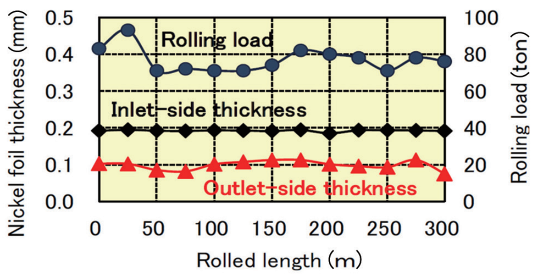


Fig. 10 Thickness amount of change of the nickel foil in the rolling process

Table 2 Characteristics of DLC film on work rolls

Color tone	Film thickness	Surface roughness	Friction coefficient	Adhesive strength	Nano-indentation		Insulation resistance
					Hardness	Young's modulus	
Gray	1.5 μm	0.046	0.130	48 N	20 GPa	190 GPa	≥1 MΩ-cm

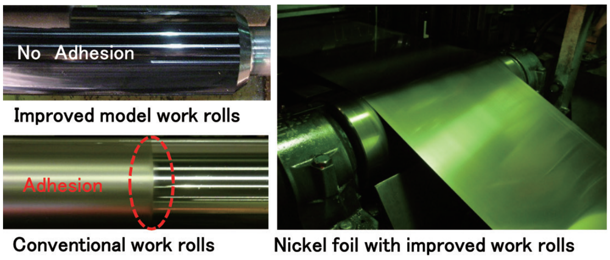


Fig. 11 Surface state of the work rolls and the nickel foil after the cold rolling examination

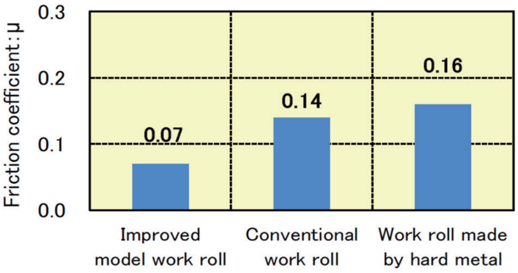


Fig. 12 Analysis results of the friction coefficient of the work rolls

that improvement of tool function by applying DLC film forming has been obtained.

Figure 12 shows the comparison of the friction coefficients obtained in the abovementioned test rollings using the improved work roll with DLC film forming, the conventional work roll without surface improvement treatment and the cemented carbide work roll. The friction coefficient was calculated from the rolling load exerted on the work roll and the frictional force based on rolling analysis. The friction coefficient of the improved work roll with DLC film forming is suppressed to a lower level as compared to those of other rolls. The high lubricating performance on the sliding part in rolling owing to the low friction coefficient contributes not only to the suppression of the adhesion, but also to the enhancement of rolling productivity.

4. Conclusion

To expand the area of application and to develop ceramic dry coating technology that has been used mainly for relatively small steel material production tools, a DLC hard film was applied to long-length cold rolling mill work rolls. As a result, a desired guideline aimed at improving the basic tool surface targets such as adhesion and or wear has been established. Hereafter, we are determined to confirm the durability etc. of the tool equipped for trial purposes based on the technology described in this article, and to promote the enhancement of tool function and cost performance by further study of the formed film structure and the method of film-forming.

Acknowledgements

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