INVESTIGATION ON RETAINED DELTA FERRITE OCCURRENCE AND ITS INFLUENCE ON HSS AND SEMI HSS STRENGTHENING AFTER THERMOMECHANICAL ROUTES

J. Tchoufang Tchuindjang\textsuperscript{1}, J. Lecomte-Beckers\textsuperscript{1}
\textsuperscript{1}University of Liege, Dpt. Aerospace & Mechanics, Metallurgy and Materials Science, Belgium

\textbf{Abstract}

Two groups of HSS grades for rolling mill rolls were studied, both belonging to the complex Fe-C-Cr-X system, where X is a strong carbide forming element.

Group 1 contained three alloys, namely A1, A2 and A3, which were mostly differentiated towards their carbon content. Group 2 was composed of M1 and M2 alloys, the latter being obtained after changing W, Cr and Mo contents of the former.

Two casting routes were considered, as Group 1 alloys were obtained from ESR process, whereas group 2 alloys were spun cast. Microstructures in the as-cast conditions were compared to that obtained after thermomechanical route and thermal treatment, respectively for Group 1 and Group 2. Light microscopy together with SEM/EDX analyses helped matrix and carbides identification.

DTA was used to enhance the crystallisation behaviour and the phase transformations of each group of alloys, with a focus on the first stage of the solidification process.

Both A2 and M1 alloys were found to be subjected to the so-called Back-Activated Primary Hardening (BAPH), as they exhibited a certain form of hardening after performing their defined thermomechanical process, while A1, A3 and M2 alloys did not.

Indeed A2 exhibited an unexpected strengthening effect during forging, while a significant increase in bulky MC carbides content was found in M1 alloy at the end of the quenching plus tempering heat treatment. Moreover, evidence of Retained delta Ferrite (RdF) occurrence was enhanced in A2 and M1 alloys, towards DTA tests.

Finally, RdF was suggested to be the major parameter leading to the BAPH phenomenon observed in both A2 and M1 alloys.

\textbf{Keywords: High Speed Steel, Differential Thermal Analysis, Delta ferrite, Carbides, Phase transformations, Back-activated Primary Hardening}

\textbf{Introduction}

High Speed Steels (HSS) are high alloy steels belonging to the complex Fe-C-Cr-X system while X is a strong carbide former element standing for Mo, Nb, V or W. Due to the presence of a large amount of hard carbides in their matrix, HSS exhibit excellent hardness, wear resistance and high-temperature properties \[1-5\].

The chemical composition and the casting parameters especially cooling rate directly
influence crystallization behavior and carbides content of HSS alloys [1-2, 5-15]. When used for rolling mill applications, HSS quality depends to a large extent on the type, the size and the distribution of carbides in the matrix, as carbides directly influence mechanical properties in service [16].

Indeed, primary and eutectic carbides usually set the grain size, as they precipitated at grain boundaries during the solidification route. Subsequent heat treatments performed at temperature ranges lower than that of eutectic carbides dissolution are known to let such carbides undissolved [17]. However, such a distribution and carbides sizing could be modified through hot working, as it is the case when ESR plus forging processes are performed to promote the compactness of the cast material.

Heat treatments are intended to promote a defined microstructure towards solid state transformations. Martensite and bainite are almost the two matrix types that are promoted in order to achieve enhanced mechanical properties, as the matrix must exhibit a hardness close to that of the widespread eutectic carbides. Tempering or quenching plus tempering routes are custom practices that are performed when a significant hardening is expected on a given HSS alloy. Indeed, the completion of the retained austenite transformation into martensite/bainite together with the fine secondary carbides precipitation at the time of the tempering stage could be strongly achieved.

Changes in alloying elements could strongly influence either stables phases or metastable fields, when considering respectively equilibrium and pseudo-equilibrium diagrams [12, 14, 16].

Passing through the delta ferrite domain at the time of the solidification can be promoted by the presence of alloying elements such as V, Mo and Cr, which are also strong carbides forming elements. But such a delta ferrite phase is reported to be mainly stable at higher temperatures ranges that are closed to the melting point [14, 19]. Since most of the works dealing with delta ferrite presence at temperature ranges around room temperature are related to ferritic stainless steels [20], there is still a need to know the influence of such a phase on the subsequent HSS thermomechanical behaviour, as soon as the casting process had been completed.

The present work deals with the use of DTA tests in order to understand the crystallisation behaviour of semi-HSS and HSS alloys, and to enhance their solid state transformations. Emphasis is laid on the decomposition of the unexpected retained delta ferrite during thermal and thermomechanical treatment.

**Materials and thermomechanical routes**
The studied alloys are named A and M series, the first grade being semi-HSS obtained from ESR plus forging route, and the second one being composed of HSS grades coming from spin casting process. The chemical compositions in weight percent are given in Table 1. Carbon content increases by 0.1% from A1 to A2, and by 0.2% from A2 to A3, while other alloying elements remained unchanged. M2 grade was obtained while changing Cr and Mo contents of M1, and while adding W that was not present in M1 grade.

Samples were obtained from bars and blocks, which had been cut out of the shell of the rolls originated from different stages of the thermomechanical route. The external diameter was around 700 mm and 800 mm respectively for spun cast rolls (M series) and ESR cast rolls (A series). The forging ratio for the barrel was set around 50%.
While using DTA tests, only the as-forged state was studied on A series, except for A2 where as-cast state was considered in addition.

M1 and M2 samples were studied in the service conditions, namely the as-cast state submitted to a heat treatment that lead to a fully tempered martensitic matrix. As preliminary quenching was carried out on M1, as the as-cast material exhibited an unexpected pearlite phase within the matrix. Such a treatment was not necessary on M2, which was composed of martensite and retained austenite at the end of the spin casting process. The tempering temperature was set at 520°C for both M1 and M2 grades, with regard to the application downstream that required an enhanced metallurgical behaviour at temperatures up to 500°C.

**Experimental methods**

Differential Thermal Analysis tests were performed on a Nestzch STA 449 device. The heating sequence of DTA test can lead to the determination of temperature ranges at which precipitates dissolved and also to the melting point of the studied alloy. In addition to the melting behaviour obtained during the heating sequence, DTA could allow the determination of the crystallization behaviour of a given alloy, namely phase transformations and particularly their temperature ranges in relation with cooling rates. Crystallization behaviour allows the prediction of primary carbides precipitation within the matrix during cooling [1, 5, 8, 10-12, 14, 15]. Thus alloying elements influence could be studied in relation with the remelting behaviour of the defined alloys during heating stage. The heating rate was chosen to be close to industrial practice obtained during the cooling stage of the casting process, despite the fact that such a casting route involved variable cooling rates on the actual roll that is to be produced.

The heating rates were set at either 5°C/min or 10°C/min for the studied samples, with each trial performed twice in order to yield an average behavior for each material. Carbides nature was determined by the means of scanning electron microscopy together with Energy Dispersive by X rays Spectrometry (EDS or EDX). Carbides volume fraction was assessed only on M series, based on quantitative metallography towards Images analysis and optical microscopy. Overall carbides volume fraction on M series was assessed through the average values obtained after different etching states.

**Results**

Microstructures of the as-cast and as-forged samples originated from A2 are illustrated on Fig. 1, whereas fig. 4 and 5 show the optical micrographs obtained from M series. DTA heating curves are respectively given at fig. 2 for A series, and fig. 3 for M series. Retained δ-ferrite (RdF) was observed on remelted and re-solidified samples from A series, obtained after DTA tests. But no evidence of RdF occurrence was made neither in the as-cast nor in the as-forged samples of A series through metallographic analysis (Fig. 1a, 1b). Contrary to optical micrographs DTA tests allowed the enhancement of RdF occurrence within the studied alloys, especially A2 (fig. 2a, 2b) and M1 (fig. 3a).

The melting process was completed at different temperatures for A and M grades. The higher melting point was found on M1 (around 1600°C, see fig. 1), while the lower melting point was obtained on M2. A series exhibited different melting points, all of which being comprised between the previous values determined on M1 and M2.
Further analyses were carried out on M series prior to A series, as the former were almost characterised, while the latter grade remained under analyses.

M1 and M2 DTA heating curves led respectively to 10 and 8 specific peaks (Fig. 3). Related phase transformations are also mentioned with a “hi” designation involving the chronological occurrence of the reaction at the time of the DTA heating sequence. The heating sequence up to complete melting of the sample gave back the thermal history of the material towards phase transformations observed while the tests went on. In fact, peaks that are illustrated on thermal diagrams involved precipitates solutionizing and phase transformations like reverse eutectoid, reverse eutectic or even reverse peritectic (Fig. 1).

Phase transformations nature and designation as illustrated in Tab. 2, were determined while combining DTA curves with subsequent SEM/EDS analyses and results from previous works [2, 4, 6, 7, 12-15, 19, 20].

M1 and M2 DTA heating curves seemed to exhibit similar peaks appearing at comparable temperature ranges, except for peak 5 only found on K1, and peaks 9 and 10 only found on A2 (see fig. 3).

Peak 5 (K1) is related to M_{7}C_{3} eutectic carbides, while peak 9 and peak 10 (on M1) involved respectively the reverse peritectic reaction and the ultimate melting point (Tab. 2). DTA heating peaks sequence could be analyse in a reverse approach, starting from the last peak (peak 10 for M1 grade and peak 8 for M2 grade) down to the first peak 1, on both alloys.

Remelting process was achieved on M1 (1600°C) at a temperature higher than that of M2 (1360°C), owing to the peritectic reaction which only existed in M1 grade. Such results inferred that the first phase to precipitate in M1 during the initial casting process was δ-ferrite (peak 10), while the solidification process began with the formation of γ-austenite on M2 (peak 8).

As the solidification process is governed by the segregation of the alloying elements within the liquid/solid interfaces, the sequence by which carbides precipitated resulted from a competition between them, depending on the overall chemical composition and on the cooling rate [1, 2, 5-15].

In the present work the lack of M_{7}C_{3} carbides in the M1 grade was probably due to the chemical composition, either for the reduced Cr and W contents or for the balance in others elements forming carbides (Mo and V).

In the same time, an additional carbide known as M₆C was found only on heat treated M2 (M2 htt) sample.

Fig. 3b shows the average carbide volume fractions as obtained from the results of the quantitative metallography done on M series.

M₂C and M₇C₃ carbides were considered as a whole on M2 series as it appeared difficult to distinguish them on a grey level scale prior to quantitative metallography.

M2 contained more carbides than M1 either in the as-cast conditions or after heat treatment route.

Total volume fraction of carbides increased respectively by 17.6% and 4.3% on M1 and on M2, after heat treatments. Meanwhile total carbides volume fraction remained alike on M1 before and after heat treatment (Fig. 3b, 6).

There was a significant increase in MC amount when heat treating M1. Indeed, MC amount jumped by 61%, from 5.4 up to 8.7% (fig. 3b, 4).

There was a drop (26% down) in M₆C content on M1 while performing quenching and tempering on the as-cast sample (fig. 5).
The $M_2C$ content lowering on M1 suggested that such carbides were likely to be transformed during heat treatment. Indeed, $M_2C$ decomposition had been reported to be an eutectoid reaction that is time and temperature depending [7, 11, 13, 17, 20]. Products of such a reaction are $MC$ and $M_6C$ carbides, their size varying with time, temperature and chemical composition of the initial $M_2C$ carbides [7, 11, 13, 17, 20].

**Discussion**

The $+3.3\%$ increase ratio of $MC$ carbides appeared to be more important than the related $-1.4\%$ drop of $M_2C$ carbides as observed on M1. From this statement, it is quite obvious that the rise of $MC$ carbides amount on M1 had an additional origin that is different from the solely $M_2C$ decomposition.

In order to explain how a slight decrease of $M_2C$ carbides could yield a more significant increase of $MC$ carbides in M1 alloy, direct transformation of acicular $M_2C$ into $MC$ at high temperature was not consistent.

A further analyze done on $\delta$-ferrite presence in M1 yield following outcomes. Peak 9 (Fig. 3a), which is related to the reverse peritectic reaction during heating mode, involved the formation of a new $\delta$-ferrite phase, as the heating mode of the alloy led to a crossing through $\delta$ field. But peak 9 seemed to exhibit a weaker area when compared to that of the following peak 10, which was involved in the melting of the newly formed $\delta$-ferrite. Then it had been assumed from the difference in the area of peaks 9 and 10 that there was already a $\delta$-ferrite phase in the as-cast sample that is known as residual $\delta$-ferrite. Evidence of untransformed $\delta$-ferrite had already been enhanced [8, 20]. The incompleteness of the peritectic reaction was reported to yield the solid state decomposition of the intradendritic residual $\delta$-ferrite through a delta eutectoid reaction that was described as the last step of the solidification process [8]. Besides, the more or less complex reaction involving the direct transformation of retained $\delta$-ferrite to yield the so-called $MC'$ carbides can be defined as a complex peritectoid reaction, with peritectoid $MC'$ carbides as a result that are larger in size [8]. Previous works involved eutectoid-like products [8, 13, 20] from the $\delta$-ferrite decomposition latter in the solidification stage.

The newly formed $MC'$ carbides are larger in size, and almost similar to the primary eutectic $MC$ carbides which precipitated at the beginning of the solidification process. Nevertheless, $MC'$ carbides have to be differentiated from eutectic $MC$. Furthermore, $MC'$ carbides are different from fine secondary carbides precipitating at the time of tempering process.

Thus, it was suggest that such complex peritectoid phase transformation being called with a specific designation known as Back-activated Primary Hardening (BaPH). The BaPH yield larger $MC'$ carbides from the decomposition of the residual $\delta$-ferrite ($RdF$), in a complex peritectoid reaction that involved more or less austenite to be associated with $\delta$-ferrite at temperature ranges above $Ac_1$. Nevertheless, almost all the previous investigations assumed a complete transformation of $\delta$-ferrite by the end of the solidification process. However, it might be assumed that $\delta$-ferrite could still exist at room temperature, depending on both metallurgical and thermophysical parameters, which are set by the HSS alloy and the subsequent casting route. Such an assumption of the residual $\delta$-ferrite existence at room temperature appeared definitely necessary in order to explain the origin of the additional contribution in $MC$ forming elements other than $M_2C$ decomposition, which yield the $3.3\%$ increase in $MC$. 


carbides after heat treatments on M1.

The same assumption of δ-ferrite existence was made on A2 which exhibited an unexpected strengthening effect during the forging process. From DTA heating curves on A series (fig. 2) it appeared that the passing through δ-ferrite filed could be predicted by the occurrence of a previous endothermic peak that arises between 1300 and 1400°C (see zone 1, on fig. 2b). This peak may stand for the MC’ melting in A2, as long as such MC’ originated from RdF decomposition that occurred earlier, during the forging process.

Work is still in progress in order to determine whether the passing through the δ-ferrite field at the end of the melting process as given by DTA test is related to the conventional reverse peritectic reaction, or to the occurrence of a RdF that remained untransformed.

Summary
Depending on their chemical composition, HSS and semi-HSS alloys can exhibit retained δ-ferrite (RdF) at the end of the casting route, when the room temperature is reached.

Such a RdF appeared to originate from the incompletion of the peritectic reaction during the solidification of the HSS alloy, when the casting parameters together with the chemical composition allowed a passing through δ-ferrite field at the beginning of the solidification process.

The occurrence of RdF in the HSS microstructure had a great influence on the subsequent thermomechanical behaviour of the alloy, especially when a re-austenitisation stage is to be performed.

Indeed, RdF appeared to decompose itself into larger MC’ carbides, through a complex peritectoid reaction, during the re-austenitisation.

This phase transformation had been set as the so-called Back-activated Primary Hardening (BaPH), as it led to a hardening effect more significant than that of the secondary precipitation arising during tempering process.

Such a decomposition of the RdF into MC’ carbides was suggested to be responsible of the strengthening effect observed in a semi-HSS alloy during the forging process.

Acknowledgments
The authors wish to thank the CATµ of ULg for SEM/EDX facilities, both MK Belgium and Åkers Group for their technical support, and Walloon Region for their financial support.
Tables:

Tab. 1: Chemical composition of HSS grades (wt %)

<table>
<thead>
<tr>
<th>Casting process</th>
<th>HSS Grades</th>
<th>Alloying elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>ESR</td>
<td>A1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>to</td>
</tr>
<tr>
<td></td>
<td>A3</td>
<td>1.0</td>
</tr>
<tr>
<td>Spin Casting</td>
<td>M1</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Tab. 2: Signification of DTA peaks and related phase transformations during heating mode on M1 and M2

<table>
<thead>
<tr>
<th>Peak Number (Related reaction)</th>
<th>Phase transformation reaction</th>
<th>Phase transformation designation</th>
<th>Peaks occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5 (h₅)</td>
<td>γ₂ + M₇C₃ → L₁</td>
<td>Reverse eutectic 1 (Direct melting of M₇C₃ carbides)</td>
<td>No Yes</td>
</tr>
<tr>
<td>P6 (h₆)</td>
<td>γ₃ + M₂C → L₂</td>
<td>Reverse eutectic 2 (Direct melting of M₂C carbides)</td>
<td>Yes</td>
</tr>
<tr>
<td>P7 (h₇)</td>
<td>MC (+ L₂' ) → L₃</td>
<td>Direct melting of primary MC carbides</td>
<td></td>
</tr>
<tr>
<td>P8 (h₈)</td>
<td>γ₄ → L₄</td>
<td>Direct melting of γ-austenite</td>
<td></td>
</tr>
<tr>
<td>P9 (h₉)</td>
<td>γ₅ → L₅ + δ</td>
<td>Reverse peritectic</td>
<td></td>
</tr>
<tr>
<td>P10 (h₁₀)</td>
<td>δ → L₆</td>
<td>Direct melting of δ-Ferrite</td>
<td></td>
</tr>
</tbody>
</table>

A grade | K grade
No | Yes
Yes
Yes
Yes
No
Figure 1a: Microstructure on as-cast A2 (Nital)

Figure 1b: Microstructure on as-forged A2 (Nital)

Figure 1c: Microstructure on re-solidified A2 after DTA test - RdF lobules (light) surrounded by fine carbides in a mixed austenite/bainite matrix (Nital)

Figure 1d: Re-solidified A2, after DTA – Lobules are RdF with sulphide inclusion in the middle that acts as a $\delta$-ferrite germ (Nital); matrix is composed of RA and martensite
Fig. 2a: DTA heating curves on A series

Fig. 2b: Enhancement of the final stages of remelting process on A series

Fig. 3a: DTA heating curves on M series

Fig. 3b: Carbides volume fraction on M series
Fig. 4: Enhancement of the sharp increase in MC carbides (light) after heat treatment on M1 (left, as-cast M1 – right, quenched and double tempered M1 – Murakami etching)

Fig. 5: Enhancement of the collapse in M2C carbides (colored) after heat treatment on M1 (left, as-cast M1 – right, heat treated M1 – Groesbeck reagent)

Fig. 6: Similar carbides volume fraction on both as-cast (left) and heat treated (right) M2 (Quasi continuous carbides network with complex M7C3/M2C/M6C (dark) and interdendritic rod-like MC (light) – Murakami etching)
Fig. 7: Carbides characterisation on as-cast M1 towards SEM/EDX analyses
7a: M1 microstructure after a deep etching of the matrix
7b: EDX map related to 7a (Mo-rich M2C, V-rich MC and Fe-rich matrix)
7c: M2C (light) and rod-like MC (grey) in a quasi-continuous network in the as-cast M1

Fig. 8: Carbides characterisation on heat treat M1 towards SEM/EDX analyses
8a: M1 microstructure after a deep etching of the matrix
8b: EDX map related to 8a (Mo-rich M2C, V-rich MC and Fe-rich matrix)
8c: Partially dissolved M2C (light needles) with fine secondary M4C3 in their vicinity and bulky and nodular MC around (and rod-like MC (grey))
REFERENCES


