

Application of Amorphous Brush-Plated Coatings to Hot Work Dies

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The results obtained during industrial trials have shown that the service life of hot work dies can be increased by 33 to 180% using the brush plating technique to prepare amorphous coatings. The coatings possess a much higher hardness, lower friction coefficient at room and elevated temperatures, good scale resistance in addition to higher surface finish, compared to uncoated dies, and thus improve the tribological performance of the dies. In this work, a study of the crystallization process, its kinetics, and the hardness variations of the coatings has been made. According to the data obtained, it can be considered that the main reason for the success of amorphous brush-plated coatings is that, during the operation, crystallization and precipitation takes place instantaneously, which results in a strong secondary hardening effect, thus leading to an increase in the red hardness of the surface layers of dies, therefore ensuring higher thermal wear resistance of the dies.

Keywords

amorphous coating, brush plating, hot work die, red hardness, thermal wear resistance

1. Introduction

THE characteristic operating conditions of hot work dies are (1) elevated temperature, usually higher than 600 °C, which causes oxidation and softening of die surfaces; (2) contact pressure is very large, often in the range of 50 to 500 MPa; and (3) plastic flow of deformed metal is rapid, and the surface oxide film is easy to break, which leads to exposure of fresh metal and produces rapid plastic wear of dies. Therefore, hot work dies fail primarily by thermal wear.^[1]

Dennis et al.^[2] first applied the brush plating technique to dies to improve their wear resistance and service life. Using Co-Mo and Co-W alloy coatings, they increased the service life of hot forging dies by 20 to 100%.^[2] The coatings possess a microgranular structure and thickness of about 13 μm. Recent research shows that metals in the amorphous state have good physical, chemical, and mechanical properties.^[3] Consequently, amorphous coatings produced by the use of brush plating techniques are expected to prolong die life even longer.

Furthermore, the technology of brush plating is very simple and adaptable, can be operated *in situ*, can be repaired, and is not limited by shape, size, material, and the treating method of dies. It is likely to be used as a surface for dies with wide practical applications.

2. Obtaining Amorphous Brush-Plated Coatings

Obtaining amorphous brush-plated coatings depends primarily on the compound of a solution, which is essential to getting the amorphous structure for coatings. The solution suitable for dies, especially hot work dies, consists of three components:

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- *Base metals*: Ni, Co, and their alloys; they are used to ensure the basic properties of coatings.
- *Alloying elements*: Primarily W, Mo, etc.; they are used to improve the service performance of coatings.
- *Vitrification elements*: Generally metalloid P, B, etc.; they are used to promote the formation of an amorphous structure.

According to experiments, two types of successful solutions and their coatings are as follows:

- *Ni-P alloy coating*: Solution has a composition (ion concentration) of 74 g/l Ni and 7.3 g/l P, pH 3.2; coating contains 9.0 to 10.2% P, rem Ni.
- *Co-W-P alloy coating*: Solution has a composition (ion concentration) of 50 g/l Co, 7 g/l W, and 1.5 g/l P; pH near 1; coating contains 3 to 5% W, 6 to 10% P, rem Co.

The brush plating voltage is 13 to 17V, and the plating stylus (anode) moves (over cathode components) with a relative velocity of 10 m/min. Usually, the thickness of sound coatings is 20 to 30 μm; the maximum is 0.1 mm. The substrate material includes primarily the hot work die steel grade 3Cr2W8V (corresponding to UNS T20821), which contains (in wt%): 0.33 to 0.38C, 2.38 to 2.90Cr, 8.25 to 8.26W, 0.38 to 0.47V, 0.17 to 0.20Si, 0.20 to 0.22Mn, 0.020 to 0.027P, and 0.005 to 0.008S, and is usually heat treated to a hardness of 46 to 52 HRC.

3. Properties of Coatings

3.1 Hardness

At room temperature, Ni-P and Co-W-P coatings have microhardnesses of about 730 and 840 HV, respectively. After tempering at 600 °C for 30 min, the hardness increased to 960 and 1150 HV, respectively. The typical hardness of hot work die steels in service ranges from 36 to 50 HRC (equivalent to 338 to 509HV).

Table 1 Surface finishes and friction coefficients of brush-plated coatings

| Brush-plated coating | Before plating | | After plating | | Coefficient of dynamic friction | |
|----------------------|--|----------------|--|----------------|---------------------------------|------------------|
| | Surface roughness (R_a), μm | Surface finish | Surface roughness (R_a), μm | Surface finish | Initial | After running in |
| Unplated die | ... | ... | ... | ... | ... | ... |
| 3Cr2W8V steel | 0.39 | ∇8 | 0.39 | ∇8 | 0.112 | 0.112 |
| Co-W-P | 0.41 | ∇8 | 0.32 | ∇9 | 0.105 | 0.102 |
| Co-W | 0.39 | ∇8 | 0.30 | ∇9 | 0.108 | 0.105 |
| Ni-9.3P | 0.35 | ∇8 | 0.25 | ∇9 | 0.104 | 0.099 |

Table 2 Surface finish variations of die steel panels having different roughnesses after brush plating

| Detail of die steel panel | Surface roughness (R_a), μm | | Surface finish | |
|----------------------------|--|---------------|----------------|---------------|
| | Before plating | After plating | Before plating | After plating |
| Actual hot-forging die | 7.0 | 1.6 | ∇4(a) | ∇6 |
| Abraded with No. 200 paper | 1.81 | 0.43 | ∇6 | ∇8 |
| Abraded with No. 400 paper | 0.95 | 0.22 | ∇7 | ∇9 |
| Abraded with No. 600 paper | 0.39 | 0.18 | ∇8 | ∇9 |
| Abraded with No. 800 paper | 0.19 | 0.15 | ∇9 | ∇10 |

Table 3 Results of wear tests

| Type of wear | Abrasive wear | | | Adhesive wear | | |
|--------------------------|--------------------|------|--------|--------------------|-------|--------|
| | Unplated 3Cr-2W-8V | Ni-P | Co-W-P | Unplated 3Cr-2W-8V | Ni-P | Co-W-P |
| Loss of weight, mg | 2.63 | 1.84 | 1.67 | 27.55 | 15.80 | 9.27 |
| Relative wear resistance | 1.00 | 1.43 | 1.57 | 1.00 | 1.74 | 2.97 |

3.2 Finish

The results of measurements with an SP-120, a product of the English company, Talysurf, indicate that, on the brush-plated 3Cr-2W-8V steel specimens abraded with No. 600 abrasive paper, Ni alloy and Co alloy coatings experienced improved finishes by 1 class (∇4 ... ∇10 are used to express the surface finish classes for reference) with almost the same effects (Table 1). On surfaces with lower finishes, the effects of brush plating are more prominent; the finishes can be increased by 2 classes (Table 2).

3.3 Wear Performance

The friction conditions of hot work dies are extremely complicated. All types of wear, such as abrasive, adhesive, and oxidation wear, etc., occur simultaneously. Tests were conducted on specially designed MMB-1 half-fixed abrasive wear test apparatus and a BJM-1 block and ring wear tester. Ring specimens had an outer diameter of 40 mm and thickness of 10 mm. In the abrasive wear test, Fe_2O_3 powder was used as the abrasive; specimens rotated at 385 rpm; blocks were made from gray cast iron having a hardness of 210 HB; a load of 9.8 N was applied. In the adhesive wear test, No. 20 motor oil was used as a lubricant, in which 10 g/l Fe_2O_3 powder is added; specimens rotated 980 rpm ($v = 1.84$ m/s); bushes were made from grade

45 steel (UNS G10450) with a hardness of 53 HRC. The load was 98 N. Test results are shown in Table 3. It is apparent that brush-plated coatings can improve the wear resistance of die steel, and the effect of Co-W-P is better than that of Ni-P.

3.4 Friction Coefficient

When measuring friction coefficient with MHK500 block and ring wear test apparatus (a Chinese standard model), rings 13 mm thick \times 49.24 mm in diameter were made from GCr15 steel (corresponding to AISI ES2100) with a hardness of 60 HRC and a finish of ∇9; the blocks had a finish of ∇8, and obtained ∇9 after brush plating. The load was 98 N; rotating velocity was 250 rpm. Initial and running-in friction coefficients are listed in Table 1, which illustrates that brush plating is capable of lowering friction coefficients.

The high-temperature friction coefficient is very important to hot work dies. It is determined on a specialized MG-200 high-temperature friction tester by the use of pin and disk method, in which pins 32 to 35 mm long \times 5 mm in diameter were made from normalized low-carbon steel, and disks 5.5 mm thick \times 45 mm in diameter were used. Rotating velocity was 700 rpm ($v = 1$ m/s), and load was 19.6 N. The experimental results are shown in Fig. 1, which indicates that, at all tem-

Table 4 Results of industrial trials on hot work dies brush-plated with Ni-P and Co-W-P alloy coatings

| Die type | No. of sets plated | Die material | Component material | Results |
|--|--------------------|---------------|--------------------|-----------------------|
| No. 2 pipe cutter dies | 90 | 3Cr 2W 8V | T10 | 180% average increase |
| No. 3 pipe cutter dies | 50 | 3Cr 2W 8V | T10 | 90% average increase |
| Cutting pliers dies | 7 | 3Cr 2W 8V | GCr15 | 52% average increase |
| Solid wrench (17 in. length) dies | 9 | 3Cr 2W 8V | 40Cr | 51% average increase |
| Solid wrench (19 in. length) dies | 7 | 3Cr 2W 8V | 40Cr | 41% average increase |
| Axle shaft gear blank dies | 10 | 5Cr Mn Mo | 20Cr Mn Ti | 90% average increase |
| Transmission counter shaft gear blank dies | 8 | 5Cr Mn Mo | 20Cr Mn Ti | 148% average increase |
| Second speed gear blank dies | 8 | 5Cr Mn Mo | 20Cr Mn Ti | 53% average increase |
| Engine connecting rod cover dies | 10 | 3Cr 2W 8V | 45Mn2 | Increase over 50% |
| Engine connecting rod cover dies | 18 | 3Cr 2W 8V | 45Mn2 | 82% average increase |
| Transmission case gear blank dies | 4 | 5Cr Mn Mo | 20Cr Mn Ti | Increase near 100% |
| Connecting rod dies | 4 | 4Cr 5Mo V 1Si | 40Cr | 33% average increase |
| Connecting rod dies | 2 | 3Cr 2W 8V | 40Cr | 67% average increase |
| Inserts for extrusion of pipes | 10 | 3Cr 2W 8V | 1Cr 18Ni 9Ti | 93% average increase |
| Core rod for extrusion of pipes | 1 | 3Cr 2W 8V | 1Cr 18Ni 9Ti | 146% increase |
| Spanner dies | 4 | 3Cr 2W 8V | 45 | Increase near 100% |
| Socket bend dies | 5 | 5Cr Mn Mo | 45 | Increase over 100% |

Note: 3Cr 2W 8V, UNS T20821; 5Cr Mn Mo, ASM VIG; 4Cr 5Mo V 1Si, UNS T20813; T10, UNS T72302; GCr15, AISI E52100; 40Cr, UNS G51400; 20Cr Mn Ti, near UNS G51200; 45Mn2, UNS G13450; 1Cr 18Ni 9Ti, UNS S32100; 45, UNS G10450

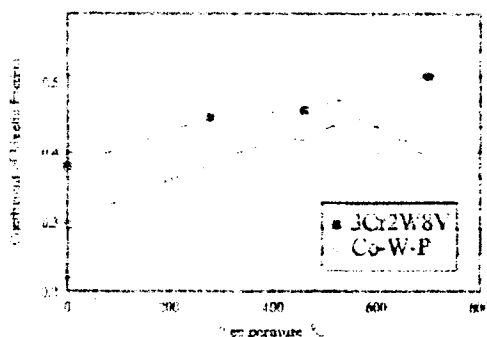


Fig. 1 Effect of temperature on friction coefficient.

peratures tested, the friction coefficients of Co-W-P coatings were lower than those of 3Cr2W8V steel.

3.5 Scale Resistance

The resistance of dies to oxidation affects their tribological behavior at high temperatures. Specimens were plates of 28 × 4 mm (diameter) with finishes of ∇7 after brush plating. They were heated in air to various temperatures, held, and oxidated for 90 min. Figure 2 shows the variations in mass increase versus temperature during oxidation. From 300 °C, the mass increase of plated specimens were much lower than that of 3Cr2W8V steel (the actual mass increase of unplated plate should be even greater because of mass loss via decarbonizing). The Ni-P coating had the least increase, which is associated with the good oxide film of Ni. More importantly, the surface appearance of unplated 3Cr2W8V steel plate changes rapidly as the temperature increases. At 550 °C, an obviously loose scale forms, and above 650 °C, it peels off. However, specimens with Ni-P and Co-W-P coatings were relatively sta-

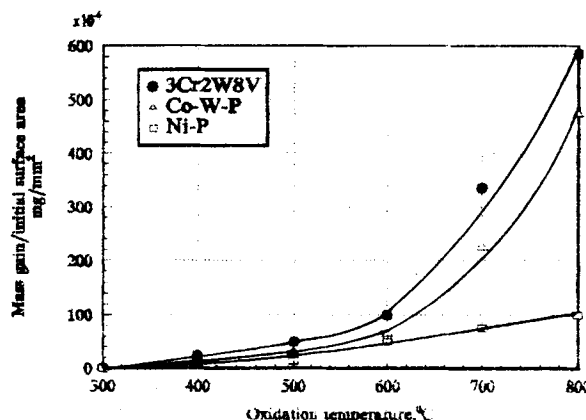


Fig. 2 Effect of temperature on oxidation (90 min at temperature).

ble; no defects such as breaking and peeling occurred, and the finishes remained acceptable up to 650 °C.

4. Industrial Trials

For several years, industrial application trials of Ni-P and Co-W-P brush-plated coatings were carried out on about 30 kinds of hot work dies in nearly 20 plants. The results are given in Table 4.

The results obtained on hot forging, hot pressing, and hot extruding dies show that, regardless of what die material was used, Ni-P and Co-W-P brush-plated coatings can both prolong die service life by 33 to 180% (above their original one). Furthermore, brush-plated coatings are also beneficial in applications such as cold work dies for blanking, forming, and deep

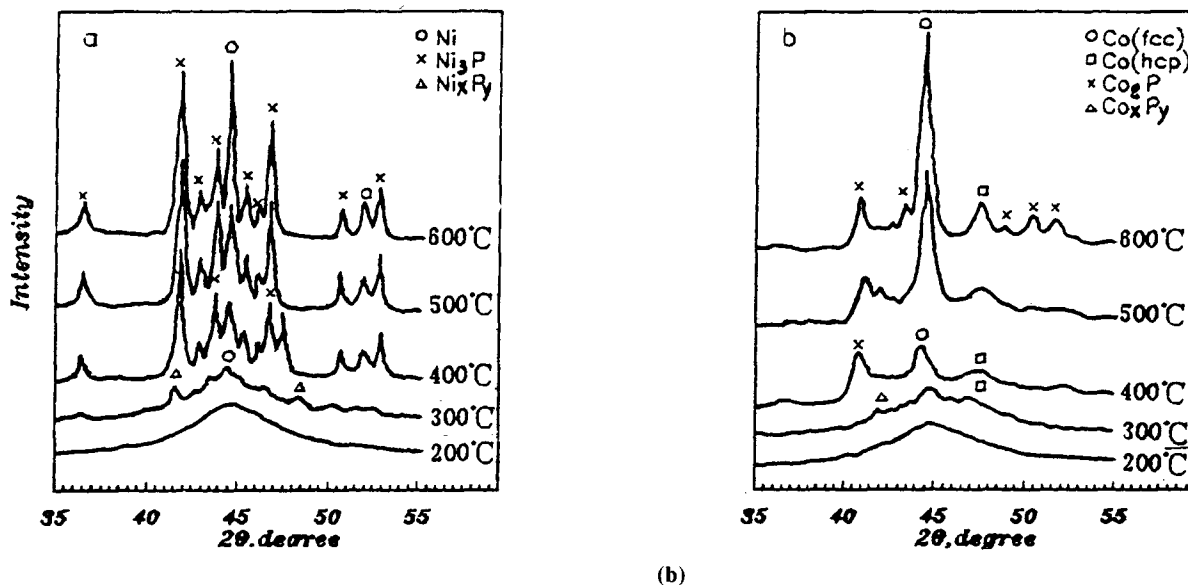


Fig. 3 X-ray diffraction patterns of the brush-plated coatings. (a) Ni-P coating. (b) Co-W-P coating.

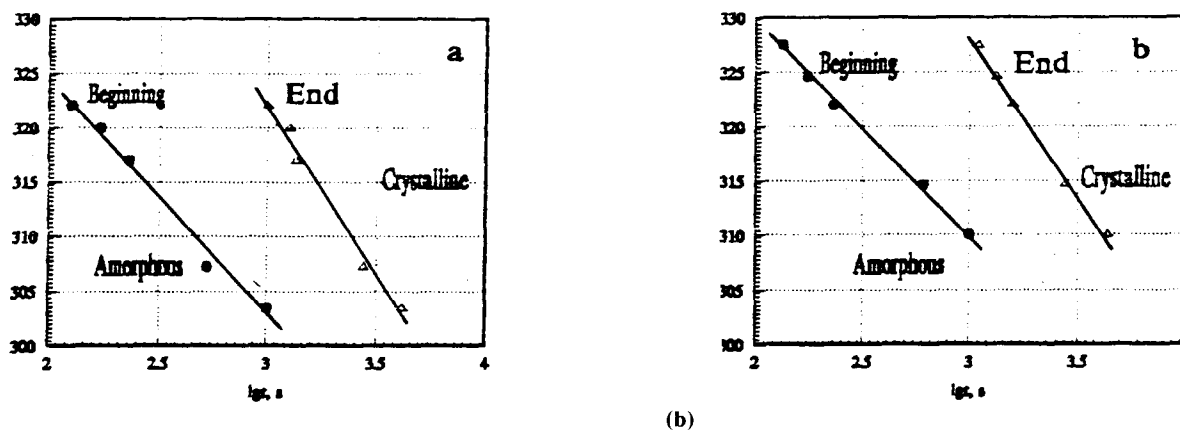


Fig. 4 Diagrams showing isothermal crystallization. (a) Ni-P coating. (b) Co-W-P coating.

drawing, as well as in such components as small cold rolls, aluminum alloy friction disks for textile industry, etc.

5. Structure and Its Transformation of Coatings

5.1 Structure of Coatings and Its Crystallization Process

A series of X-ray diffraction patterns taken from Ni-P and Co-W-P brush-plated coatings heated for 2 h at various temperatures in argon are shown in Fig. 3. Below 200 °C, diffraction patterns have the typical characteristic shape of amorphous swelling, which indicates that the coatings possess an amorphous structure. From 300 °C, sharp peaks gradually rise on the curves, as coatings transform into the crystalline state. Above 600 °C, an analysis of diffraction peaks shows that

the Ni-P coating transforms into a two-phase structure consisting of Ni and Ni₃P. The Co-W-P coating possesses a structure consisting of Co₂P phase and a cobalt-base solid solution with primarily fcc lattice mixed with a secondary cph lattice.

5.2 Kinetics of Crystallization

Under actual operation conditions, because crystallization from the coatings is not equilibrium, the process should be characterized by its kinetics or kinetic parameters. According to a thermal analysis experiment, and using the Johnson-Mehl-Avrami and Arrhenius equations, the crystallization activation energy of Ni-P coating is measured to be 192 kJ/mol, and its Avrami exponent is 2.7.^[4] The crystallization activation energy of the Co-W-P coating is 215 kJ/mol, and its Avrami exponent is 2.9.^[5] It follows that Co-W-P is more thermostable than Ni-P. In Ref 4 and 5, on the basis of thermal analysis curves, the

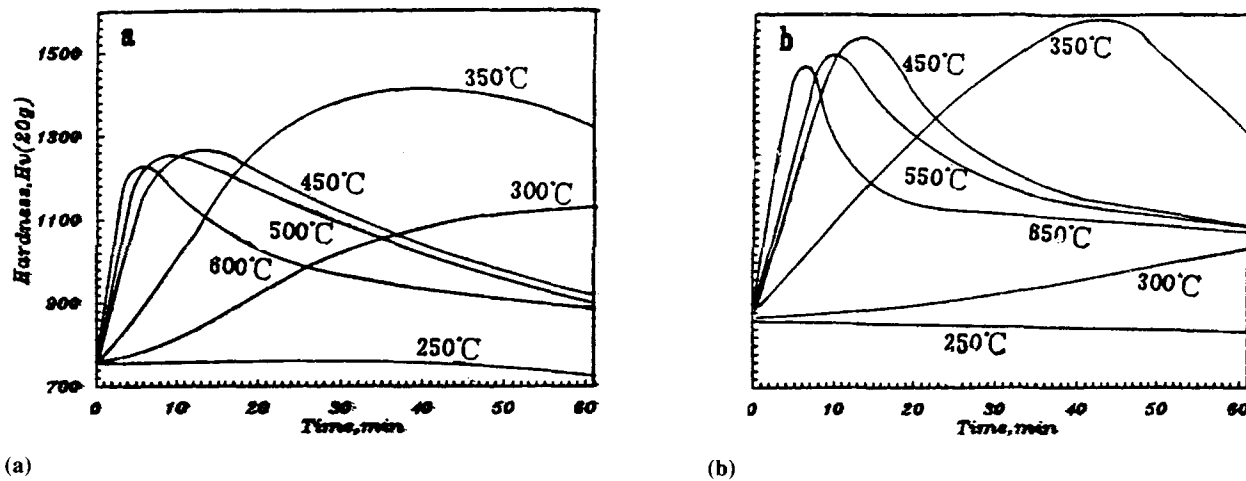


Fig. 5 Hardness variations in brush-plated coatings after heating at various temperatures. (a) Ni-P coating. (b) Co-W-P coating.

authors constructed the diagrams of isothermal crystallization of Ni-P and Co-W-P coatings, as shown in Fig. 4. Extrapolating the end line of crystallization along the $t \rightarrow 0$ direction to approach the initial ordinate, one can conclude that the crystallization processes of Ni-P and Co-W-P coatings may finish instantaneously at temperatures about 409 and 415 °C, respectively.

5.3 Precipitation Hardening during Crystallization

The coatings were heated and held in vacuum. Hardness was measured at room temperature and is shown in Fig. 5. At 250 °C, hardness barely varies with time, decreasing only slightly after 30 min. Above 300 °C, the Ni-P and Co-W-P coatings crystallize, and the high hardness dispersoids, Ni₃P and Co₂P, precipitate, which causes the coating hardness to increase. With time, the dispersoid phases grow and the hardness of the coatings decreases. Then, a normal precipitation hardening process occurs. However, note that during brush plating the supersaturation amount of P is relatively high, and phosphide will precipitate in larger amounts than under normal conditions. Consequently, the coatings can still maintain higher hardness than in their amorphous state, even though the size of the precipitated phase increases. The hardnesses of Ni-P and Co-W-P coatings are then about 900 and 1100 HV, respectively.

6. Discussion

At the forming instant of a hot work die, the impression surface temperature rises sharply. If water-base graphite lubricant is used, the thickness of the surface layer whose temperature is higher than the tempering temperature is thinner than 0.1 mm.^[6] Although brush plating presently cannot guarantee this thickness, it can significantly lower the die steel temperature and postpone the softening process.

Because of high hardness, good finish, relatively low friction coefficient, the coatings improve the tribological performance of dies. They are extremely beneficial to the procedure of drawing forgings from die impressions, and can shorten the

staying time and lower the die temperature. Additionally, they also increase productivity.

More importantly, during die operation, the coatings are heated suddenly above their instantaneous crystallization temperatures. The crystallization and precipitation processes are then completed instantaneously, which produces a strong secondary hardening effect that relies on the precipitating of the disperse hardening phase and ensures a relatively higher red hardness of the die surface (at least in approximately 2 hours limit of the service life of hot work dies), which improves the thermal wear resistance of dies. This is the main reason why the amorphous brush-plated coatings can increase the life of hot work dies.

7. Conclusions

Ni-P and Co-W-P coatings achieved by the use of brush plating possess high hardness (about 730 and 840 HV, near 1400 and 1600 HV after proper heat treatment), relatively low friction coefficient, good wear resistance, strong oxidation resistance, and can improve the surface finish of dies by 1 to 2 classes. Applying Ni-P and Co-W-P brush-plated coatings to hot work dies can increase their service life by 33 to 180% and bring about a considerable economic effect. Brush plating is a useful surface technique for dies and molds. The main reason why the use of Ni-P and Co-W-P brush-plated coatings improves the service life of hot work dies is that, during die operation, crystallization and precipitation processes take place simultaneously, which produces a secondary hardening effect and causes a relatively high red hardness, therefore ensuring good thermal wear resistance of the surface layers.

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