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1 Introduction

Rolls used in steel manufacturing processes must satisfy various performance requirements. Because these rolls come into direct contact with the steel strip, they have an important effect on the surface quality of the strip. In particular, surface-modifying technologies have been developed and introduced with the process rolls that are used in cold rolling, coating, and stainless steel production equipment in order to increase the reliability of these rolls in response to higher strip quality requirements and the expanded variety of manufacturing processes. Among these, a large number of thermal spraying technologies[1,2] have been developed, and various types of materials have been applied up to the present time.[3]

Thermal spraying refers to a method of surface modification in which a powder or wire material is sprayed at high speed onto a base material while in a semi-molten state to form a coating. As features of thermal spraying, in comparison with other surface modification methods such as CVD (chemical vapor deposition) and PVD (physical vapor deposition), the speed of coating formation is extremely high, and a number of material types can be deposited by thermal spraying because this method has virtually no restrictions related to the material properties of the object being treated. Moreover, because the temperature of the base material can be held to under 150°C during spraying, this method also offers other advantages. For example, heat strain of the type that occurs during overlay welding for roll hardening is not a problem, and recycling repairs can be carried out at a comparatively low cost. However, the corrosion resistance of sprayed coatings is not adequate because fine pores remain in the coating,[4] and there are cases in which peeling under impact is a concern because the coating and base material are bonded mechanically. To solve such problems, sealing treatment technology or

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multi-coating techniques and heat treatment (fusing) technologies have been developed and are applied as required by the application.

This paper presents a brief explanation of the various types of surface-modifying technologies using thermal spraying which have been developed for process rolls up to this time, and describes the elucidation of the mechanism of build-up which forms on the surface of annealing line hearth rolls during the production of high strength steel strip, together with a newly developed technology for alleviating and preventing this problem.

2 Surface Modification Technologies for Various Types of Process Rolls

This chapter describes the surface modification technologies applied to bridle rolls, which have a tension controlling function, conductor rolls, which have a conductive function, tension meter rolls, which have a strip tension detecting function, and deflector rolls, which are used to change the direction of strip travel.

2.1 Bridle Rolls

The bridle roll is a type of process roll that is used to control strip tension. With these rolls, wear resistance is necessary in order to maintain this function over the long term without the occurrence of slips. Conventionally, these rolls were coated by chrome plating, but life was short due to wear. For this reason, WC cermet, which has high hardness among cermet coatings, was selected and applied by thermal spraying. However, unlike the chrome plated surface, WC cermet is a continuous body with a sharp surface shape, and causes dents on the steel strip if left in the as-sprayed condition. Therefore, a technique of polishing by buffing was developed to give the roughness peaks the same rounded shape as the chrome plated surface, and to give the WC coating a similar friction coefficient. Specifically, it was found that, with the bearing length ratio (mr) specified in JIS B0601, virtually the same roughness profile as that of a chrome plated surface can be obtained if the bearing length ratio of the 1/2 maximum height (Ry) from parts showing roughness peaks can be reduced to the same value as the chrome plated surface, and a buffing technique for controlling roughness in this manner was developed. **Figure 1** shows the results of an investigation of the relationship between friction and the bearing length ratio when the surface roughness Ra is 6~7 μm. In this case, it can be understood that the WC sprayed surface has basically the same friction coefficient as the chrome plated surface when buffing is performed two times, and a similar roughness profile is obtained. This technique made it possible to prevent the occurrence of dents on steel strips and extend the life of the WC sprayed rolls by more than five times in comparison with the conventional chrome plated rolls.[5]

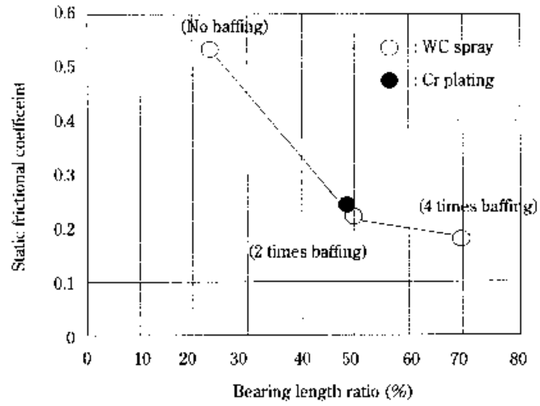


Fig. 1 Relation between bearing length ratio and static frictional coefficients of bridle roll

Further, if a WC-Co cermet thermal spray coating is used under a corrosive environment, Co, which is the WC binder, tends to corrode. For this reason, a Cr-added WC-Co-Cr cermet coating and a WC-Cr_3-C_2-Ni cermet coating, which uses Ni as the binder, were introduced,[6,7] establishing an appropriate selection of materials depending on the level of corrosion. For wet environments, a multi-coating was developed, in which the WC-Cr_3-C_2-Ni cermet is applied by thermal spraying to an undercoat, which also serves as a sealing technique. This type of coating achieves a life more than three times longer than that of conventional high carbon, high alloy overlay welding hardened rolls.

On the other hand, coating improvements have also been achieved through progress in thermal spraying technology. With high speed flame thermal spraying equipment, ultra-high speed powder spraying has been realized, the feed rate has been made uniform and the coating forming speed has been increased,[8] and the traverse accuracy of the thermal spray gun has been improved. As a result, it has become possible to form a finer coating and improve adhesion, and reduce undulations during spraying. At the same time, progress has also been made in analyzing the crystal structure of the thermal spraying powder. Based on this work, by using a granulation sintering powder with WC cermet, it is possible to obtain a coating that contains little W_2C in comparison with melting pulverized powder. The appropriateness of these improvement techniques for steel strips has also been evaluated quantitatively, and high steel strip quality, high productivity, and long roll life have been realized.

2.2 Conductor Rolls

Conductor rolls, which have an electrical conducting function as the cathode pole in the tin plating section, are required to provide corrosion resistance against strongly acidic solutions that contain mixed hydrochloric acid, fluoric acid, and other acids. Conventionally, these rolls have been chrome plated, and their life was short due to corrosion. Therefore, SFWC 2 type self-fluxing

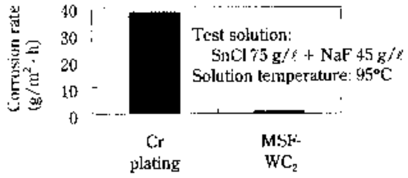


Fig. 2 Comparison of corrosion rate between MSF-WC_2 and Cr plating used for conductor roll

alloys, as specified in JIS H8303, which possess electrical conductivity and provide excellent corrosion resistance and wear resistance, were evaluated and introduced. In an immersion test, as shown in **Fig. 2**, the corrosion rate was reduced to less than 1/10 that of chrome plated material. However, it was expected that there would be cases in which the WC material peeled off, the plating components precipitated in the tracks left by the peeling, and this would cause dents on the strip. For this, a thermal spray coating was developed by applying the cermet in a flattened form by gas plasma spraying, thus preventing peeling of the WC and reducing the peeling tracks. As a result, roll life has been extended to more than five times that with chrome plated rolls, and dents have not been a problem.[9)]

2.3 Deflector Rolls and Tension Meter Rolls

Deflector rolls and tension meter rolls are required to provide wear resistance and corrosion resistance. Therefore, a coating improvement technology was developed in order to achieve a dramatic increase in the wear resistance of Ni-base self-fluxing alloys, which possess excellent corrosion resistance. Specifically, a technique for producing a fine coating was developed by adding metal carbides (metal carbides with ductility), which resist peeling from the alloy matrix, in amounts of up to 50 mass%, and fusing this coating. As a result, roll life has been extended to more than three times that of the conventional SUJ rolls.[10,11)]

3 Technology for Preventing Buildup on Hearth Rolls

3.1 Description of Problem

Hearth rolls, which convey the steel strip through the annealing section of continuous annealing lines and similar equipment, must possess resistance to high temperature wear and thermal shock due to cyclical heating and cooling. Normally, in lines where the temperature of the roll itself is less than 850°C, Cr_3-C_2-NiCr is applied by thermal spraying in order to reduce wear under high temperature conditions. In rolls used at temperatures of more than 850°C, the thermal spraying material is MCrAlY,[12–14)] which is mainly used in gas turbines and jet engines, with added oxide ceramic material. The purpose in this case is to prevent Fe type buildup, as well as to secure wear resistance. Here, it should be mentioned that the M in this MCrAlY is the main composition system, comprising Co, Ni, and Fe, and Cr and Al are protective oxidation film forming elements. Y is an element that has the function of strengthening and maintaining the oxidation film.

In recent years, increasing production of high strength steels has caused buildup problems with this conventional coating material. These steels, which have been developed and commercialized to meet the need for weight reduction in the automotive industry, are strengthened by adding Si, Mn[15)] and P, which form solid with Fe. However, because these elements are easily oxidized, they tend to concentrate at the strip surface during annealing.[16)] These concentrated oxide compounds then build up on the thermal sprayed coating on the hearth roll barrel. As a result, there has been a remarkable increase in quality-related rejects due to the transfer of these substances back to the steel strip. In other words, with thermal sprayed coatings of MCrAlY materials that conventionally contained added oxide ceramics, it became impossible to provide adequate assurance of resistance to buildup on the roll surface as the amount of high strength steel strip increased.

3.2 Elucidation of Mechanism of Buildup by Investigation of Actual Condition of Coating

The coating in areas with buildup was sampled from the surfaces of rolls that had been used for approximately five years in the soaking section of a continuous annealing line, and SEM and chemical analysis were performed on the surface and the cross-sectional direction. **Photo 1** shows an SEM surface micrograph. The largest amount of buildup can be seen in the black area labeled 1. An analysis of the surface by EDX showed that the area labeled 1 consisted almost entirely of Mn, whereas, the surrounding area, which is labeled 3, showed a reduced level of Mn and an increased level of Al. An SEM cross-sectional micrograph of area 3 and the EPMA scanning images of Mn, Al, and O on the surface (**Photo 2**) were taken, and it was found that the Al which had diffused from the spray coating was distributed virtually uniformly in the concentrated Mn. The results of a surface X-ray diffraction analysis of this area identified MnO, Al_2O_3, and spinel type compound oxides of $MnAl_2O_4$. From this, it was understood that, at the interface between the buildup part and the coating, a solid reaction occurred between Al which diffused[17)] from the coating and Mn compounds that had concentrated at the surface, resulting in a strong buildup.

3.3 Analysis of Reaction Products by Simulation

In order to clarify theoretically that the Al diffused from the coating side and the compounds of Mn which had concentrated at the surface from the steel strip formed compound spinel type oxides by a solid reaction, the reaction behavior of the steel strip and the thermal

Photo 1 SEM surface micrograph of build-up portion

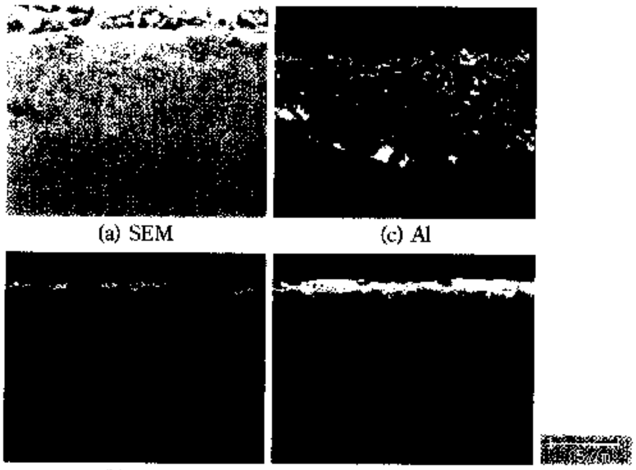


Photo 2 SEM cross-section micrograph and EPMA scanning image of Mn, Al and O at position No. 3

spray coating in the annealing furnace was analyzed using a thermodynamic chemical equilibrium computation software called ChemSage.[18] The calculated results are shown in **Table 1**, and indicate that in a solid reaction between the concentrated Mn compounds generated from the steel strip and the thermal spray coating, $MnAl_2O_4$, which is a spinel type oxide of MnO and Al_2O_3, will form in the temperature range of 700~950°C, regardless of the annealing furnace atmosphere.

Further, a chemical potential map was prepared using simulation software MALT 2[19] in order to verify that these compound oxides may in fact appear. In preparing the map, a temperature of 970°C and N_2 partial pressure of 1 MPa were used. The results are shown in **Fig. 3**. The partial pressure of oxygen equivalent to that in actual annealing furnaces corresponded to the oxygen partial pressure region in which spinel type compound oxides form by a reaction between Mn in the steel and Al in the coating, indicating that it is possible for these substances to appear under actual operating conditions.

Table 1 Stream constituents with simulation program 'ChemSage'

Constituents	Amount (mol)
H_2/gas/	3.00×10^{-2}
N_2/gas/	9.70×10^{-1}
O_2/gas/	6.00×10^{-6}
CO/gas/	1.50×10^{-4}
Mn	1.33×10^{-3}
Fe	1.44×10^{-1}
Co	1.06×10^{-2}
Cr	5.54×10^{-3}
Al	3.20×10^{-3}
Y	1.04×10^{-3}
Al_2O_3	1.26×10^{-3}
C	1.92×10^{-3}

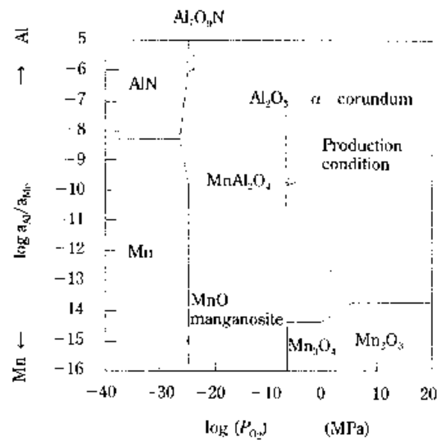


Fig. 3 Chemical potential map of Al-Mn-O system at 970°C

It might also be noted that a similar reaction involving Cr in the coating is conceivable. The above considerations suggest that it is possible that a solid reaction resulting in the formation of spinel type compound oxides due to Mn buildup may proceed in the temperature region of 700~970°C when the partial pressure of oxygen ($\log P_{O_2}$) is in the range of −24~5.

3.4 Study of Mn Buildup Resistant Material in Laboratory Tests

From the results of the investigation of the actual coating and the simulation described above, it was inferred that reducing the Al content of the MCrAlY coating material and suppressing the outward diffusion of Al provide an effective method of reducing and preventing Mn buildup with thermal spray coatings having an MCrAlY base. However, the relationship between Mn buildup and the ceramics that are added to MCrAlY had not been investigated previously. Therefore, the relationship between Mn buildup and the Al content of MCrAlY and amount and type of ceramic material was investigated by laboratory Mn buildup tests. As shown in **Table 2**, test pieces were prepared using eight types of coating material containing varying amounts of Al and amounts and types of ceramics. These coatings were applied to an SUS base metal 25 mm square and 10 mm in thickness. The test results, as shown in **Table 3**, were adjusted so that the dew point would in all cases be from −30 to −20°C in an atmosphere of 3%H_2-N_2 at a temperature of 950°C. The tests were conducted using the method shown in **Fig. 4**, in which high tensile steel sheets were placed in uniform contact with the test specimens and exposed for an extended period of time in an atmosphere furnace. The EDX analysis values of the coating surfaces after the test are shown in **Fig. 5**. The Mn content increased basically in proportion to the Al content of the surface, and both the surface Al and Mn increased as the Al content of the MCrAlY increased. It was also found that Mn decreased as the amount of ceramic addition increased, and the C ceramic was more effective than the A ceramic in reducing the amount of Mn. In other words, the amount of Mn varied depending on both the amount of ceramic addition and the type of ceramic added. The above indicates that reducing the Al

Table 2　Characteristics of spray coating

	No.	1	2	3	4
Thermal coating	Each MCrAlY + Ceramics	CoCr12AlY	CoCr12AlY + 10 mass% A metal oxide ceramics	CoCr12AlY + 20 mass% A metal oxide ceramics	CoCr8AlY
Base metal	No.	5	6	7	8
	Each MCrAlY + Ceramics	CoCr8AlY + 10 mass% A metal oxide	CoCr8AlY + 20 mass% B metal boride ceramics	CoCr8AlY + 10 mass% C metal oxide ceramics	CoCr8AlY + 20 mass% C metal oxide ceramics

Table 3　Test conditions

Dew point	(°C)	−30∼−20
Atomosphere		3% H_2-N_2
Hearth temperature	(°C)	950
Test time	(h)	60

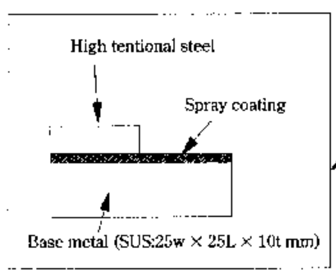


Fig. 4　Outline of test apparatus

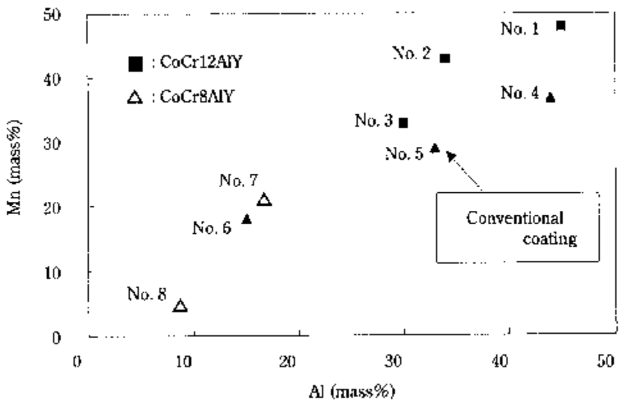


Fig. 5　Results of EDX analysis on sample surface

content is effective in preventing Mn buildup, and ceramic addition is effective in suppressing the outward diffusion of the Al in MCrAlY.[20] It is therefore considered that determining the proper type and amount of ceramic material provides an effective method of preventing Mn buildup.

3.5 Design of Thermal Spray Material and Basic Performance Evaluation

A material was designed and specimens were prepared using MCrAlY with reduced Al and a ceramic that had the effect of suppressing the outward diffusion of Al. These test pieces were used to evaluate thermal shock resistance and high temperature wear resistance, which are fundamental performance requirements in hearth roll material. The conventional coating was used as a comparison material.

3.5.1 Evaluation of thermal shock resistance

Test pieces were prepared by spraying the developed coating on an SUS base metal 50 mm square and 10 mm in thickness. The test was conducted by repeatedly heating the test pieces to 1 000°C in a heating furnace with an air atmosphere, holding for 15 min, and water cooling for 15 min. This cycle was repeated a maximum of 20 times, and if no abnormalities were found, the piece was considered to pass. As a result, as with the conventional coating, no peeling of the developed coating was observed up to 20 cycles, and no oxides or other abnormalities were found. Accordingly, the developed coating is estimated to have satisfactory resistance to thermal shock.

3.5.2 Evaluation of high temperature wear

The hardness of the coating was measured using a high temperature microscope hardness gauge, based on JIS Z-2252. The measurement load at this time was set at 100 gf. The results are shown in **Fig. 6**. In the range of temperatures from room temperature to 400°C, the conventional coating showed higher hardness and the difference in hardness was large. However, when the

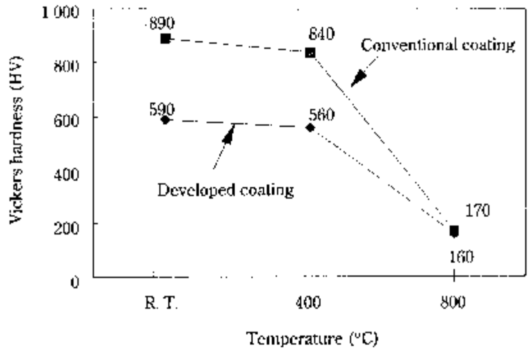
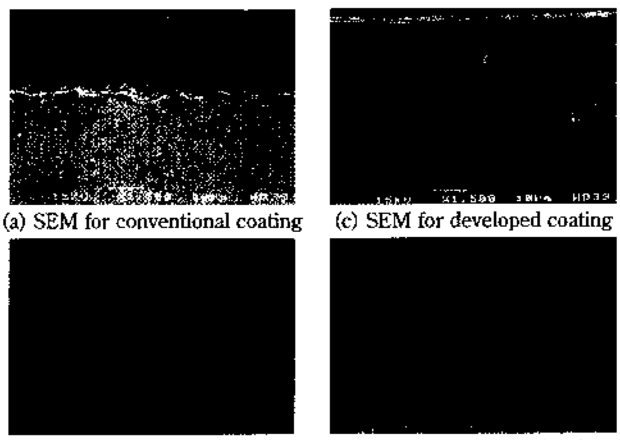


Fig. 6 Comparison of hardness between conventional coating and developed coating

temperature was increased to 800°C, the difference in hardness was virtually within the measurement error range. Accordingly, the new coating is estimated to have substantially the same high temperature wear resistance as the conventional coating when used at 850°C or higher.

3.6 Reliability of Mn Buildup Resistance in Laboratory Tests

An Mn buildup test was performed using the test conditions shown in Table 3 and the test apparatus shown in Fig. 4. **Photo 3** show the SEM cross-sectional micrographs and Mn surface analysis results of the conventional coating and the developed coating after the test. In the conventional coating, a concentration of Mn compounds built up on the coating, and Al and compound oxides formed in the surface layer of the coating. On the other hand, in the developed coating, virtually no Mn buildup could be observed.



(a) SEM for conventional coating (c) SEM for developed coating

(b) SEM of Mn for conventional coating (d) SEM of Mn for developed coating

Photo 3 SEM cross-section micrograph and EPMA scanning image of Mn, showing effect of build-up preventing (a), (b): conventional coating, (c), (d): developed coating

Table 4 Results of EDX analysis for conventional coating and developed coating

(mass%)

		Conventional coating	Developed coating
Surface	Mn	49.6	20.4
	Al	43.5	4.1
Cross section	Mn	23.5	3.1
	Al	59.0	3.0

Table 4 shows the results of a chemical analysis of the surface and cross section by EDX. From the analysis of Mn and Al on the surface, it can be understood that the Mn content of the developed coating was reduced to one-half that of the conventional coating, and the Al content was reduced to less than 1/10. From the analysis of Mn in the cross-section, the Mn content of the developed coating was approximately 1/7 that of the conventional coating, and inward diffusion was very slight.

From the results described above, it is considered that the developed coating has excellent resistance to Mn buildup in comparison with the conventional coating.

3.7 Total Evaluation in Production Equipment

Rolls with the developed coating and conventional coating were installed at adjacent positions in the soaking zone of a continuous annealing line and compared. The results showed that Mn buildup can be reduced from that in rolls with the conventional coating, contributing to a reduction in quality-related rejections of steel strips caused by buildup. Further, it was also possible to maintain the same level of surface roughness as in rolls with the conventional coating, showing that high temperature wear resistance is not a problem. At present, rolls where Mn buildup is a potential problem are being replaced with rolls coated with the newly developed material.

4 Conclusion

To extend the life of the process rolls used in steel manufacturing lines, research and development were carried out to establish the optimum material property design technology and surface modification technology by thermal spraying. The following results were obtained.

(1) For WC cermet thermal spraying of process rolls,
  (a) A roughness control technology was developed that satisfies the mutually contradictory performance requirements of slip resistance and dent resistance.
  (b) In order to improve corrosion resistance and enable long term use under wet environments, a multi-coating was developed in which WC-Cr_3C_2-Ni cermet is applied by thermal spraying to an undercoat, which also serves as a sealing treatment technique.

With these technologies, the life of rolls has been extended to more than three times that of the conventionally used chrome plated rolls.

(2) For conductor rolls, a thermal spray coating with reduced peeling tracks was developed by applying a self-fluxing alloy containing WC cermet by gas plasma thermal spraying, flattening the WC, and performing fusing treatment, thereby preventing peeling of the WC. This has made it possible to prevent dents, extending the life of conductor rolls to more than five times that of the conventional chrome plated rolls.

(3) For deflector rolls and tension meter rolls, a technology was developed which makes it possible to produce a fine coating by adding carbides that do not peel to a self-fluxing alloy in amounts of up 50 mass%, extending roll life to more than three times that of the conventional SUJ rolls.

(4) For hearth rolls,

(a) The actual condition of the conventional MCrAlY alloy thermal spray coating was investigated to elucidate the mechanism of Mn buildup. It was found that Mn adheres to the thermal spray coating, and compound oxides form by a solid reaction between this Mn and Al that diffuses outward from the interior of the coating.

(b) In an analysis of reaction behavior by simulation, it was found that spinel type compound oxides form in the temperature range of 700~950°C regardless of the furnace atmosphere. Based on the fact that the partial pressure of oxygen equivalent to that in commercial annealing lines is included in the region where formation occurs, the appearance of these oxides is considered possible.

(c) In laboratory tests of Mn buildup, it was found that reducing the Al content of MCrAlY is effective in preventing Mn buildup, and addition of ceramics is effective in suppressing outward diffusion of Al. Further, by determining the proper type and amount of ceramic material, it is possible to prevent Mn buildup.

(d) Laboratory tests confirmed that the newly developed material has excellent resistance to thermal shock, high temperature wear, and Mn buildup in comparison with the conventional coating. The new coating was also evaluated in an actual annealing line. The results showed that quality-related rejections of steel strip originating in buildup can be reduced and high temperature wear is not a problem.

It is considered that these results will contribute to higher quality and high productivity in steel strip products in the future.

In closing, the authors wish to express their sincere appreciation to all those concerned at Praxair Surface Technologies K. K., Tocalo Co., Ltd. and Dai-ichi High Frequency Co., Ltd. for their cooperation in the development of the surface-modifying technologies using the thermal spray method discussed in this paper.

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