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ABSTRACT

Some trials with graphite Hi-Cr iron rolls have been done mainly in Japan, for the rolling of stainless steel. This material could lead to good compromise between oxidation, wear and thermal behaviour.

By using thermal analysis and resistometry, the conditions for secondary graphite formation have been studied. The amount and volume of free graphite may be strongly increased by a suitable heat treatment, allowing a good thermal conductivity as well as high wear and mechanical properties.

1. INTRODUCTION

For long time ICDP rolls were used in all the finishing stands of many hot strip mills. About twenty-five years ago they have been replaced by high chromium (Hi-Cr) iron rolls in the front stand of finishing mills.

For the last years high speed steels (HSS) rolls have been introduced in the hot strip mills. Nowadays they are used in the front stand of a finishing section (mainly in Japan). HSS rolls are wear resistant and can therefore be used for longer rolling campaigns, increasing the hot strip mill productivity.

As far as the finishing section is concerned, some trials done to use Hi-Cr rolls ends to failure due to sticking problems connected with the oxidation behaviour of roll surface. HSS rolls are used in those stands only in some mills in Japan.

Last finishing suffers from high wear which affects gauge accuracy, strip profile and frequency of roll changes. ICDP rolls offer a good compromise between resistance to thermal stresses existing at that stage of the mill and good wear resistance.

For development of a new grade the main requirements are

- good oxidation and thermal behaviour,
- high wear resistance
- good resistance to rolling incidents.

Hi-Cr cast iron possesses excellent wear resistance due to the presence of hard chromium carbides but its thermal conductivity is low. A graphite precipitation could contribute to an improvement in thermal conductivity and serve as lubricant prohibiting the sticking. In high chromium cast iron only chromium carbides are present. However, it is possible to get crystallised graphite in the as-cast state by adjusting the composition.

Some trials with graphite Hi-Cr rolls have been done in hot strip mill, mainly in Japan, for the rolling of stainless steel.

In the first part of this paper, we will compare the properties (mechanical and chemical as well as in service such as hot hardness ...) of the roll materials currently used in hot strip mill i.e. Hi-Cr iron, HSS, ICDP to the properties of graphite chromium iron. We will point out the good results of this last one which can lead to an optimised compromise between oxidation, wear and thermal behaviour.

In the second part, we will summarise the results of a study aimed to examine the graphite formation conditions in a high chromium iron and the effect of an austenite destabilisation heat treatment on the graphitisation. The amount and volume of free graphite may be strongly influenced by a suitable heat treatment, allowing to increase the thermal properties.

2. COMPARISON BETWEEN ROLL GRADES USED IN THE FINISHING SECTION OF HOT STRIP MILLS.

During hot rolling, work rolls are submitted to alternate cycle of heating and cooling. That thermal fatigue induces the appearance of cracks at the roll surface. To reduce the cracks depth, ultimate tensile strength as well as compressive yield strength have to be as high as possible. Moreover, well dispersed carbides in the matrix reduce the propagation of the cracks.

The interface between the roll and the strip is also of prime importance. It is well known that a low friction coefficient reduces the rolling force and power. On top of that, sticking friction conditions must be avoided. They can lead to local welding or to rolled in scale. The control of the oxide layer on both roll and strip surface is deciding.

As far as the last finishing stands are concerned, the low rolling temperature met in those stands involves that the roll oxidation must be adjusted to rolling conditions.

2.1 New alloys for work rolls

In the early stands of the finishing section, work rolls must sustain hot wear and have a good fire cracks resistance. The use of high chromium iron in those stands is still common in many hot strip mills.

Recently, alloys stemming from the high temperature tool steels (HSS) have been introduced in those stands. Due to the presence of very hard MC carbides, as well as M_6C and M_2C carbides, their wear resistance is very often more than twice the Hi-Cr iron one.

However spalling resistance of HSS rolls is sometimes very poor compared to high chromium iron rolls. Marichal-Ketin developed [(1)] a new grade which gives a good compromise with regards to a low friction coefficient as well as a high crack and wear resistance.

The 16 - 18 % chromium content of high-chromium iron rolls explains their low oxidation kinetics and why they are not suitable for the last stands of the finishing section. HSS rolls have an outstanding wear resistance but are sensitive to cobbles.

In most of the HSM, ICDP rolls are still used in the last stands. Their low level of chromium favours the oxidation kinetics. However, that grade suffers for a poor wear

resistance due to the low hardness of its carbide : Fe_3C cementite.

A good compromise between these alloys could be founded in creating a special grade based on a high chromium iron with free graphite. That new grade contains, like the Hi-Cr iron, M_7C_3 carbides which are harder than the cementite carbides present in the ICDP. Free graphite which is thought to delay the crack propagation is also found as in the ICDP. Moreover the presence of graphite could contribute to the improvement of thermal conductivity and serve as lubricant prohibiting the thermal sticking.

It is possible to obtain crystallised graphite in the as-cast state by modifying the composition of chromium iron as shown in the literature [2,3] .

Two laboratory castings G1 and G2 , in the range defined in table I, have been used to identify the possibilities of the graphite chromium iron. G2 possesses lower nickel content to optimise the oxidation behaviour as it will be seen in the part concerning the oxidation properties (Fig.3).

High level of Ni and Si are used to obtain free graphite precipitation. The microstructure of the alloy consists of nodular graphite, M_7C_3 chromium carbides and a martensitic matrix. In the as cast state the level of residual austenite is rather high due to the high nickel content. A tempering heat treatment leads to a destabilisation of the austenite. To be effective the treatment has been done between 490°C-510°C (fig. 1) leading to a hardness in the 650-700 HV 30 range.

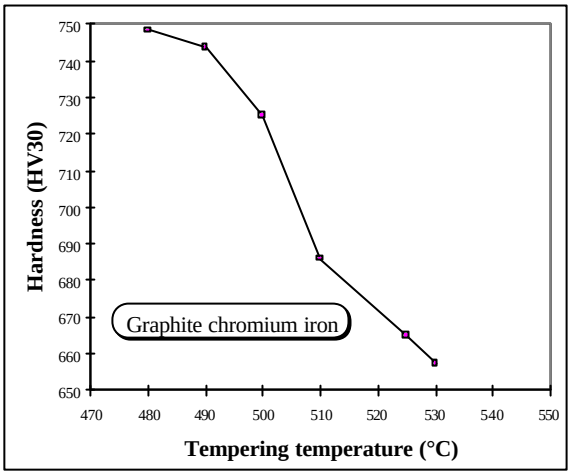

Fig. 1 - Hardness of graphite chromium iron after heat treatment.

2.2. Properties of the alloys

The properties of the graphite chromium iron have been compared to those of ICDP, Hi-Cr iron and HSS.

Alloy	C %	Si %	Ni %	Cr %	Mo %	V %	W %
ICDP	3.2/3.5	0.9/1.1	4.2/4.5	1.6/1.9	0.3/0.4	-	-
Hi-Cr	2.7/2.8	0.4/0.6	1.2/1.4	17.0/18.0	1.2/1.4	-	-
HSS	1.5/2.0	0.5/1.0	1.0/1.5	5.0/7.0	2.0/5.0	3.0/5.0	1.0/3.0
Hi-Cr +graphite	3.3/3.5	1.8/2.2	4.0/5.0	7.0/8.0	1.3/1.5	<0.50	-

Table I - Composition of the ICDP , Hi-Cr , HSS iron and graphite chromium iron.

a. Hot hardness

The temperature in the roll gap where a sliding between the strip and the roll occurs ranges between 500 and 600°. It is well known that a high hot hardness at these working temperatures leads to a good wear resistance.

Fig. 2 compare the hot hardness of the different alloys.

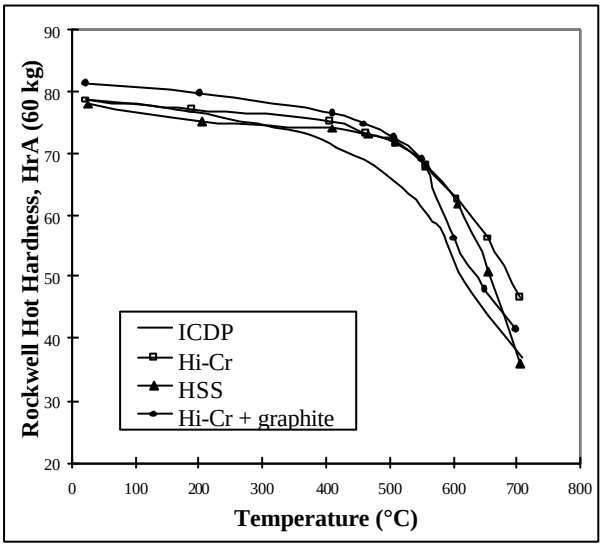

Fig. 2 - Hot hardness of ICDP, Hi-Cr, HSS iron and graphite chromium iron.

The HSS and Hi-Cr iron have the highest hot hardness. For graphite chromium iron the hot hardness is higher than ICDP. It can be expected that in the working conditions its wear resistance will be better than ICDP.

b. Mechanical properties

Table II illustrates the results.

Mechanical properties in compression are higher for graphite chromium iron than for ICDP and Hi-Cr iron. But elongation is rather low which may increase the sensitivity to rolling incident. The role of thermal treatment is rather important and a higher treatment temperature could increase the elongation.

The ultimate tensile strength is higher than the one of ICDP. With regards the Young modulus at room temperature, it equals 200.000 Mpa.

c. Oxidation kinetics

Sticking problem of the strip to the rolls in the last stands of hot strip mill is often connected to the roll oxidation kinetic.

Alloy	Compression Yield strength	Compression Rupture strength	Compression Elongation	Ultimate Tensile Strength	Hardness
	(MPa)	(MPa)	(%)	(MPa)	HV30
ICDP	1400-2200	1800-2500	1 to 3	350-450	650-700
Hi-P	1600-1800	2000-2800	5 to 10	700-800	600-650
HSS	1900-2100	2800-3000	17 to 19	1000-1100	620-640
Hi-Cr +graphite	2000-2200	2600-2800	2 to 3	550-600	690-710

Table II - Compression and tensile tests results (20°C).

The oxidation kinetic in humid atmosphere was measured by a simulation of oxidation conditions existing in the roll gap. The samples of the tested materials are kept in a tubular furnace heated at 575°C during 24 hours. This furnace is charged by wet air saturated by water at 60°C. Fig. 3. illustrates the results.

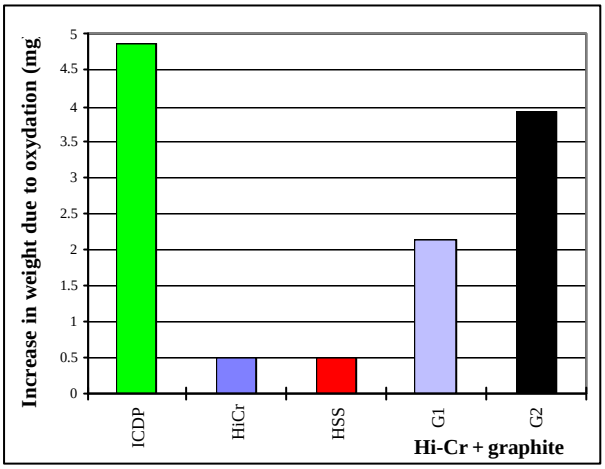

Fig. 3 - Oxidation behaviour of ICDP, Hi-Cr, HSS iron and graphite chromium iron.

ICDP iron is the alloy that is more sensitive to oxidation alloy. This observation fits well with the industrial experience. Hi-Cr iron and HSS alloys show a slow oxidation kinetic. These alloys could not replace the ICDP iron in the last stands of a finishing mill. However the oxidation kinetic of the graphite chromium iron is nearly as fast as the ICDP iron. We may think that the sticking problem of the strip upon the rolls could be avoided be using this new alloy. In top of that a better control of the oxidation kinetics is possible by optimising the composition : we can observed that the oxidation is higher for the G2 alloy containing less nickel than the G1 alloy.

d. Results

The graphite chromium iron is an excellent alternative to be used in the last stands of finishing mill and to replace ICDP.

Its oxidation kinetic is likely to avoid the sticking problem like ICDP. The hot hardness in the 500-600°C range is higher than ICDP leading to higher hot wear resistance and the mechanical properties are also better than ICDP.

These positive results lead us to conduct further studies in order to optimise the properties of the graphite chromium iron.

It has been pointed out that the presence of graphite is thought to delay the crack propagation, contribute to the improvement of thermal conductivity and serve as lubricant prohibiting the thermal sticking.

The shape and the amount of graphite is thus rather important.

That is why laboratory researches have been conducted on the improvement of graphite precipitation during solidification and during heat treatments.

3. STUDY OF GRAPHITE PRECIPITATION

The technique of differential thermal analysis (DTA) was used to study structural transformation and especially the graphite precipitation.

Differential thermal analysis (DTA) is a technique in which the sample is heated (or cooled) following a temperature schedule and which can detect any endothermic or exothermic type transformation. Any phase change leads to variations in the sample temperature. The difference in temperature between the sample and the programmed temperature is monitored against

time or temperature while the temperature of the sample is programmed. With the DTA method, any transformation even the small one, can be detected (fusion, solidification, decomposition,...).

3.1. Solidification

The solidification of G2 (table I) graphite chromium iron was studied by DTA. The sample was heated from 20°C to 800°C with a speed of 10°C/minute and then from 800°C up to 1500°C at 2°C/minute.

The sample was maintained at 1500°C in the liquid state during 15 minutes and then cooled up to 400°C with a constant speed of 2°C/minute. The solidification curve is illustrated at the figure 4. Three different peaks have been reported at high temperature during solidification (table V).

Solidification			
Peak	T start	T Max peak	T end
	(°C)	(°C)	(°C)
1	1491.09	1435.32	1360.32
2	1360.32	1348.78	1331.47
3	963	950	921.86

Table V - DTA results - Solidification of graphite chromium iron.

The two high temperature peaks (1, 2) are related to the formation of the carbides M_7C_3 and to the eutectic M_7C_3-γ. The third peak (3) is related to the formation of primary graphite. The graphite maximum peak temperature (950°C) is the same as in reference [2].

The presence of graphite is due to the influence of the alloying elements such as

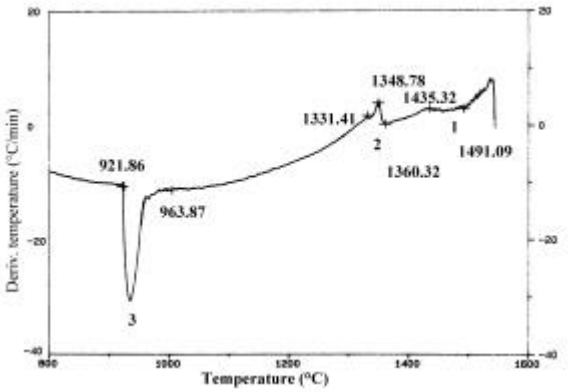

Fig.4 - DTA curve - Solidification of graphite chromium iron.

nickel. Following [3] without the presence of nickel and silicon, it is difficult to form graphite.

3.2. Austenite destabilisation heat treatment

DTA experiments and RX measurements have been used to study the formation of secondary graphite during high temperature heat treatment. As the precipitation of graphite has been shown to appear at 950°C, the temperature range for heat treatment is higher because in that case the thermal activation of the transformation is more favourable.

The sample has been heated to 1000 - 1050 and 1200°C at a speed of 10°C/minute, hold during 30 minutes at this temperature and then cooled at a speed of 5°C/minute. The heating and cooling transformations have been studied using DTA.

During this destabilisation heat treatment the matrix is transformed into austenite and some dissolution of the chromium carbides and primary graphite appears. During cooling the free graphite diffuses together and forms clusters.

The temperature corresponding to secondary graphite formation (Tpeak Max)

during cooling increases with the temperature of heat treatment as shown in table VII.

T treatment	T peak Max graphite formation
1000°C	960°C
1050°C	965°C
1200°C	985°C

Table VII - T° secondary graphite formation - DTA experiments.

Due to thermal activation resulting from treatment at higher temperature the moving of carbon atoms and their concentration is easier and occurs at higher temperatures.

To confirm these results different techniques have been used : differential calorimetry, dilatometry and resistometry. The general principle of these techniques is to analyse the variations of a property (heat capacity, thermal expansion, resistivity) depending closely to the structure as a function of the temperature programme.

Differential resistivity is a very sensitive method to study microstructure transformations and is well adapted to confirm our DTA results. We find again that the temperature of the secondary graphite precipitation increases with the temperature of the heat treatment and also with the cooling rate as shown in table VIII.

The same conclusions have been made in similar calorimetry and dilatometry experiments [4].

After treatment by DTA and resistometry experiments, the specimens were used for microstructure studies. The samples

T treatment	cooling rate	Tpeak Max graphite formation
1000°C	5°/min	963°C
1000°C	1.25°/:min	971°C
1100°C	5°/min	965°C
1100°C	1.25°/:min	980°C

Table VIII - T°secondary graphite formation - resistivity experiments.

have been examined using scanning electronic microscopy (SEM) and scanning Auger microscopy (SAM). The Auger electron spectometry is a typical surface chemical analysis technique . In our case it allows us to obtain good chemical analysis of the phases with depth and lateral resolution such as fine particles could be analysed without interference.

Figure 5 illustrates the microstructure of heat treated (in DTA experiments) samples. We can observe the presence of carbides, the matrix and graphite flakes. The amount of graphite is greater than the one observed in as-cast sample (fig. 6). We noticed that the amount of graphite increases with the temperature of destabilisation treatment : we have 3 % of graphite for treatment at 950°C, 6 % of graphite at 1100°C and 10 % graphite at 1200°C. In comparison, the amount of graphite in the non-treated specimen is in the range 1 to 2 %.

This is in total agreement with the observations of DTA and resistivity : the concentration of carbon atoms is greater after treatment at higher temperature. This allows the formation of bigger cluster during cooling.

RX examination on these samples lead to the same conclusions. The intensity of the peak corresponding to graphite is rather weak

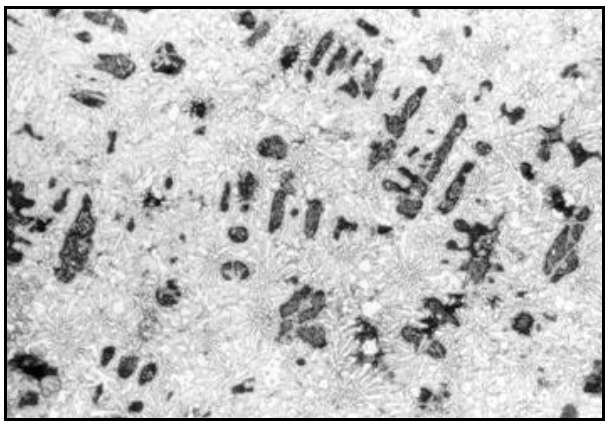

Fig.5 - Microstructure of heat treated sample - (DTA - 1200°C) - etched sample.

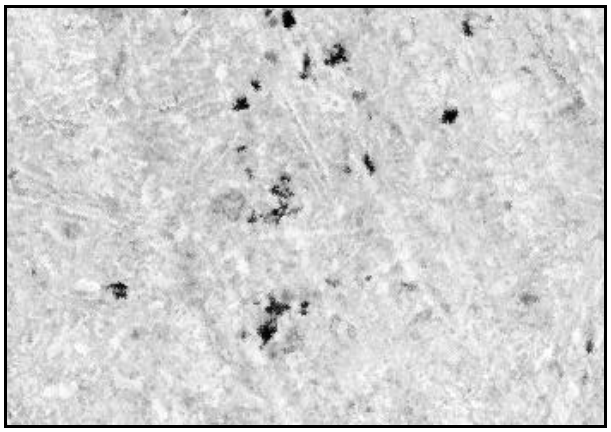

Fig.6 - Microstructure of as-cast sample - etched sample.

in the as-cast sample (fig. 7). Graphite appears during heat treatment (fig. 8). The intensity of this peak is greater after DTA treatment at 1100°C(cooling rate :5°/min - curve a)than at 1000°C(cooling rate :5°/min - curve b).

After thermal treatment, the shape of graphite is rather irregular in comparison with the shape before treatment (fig. 9).

By using backscattered electron microscopy analysis on these graphite flakes(fig. 10) the structure is well defined : in the center we have a dark compact structure of pure graphite and around this core, graphite

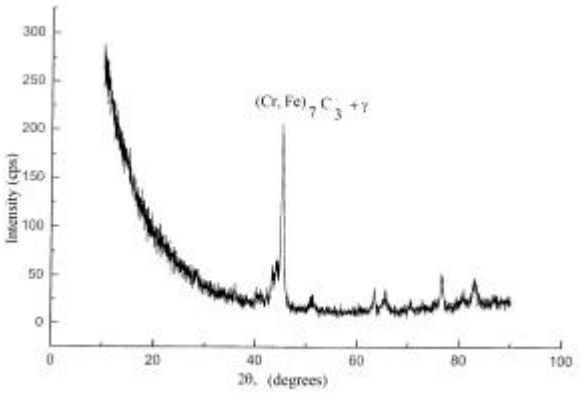

Fig. 7 - RX spectrum on as-cast sample.

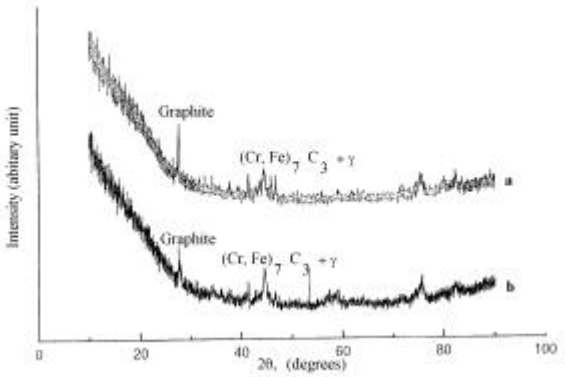

Fig. 8 - RX spectrum on DTA samples.

mixed with carbides. Further on the structure is made of round particles of graphite dispersed with carbides.

It is quite clear that graphite precipitation occurs during heat treatment mainly by decomposition of the complex chromium carbides.

Microstructure chemical analysis after heat treatment using Auger Electron Spectrometry indicates that the graphite phase contains (in weight) 98.95 %Carbon, the carbides contain Carbon (12.34%), Chromium (31.2 1%), Iron (50.31%), Vanadium (2.35%) and Molybdenum (2.15%) and that the matrix is composed of Iron (84.64%) with Chromium

(5.25%), Nickel (3.14), carbon (3.45%) and Silicon (1.85%).

Fig.9 - Microstructure of heat treated sample
- (resistivity - 1100°C - 5°/min)
SEM - etched sample.

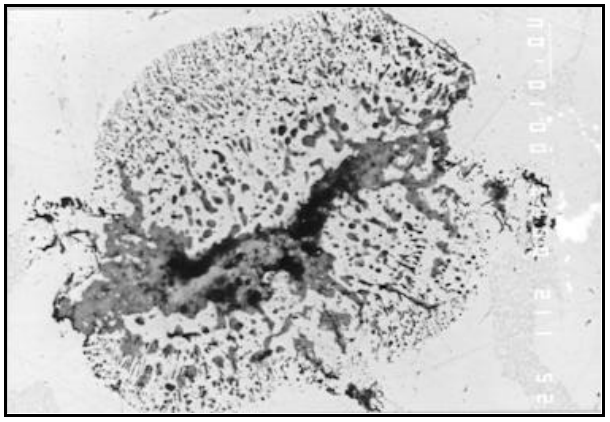

Fig.10 - microstructure of heat treated sample
- (resistivity - 1100°C - 5°/min)
- SAM - non etched sample.

4. CONCLUSIONS

In the as-cast conditions graphite precipitation in high Ni and Si chromium cast iron occurs at a temperature of 950°C. It is possible to increase the amount of graphite up to 10% in volume by secondary graphite precipitation. This can be obtained by high temperature austenite destabilisation. The shape and the amount of graphite depend on the treatment temperature. Graphite precipitation occurs by decomposition of the M_7C_3 chromium carbides. The amount of secondary graphite is also greater after treatment at higher temperature.

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