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Plasma Spraying of High-Nitrogen-Bearing Steels for Wear-Resistant Coatings and Structural Applications

S. Khatri, R. Smith, P. Jokiel, E. Lugscheider, and M. Bohley

Thermally sprayed coatings of high-nitrogen-bearing steel for corrosion resistance and wear applications were investigated. High-nitrogen steels represent a new class of engineering materials. Additions of nitrogen enhance the strength, corrosion resistance, and hardness of austenitic stainless steels without sacrificing low-temperature ductility and fracture toughness. In addition, the precipitation of nitrides at the grain boundaries is slower compared to that of ferrous carbides, thus increasing the elevated-temperature use of the steels. The objective was to take advantage of these properties and produce high-nitrogen steels via plasma spraying. An Fe-18Cr-18Mn steel with 0.61 wt% N was air and vacuum plasma sprayed over steel and aluminum substrates. Plasma spraying was conducted with Ar/H$_2$, Ar/He, and Ar/N$_2$ plasma gases in air, vacuum, and nitrogen atmospheres. It was found that the nitrogen atmosphere increased the nitrogen and nitride content of the coatings and improves wear and corrosion properties. The sprayed coatings were characterized for nitrogen and oxygen content, porosity, hardness, and wear resistance.

Keywords
nitrogen steels, plasma spraying, reactive spraying, wear resistance coatings

1. Introduction

PRELIMINARY investigations have shown that reactive plasma spraying can consolidate nitrided steel powders and even nitride the steels during in-situ deposition. These results indicate that plasma spraying is a potential method for producing coatings or structurally nitrided steels. Figure 1 illustrates the general principles of reactive plasma spray forming, which combines conventional plasma spraying with steel particles injected into thermal plasma jets for heating. Nitrogen-bearing gases are injected into these thermal jets, where they dissociate and ionize to form N$^+$, which either reacts with the matrix to form nitrides or goes into solution. Opportunities exist for producing an entirely new class of tribological coatings or functionally graded steels in which high-nitrogen steel can be placed in the locations where it is needed. The process can consolidate nitrided powders without substantially lowering their N$_2$ contents and can even enhance the N$_2$ contents.

Coating applications for automotive components and other industrial parts that are currently hard chrome plated may be developed, especially where more conventional tungsten carbide/cobalt cermet-type coatings cannot be justified economically. Suitable replacement coating materials and processes are being sought to eliminate hard chrome plating due to its detrimental environmental impact. The inherent strength and corrosion resistance of high-nitrogen steels may make them suitable replacement materials for hard chrome plating; plasma spraying, especially reactive plasma spraying, is a promising coating or forming process. This investigation has been conducted both to evaluate the reactive plasma spray process for nitrogen steels and to characterize the coatings.

High-nitrogen steels represent a new class of engineering materials. Nitrogen occurs universally in all steels. Although its solubility under normal processing conditions is low, it can exert a large influence on the properties of steel. Some of these effects can be detrimental—for example, embrittlement. Often, however, nitrogen has beneficial effects, which in recent years has resulted in efforts to develop new processing techniques and alloys for enhanced nitrogen content in steels. Additions of nitrogen have been shown to enhance the strength, corrosion resistance, and hardness of austenitic stainless steels without sacrificing low-temperature ductility and fracture toughness (Ref 1-4). Also, precipitation of nitrides at the grain boundaries has slower reaction kinetics than ferrous carbides. Hence, nitrogen acts as an austenite stabilizer, offers solid-solution

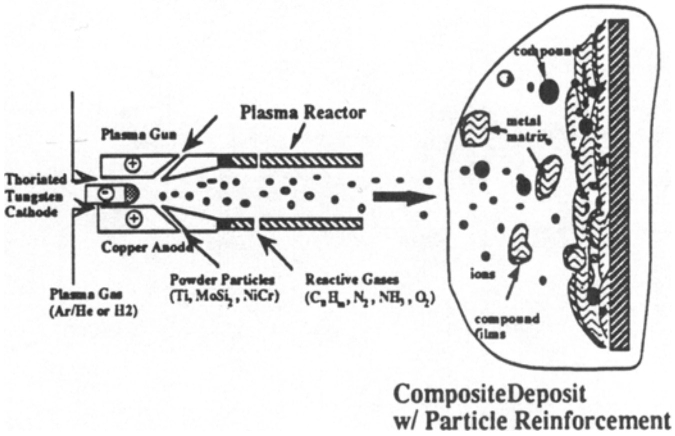

Fig. 1 Schematic illustrating the general principles of reactive plasma spray forming

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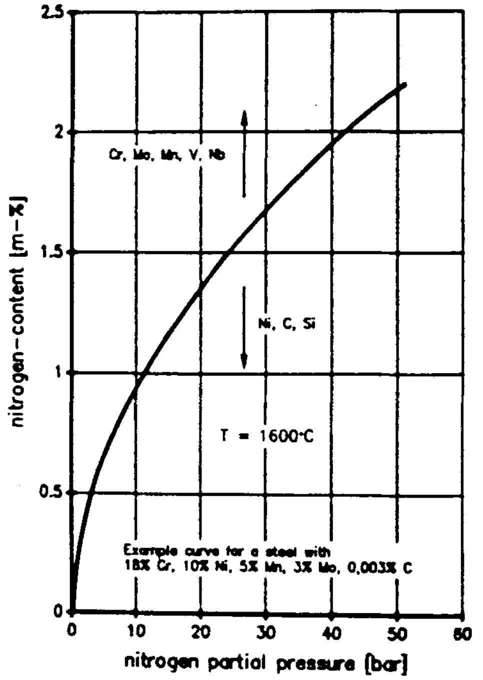


Fig. 2 Influence of pressure and alloying elements on the N_2 concentration of an austenitic steel

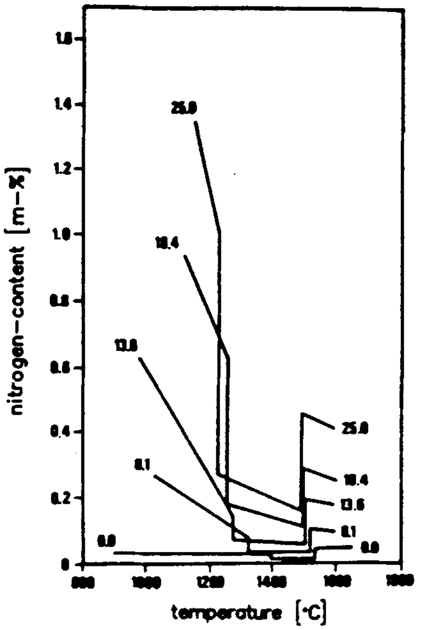


Fig. 3 Nitrogen solubility of iron-chromium alloys in equilibrium with an atmosphere of 0.101 MPa nitrogen

strengthening, improves pitting corrosion resistance, and can be used as a substitute for more costly nickel (Ref 5).

Many of the beneficial effects of nitrogen are due to its interaction with the alloying elements present. These interactions may involve precipitation reactions to form nitrides and/or carbonitride clusters or zones in either ferrite or austenite phases. These interactions influence solid-solution hardening, precipitation hardening, grain growth, hardenability, work hardening, and creep resistance. Because nitrogen, like carbon, occurs as an interstitial alloying element in ferrite and austenite, it can form Fe-N austenites and martensites with tempering and transformation behavior analogous to Fe-C systems. These steels range from simple carbon-manganese steels to high-strength low-alloy, creep-resisting iron-chromium, and austenitic stainless steels. Many times, efforts to incorporate higher amounts of nitrogen into steels have led to the development of new alloys, such as iron-chromium-manganese and iron-vanadium-titanium. Chromium and manganese increase the solubility of nitrogen in steels to a large extent. Figure 2 shows the influence of pressure and alloying element concentrations on the solubility of nitrogen in steels (Ref 4). Figure 3 shows the solubility of nitrogen in steel as a function of chromium content and temperature (Ref 6).

Incorporating nitrogen in steels in a controllable fashion has presented numerous challenges. Some of the methods for processing nitrogen steels include melting and casting under nitrogen pressure, addition of nitrogen-bearing materials during electroslag remelting, use of a nitrogen-rich master alloy, use of powder metallurgy (P/M) processes with nitrogen gas atomization, and bubbling of nitrogen plasma and/or nitrogen gas through the molten steel.

2. Plasma Spraying of Nitrogen Steels

Although extensive research has been conducted on nitrogen-bearing steels, these steels have not been fully exploited in terms of commercial application. The application of nitrogen steels is limited by the low solubility of nitrogen in liquid steels. Further difficulties are associated with incorporating high amounts of nitrogen into the steels and processing of nitrogen steels without loss of nitrogen. The nitrogen content of steels can be increased by increasing nitrogen pressures during melting and/or spraying. Powder metallurgy techniques successfully utilize the former method, that is, increasing the melt atmosphere pressures to increase the nitrogen content. On the other hand, thermal spray deposition techniques can increase the nitrogen content by increasing the chamber pressure and utilizing the higher reactivities of N^+ ions in a nitrogen plasma.

This research focuses on the thermal and plasma spray deposition of nitrogen steel powders with the goal of advancing a new approach to the processing of nitrogen-strengthened steels and composite materials while furthering the understanding of thermal plasma materials synthesis. Plasma spraying is a potential method for processing steel powders with higher nitrogen contents. It is anticipated that spraying under favorable conditions (e.g., high-pressure nitrogen or ammonia environments) will result in increased solubility of nitrogen in the matrix. For successful implementation of thermal plasma materials synthesis, the major scientific challenge lies in controlling the synthesis of products through optimized reactions and processing. By suitable selection of the reacting species, their concentration, and the atmosphere, the nitride phases formed, the nitrogen content of the steels, and thus the coating characteristics (e.g., hardness, strength, and corrosion resistance) may be controlled.

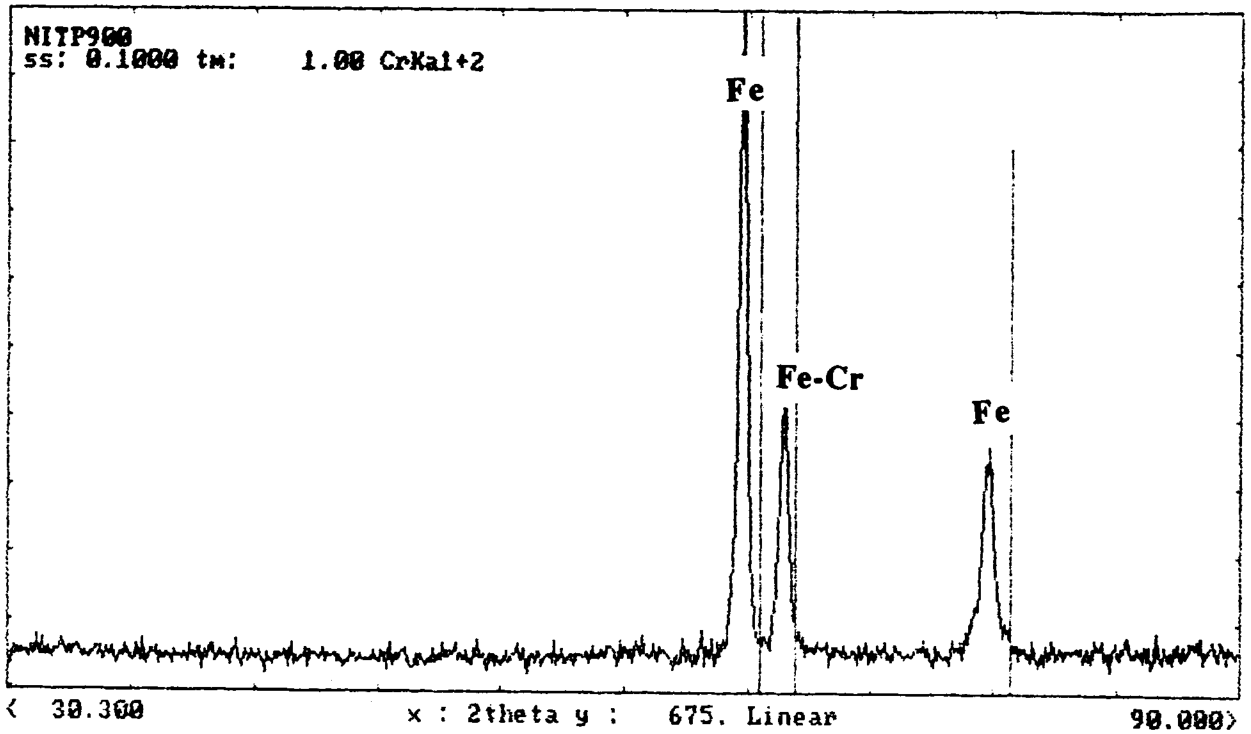


Fig. 4 XRD pattern of as-received P900 powder

Preliminary research has been aimed at spraying nitrogen steel coatings via air plasma spraying (APS) and vacuum plasma spraying (VPS) for tribological applications. It is believed that lower-cost nitrogen steel coatings may have potential use in high-volume applications—for example, cylinder liners for automotive engines. It is anticipated that steels of various compositions and nitrogen contents could be produced in air and controlled atmospheres by the plasma spray process. The sprayed coatings and powders must be evaluated for hardness, porosity, wear properties, composition, cleanliness, and change in nitrogen content. Feasibility studies are already in progress; preliminary data on these coatings look encouraging and are presented in the next section.

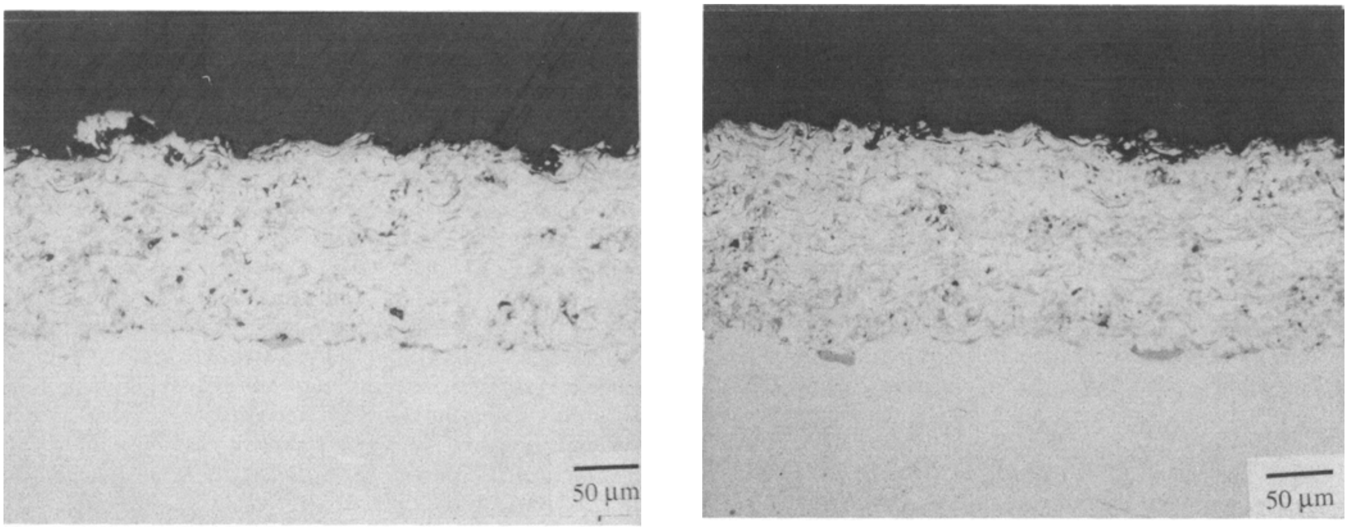
3. Experimental Procedures

Air and vacuum plasma spraying of P900 nitrogen-bearing powder was conducted on steel substrates. The APS experiments were conducted using an EPI-93 anode plasma gun. Typical spray distance was 100 mm, and a current of 1100 A and power of 55 kW were utilized. All coatings were sprayed with argon as the primary plasma gas and helium, hydrogen, and nitrogen as secondary gases. The argon flow rate was maintained at 55 slm for all APS experiments. Helium and H_2 flow rates of 20 and 3 slm, respectively, were utilized. To study the effect of N_2 as the secondary plasma gas, three different flow rates—10, 15, and 20 slm (standard liters per minute)—were analyzed.

The vacuum/controlled-atmosphere plasma spray experiments were conducted using an F-4 plasma gun. Typical spray distance was 215 mm, and a current of 860 A and power of 50 kW were utilized. The flow rate of the argon plasma gas was 30 slm. Flow ratios for Ar/N_2, Ar/He, and Ar/H_2 plasma spraying were 30/8, 30/12, and 30/6 slm, respectively. The Ar/He and Ar/H_2 plasma spray runs were conducted in vacuum, whereas the Ar/N_2 plasma experiments were conducted with N_2 back pressures of 450 and 760 torr, respectively.

Metallography and microhardness examinations were conducted on specimens. Vickers hardness testing was used to determine microhardness using 300 gf loads and reported as a mean for eight indentations. X-ray diffraction (XRD) patterns were obtained using a Siemen's model D500 (Siemens Corp., New York, NY) diffractometer to identify the phases present in the plasma-sprayed coatings. Leco (Leco Corp., St. Joseph, MO) gas analysis was conducted to determine the nitrogen content in the coatings and the powders both in atomic form and as nitrides.

Pin-on-disk (POD) sliding wear tests were conducted according to ASTM standard G99-90 on selected Fe-45Cr-0.45C (F90) deposits sprayed with and without nitrogen as the secondary plasma gas. Type 4340 steel wear disks (60 mm diam by 10 mm thick) were reactively plasma spray coated with steel powders up to 250 μm thick. Wear behavior, friction, and total wear scar cross-sectional area were then measured after sliding a 10 mm diam SAE 440 stainless steel ball at room temperature (20 °C) under dry and lubricated (SAE 1040 oil at 1 drop every 10 s) conditions at 15 and 30 N loads. The tests selected for this



(a) (b)

Fig. 5 Micrographs of APS coatings of P900 powder with Ar/He plasma gases (a) and with Ar/N_2 plasma gases, with N_2 at 15 slm (b)

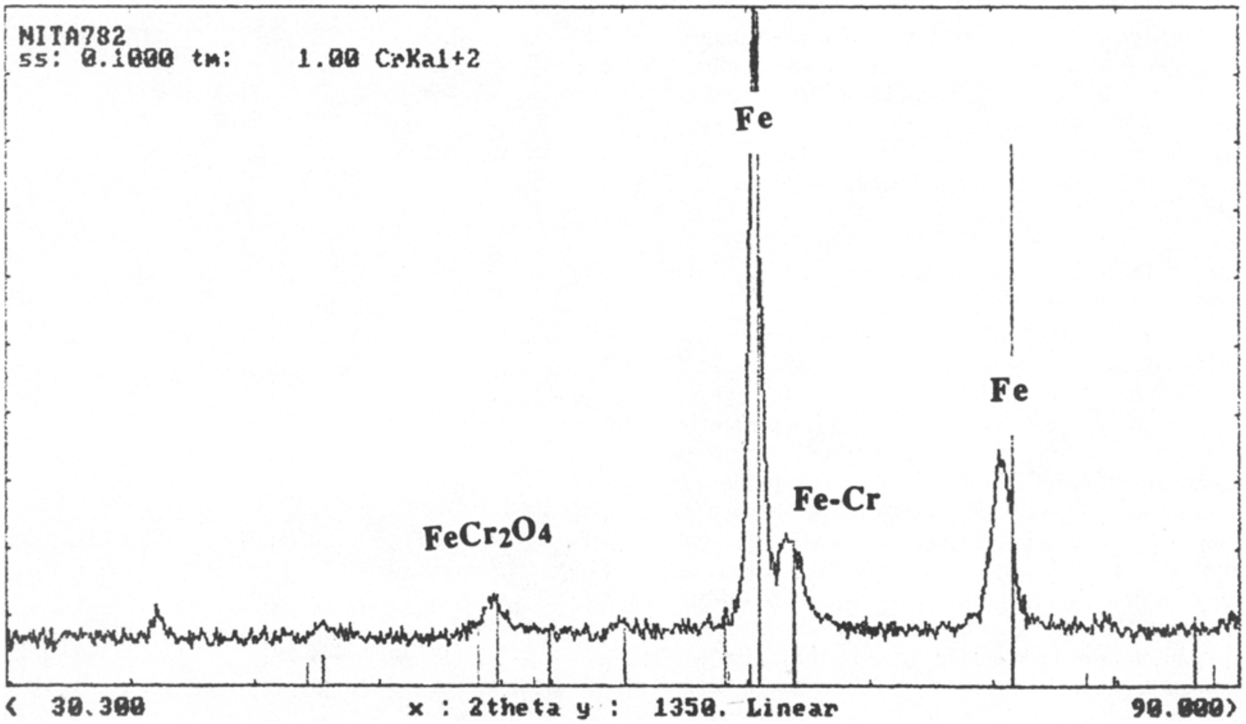


Fig. 6 XRD pattern of APS coatings of P900 powder with Ar/N_2 plasma gases (N_2 at 15 slm)

composition were chosen to directly determine the wear properties of the sprayed coatings.

4. Results and Discussion

The nitrogen-bearing steels were studied by spraying P900 austenitic steel powders (Fe-18Cr-19Mn), a powder composition developed under German government sponsorship with 0.39 wt% N_2, onto a mild steel substrate using APS and VPS methods. An XRD plot of the as-received P900 powder is shown in Fig. 4. The powders show the presence of iron with carbon and chromium solid solution. The peaks show a shift due to lattice stretching caused by the presence of manganese. Air plasma spraying was conducted with argon as the primary gas and with helium, H_2, and various amounts of N_2 as the secondary plasma gas. For vacuum-chamber plasma spraying, similar plasma gas compositions were utilized; however, spraying was also conducted under various nitrogen-atmosphere pressures.

4.1 *Air Plasma Spraying*

Figures 5(a) and (b) are representative optical micrographs of nitrogen steel APS coatings on steel substrates with helium and N_2 as secondary plasma gases. The coatings show good bonding to the substrates. Nonmelted particles are present, especially in the coating produced by spraying with the colder Ar/He plasma gas. As expected, the coatings show the presence of oxides (gray regions). With increased nitrogen flow rates in the Ar/N_2 plasma gases, the coatings, due to the hotter nature of the plasma jet, show fewer nonmelted particles. X-ray diffraction patterns of the plasma-sprayed coatings reveal the presence of oxides in addition to iron-carbon and iron-chromium peaks. The oxides are believed to be a mixture of iron-chromium, manganese-chromium, and iron-manganese oxides, as represented in the XRD plots. Although not very clear, the XRD plots of coatings sprayed with N_2 plasma gas sometimes indicate the formation of manganese nitrides (Fig. 6).

The hardness measurements and their standard deviations are listed in Table 1. The lowest hardness is seen for coatings with Ar/He plasma gases. The hardness is higher with use of Ar/H_2 plasma gases, and maximum hardness is obtained for Ar/N_2 plasma-sprayed coatings. The higher hardness of the coatings with Ar/H_2 and Ar/N_2 can be attributed to hotter plasmas, resulting in higher oxidation. Also, it is probable that nitrides are formed (as seen in the XRD plots), further contributing to the additional increase in the hardness of the Ar/H_2 sprayed coating.

Table 1 lists the nitrogen contents of the as-received powder and the APS coatings. As can be seen, the nitrogen content of the coatings is higher than that of the as-received powder. Use of Ar/He and Ar/H_2 plasmas increased the nitrogen content to 0.5 wt% or more, at least a 25% increase compared to the baseline N_2 content (0.39 wt%). The nitrogen is picked up from the atmosphere. Even higher nitrogen contents can be obtained by using nitrogen plasmas. A nitrogen content of 0.641 wt% is obtained after spraying P900 powders with Ar/N_2 plasmas, as compared to 0.39 wt% for the as-received powder—an increase of almost 65%. It is clear that both the plasma gases and the background atmosphere N_2 content have a significant effect on the nitrogen contents of the sprayed coatings. Additional studies must be conducted to determine the exact phase nature of the nitrogen in the coatings (whether nitrogen is present in solid solution or as distinct nitride phases).

Table 1 Vickers hardness and nitrogen contents of the various APS coatings

Plasma gas	Hardness, HV (300 gf)	Standard deviation	N_2 content, wt%
P900	...	...	0.39
Ar/He	324.4	21.1	0.499
Ar/H_2	388.4	19.7	0.487
Ar/10 slm N_2	417.2	16.7	...
Ar/15 slm N_2	423.4	26.4	...
Ar/20 slm N_2	417.6	37.6	0.641

4.2 *Vacuum Plasma Spraying*

A chamber was used to contain the process and was evacuated to below 200 μm Hg before backfilling with argon or N_2 to the desired pressure. Similar to the APS coatings, spraying was conducted with Ar/He, Ar/H_2, and Ar/N_2 plasmas, with argon as the primary gas. Figure 7 shows a micrograph of a coating sprayed with argon and helium as the primary and secondary plasma gases, respectively. This coating was sprayed with a chamber pressure of 200 torr argon atmosphere. Bonding between the coating and the substrate was poor. The debonding was more noticeable when Ar/H_2 plasma gases were utilized. The colder Ar/He plasma also resulted in a large quantity of

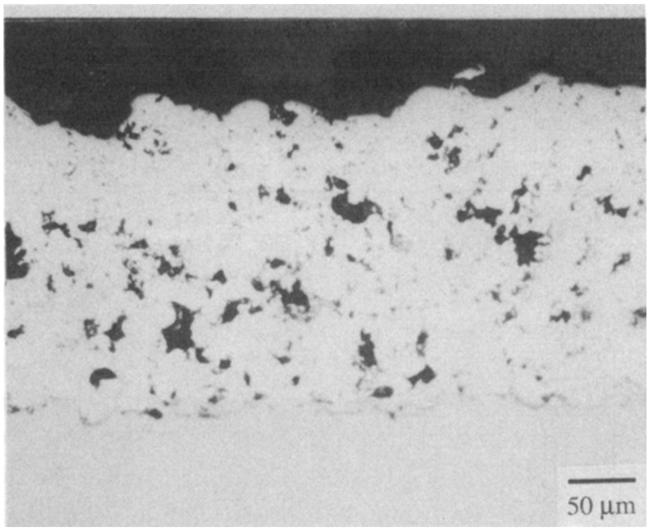


Fig. 7 Micrograph of VPS coating of P900 powder with Ar/He plasma gases

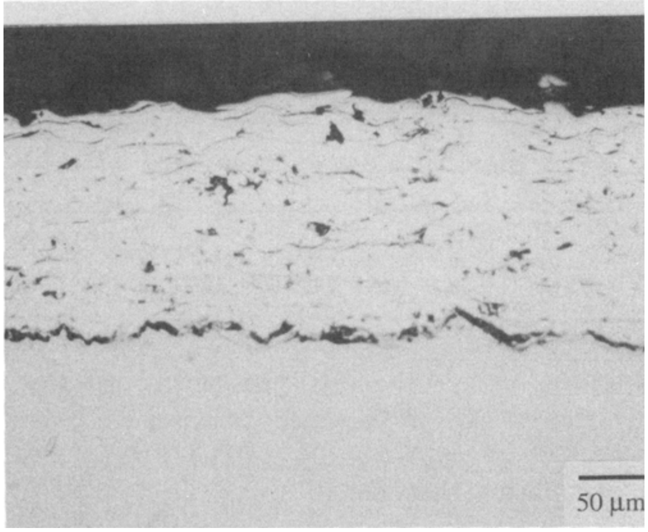


Fig. 8 Micrograph of VPS coating of P900 powder with Ar/N_2 plasma gases (N_2 chamber pressure of 450 torr)

nonmelted particles, leading to extensive porosity in the coating. The debonding was probably a result of substrate surface preparation techniques and/or thermal residual stresses generated during cooling of the splats upon impingement on the substrate. Similar coating experiments using P900 powders and Ar/H_2 plasma gas with a preheated substrate resulted in good bonding (Ref 7). These results lead the authors to believe that coating residual stresses play an important role during VPS of P900 nitrogen steel powders.

Figure 8 is a micrograph of nitrogen steel coatings sprayed with Ar/N_2 plasma gases in a nitrogen atmosphere with a chamber pressure of 450 torr. As with the Ar/H_2 plasma gas coatings, use of Ar/N_2 plasma also results in debonded coatings. As Ar/N_2 plasma is hotter than the Ar/H_2 plasma, the effect of thermal stresses is even more significant. This is seen in the form of intrasplat porosity (Fig. 8). Controlled-atmosphere spraying resulted in lower, almost negligible amounts of oxides, as evident by the absence of gray areas. It is hypothesized that the microstructural results of air and vacuum plasmas suggest that the presence of small amounts of iron oxides is useful to maintain the integrity of the coatings. Because iron oxide has a lower melting point than steel, it serves as a compliant layer upon solidification of the steel droplets and partially relieves thermal stresses generated upon solidification.

The results of microhardness testing of the controlled-atmosphere sprayed coatings are listed in Table 2. The hardness values of the VPS coatings are lower than those of the APS coatings (see Table 1). The lower hardness values are due to the absence of oxides in VPS coatings. It is difficult to comment on the variation of the coating hardness values with change in plasma gas composition and atmosphere, because coatings other than those with Ar/H_2 gas resulted in extensive porosity due to either nonmelted particles or microcracks from thermal stresses. The nitrogen content of the coatings is lower compared to the as-received powder particles. Nitrogen solubility is lower in the liquid steel compared to the solid phase. Thus, absence of a nitrogen atmosphere may have resulted in the evolution of nitrogen from the molten droplets.

The XRD plot of the coating sprayed with Ar/N_2 plasma is shown in Fig. 9. The plot shows the absence of oxides and the presence of phases similar to those in the as-received powder (i.e., iron-carbon and iron-chromium). However, the relative intensities of the peaks have changed and must be further analyzed.

Table 2 lists the nitrogen contents of the as-received powder and the VPS coatings. The results show that no significant change in N_2 content occurs after spraying with Ar/He plasmas. These results are encouraging. Use of Ar/N_2 plasma in a 450 torr nitrogen atmosphere results in an increased N_2 pickup of

Table 2 Vickers hardness and nitrogen contents of the various VPS coatings

Plasma gas	Hardness, HV (300 gf)	Standard deviation	N_2 content, wt%
P900	...	...	0.39
Ar/He	262.3	31.3	0.392
Ar/H_2	314	24.2	...
Ar/N_2 (450 torr)	274.6	39.2	0.538
	234.8	32.7	...
Ar/N_2 (760 torr)	223.7	17.8	...

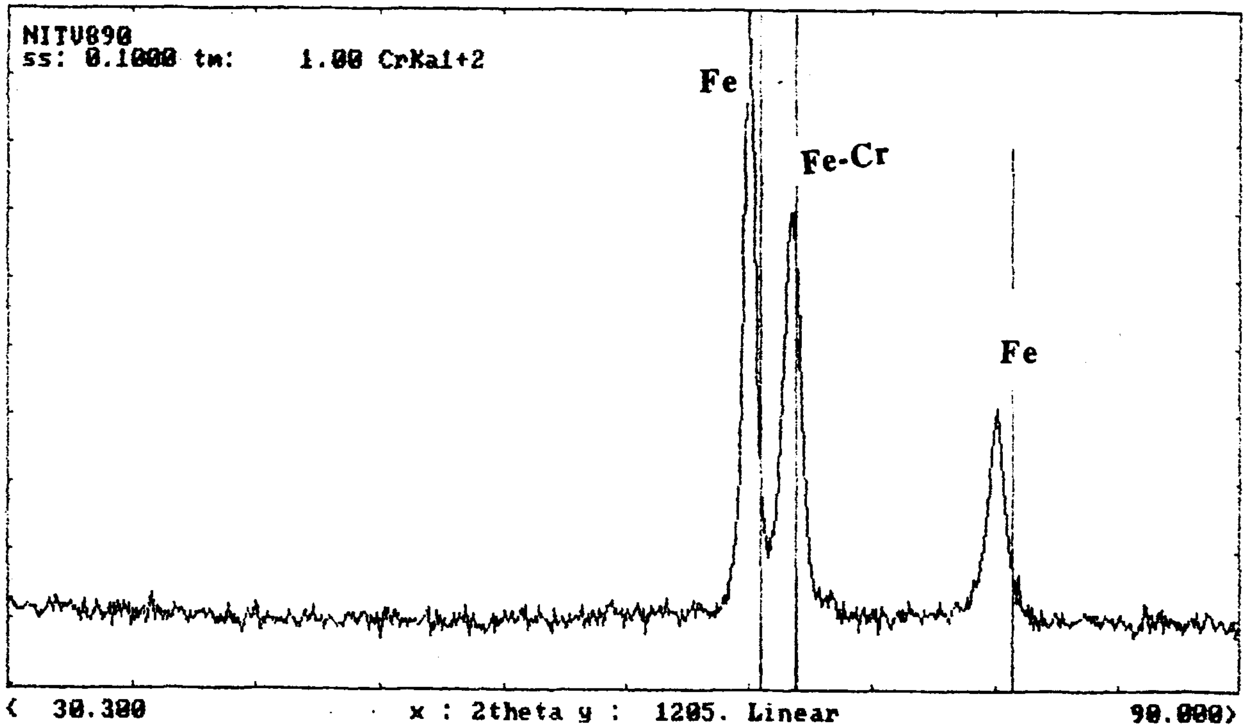


Fig. 9 XRD pattern of VPS coating of P900 powder with Ar/N_2 plasma gases (N_2 chamber pressure of 450 torr)

about 40% (0.54 versus 0.39 wt%). Use of Ar/He and Ar/H_2 plasma gases increases the nitrogen content by 0.1% or more. The nitrogen is picked up from the atmosphere. Even higher nitrogen contents can be obtained by using nitrogen plasmas. A nitrogen content of 0.641 wt% is obtained after spraying P900 powders with Ar/N_2 plasmas as compared to 0.39 wt% for the as-received powder, an increase of almost 65%. As in APS, it is anticipated that the plasma gas as well as the background atmosphere will influence the nitrogen content of the coatings. However, due to better control of atmospheric content and pressure, the VPS technique can potentially increase nitrogen content in the coatings.

4.3 *Wear Resistance Results*

Wear tests were not conducted directly on P900 samples, but to compare the effect of nitrogen on wear resistance, POD wear tests were conducted on sprayed high-chromium steel coatings. These coatings were made from F-90 (Fe-45Cr-0.45C) powders sprayed onto steel and aluminum substrates. Figure 10 presents the results of several unlubricated and lubricated tests of sprayed F-90 coatings and cast iron to show the influence of nitrogen in the plasma jets. Unless otherwise noted in Fig. 10, all the substrates were AISI 4340 steel. The cast iron comparison is presented because cast iron is presently the standard engine liner material. In most cases, the sprayed F-90 has lower wear resistance than the cast iron, especially when lubricated. The non-nitrogen-containing plasma-sprayed coatings showed higher wear resistance than the coatings sprayed with nitrogen-containing plasma. Figure 10 also shows the effect of graphite in the coatings. At lower loads, wear resistance improves with added graphite, but at higher loads, wear resistance decreases. This is probably due to the poor cohesion of the plasma-sprayed coatings with the substrate. The coefficient of friction of the plasma-sprayed F-90 coatings was similar to that of cast iron in lubricated state (0.06 to 0.08). In the unlubricated state, however, the F-90 steels had friction coefficients much lower than that of cast iron (0.6 for F-90 versus 0.8 for cast iron). Overall, the results summarized in Fig. 10 clearly indicate the potential for improved sliding wear resistance using reactively sprayed nitrogen steel coatings.

5. Conclusion

Reactive plasma spraying shows potential as an economical method for the synthesis of nitrogen-bearing steels. Results have shown that the nitrogen content of the steels can be significantly increased through the use of plasma spray techniques. The nitrogen gas, both as part of the plasma gas chemistry and in the background, affects the nitrogen content of the coatings. Air plasma spraying increases the nitrogen content with or without use of a nitrogen plasma gas. Without nitrogen in the plasma, the nitrogen content increases from 0.39 wt% to about 0.5 wt% (an increase of 25%). This is attributed to diffusion of nitrogen from the atmosphere to the molten nitrogen particles in the plasma jet. With 20 slm nitrogen in the plasma, the nitrogen content of the coatings almost doubles to 0.641 wt%. The integrity of the coatings sprayed in air seems acceptable. The coatings are devoid of any porosity and/or cracks due to thermal stresses. As expected, oxides are present in the coatings.

Similar to the APS coatings, the nitrogen content of vacuum/controlled-atmosphere sprayed coatings increases with the presence of nitrogen in the plasma gases and in the background atmosphere. No nitrogen content change was observed in coatings sprayed without nitrogen, thus leading to the conclusion that no loss of nitrogen results in the sprayed coatings.

F-90 steel sprayed coatings in the lubricated and unlubricated conditions show an improvement in sliding wear performance after 10,000 cycles.

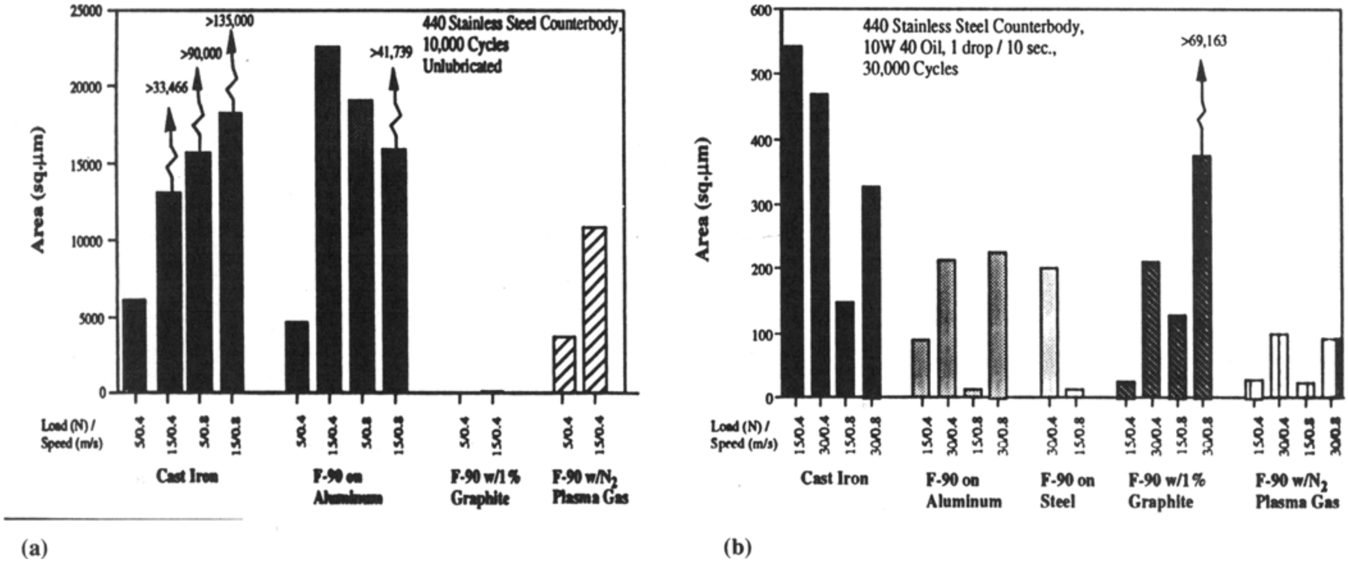


Fig. 10 Comparative POD test results for reactively sprayed nitrided steels in the unlubricated (a) and lubricated (b) condition

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References

1. M.O. Spiedel et al., *High Nitrogen Steel Proceedings* (Aachen, Germany), Metals Society, 1992
2. K.J. Irving et al., *J. Iron Steel Inst.*, Vol 199 (No. 10), 1961, p 153-175
3. X. Zheng et al., *High Nitrogen Steel Proceedings* (Aachen, Germany), Metals Society, 1992, p 320-325
4. B. Anthamatten et al., *High Nitrogen Steel Proceedings* (Lille, France), Metals Society, The Institute of Metals, 1988, p 46
5. I.A. Torkhov et al., *J. Met.*, No. 12, 1978, p 20-27
6. P. Menzel et al., *High Nitrogen Steel Proceedings* (Aachen, Germany), Metals Society, 1992, p 365
7. R. Smith and R. Knight, in *11th Int. Symp. on Plasma Chemistry* (Loughborough, U.K.), Vol 1, John Harry, Ed., 1993, p 139-144