Influence of Carbide Precipitation on Hot Hardness of High Speed Steel Rolls

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INTRODUCTION

When generating a new rolling mill roll grade the rollmaker has to face several challenges. A new chemical composition and related heat treatments have to be developed in order to manufacture a reliable roll with high performance in operation, but all the parameters connected with the manufacturing process also have to be fixed, mainly those invloved in to the interface between shell and core materials.

On the basis of information received from Japanese Hot Strip Mills and relating to a new grade with very high performance, Marichal Ketin started the development of High Speed Steel (HSS) rolls in 1992.

In the late nineties, after many laboratory and industrial trials with different compositions, a grade called Kosmos was considered as the standard grade. More than 600 rolls have been delivered in 30 Hot Strip Mills with good results in performance and reliability in operation.

From a metallurgical point of view, the behaviour of a roll in a mill may be connected to the various components of its microstructure. The main characteristic of the HSS structure is the presence of different kinds of very hard eutectic carbides whose nature, shape, size and distribution are the result of the alloying elements content as well as the solidification rate.

The chemical composition of Kosmos optimises the precipitation of three kinds of eutectic carbides: MC, M_2C, M_7C_3.

Large amounts of very hard MC eutectic carbides greatly improve the wear resistance, but overly large amounts can lead to an increase in the friction coefficient and even chattering. The hard M_2C eutectic carbides are also very wear resistant. However, when the carbide precipitates mainly in the flake morphology it makes the material very brittle and the resistance to mill incident may becomes very poor. Due to its high Chromium content the M_7C_3 eutectic carbide may have a beneficial effect on the roll oxidation behaviour. However that carbide is rather soft compared to MC and M_2C.

When a roll grade is considered as common world-wide, each rollmaker tries to improve the performance of its rolls, either by using another manufacturing process or another chemical composition.
This is the case with the Indefinite Chill Double Pour whose first development was done in the USA in the forties and is still being used as work roll in the last finishing stands of Hot Strip Mills and in Heavy Plate Mills with basically the same analysis. However, in more than fifty years two main changes have been done. One concerns the manufacturing process: most of these rolls are now cast by spincasting instead of the overflow or slide gate system. The other concerns the composition, many mills are now using micro-alloyed, also called enhanced grade, which contains very low amounts of hard MC carbides within their structure.

The development of HSS now follows the same history as that of the ICDP. Without modifying the manufacturing technique, Marichal Ketin introduced on the market about four years ago a new improved grade, called Aurora, in order to get better performance. About forty rolls are now in operation in various Hot Strip Mills.

This paper will illustrate the choice of the alloying elements and their content in the current grade. By using sophisticated laboratory examination techniques such as differential thermal analysis, scanning electron microscopy and image analysis, the metallurgical parameters of Aurora grade will be described and compared to those of the Kosmos grade. An attempt will also be made to connect all our laboratory results to the good behaviour of the alloy in operation in the early stands of Hot Strip Mills.

ROLLS CHARACTERISATION

Rolls characteristics are fixed by the composition, solidification rate and heat treatments. Many tool steels are described by their equivalent Tungsten (Weq) which equals (2Mo+W). Generally speaking, it means that two atoms of Tungsten have a similar effect on the material as one atom of Molybdenum. Some publications describing structural investigation on tool steels with the same Weq and various Mo and W content have shown that a high Molybdenum content [1], [2], [3]:

- decrease the total amount of eutectic carbides and the alloying elements content of the metallic matrix is thus increased;
- promote the MC eutectic carbide precipitation.

Effects of alloying elements in Aurora and Kosmos grade

Figure 1 shows the relationship between Carbon content, Tungsten equivalent and morphology of the eutectic carbides.

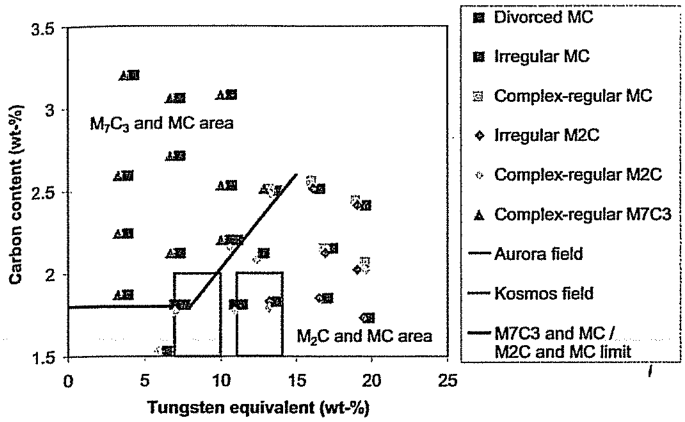

Fig. 1 Influence of C and Weq contents on type and morphology of eutectic carbides[4]

Kosmos and Aurora composition are described in table 1.

Table 1 - Composition of Kosmos and Aurora (%-wt)

The main differences between these grades are:

	C	Cr	Weq	Mo/(Mo+W)	V
KOSMOS	1.5/2.0	5.0/7.0	7.0/10.0	0.6/0.7	4.0/6.0
AURORA	1.5/2.0	3.0/5.0	11.0/14.0	0.9/1.0	4.0/6.0

- Aurora contains less Chromium than Kosmos. The purpose is to decrease the amount of Chromium carbide (M_7C_3);
- the Weq and the Mo/(Mo+W) ratio are both higher for Aurora than Kosmos.

We notice in figure 1 that such compositions lead to a shift of the Aurora field from the M_7C_3-MC domain to the M_2C-MC domain.

Heat treatments

HSS rolls are heat treated in order to get a hardness of 78/83 Sh.C. Such a hardness is now used by many roll makers because it gives the best compromise between wear and mill incidents resistance.

For Kosmos, the high hardness of the as-cast microstructure containing only austenite and martensite allows us to get the required hardness by tempering only. In the case of Aurora, its lower Chromium content induces a soft as-cast structure containing austenite and bainite. A normalisation followed by austenitisation and air quenching have to be performed before the tempering treatments to get a hardness in the 78/83 range.

Material tested

The samples analysed correspond to real industrial conditions for work rolls used in the early finishing stands of Hot Strip Mills with a diameter in the 700/800 millimetres range. The rolls were manufactured by the centrifugal vertical spincasting process. Pieces are cut off from the roll shell in the as-delivered state to obtain samples corresponding to different depths of the working layer. They were used for microstructure characterisation and mechanical testing.

The characterisation of the microstructure was done using various techniques:

- differential thermal analysis (DTA) to study the solidification sequence;
- scanning electron microscopy (SEM) to perform the analysis of carbides;
- image analysis to quantify the volume fraction of carbides and the grain size.

Some correlations were also made with related mechanical properties:

- compression test;
- hot hardness.

SOLIDIFICATION SEQUENCE

The differential thermal analysis technique (DTA) was used to investigate the solidification sequence and especially the carbides precipitation. Differential thermal analysis (DTA) is a technique in which the sample is heated (or cooled) in accordance with 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. With the DTA method, any transformation even the small ones, can be detected (fusion, solidification, decomposition...).

Generally, during DTA, one phase transformation appears on the test record as one peak at a given temperature (figure 2a). On the other hand, if two transformations can occur at similar temperatures, the two resulting peaks can match together. In this case, the different peak transformations are difficult to separate (figure 2b). The occurrence of overlapping peaks is frequently observed in high alloyed steels and particularly during fusion and carbides dissolution.

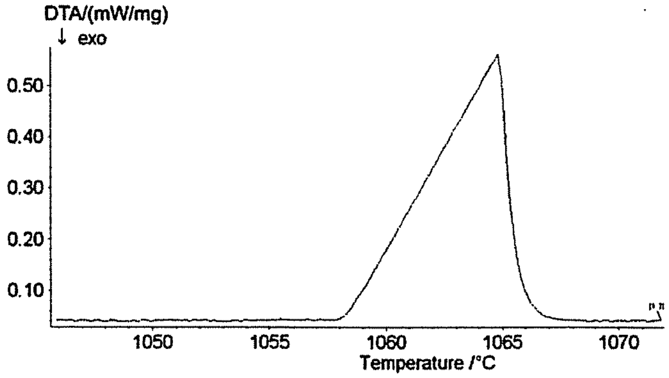

Fig. 2a DTA signal with one peak transformation

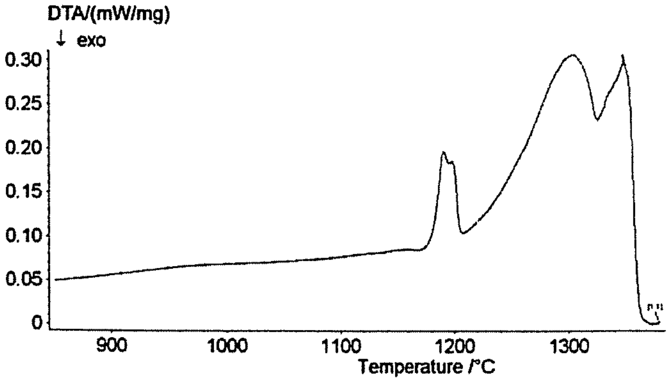

Fig. 2b DTA signal with peaks overlapping

The experimental conditions were heating from room temperature up to 1620°C with a 5°C/min rate. This rate was chosen in order to get as close as possible to industrial conditions. The experiments were limited to 1620°C which is the temperature limit of the DTA apparatus.

In our DTA experiments, we observed different peaks at high temperatures. Each peak or overlapping peak corresponds to a transformation. Figure 3 and table 2 compare the behaviour of Kosmos and Aurora grades.

During heating, we observed (Fig. 3):

- the reverse austenitic transformation (peaks 1, 2 and 3);
- the dissolution of the carbides $M_{23}C_6$ existing in the tempered matrix (peak 4);
- the dissolution of the eutectics carbides (peaks 5, 6 and 7);
- either the fusion of austenitic matrix (peak 8 for Kosmos) or the reverse peritectic transformation and the direct formation of liquid from "intrinsic" ä ferrite (peaks 8 and 9 for Aurora).

The last peak (peak 9 for Aurora) is not completed for the selected heating rate, of 1620°C. This last point requires further investigation.

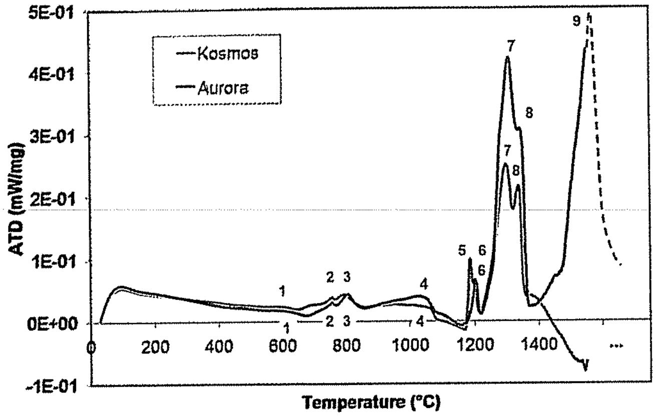

Fig. 3 DTA curve during heating

Table 2 - Temperatures of peak transformation in Kosmos and Aurora during heating

	KOSMOS		AURORA		
Nr	T° peak max (°C)	Transformation	Nr	T° peak max (°C)	Tranformation
1	595	Reverse austenitic transformation	1	610	Reverse austenitic transformation
2	752		2	755	
3	790		3	805	
4	1029	$\gamma+M_{23}C_6\rightarrow L$	4	1027	$\gamma+M_{23}C_6\rightarrow L$
5	1186	$\gamma+M_7C_3\rightarrow L$	5	---	---
6	1201	$\gamma+M_2C\rightarrow L$	6	1205	$\gamma+M_2C\rightarrow L$
7	1298	$\gamma+MC\rightarrow L$	7	1344	$\gamma+MC\rightarrow L$
8	1338	$\gamma\rightarrow L$	8	1311	$\gamma\rightarrow\delta+L$
-	---	---	9	> 1550	$\delta\rightarrow L$

When comparing the heating curves for Aurora and Kosmos (Fig. 3 and table 2), we observe for Aurora:

- there is no eutectic carbide M_7C_3;
- an increase of the peak maximum temperature of the dissolution of eutectic carbide MC;
- the presence of a reverse peritectic transformation.

The lack of eutectic carbide M_7C_3 in Aurora grade can be explained by the decreasing of the Chromium content, the principal element in the formation of carbide M_7C_3.

The reverse peritectic reaction is the transformation that occurs during the heating, starting from a solid austenite phase and leading to a mixture of solid delta ferrite and a residual liquid. The presence of intrinsic ferrite delta at the end of heating could be allowed by the presence of alpha stabilizing elements (Si, Mo, Cr).

Generally speaking, during solidification, two types of delta ferrite can be observed:

- the *"intrinsic" delta ferrite* appears as the result of the beginning of the solidification sequence and is transformed completely by peritectic reaction in austenite ($L+\delta\rightarrow\gamma$);
- the *"residual" delta ferrite* remains until room temperature is reached due to the uncompleted peritectic transformation.

"Residual" delta ferrite can be identified in the DTA heating mode, as the inversion of DTA curve slope in the temperature range of 1050°C to 1300°C [1].

Aurora grade contains "intrinsic" delta ferrite and no "residual" delta ferrite. The Aurora's heating curve doesn't show the inversion corresponding to residual delta ferrite.

The presence of "intrinsic" delta ferrite in Aurora and not in Kosmos is due to the presence of the higher Molybdenum content in Aurora. In[3], thermal analysis results showed that Molybdenum is a ferrite stabilizing element and so it could be expected that Aurora will also contain more carbides resulting from eutectoid decomposition of delta ferrite.

EUTECTIC, SECONDARY CARBIDES AND MATRIX

The Kosmos and Aurora microstructure consists of a matrix containing the products of austenite decomposition (tempered martensite) with precipitated globular secondary carbides and eutectic carbides distributed both in the interdendritic and intercellular region.

The nature and morphology of the eutectic carbides are influenced by solidification rate and chemical composition. In conventional High Speed Steels:

- MC carbide dissolves mainly Vanadium;
- M_2C carbides are rich in Molybdenum and Tungsten and can dissolve some Chromium;
- M_7C_3 are rich in Chromium.

The identification of carbides in Kosmos and Aurora was made by electron microscopy (SEM) combined with EDAX microanalyses. Figures 4 and 5 illustrate the microstructure. In Aurora and Kosmos, three types of carbides were identified: MC, M_2C, $M_{23}C_6$ (Fig. 4 and 5). In Kosmos, carbide M_7C_3 was found in addition (figure 4) [6]. MC, M_2C, M_7C_3 are eutectic carbides. It means that they precipitate from the liquid. $M_{23}C_6$ are very fine secondary carbides fully dispersed within the matrix.

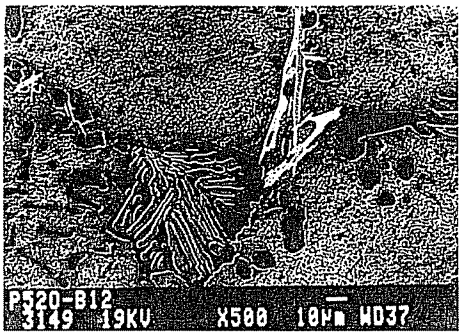

Fig. 4a Cluster of MC (black), M_2C (in white) and M_7C_3 (black) in Kosmos grade

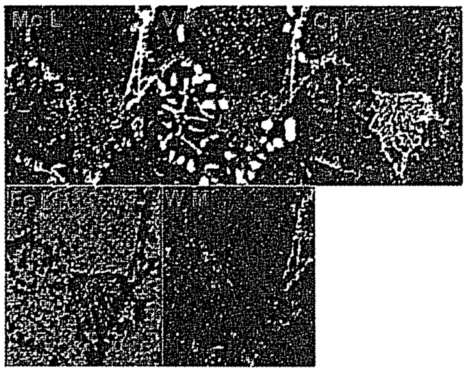

Fig. 4b EDX on figure 4a

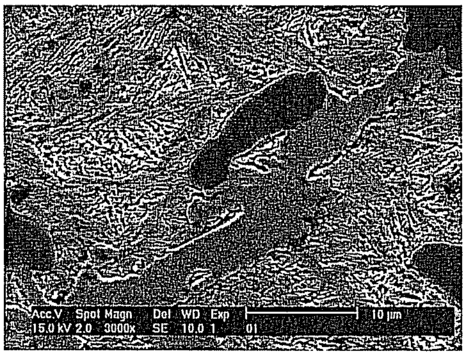

Fig. 5a Cluster of MC (black) and M_2C (grey) in Aurora grade

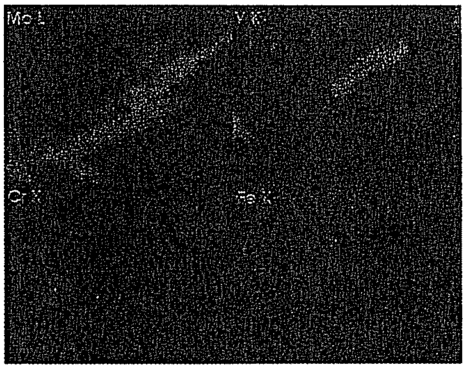

Fig. 5b EDX on figure 5a

In Kosmos and Aurora grades, the eutectic carbides have the same morphology:

- the divorced MC are characterised by a idiomorphic morphology as isolated massive crystals (Fig. 4 and 5);
- the irregular M_2C are characterised by a platelike morphology as an acicular shape (cluster of rod-like particles) (Fig. 4 and 5);

The complex-regular M_7C_3 present in Kosmos are characterised by a complex fan-shaped distributed as a continuous network (Fig. 4).

Figure 1 shows the relationship between the C content, Tungsten equivalent and morphology of eutectic carbides[4]. Table 3 compares the nature and the morphology of carbides obtained by SEM and those given by[4].

Table 3 – Nature and morphology of carbides

	KOSMOS 1.5/2.0% C 7.0/10.0% Weq	*AURORA* 1.5/2.0% C 11.0/14.0% Weq
Nature and morphology of carbides obtained by scanning electron microscopy (present study - figures 4 and 5)	Divorced MC Irregular M_2C Complex-regular M_7C_3	Divorced MC Irregular M_2C
Nature and morphology of carbides for similar composition with lower V content (given by reference 4)	Divorced MC Complex-regular MC Complex-regular M_2C Complex-regular M_7C_3	Divorced MC Complex-regular MC Irregular M_2C Complex-regular M_2C

The difference in carbides morphology between our results and those given by[4] is due to lower V content.

The results of Zaf quantification EDAX microanalyses of MC, M_2C, M_7C_3 and the matrix are shown in table 4.

Three parameters have been used:

- Weq (2Mo+W) of the matrix which is related to the solid solution hardening effect;
- Eq.Cr (Cr+1.5Si+Mo) of the matrix which gives the alphagen power;
- Weq/Cr of eutectic carbides which is the parameter we propose to characterize the hardening effect of alloying elements in MC and M_2C eutectic carbides.

Table 4 - Zaf quantification (wt-%)

	KOSMOS				*AURORA*		
	MC	M_2C	M_7C_3	Matrix	MC	M_2C	Matrix
MoL	18	39	12	2	34	68	6
V K	52	12	9	2	58	14	1
CrK	7	16	33	5	6	11	5
FeK	4	8	39	85	2	7	84
W L	19	25	7	2	-	-	-
SiK	-	-	-	1	-	-	1
MnK	-	-	-	1	-	-	1
NiK	-	-	-	2	-	-	1
Weq	-	-	-	6	-	-	12
Eq.Cr	-	-	-	8.5			12.5
Weq/Cr	7.9	6.4	-	-	11.3	12.4	-

When comparing the nature and composition of carbides and matrix of Aurora and Kosmos, we observe in the case of Aurora that:

- there are no M_7C_3 which can be explained by the decrease of Chromium content;
- the carbides MC and M_2C are:
  - richer in Molybdenum;
  - poorer in Chromium and Tungsten;
- the parameter Weq/Cr is higher;
- the matrix is richer in Molybdenum and its Weq is higher;
- the parameter Eq.Cr is higher which explains the existence of the peritectic transformation in Aurora.

Table 5 gives a summary of the nature, composition, morphology, distribution of eutectic and secondary carbides in Aurora and Kosmos.

Table 5 – Characterisation of carbides

	Composition		Characterisation ESEM *Distribution and morphology*	
	KOSMOS	*AURORA*	*KOSMOS*	*AURORA*
MC	V rich (Mo, W, Cr)	V rich (Mo, Cr)	Divorced and idiomorphic	
M_2C	Mo, W rich (V, Cr)	Mo rich (V, Cr)	Irregular and platelike	
M_7C_3	Cr rich (V, Mo, Fe)	-	Complex-regular Fan-shaped	-
$M_{23}C_6$	V rich	V rich	Regular and globular	

DENSITY OF CARBIDES

The total volume fraction of eutectic carbides and the volume fraction of each of them depend mainly on the chemical composition, the effect of the cooling rate being less significant[4]. The total volume fraction of eutectic carbides in High Speed Steels for Rolling mill rolls ranges from 9% to more than 15%, which is one of their main characteristics[4].

Figure 6 gives the volume fraction of the MC, M_7C_3 and M_2C eutectic carbides in Kosmos and Aurora as obtained in our image analysis study. The amount of MC and M_2C is higher in Aurora (8.5%) than in Kosmos (6.9%). But as there is no M_7C_3 the total volume fraction of eutectic carbides is higher in Kosmos (14.3%) than in Aurora (8.5%).

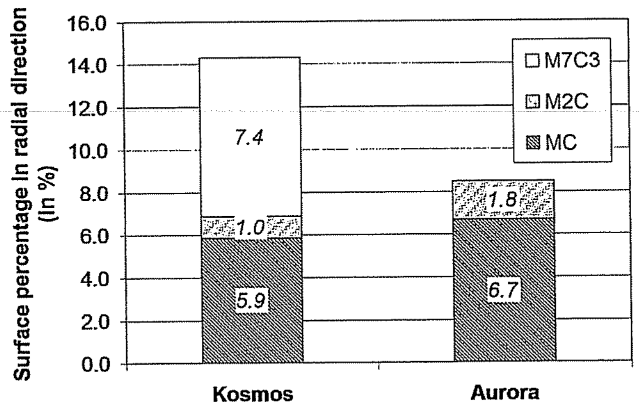

Fig. 6 Surface percentage of carbides in radial direction for Kosmos and Aurora

The amount of M_7C_3 eutectic carbides decreases when the Chromium content decreases. These carbides are rich in Iron, Chromium and other alphagen elements. The M_7C_3 is replaced by other carbides which contain mainly Vanadium, Molybdenum and Tungsten.

MECHANICAL PROPERTIES

Figures 7 and 8 compare the properties of Aurora and Kosmos for with regard to compression and hot hardness test.

The maximum stress is higher in Aurora (3203 N/mm²) than in Kosmos (2440 N/mm²).

Another main characteristic of Aurora compared to Kosmos is its high hardness level at temperatures in the 500/600°C range (figure 8).

This is in line with all the observations. The matrix in Aurora is more resistant because its WeQ is double (12) that of WeQ in Kosmos (6) (table 3). The Aurora grade contains less carbides than the Kosmos grade but these carbides are harder: there are no soft carbides such as M_7C_3. Moreover, the MC and M_2C carbides increase in quantity and they are harder because they are richer in WeQ and poorer in Cr as described by the parameter WeQ/Cr (table 3).

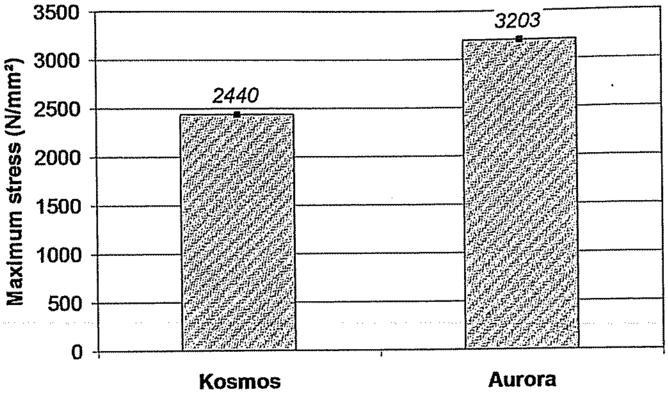

Fig. 7 Compression test

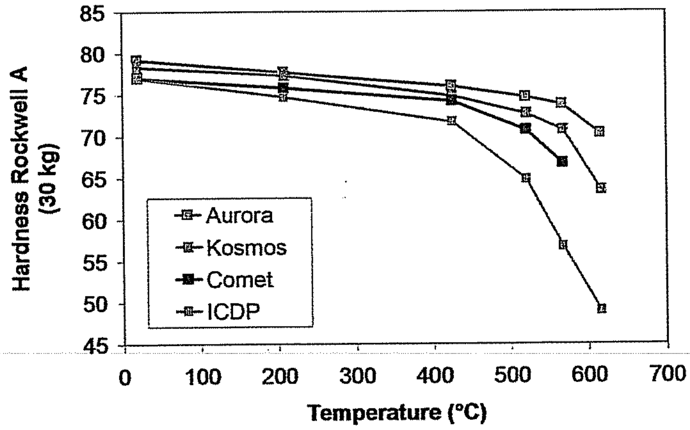

Fig. 8 Hot hardness

INDUSTRIAL RESULT

Figure 9 compares the performance of both grades in stand 2 of a CSP (Compact Strip Mill). The outputs are expressed in kilometres of tons rolled in the stand per millimetre of stock removal. The performance of Aurora is 14% higher for Aurora (2606 km/mm) than for Kosmos (2282 km/mm).

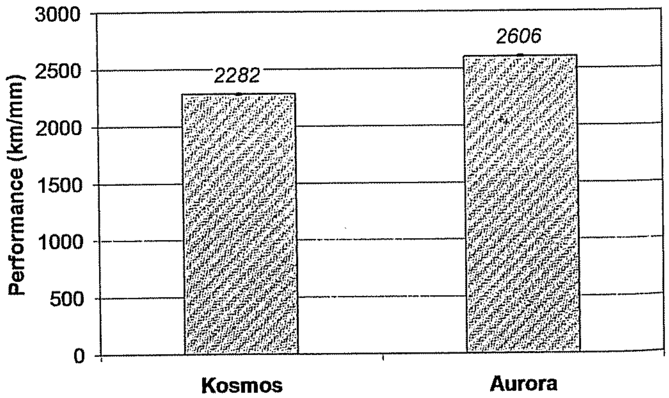

Fig. 9 Performance in stand 2 of a CSP

CONCLUSION

An overview of the development of High Speed Steel over the last century shows that it was strongly connected to the price and availability of alloying elements such as Molybdenum, Tungsten, Vanadium and Niobium.

When starting the development of Aurora grade, the price of those alloying elements was in the 6/7 € range. The total cost of alloying elements was the same for both grades.

It is clear that the big increase in the price of alloying elements since 2004, mainly Molybdenum (10x), affects the manufacturing cost of the different HSS grades. The cost of the alloying elements is higher for Aurora than for Kosmos. Due to that difference, Aurora will have to show very good performance and reliability to compete with Kosmos.

The Aurora grade presents big differences compared to the Kosmos grade:

- there are no eutectic carbides M_7C_3;
- a decrease in the total amount of carbides but an increase in the quantities of MC and M_2C's carbides;
- harder MC and M_2C carbides with higher parameter Weq/Cr;
- a more alloyed and more resistant matrix with higher Weq;
- a high hardness level at temperature in the 500/600°C range;
- a higher maximum stress.

This is in line with other scientific studies such as references [1], [2], [3] and [4].

The decrease of Chromium and the increase of Weq content in High Speed Steel makes it possible to obtain a more resistant matrix and harder eutectic carbides. The matrix is more resistant due to higher Weq content. The eutectic carbides present in the structure are harder due to the fact that the amount of soft carbides such as M_7C_3 is small or equal to zero and that the amount of hard carbides such as MC or M_2C is high. Moreover, these carbides are harder due to the higher Weq content and lower Cr content. This explains the better mechanical properties of grades containing low Chromium and high Weq content.

The performance of the Aurora grade is better than that of the Kosmos grade. This result is in line with the mechanical as well as metallurgical properties described in the present study. The higher manufacturing cost of Aurora compared to that of Kosmos may be compensated by its better performance and properties.

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Notes: