NON-STICKING FURNACE ROLLS FOR STEEL PRODUCTS TO IMPROVE SERVICE LIFE AND PRODUCT QUALITY IN CONTINUOUS ANNEALING AND GALVANIZING LINES: PRELIMINARY STUDY ON CHEMICAL INTERACTIONS AND PICKUP MECHANISM

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ABSTRACT

Thermal spray cermet coatings are successfully applied on furnace rolls in continuous annealing and galvanizing lines. However, when processing HSS/AHSS with high Mn and/or high Si content, pickups can be formed on the rolls working in the different furnace zones.

The aim of this study was to acquire knowledge on the pickup mechanisms and the chemical interactions occurring between Cr_3C_2-NiCr and Al_2O_3-Co based matrix coatings and steel grades as a function of factors such as dew point, furnace temperature, surface roughness, etc.

Coatings were made to interact with pre-oxidized steels characterized by different levels of Mn and of Si by high temperature static reactivity tests and low temperature dynamic tests, which allow the friction of a roll on a steel strip at controlled temperature and furnace atmosphere. The interaction surfaces were then characterized by XRD, GDOES, AES, SEM-EDS.

The high temperature interaction tests results indicate that when aged cermet coatings have at their surface Cr_2O_3 and/or Al_2O_3, then $MnAl_2O_4$ and $Mn_{1.5}Cr_{1.5}O_4$ spinels will form with all the steels that have a sufficiently high Mn content. However, if coatings are aged at a DP of -30°C/-40°C, a nitride surface layer is produced that seems to affect the interactions with MnO.
Dynamic tests at low temperatures results indicate that coating roughness strongly influences pickups and must be limited as much as possible.

KEYWORDS

Cermet coatings, thermal spray coatings, furnace rolls, CAL, CGL, pickup mechanism, HSS.

INTRODUCTION

Thermal spray cermet coatings are currently being applied on furnace rolls working in continuous annealing lines (CALs) and continuous galvanizing lines (CGLs) processing High Strength Steels (HSS). Mandatory properties for such coatings are to have high resistance against wear, thermal shock and pickup of selectively formed oxides or iron dust particle matter from the steel strip to the roll's surface. More severe issues regarding the pickups have arisen since the production of AHSS/HSS containing elevated levels of Mn and Si and when adopting higher line speeds needed to increase the productivity [1, 2].

The pickups on furnace rolls may occur by either a mechanical mechanism due to slippage between the roll and steel strip or a reaction mechanism involving chemical interaction between the coating on the rolls and the oxides formed during the selective oxidation on the steel strip at the low oxygen partial pressure of the furnace atmosphere. Once pickup occurs, it will accumulate on the rolls and damage the steel strip that is being processed.

The rolls which give rise to pickups can be in the different furnace zones (heating, soaking, cooling and over-aging). In all zones the furnace is kept under a reducing H_2-N_2 atmosphere, with a dew point that can vary between -50°C and -20°C. The temperature of the heating and holding zones is between 750 and 850°C whereas that of the cooling and over-aging zones is under 500°C. Therefore, according to the different location of the rolls, the pickup mechanism is expected to be diverse.

In this paper are presented some of the results of the preliminary study from a RFCS Project funded by EC, to acquire knowledge on the pickup mechanisms and the chemical interactions occurring between thermally sprayed Cr_3C_2-NiCr and Al_2O_3-Co based matrix cermet coatings and steels characterized by different composition, as a function of factors such as furnace temperature and dew point, coating's surface roughness, etc. The aim was to evidence the furnace conditions and coating roll features that have a major role on the pickup formation.

EXPERIMENTALS

Commercial thermally sprayed Cr_3C_2-NiCr and Al_2O_3-Co matrix coatings were used to reproduce pickups by the interaction with the selective oxidation covering the steel strip samples containing different levels of Mn, Si and Al wt% (see Table 1), as well as a TWIP steel containing 23% Mn.

Table 1: Chemical composition of steel grades (wt%)

Steel grades	Mn	Al	Si	Cr	C	P	Cu	Ni	Mo	S
HSS1	0.25	0.15	1.40	0.15	0.003	0.07	0.15	0.15	0.05	0.008
HSS2	1.55	1.30	0.10	0.50	0.120	0.02	0.1	0.1	0.1	0.003
DP980	2.7	0.15	0.30	0.30	0.09	0.008	-	-	-	-

The interaction was performed by high temperature static reactivity tests and by low temperature dynamic tests, which allow the friction of a roll on a steel strip at controlled temperature and furnace atmosphere. The interaction surfaces were then characterized by XRD, GDOES, AES, SEM-EDS.

The static reactivity tests consisted in putting in contact the aged coatings (flat samples) with the steel strips covered with selective oxidation, in a laboratory furnace. Ageing of the coatings and oxidation of the strip samples was carried out at 900°C for 120 hours with the atmosphere of N_2–7% H_2 and the dew point kept either at -20°C, -30°C or -40°C. For the interaction step, the temperature was held at a temperature of 900°C for 120 hours days in a N_2–7% H_2 atmosphere. Steel samples after oxidation were analysed by GDOES quantitative depth profiling, whereas coating samples were analysed by XRD and SEM-EDS analysis.

A NSR (NoStickRoll - Fig. 1) equipment has been specifically developed to allow reproducing the friction and consequently the pickup, which occurs at the exit of the industrial lines at low temperature (500°C), and also the reactivity of the coatings at high temperature (900°C). Two coated rolls turn on a steel to reproduce the friction between the coating and the strip at a controlled temperature and under a classical furnace atmosphere (5%H_2/DP-30°C).

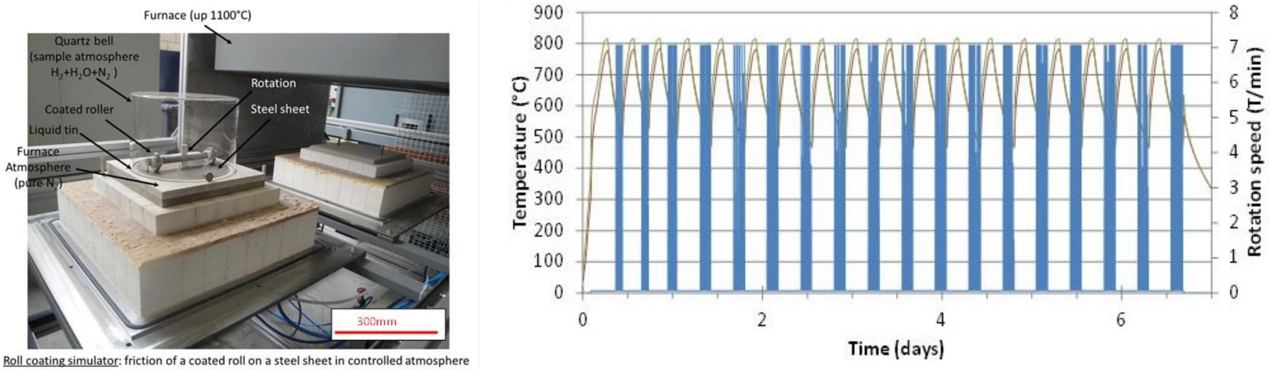

Fig. 1: NoStickRoll (NSR) equipment developed for the pick-up study and example of thermal cycle applied with sequential friction (blue section).

RESULTS AND DISCUSSION

Interaction at high temperature

In order to investigate the chemical reactions occurring between the cermet coatings and the 4 steel strips at high temperatures, the oxidation conditions were set to form different oxide layers. In Fig. 2 and Fig. 3 are shown the GDOES depth profiles of the oxidised steels with a dew point of -20°C and -40°C. The composition of the surface oxide is affected by the steel composition and the oxygen partial pressure of the atmosphere. MnO can always be formed on the strips surface under the possible conditions in the furnace and its amount depends on Mn content in the steel. SiO_2 is formed on the HSS1 steel surface only under the drier atmosphere conditions.

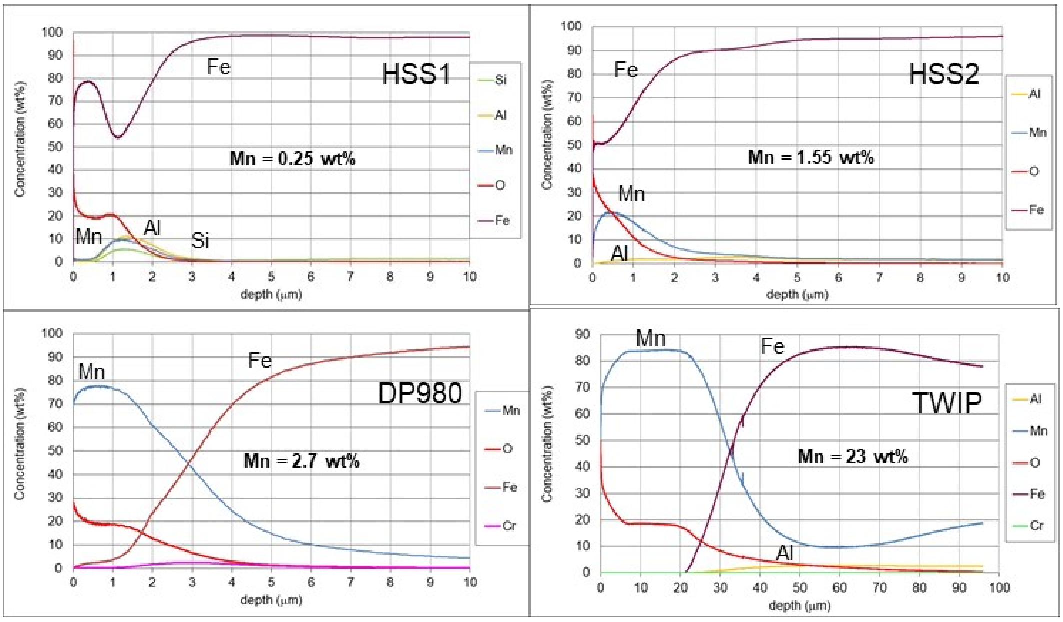

Fig. 2: GDOES quantitative depth profiles of the steel samples after oxidation at 900°C in 7% H_2-N_2 with DP of -20°C

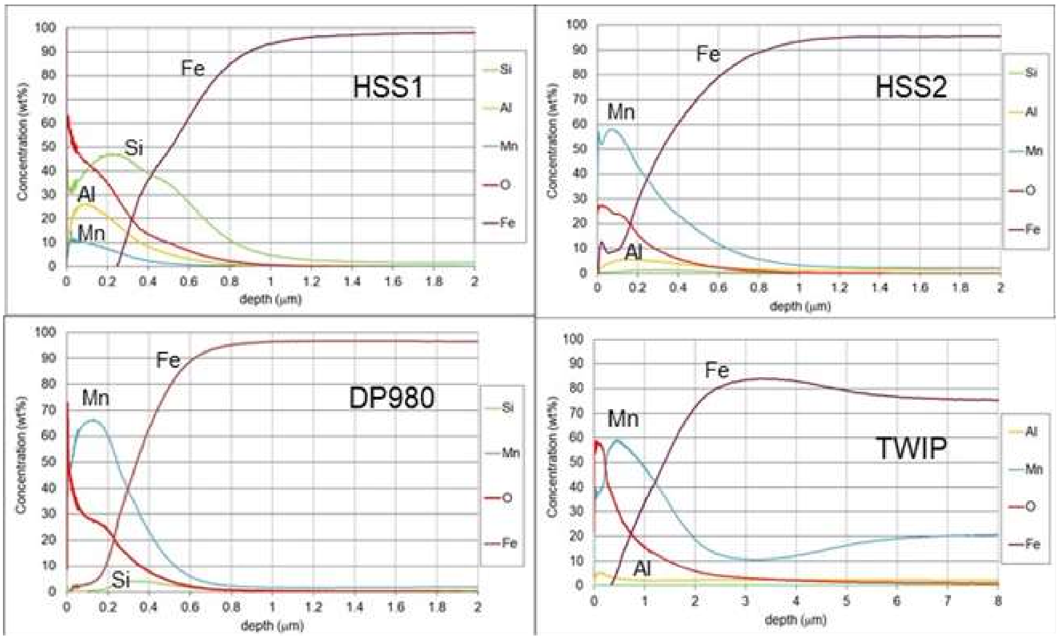

Fig. 3: GDOES quantitative depth profiles of the steel samples after oxidation at 900°C in 7%H_2-N_2 with DP of -40°C.

The standard Gibbs Energy values of chemical reactions of MnO with pure oxides like SiO_2, Al_2O_3, and Cr_2O_3 in the considered range of temperature are reported in Fig. 4. The thermodynamic order of the possible reactions of MnO with the pure oxides is: Cr_2O_3 > Al_2O_3 >SiO_2 throughout the wide temperature range. Therefore, steels containing over 0.5% of Mn will always be able to form, in the classical annealing conditions, the Cr_2O_3.MnO and Al_2O_3.MnO spinel phases. The kinetics of such spinel formation will depend on the temperature at which the rolls are working in the furnace.

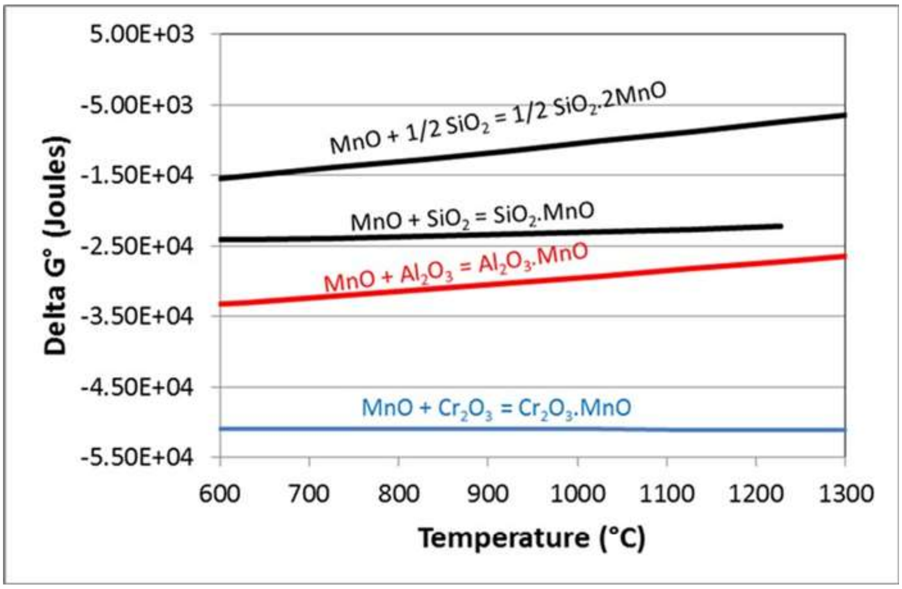

Fig. 4: Values of Gibbs energy change of MnO reactions with pure oxides (ThermoCalc©, SSUB3 module).

The XRD patterns of the aged cermet coatings before and after interaction with the selectively oxidised TWIP steel grade at a dew point of -20°C is shown in Fig. 5. It appears that both coatings form Cr_2O_3 at their surface due to the oxidation of the metal chromium in the Co and Ni base matrix, and of the chromium carbide. Once formed, Cr_2O_3 reacts with MnO of the TWIP steel making $MnCr_2O_4$ or $Mn_{1.5}Cr_{1.5}O_4$ spinels[3]. Similarly, such reaction occurs on HSS2 and DP980 steel grades. Results on Al_2O_3-Co based coating indicate that also the reaction between MnO and Al_2O_3 occurred, producing $MnAl_2O_4$ spinel.

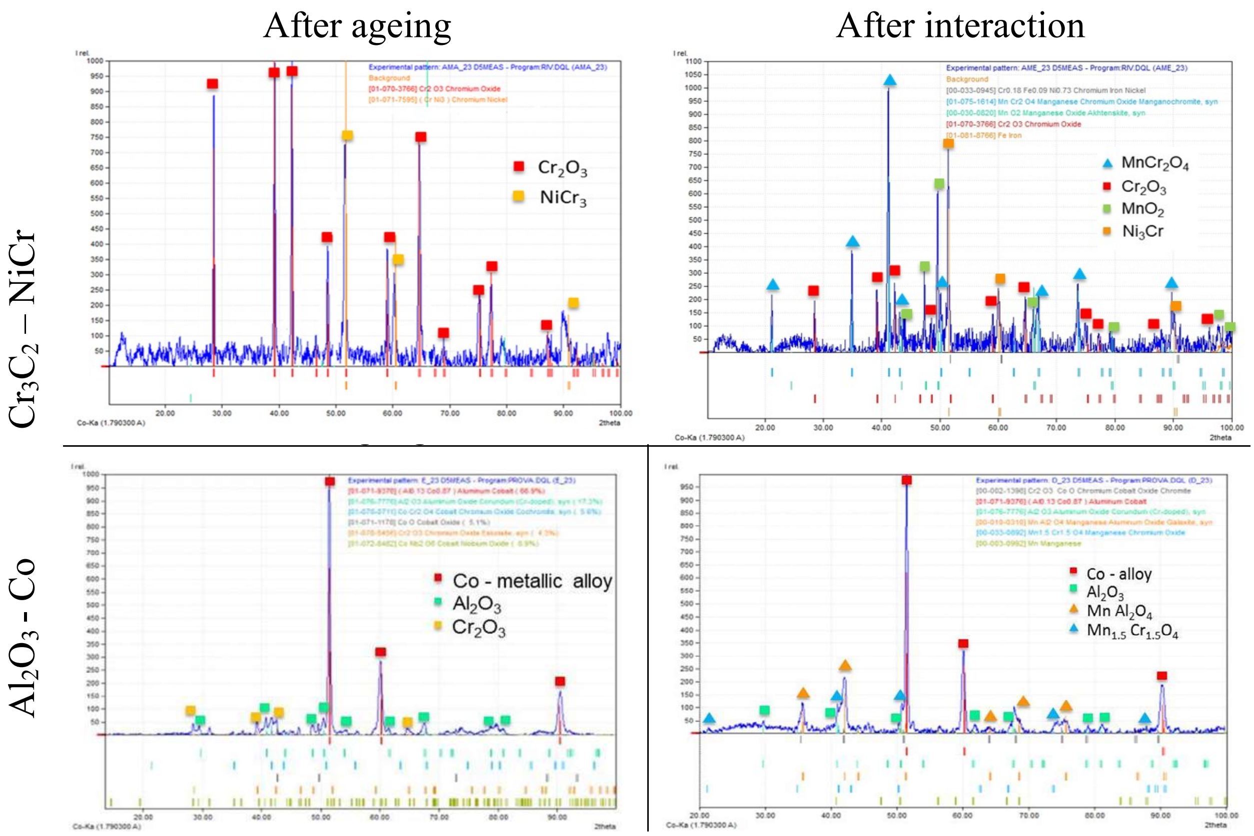

Fig. 5: XRD results of Cr_3C_2 – NiCr and Al_2O_3-Co based matrix coatings after ageing and after interaction with TWIP steel, DP: -20°C.

Indeed, as shown in Fig. 6 by the SEM/EDS mapping in cross-section, the Mn selective oxidation clearly sticks on both coatings and follows the surface topography, which indicates a good ductility of this oxide at high temperature. The Mn oxide pickup is also reported to be present on industrial rolls located in the soaking zone, but without influencing in a significant way the product quality. This could be related to the high ductility of the Mn selective oxides, which finally make a smooth and continuous oxide over the whole surface roll thus not scratching the steel coil being processed.

Moreover, Fig. 6 also shows that Mn diffuses through both the Co and the Ni matrix inside the coatings. Finally, a clear coating nitriding can be noticed, which indicates a possible decomposition of the nitrogen at high temperature in drier atmospheres (DP = -30°C and -40°C).

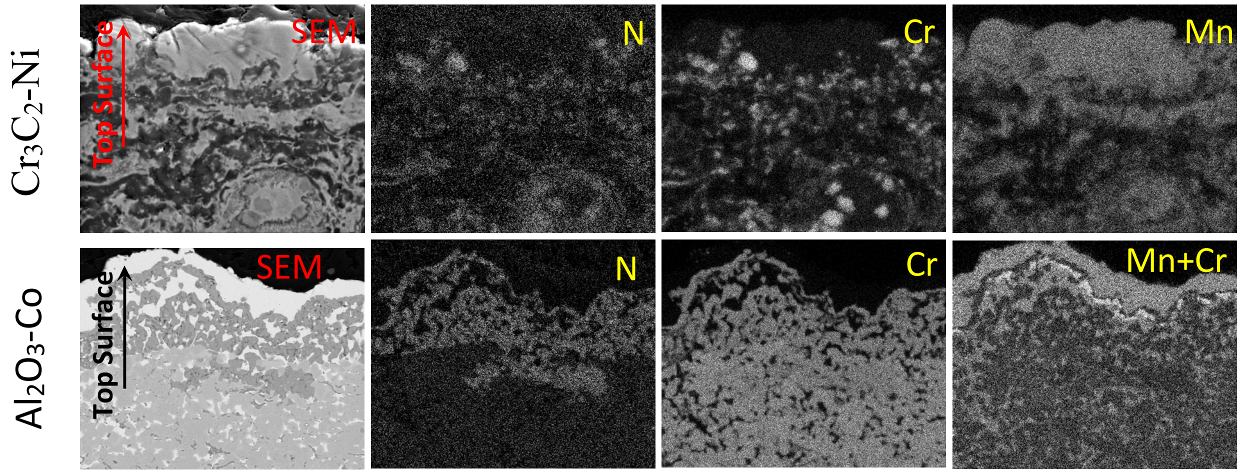

Fig. 6: SEM mapping shows nitriding and Mn oxide sticking and diffusion inside the coating (900°C; DP=-30°C)

Fig. 7 shows XRD patterns of the aged Cr_3C_2-NiCr coating before and after interaction with the pre-oxidised TWIP steel with a dew point of -40°C. The results indicate that coating after ageing in dry atmosphere, produces the formation of Cr nitride at the surface that doesn't seem to have reacted with the MnO formed on the TWIP steel.

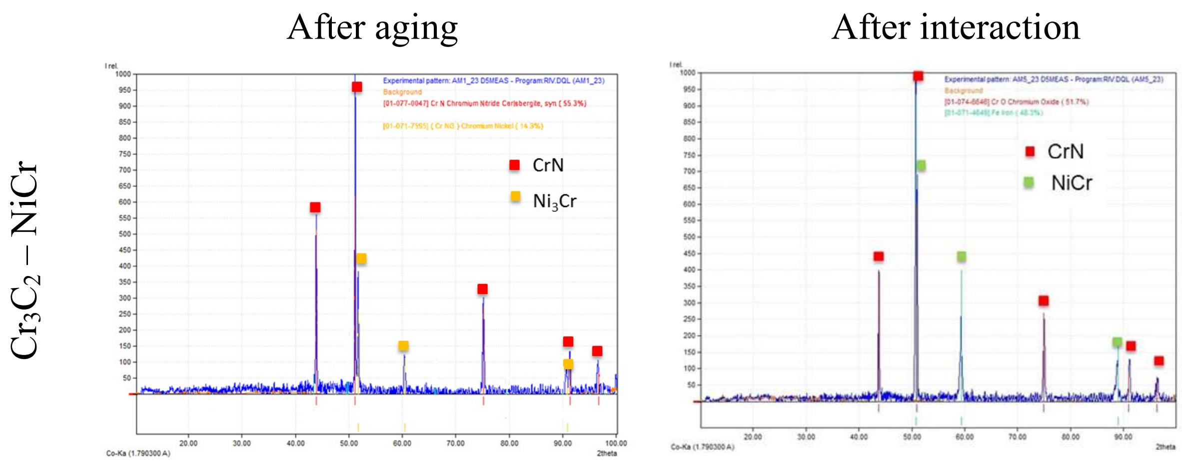

Fig. 7: XRD results of Cr_3C_2 – NiCr based matrix coatings after ageing and after interaction with TWIP steel at DP-40°C.

Friction at low temperature (500°C)

For the furnace rolls working in the cooling and over-aging zones of CALs and CGLs, the iron pickup, with some manganese oxides, is the main industrial problem reported up to now. Silicon oxide pickup are also noticed when electrical steels are processed on continuous annealing lines. Iron pickup is however more severe for the rolls because a sintering process occurs between the iron fines and the Co or Ni matrix of the coating. Therefore, the rolls must be dismounted from the line and machined or replaced. In the case of the formation of silicon oxides pickup, the counter measurement to clean the rolls is to process silicon free coils that allows the progressive removal of the non-sintered oxides.

To simulate iron pickup formation, a friction test has been performed at 500°C on the NSR equipment by the continuous rotation of the non-aged Cr_3C_2-NiCr coated roll on the HSS2 strip for 3 days at 7 T/min. The coating has surface roughness Ra of 3.5µm and Rz of 23µm.

Fig.8 shows some pictures of the roll after the friction test. Pickups seem to be randomly dispersed on the roll. Preferential pickup can also occur along over-thicknesses. The red squares indicate where punctual analyses have been done. The lateral view shows that the pickup seems to be made of an agglomeration of a lot of particles.

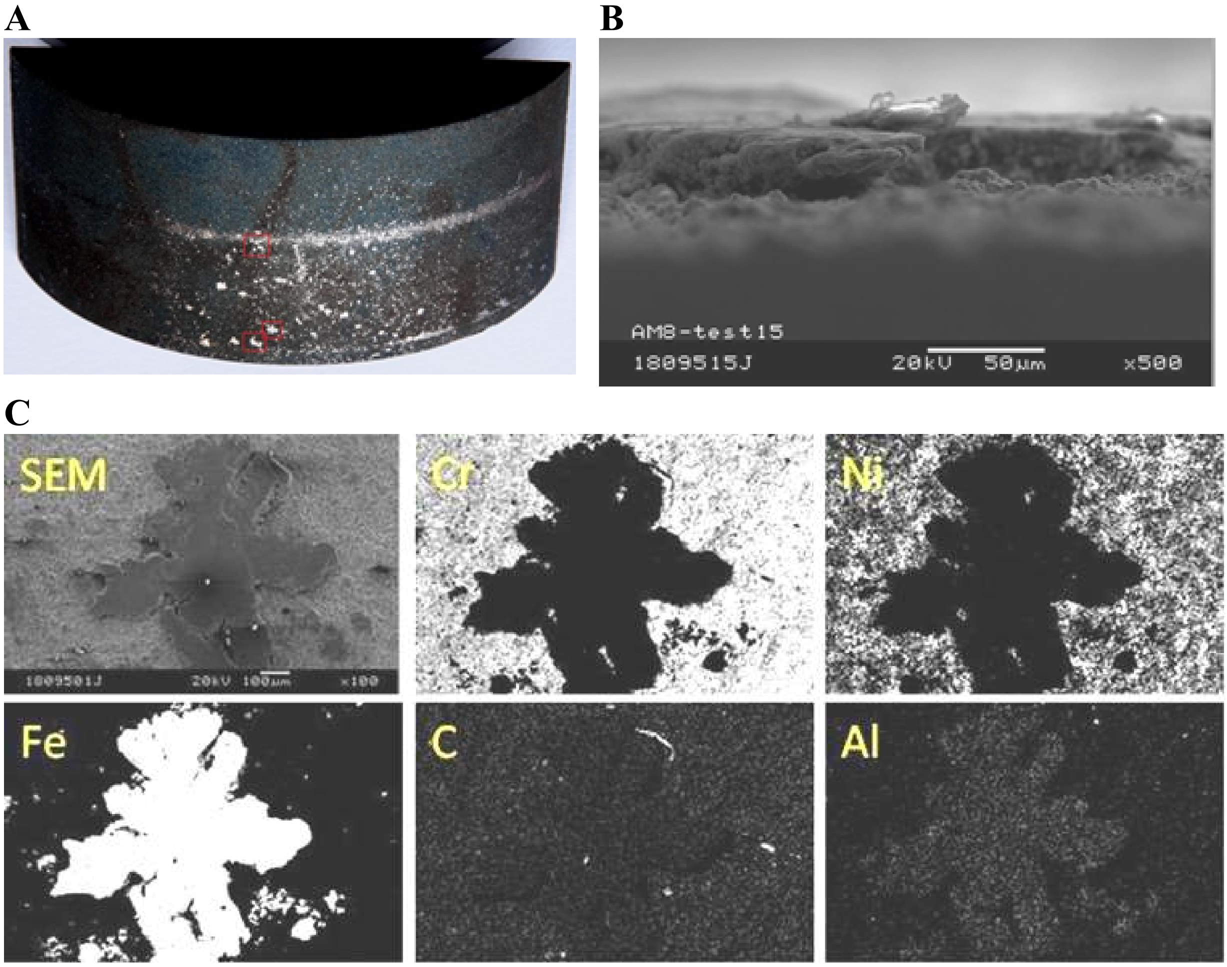

Fig. 8: (A) Photo of the Cr_3C_2-NiCr roll showing pickups; (B) SEM lateral view of a pickup; (C) SEM-EDX mapping around a pickup (top view).

These particles are mainly made of metallic iron with some Al, Cr, Si randomly dispersed in the pickup. These alloying elements come from the HSS2 steel grade.

The SEM mapping and analyses in cross section confirm the presence of low Al, Cr amounts in the pickup (Fig. 9 and Fig. 10). No chemical interaction is visible between the steel pickup and the Cr_3C_2-NiCr coating, but iron sintering can only concern a thin thickness. The adhesion is mainly due to high coating roughness as it can be noticed in Fig. 9.

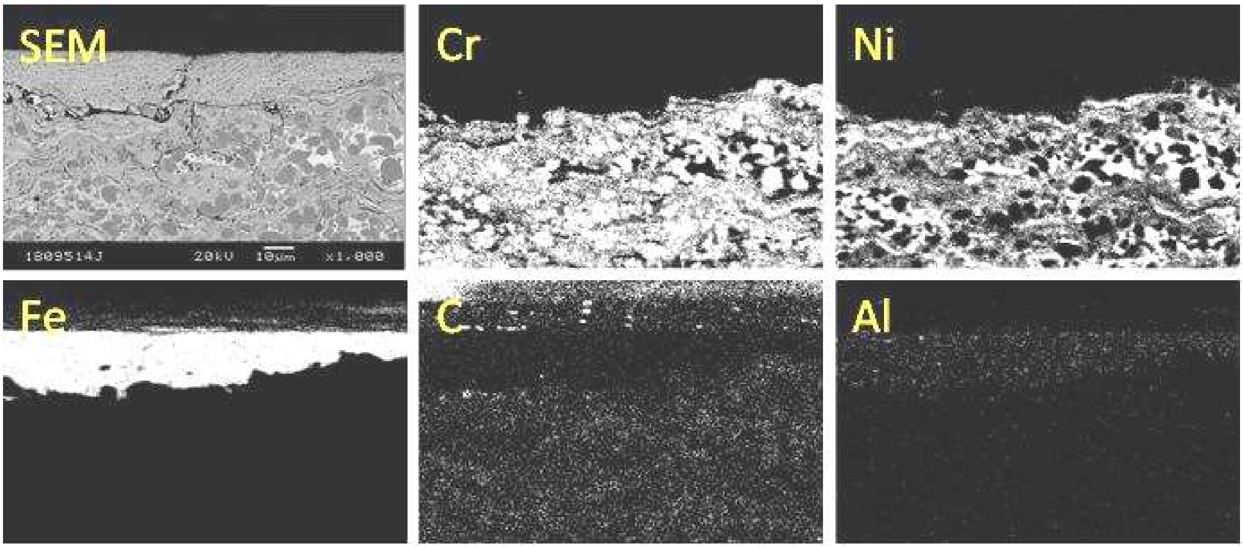

Fig. 9: SEM mapping in cross section under a pick-up from HSS2.

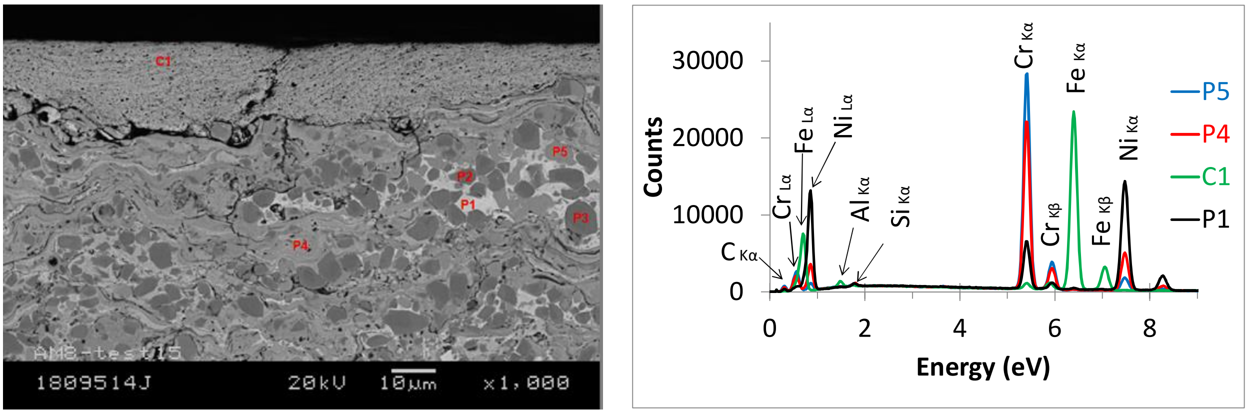

Fig. 10: SEM-EDX in cross section analyses under a pickup from HSS2.

The same friction test has been performed on the Al_2O_3-Co based matrix coating at 500°C by a continuous rotation during 3 days at 7 T/min. The coating has lower surface roughness values: Ra of 0.85µm and Rz of 6µm. In this case, quite no Fe pick-up was noticed on the coating after friction. This is attributed to the low roughness associated with this coating.

According to these results, a decrease of the roll roughness can help solving the pickup problem at low temperature. However, also the sintering of metallic iron particles with the Co/Ni metallic matrix of the cermet coatings must be avoided. Indeed, a pure oxide coating should contrast such adhesion of the metallic iron particles, but it also has to be wear and thermal shocks resistant (from 500°C to room temperature). Therefore, some ZrO_2-based coatings with an intermediate bond coat have been tested, but the insufficient hardness of these oxides has induced an important powdering of the coatings. Further developments are foreseen with, for example, the test of a nitride cermet coating to avoid a sintering with iron while keeping a correct coating hardness.

Concerning the silicon oxide pickup issue, research work is ongoing to find solutions. A high coating hardness with a low roughness should limit the pickup occurrence. A reduction of the external selective oxidation of silicon by an adaptation of the annealing conditions should also mitigate the pickup.

CONCLUSIONS

Differences in the pickup behaviour of Cr_3C_2-NiCr and Al_2O_3-Co matrix cermet coatings occur according to the temperature in which the furnace rolls are working in.

For rolls in the soaking zone, the main pickup observation on industrial rolls is selective oxidation (MnO, etc.) covering the strips, which can react with the Cr_2O_3 and/or Al_2O_3 on the coated rolls forming the spinel phases because we are at high temperatures. Laboratory trials also indicate that Mn oxides are probably quite ductile.

In principle, a non-sticking cermet coating should avoid adding Al and/or Cr in the Ni and Co matrix, in order to supress spinel phase formation. However, as the high ductility of the MnO induces the formation of a smooth layer, this reaction doesn't seem to have a real critical impact on the strip quality. As alternative, a stable oxide should be considered, such as a ZrO_2 based coating. Finally, if a low dew point (DP-40°C) can be kept in the soaking zone, a nitride surface layer is produced which seems to reduce the interactions with MnO. It can be therefore anticipated that a nitride roll should allow limiting oxides reactivity at high temperature and in low oxidation potential atmospheres.

For rolls in the cooling and over-aging zones, the main industrial problem reported up to now is attributed to the presence of iron pickups with some manganese oxides. Also, silicon oxide pickups are noticed when processing in the CALs steel grades with high levels of Si.

Dynamic tests indicate that coating roughness strongly influences all pickup formation at low temperatures. The metallic Fe particles on the strip can be picked up and then sintering occurs with the metallic Ni, Co of the coatings, which need the removal of the roll from the line. When SiO_2 is formed on the strip in the soaking area it can be pick-up by the rolls working in the lower temperature zones but will not react with the cermet coatings and can be more easily removed (no chemical bonding).

As alternative, an oxide coating could be utilized as the potential sintering of metallic iron with oxides is very low, which is expected to suppress sintering. However, the hardness of the tested coatings is not sufficient, which induces a powdering of these oxide coatings during friction. Here again, a hard nitride coating could allow limiting iron reactivity. Further research work is being carried out.

ACKNOWLEDGMENT

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