

MANAURITE® DRX

Advanced microalloyed steel for Midrex® type reformer tubes

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Microalloys have become an industry standard in the supply of reformer tubes. However, behind the word, and although we are talking indeed of "micro" additions, the selection of those alloying elements, so important for creep resistance, have evolved significantly. As a result and after extensive internal and external creep tests, Manoir has introduced in 2009 a new alloy for reformer tubes that is gaining momentum. This article is a summary of the steps undertaken to have reached this position.

INTRODUCTION

In the production of reforming gas for the DRI plants, one of the strategic pieces of equipment of the plant is the steam reformer furnace. The reformer tubes inside that furnace are designed in dimensions to stand for a minimum of 100,000 hours at approximately 1050°C, and up to 2.5 bars of pressure, and to provide the desired plant output. The key features we ask those tubes to have are creep resistance at higher and higher temperatures, and to a degree, ability to withstand thermal cycles.

The current DRI Midrex® type tube technology contains several alloy combinations. Currently the vast majority of the catalyst tube are 25-35MA in the lower section (typically Manaurite® XM in Manoir's literature) and HV (28-48 -5W, called Manaurite®50W in Manoir's literature) in the upper (hot section) of the tubes. Some tubes are equipped with 25-35 MA with HV-MA in their upper part. Current alloy combination provides 8-10 years' service.

Having been involved for more than 50 years in the production of spun cast tubes for high temperatures applications, Manoir is pleased to provide to the market a proven alloy called **Manaurite® DRX**. The specific properties of Manaurite® DRX allow:

- **Increase temperature capability to 1135°C**
- **Enhance creep strength over current alloys**
- **Easy manufacturing, regardless of investment casting, sand casting or centrifugal casting**
- **Improved weldability after ageing**
- **Balanced tube life with catalyst life.**
- **Competitive reformer tube based on lower nickel content**

CREEP FAILURE MECHANISM

Creep properties improvements over the years have been achieved by finding alloying elements (macro or micro) that, combined with the carbon present in the tube metallurgy, form carbides [Sourmail, 2001]. Those carbides act as strengtheners that will limit creep deformation. However, creep deformation, as low as it may be, will inevitably occur, leading to the formation of creep voids dispersed in the material (step 1 in Figure 1). These creep cavities will become progressively more numerous as well as larger (step 2). Eventually, they will coalesce to form first microcracks, and then macro-cracks, synonym of global failure of the tube, as illustrated in steps 3 to 5 of Figure 1.

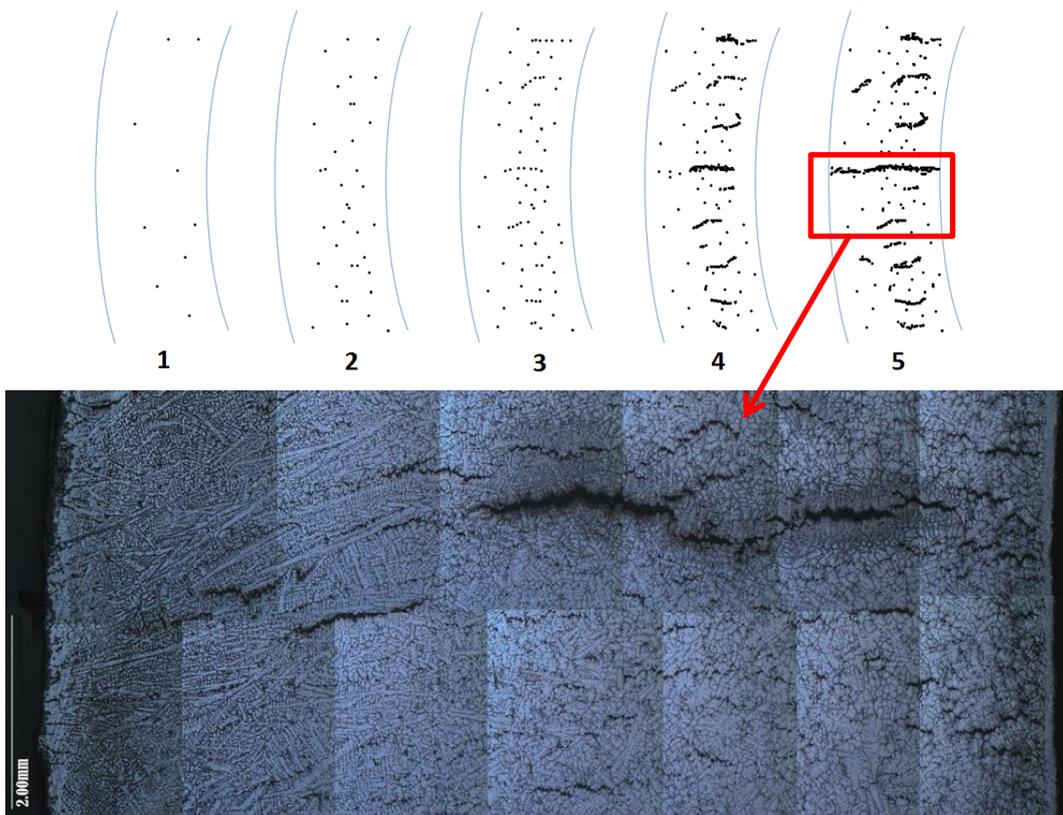


Figure 1: Failure of a reformer tube by coalescence of creep voids.

The end of the story – or failure – is somehow inevitable. However it can be both delayed in time and (partly) predicted.

The delay of creep rupture in time, at a constant plant output, can be addressed by working on the microstructure and therefore mechanical properties of the heat-resistant alloys in use.

Prediction of creep failure is possible if proper non-destructive techniques are used to evaluate tube damage on a reliable basis in order to establish an optimized revamp schedule.

Part of the process is to avoid, or delay, the coalescence of carbides that is observed after long exposure to high temperatures.

THE ORIGIN OF CREEP RESISTANCE

One of the specific goals that have led to the continuous evolution of heat-resistant steels over the years is to achieve the highest creep properties at service temperatures. For that purpose, a deep understanding of the relationships between microstructure and mechanical properties is required.

The starting point was the use of austenitic stainless steels. Indeed, austenite steels, with their face-centered cubic crystallographic structure, are well-known for maintaining better creep properties at higher temperatures than ferritic steels, which have a base-centered cubic structure. Furthermore, austenitic steels are not subject to phase transformation during temperature changes. These two points largely explain why all heat-resistant steels used in steam-reformers and steam-crackers (another high temperature application requiring cast spun tubes) are austenitic stainless steels. However, creep properties are not only ruled by crystallographic structure, but also by carbides size, spatial distribution and thermal stability.

In creep resistant steels, the role of carbides is to inhibit deformation mechanisms: preventing both the sliding of grain boundaries and the gliding of dislocations. This role is illustrated by Figure 2, which shows how dislocation glide is stopped on carbides and grain boundaries in heat-resistant steel.

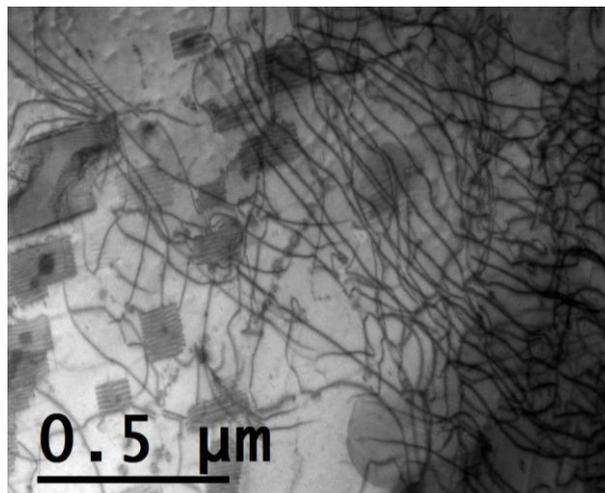


Figure 2: Dislocation pinned on carbides and grain boundaries in a heat-resistant steel.

The finer and the more homogeneously distributed the carbides are, the better the creep properties are. Therefore, part of the continuous evolution of heat-resistant steels has been to aim for the most efficient carbide precipitation. To have optimum properties, this carbides population must form adequately and, over all, must maintain itself throughout time. In that sense the growth and coalescence of carbides, due to temperature exposure and shown in Figure 3, must be avoided.

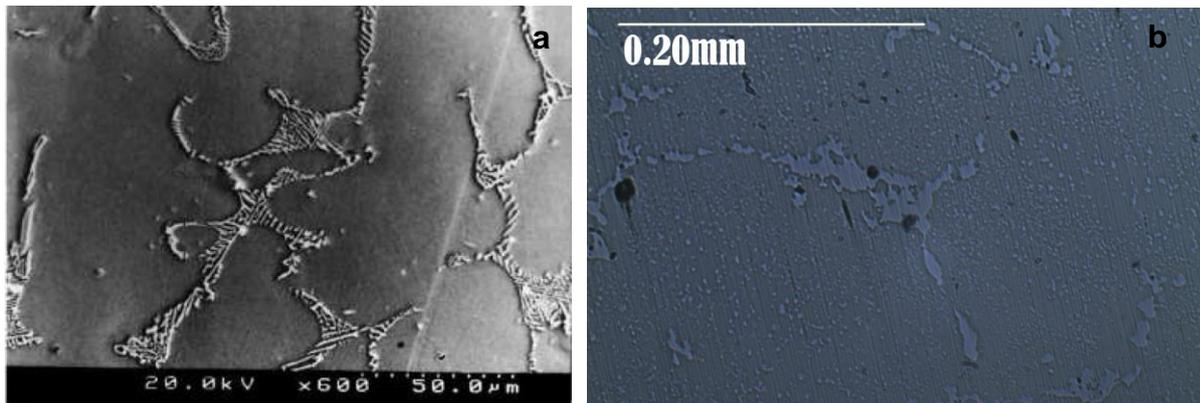


Figure 3: Microstructure of HK40 in as-cast state (a, [Kaya, 2002]) and after service (b). In aged state, primary eutectic carbides have coalesced: their shape has become rounded and the lamellar eutectic structure is no longer visible. Some creep voids and secondary carbides are also observed after service.

MICROSTRUCTURAL EVOLUTION OF HEAT-RESISTANT ALLOYS

As early as in the 1950's, the first widely used alloy for reformer tubes application was HK40, which was basically a Fe-based alloy composed of: 25% of Cr to ensure creep and oxidation resistance, 20% of Ni to maintain an austenitic structure and 0.4% of C. This high carbon content, as compared to similar wrought alloy, coupled with a high quantity of available Cr, leads to the formation of chromium carbides.

Two main categories of carbides coexist in heat-resistant austenitic stainless steels.

-The larger ones are interdendritic carbides. They form during the rapid solidification of the alloy (by centrifugal casting) and are therefore called "primary carbides" (see Figure 4a).

-"Secondary carbides" do precipitate during thermal ageing of the alloy. They form a finer and denser distribution of obstacles to dislocation glide (see Figure 4b).

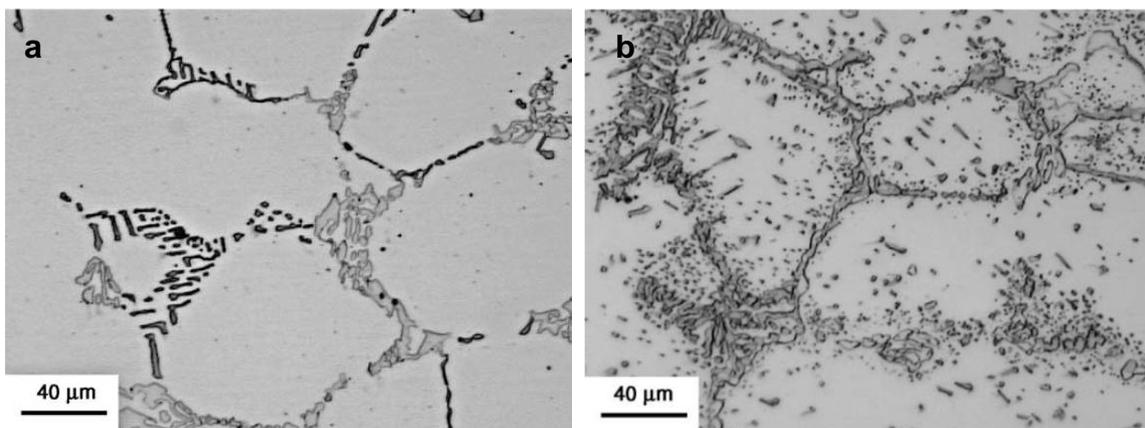


Figure 4: Microstructure of HP-Nb alloy. (a) As-cast. (b) After ageing for 1000h at 900°C. [Almeida, 2003].

In the 1960's, the chromium to nickel ratio was optimized to enhance creep properties as well as to limit sensitivity to ageing embrittlement and improve carburization resistance. HK40 was progressively replaced by HP alloy, with still 25% of Cr but 35% of Ni. Figure 5 illustrates the disappearing of one brittle phase, sigma phase, between HK40 and HP.

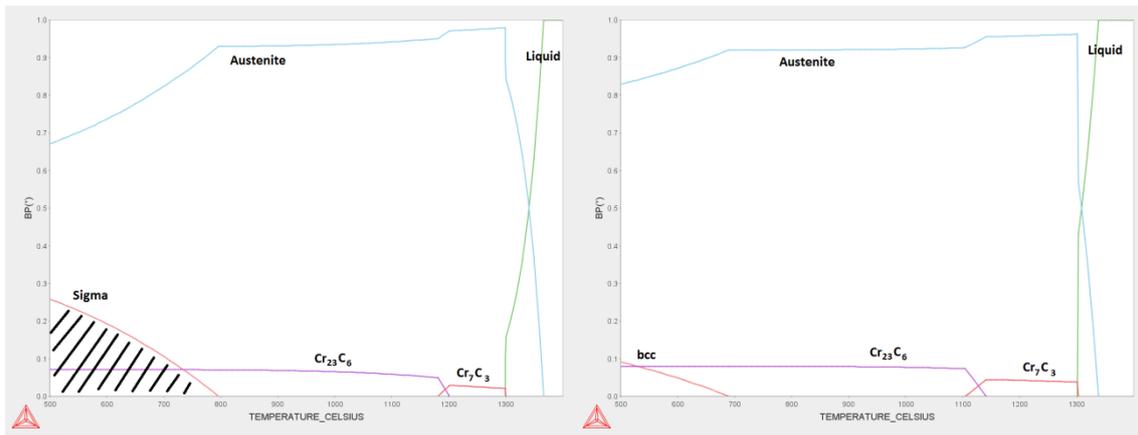


Figure 5: Thermodynamic calculations of HK40 (left) and HP (right) indicating the disappearance of sigma phase precipitation in HP alloy. Calculations were carried out using ThermoCalc® software.

HP alloy is the mother alloy of the 25Cr/35Ni family. Since then, the evolution of 25/35 steels has never stopped. Manoir to this end released Manaurite® 36X by introducing Niobium (Nb) as an alloying element. This is how HP-Nb alloys happened. This alloy was since widely introduced in applications like ammonia, methanol, and hydrogen plants. The basic idea was to increase the operating temperature of HP alloys by improving the resistance of carbides to coarsening and coalescence. Addition of niobium enables to form a new type of carbides - namely MC type, where M is mainly niobium - as well as it modifies the structure of M_7C_3 and $M_{23}C_6$ carbides. These changes lead to a higher stability of the carbides at high temperatures, and therefore to a better resistance to coarsening and coalescence.

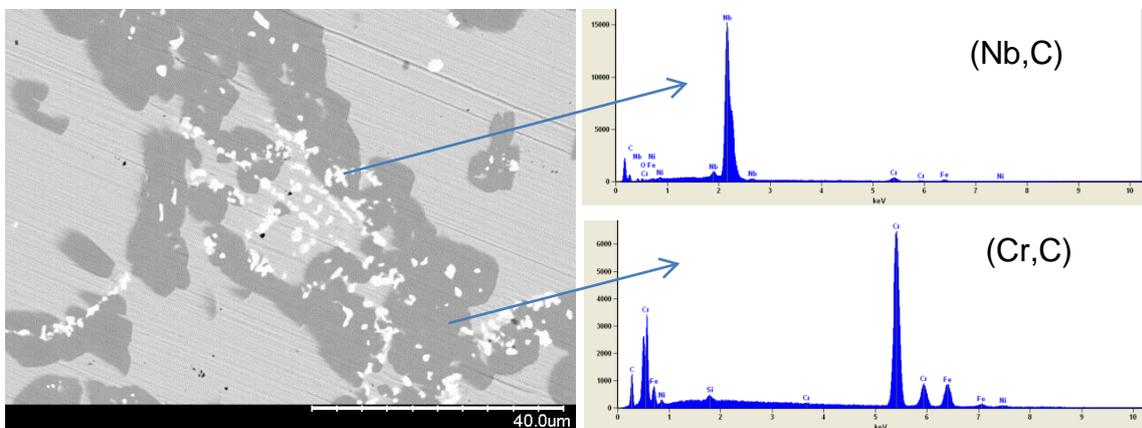


Figure 6: SEM observation and corresponding EDX spectrums of both chromium and niobium carbides in aged HP-Nb alloy.

Then, subsequent micro-additions of other carbide formers (Ti, Zr, W,..) led to the “HP-Nb-MA” (Micro-Alloyed) steels. Manoir industries introduced to the market various alloys in this category, Manaurite® XM being the most advanced one up to a recent past. The role of these micro-additions is to form even finer primary and secondary carbides with a high resistance to coarsening [Almeida, 2003].

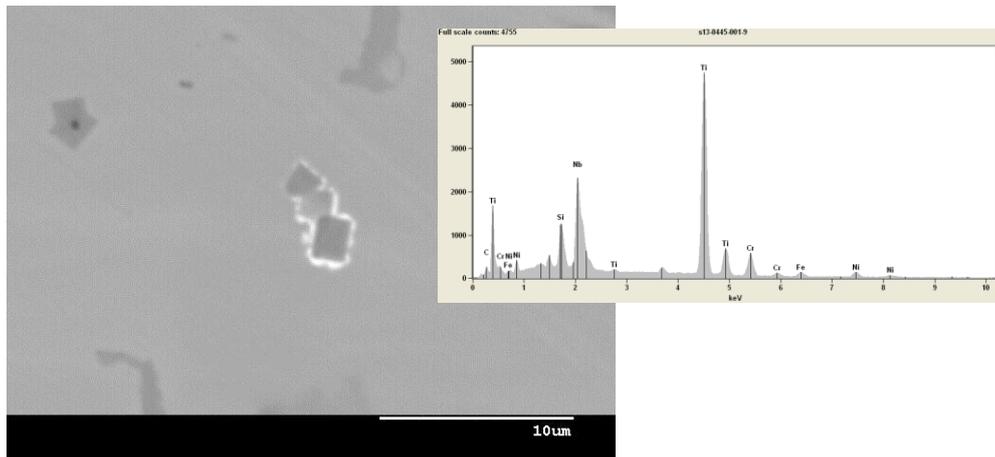


Figure 7: Titanium carbides observed in a heat-resistant alloy containing 0.02wt.% of titanium.

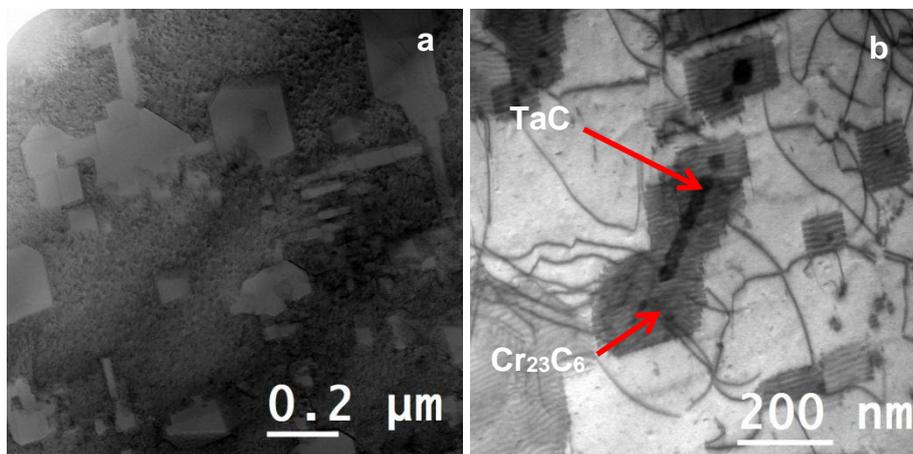
For decades, Manoir Industries has kept on improving the creep properties of its proprietary alloys. Manaurite®XM (25-35-Nb-MA) has progressively replaced Manaurite®36X (25-35-Nb) over the years.

However, Manaurite®XM has been continuously optimized by Manoir’s R&D department: optimized content of common micro-additions (Ti, Zr, W), improvement of ageing properties by Mn and Si content adjustment, and introduction of other elements such as carbides formers (V, Ta,...), rare earths (Y, Ce,...) or other beneficial elements (Hf, B,...).

Micro-additions of rare earths are known for obtaining a higher adherence of oxide layers ([Cueff, 1998], [Shao, 2012]), which is mainly of importance for steam-crackers. They also help in improving high temperature mechanical properties by inhibition of deleterious effects of sulphur segregation to grain boundaries [Chen, 2011].

Recently introduced carbide formers will also form secondary carbides, even smaller than with usual carbide formers. Such small carbides, whose size can be as low as 10 nm, are shown in Figure 8. They tend to form on existing defects of the crystalline structure (dislocations, stacking faults). They will act both as dislocation barriers, but also as nucleation sites for chromium carbides, as observed in Figure 8. Therefore, a more dispersed distribution of complex-chromium carbides is obtained.

Addition of these new elements demands specific melting procedures, in order – for example - to protect elements most likely to be oxidized. Melt protection as well as use of sacrificial elements is required.



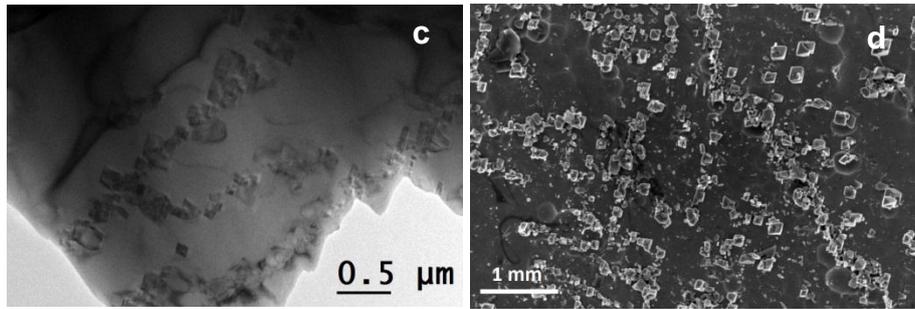


Figure 8: TEM and SEM observations of multiple shape carbides. A complex structure of chromium carbides growing on tantalum carbides can be observed in (b).

The various evolutions above mentioned have resulted in Manaurite®DRX grade, specifically designed for its high creep resistance and therefore dedicated to DRI steam-reformer applications. Manaurite® DRX is an advanced alloy of 25-35 Nb-Ma specifically tailored for Midrex® type reformers.

STABILITY OF CARBIDES WITH RESPECT TO TEMPERATURE

Resistance of carbides can be observed at two scales, which are concomitant in service: the time scale, and the temperature scale. As much as possible, carbides size should not be modified by long-term exposure to high temperature.

The effect of temperature can be deduced from infinitely long ageing treatment at different temperatures. It can also be deduced from thermodynamic calculations, simulating the equilibrium state reached after an infinitely long time at a given temperature. Results from thermodynamic calculations using ThermoCalc software are shown in Figure 9. They illustrate that the stability domain of $M_{23}C_6$ type carbides has been extended with grade evolution from HP to HP-Nb and then to Manaurite®XM. It also shows that MC type carbides have an even higher temperature limit (also visible in Figure 6). If the operating temperature is higher than the maximum temperature of given carbide, it will eventually dissolve in the matrix.

Below their higher temperature limit, carbides are stable on a thermodynamic basis. However, their size and distribution will evolve with time. At the very beginning of ageing, carbides will precipitate and grow. Precipitation rate is commonly proportional to the square root of time. Then carbides will start to coalesce: larger carbides will grow at the expense of the smaller ones (that will disappear). This growth is all the faster as the carbides are large [Lifshitz, 1961]. Therefore, the smaller the initial carbides are, the higher is the resistance to coalescence. Use of rare earths, forming very small carbides as shown in Figure 8, thus does also prevent coalescence from occurring.

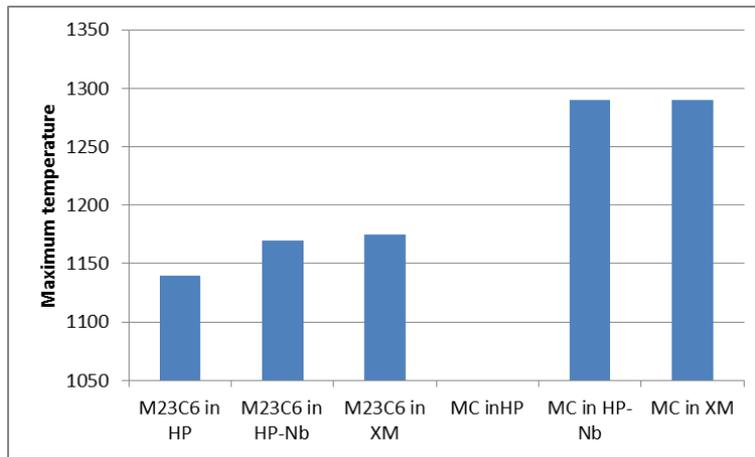


Figure 9: Maximum temperature of various carbides as determined by thermodynamic calculations.

INCREASE IN MECHANICAL PROPERTIES

Figure 10 and Figure 11 represent the 100,000 h creep strength of several heat-resistant alloys with respect to temperature. It shows the continuous increase of properties from HK40 up to Manaurite®DRX material. This continuous trend of improvement was driven by the optimization of chemical compositions, more specifically, carbide forming elements and their balance. However, simply adding carbide formers is definitely not enough: the fine tuning of the general composition is necessary to ensure the homogeneous distribution and thermal stability of carbides but also to prevent the formation of undesirable phases (like sigma phase, G-phase etc...). The solid solution strengthening is also a key to ensure good creep properties and can only be achieved by a precise balance of all elements.

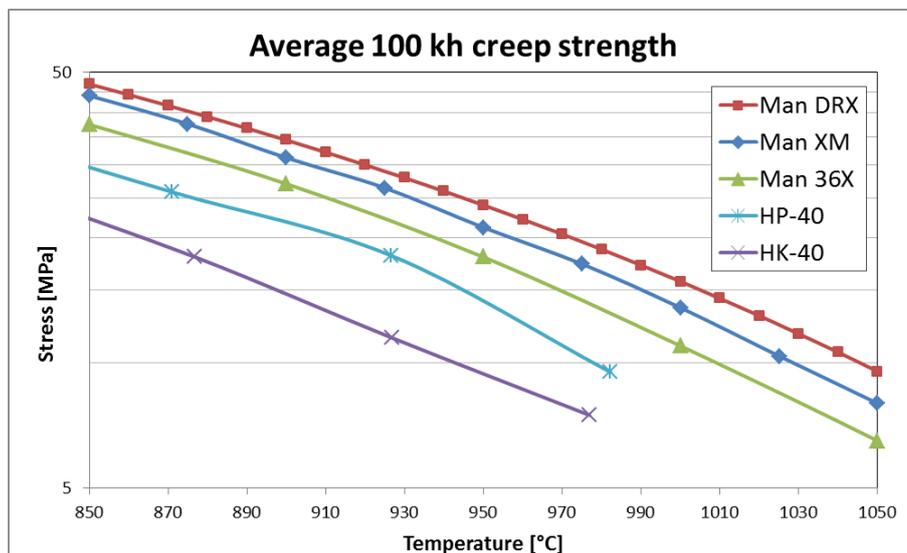


Figure 10: Average 100,000h creep strength of refractory alloys used for catalyst tubes, from HK40 to Manaurite®DRX.

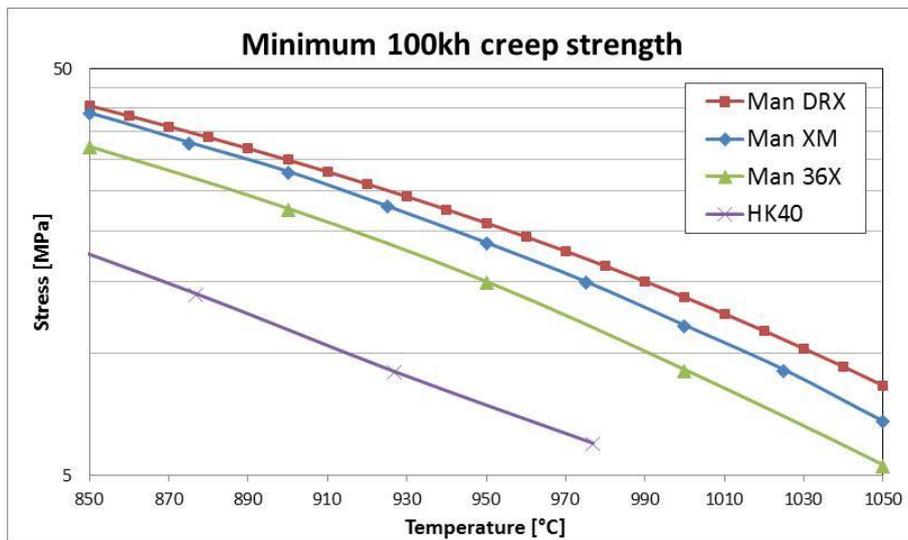


Figure 11: Minimum 100 000h creep strength of refractory alloys used for catalyst tubes, from HK40 to Manaurite®DRX.

Such statement implies that very wide ranges of chemical compositions (e.g. a 6% range for Ni content as it can be observed in some published data) are clearly unrealistic to ensure specific creep properties with reasonable ranges between minimum (95% confidence interval) and average strengths. One can claim that those wide ranges are published to protect know-how, which is arguable.

Equally unrealistic are specifications or suppliers claiming to control undesirable elements (e.g. Bi) as low as 5 ppm. Standard production control apparatus for chemical composition cannot simply ensure such low levels.

In any event, if the deleterious effect of various elements (Pb, Bi, Sn, etc...) is definitely proven and admitted by the industry, the actual acceptable boundaries are generally of the order of 20 ppm, 50 ppm or even 100 ppm.

The control of micro additions is much easier since the quantities involved are larger than 0.01%. The key points are related to the elaboration process during fusion/melting and the balance between all these elements. As previously stated, current alloys take their creep resistance from a combination of several micro-alloying elements like Ti, Zr, Ta, W etc... If titanium is now widely known, recognized and used, simply having "a lot" of it is definitely not enough and might even be negative. If correctly introduced, dispersed, combined and balanced with other carbide builders, even a Ti content as low as 0.02% can be enough to ensure the desired creep strength.

HOW TO ASSESS CREEP RESISTANCE?

To plot a creep curve, actual creep tests are carried out. Design conditions require predicted lifetimes of at least 100,000h and more and more often 200,000h or 300,000h. Knowing that 100,000h represent more than 11 years, usual extrapolation practices (e.g. according to Dutch Stoomwezen code, for example) allow a factor 3 between actual data and extrapolated creep curves.

It means that these curves need to be based on some tests of at least 33,000h in addition to the usual short term (~100h) creep tests. Of course, such very long term properties at very high temperatures are the most difficult to check or verify. This is the reason why third party tests by independent laboratories for at least mid term (>1000h) durations are so important to assess the relevance and seriousness of a creep curve presented on a commercial brochure. Larson

Miller curves enable to gather within a given range of temperatures (this range, to be valid, must correspond to similar creep mechanisms) the various stress/lifetime obtained in testings.

A Larson Miller curve that is more likely a line rather than a curve and is “very straight” on a large temperature range is often an indication that this curve has been possible vastly extrapolated.

Figure 12 shows the Larson Miller creep curve of Manaurite®DRX based on internal creep data obtained at Manoir in addition to two sets of creep data taken from a random sampling of Manoir production, on different tubes thicknesses and carried out by independent laboratories (TNO-NL) within two separate studies for durations from 200h to much more than 1000h. This curve is voluntarily conservative and pessimistic on its right side (were collecting data is long and expensive) and shows a drop for high LMP values.

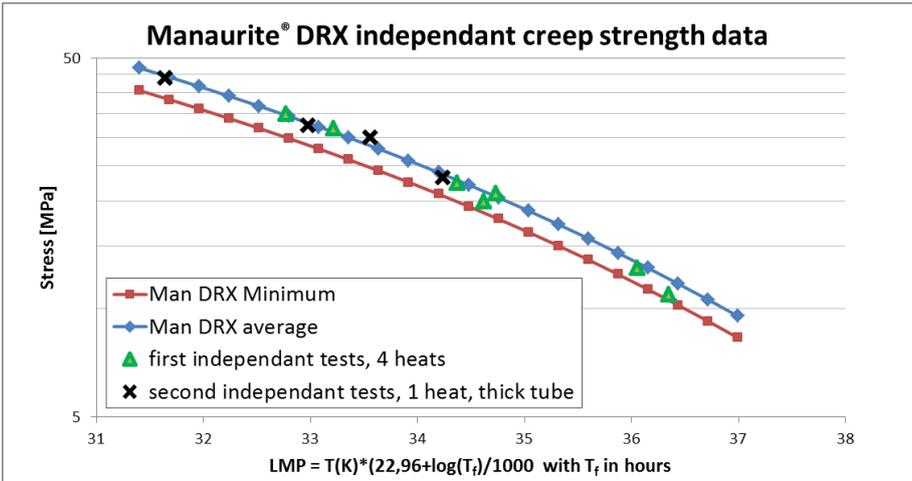


Figure 12: Comparison of independent creep tests with Manoir’s creep curves on five different heats.

DESIGNING THE EQUIPMENT

As the number of data in the high LMP range are necessarily limited and as the safety margins are continuously reduced for the sake of cost optimization in design, having such a conservative approach is needed. Indeed, no matter how detailed and severe the quality controls can be (e.g. Eddy Current, Xrays, Mechanical Testings etc...), no NDT is perfect. In an industry where a clear trend towards larger and more concentrated plants exists, a single failure has necessarily more severe consequences.

Therefore, optimizing the equipment to the ultimium design by making first –hand savings may be a very short sighted approach. It is actually safer to stick to actual and proven data and avoid obvious extrapolations to ensure reliability for key components that remain long term investments and not simple commodities only driven by price.

CONCLUSIONS

From the beginning of HK40 to the current Manaurite®DRX grade, several steps of chemical composition optimization were achieved. The use of “Micro Alloying” (MA) governed the last two generations, namely Manaurite®XM and Manaurite®DRX grades, to become respectively a standard for one, and a very interesting potential for improvement for the second. Manaurite® DRX is therefore a suitable substitute to the standard 28-48W alloy (named Manaurite® 50W in Manoir’s literature).

Manaurite® DRX temperature limit is up to 1135°C. The major benefits of this alloy as a substitute are numerous:

- Better creep strength due to specific micro additions
- Improved ductility after ageing. Indeed 28-48 W alloy tends to form large Tungsten carbides which decrease ductility after ageing.
- Significant commercial impact as the alloy contains 35% of nickel nominal in lieu of the 48% of the existing alloy.

Creep resistance superiority of Manaurite® DRX over current HV grade represents definitely a plus to end users as shown on Figure 13 and Figure 14.

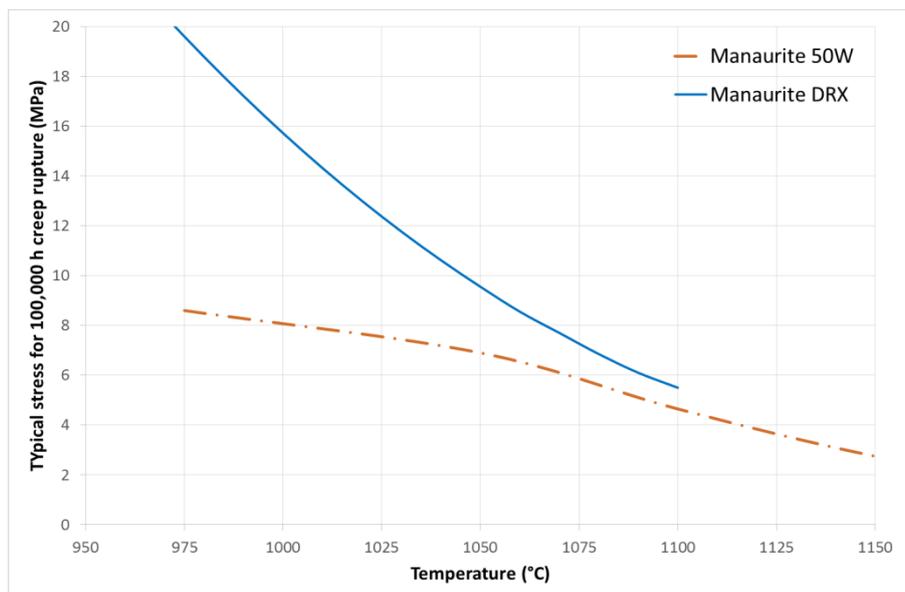


Figure 13 – Comparative average creep properties of Manaurite DRX and Manaurite 50W

The difference in creep resistance shown in Figure 13 can be turned into comparative lifetime, as described Figure 14 for a stress of 6 MPa. For a lifetime of 100,000h (11.4 years), an increase of 20°C is obtained when using Manaurite DRX instead of standard Manaurite 50W.

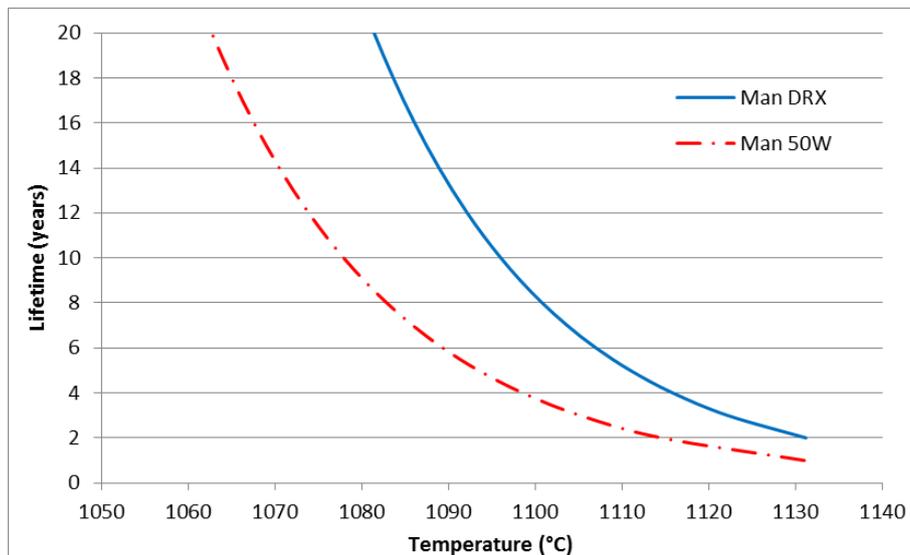


Figure 14 – Comparative lifetime of Manaurite DRX and Manaurite 50W.

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