MANOIR INDUSTRIES

Manaurite® XMR

reducing down reformer tubes wall thicknesses a step further

Background

In the petrochemical industry, there are limited applications where high temperatures are a real challenge for materials to withstand. Among those are 4 major businesses: ethylene production by means of steam cracking, and production of ammonia, methanol, and hydrogen & syngas by means of steam reforming. In those applications, the ability of materials to withstand creep is put to the real test as temperatures rank from 870°C to 1100°C.

The industry has used tubes produced by centrifugal casting process, cast in what is commonly called ''high alloys'', or HP modified, namely materials containing at least 25% Cr and 35% Nickel and micro additions.

Manaurite XM, an industry standard

In the 80's, while most of the industry was still operating furnace tubes in HK40 material, Manoir Industries came up with a real breakthrough by designing consecutively Manaurite 36X (becoming HP), enhanced a few years later by microalloying additions and then caleld Manaurite XM.

The first Manaurite XM tubes were installed in both ethylene crakers and reformer furnaces in the very early 80's.

Manaurite XM (Man.XM), in those years, was designed to withstand creep elongation at high temperature, whilst also being able to be welded after ageing. Carburization resistance also was one of its features although this property was further developed through another alloy. As such Man XM was designed, from its properties and chemical compositions, to suit both applications, i.e. reforming and steam cracking.

This alloy has been since installed worldwide and became an industry standard.

Latest findings

Following the growing demand for Hydrogen production, hydrogen producers are more and more engineering their plants to run more than the designed 100 000 hours and tubes, as a result have become thicker.

A reformer tube designed for more than 100 000 hours as per API 530 sees its thickness increasing significantly. As a result, both the heat transfer and the ability for the tube to accomodate stress relaxation during thermal cycles will be less.

Thermal cycles induce cracks within the tubes in service as during thermal cycles, tube OD and ID do not cool down or heat up at the same speed.

Heat transfer is also directly affected by the tube thickness and the thicker the tube is, the less efficient it is.

Based on track record and metallurgical knowledge, Manoir Industries has modified the composition of its Man.XM to customize it to reformer tubes applications.

	Manaurite® XM		Manaurite® XMR	
Element	Min %	Max %	Min %	Max %
C	0.40	0.45	0.40	0.50
Mn		1.50	0.30	1.0
Si	1.2	2.0	0.60	1.20
P		0.03		0.03
S		0.03		0.03
Ni	32.0	35.0	32.0	35.0
Cr	23.0	27.0	23.0	27.0
Mo		0.50	0.50	0.50
Nb	0.50	1.0		1.0
TiZr	Add	Add	+ others	-
Cu		0.25		0.25
Pb		20 ppm		20 ppm

Fig.1—Chemical composition of Manaurite® XM and Manaurite® XMR

Modified / Unchanged

As indicated in Fig.1, Mn and Si have a direct effect on corrosion resistance and those 2 elements can therefore be lowered for reformer tube applications. As these changes modify the titanium yield, some further melting paractices changes took place accordingly.

By using dedicated production equipments for melting/casting, above mentioned composition changes and the use of another microalloying element, creep properties of Man.XM have been tremendously improved to reach some 15% increase. This alloy is now called Man.XMR.

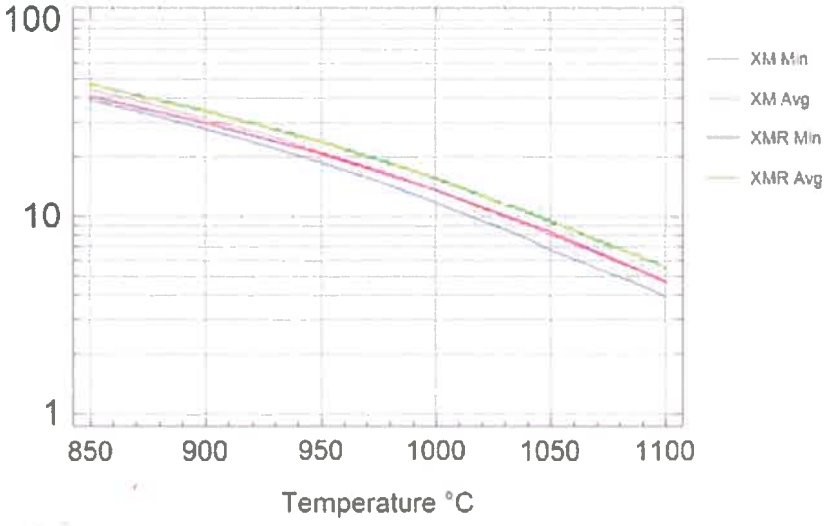

Fig 2.: Comparative 100 000 hours creep rupture data Manaurite® XMR vs Manaurite® XM

Implications on tube manufacturing

The above mentioned composition changes are, from a production standpoint, considered as minor and do not affect the ability of the material to ability of the material to be cast, machined, or welded.

Fig.3 shows the impact on 1 example this new alloy has on tube wall thickness calculations. It is worth mentioning that the thinnest the tube is, the better it will behave to accomodate stresses during thermal cycles. Additionnaly, weight is going to be significantly reduced, and so will be price.

Design pressure P	2.59 MPa		
Design temperature T	1003°C		
Tube ID	114.3 mm		
Time of rupture t	100 00 hours		
	Manaurite® XM	→	**Manaurite® XMR**
Creep rupture allowable stress (min.values) Sr	11.36 MPa	→	**13.33 MPa**
Calculation as per API 530	MSW = (PX ID) / (2 x Sr – P)		
MSW (mm)	14.7	→	**12.3**
OD = ID + 2 x MSW +1.6 mm outside roughness	145.3 mm	→	**140.5 mm**
Weight per meter	54.78 kg/m	→	**46.05 kg/m**

Fig 3.: Wall thickness & weight per meter impact based on API 530 calculations

Third party laboratory tests

In order to assess the accuracy of the creep tests results Manoir Industries has found internally, a European laboratory well known for its long lasting involvement in creep research. TNO, in the Netherlands, was asked to perform similar tests in order to position the various data points on the creep curve. Those data are shown on Fig 4.

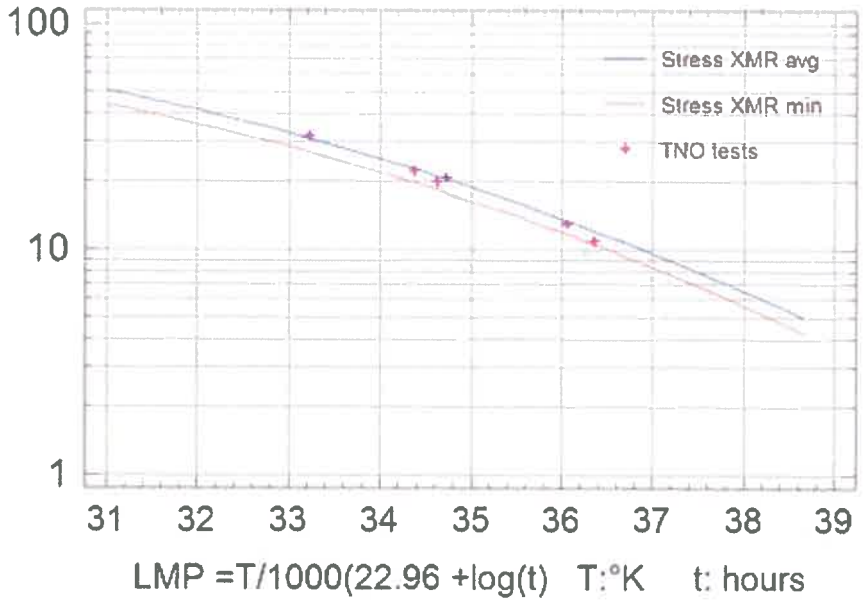

Fig 4.: Man XMR creep rupture tests results

Options for the use of this alloy

Manaurite XMR can provide multiple benefits:

1) for an engineering company by offering lighter tubes and therefore lower the overall plant Capex,

2) to the maintenance people by, in the event the existing tubes remain unchanged, increasing the life significantly,

3) to the process people by taking advantage of the thinner wall to increase catalyst volume.

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« Creep properties of Manaurite® XM have been tremendously improved to reach some 15% increase. This alloy is now called Manaurite® »

		Manaurite® XMR		
	Base case Manaurite® XM	Option 1	Option 2	Option 3
	N/A	*Same dimensions*	*decreased OD*	*Increased ID*
OD	144.6	144.6	**142.2**	144.6
ID	121	121	121	**122.6**
Thickness	11	11	9.8	10.2
Weight	606	606	**547**	**573**
Length	13500	13 500	13 500	13 500
Catalyst volume	100	100	100	**102.6%**
Calculated life	100 000 hours	**210 335 hours**	100 000 hours	100 000 hours

The table summarizes all the above

Additional considerations

The decrease of thickness as per option 3 above can provide potentialy the followin benefits:

- as thickness is less, heat transfer improvment can lead to a reduction in firing of approx. 0.4 %,

- at equal firing rate, the increase of throughput can reach up to 0.4 %,

- the increase in diameter can allow an increase in throughput of 7 % also, with a firing rate increase of up to 7%.

Those values have been modeled using Katalco ''Primary'' simulation tool, and using quadralobe catalysts from Johnson Matthey, with tubes of slightly different dimensions.

« This alloy is manufactured since 2009 in our both plants of Yantai and Pîtres. »

Applications	Tube quantity	End destination	Manoir manufacturing location
Ammonia	336	Iran	Pîtres
Methanol	300	Venezuela	Pîtres
Hydrogen	714	Russia	Yantai
Ammonia	408	Russia	Yantai
Hydrogen	410	Venezuela	Pîtres
Hydrogen	144	USA	Pîtres
Hydrogen	32	China	Yantai
Hydrogen	404	Russia	Yantai
Hydrogen	184	Saudi Arabia	Yantai

Major references for the alloy Manaurite® XMR with a total of about 4,000 tubes produced to date.

Conclusions

While it is clearly established that a breakthrough in creep properties could hardly be achieved as nearly all possible combinations have been tried, Manaurite XMR provides the industry with a technical solution that will have a definite impact of Capex for the engineering companies when it comes to sesigning a new plant. For end users, the creep properties gains can be translated by an extra capacity if the gain is used to increase the tube ID.

In any case, gain in weight and therefore in prices for this item are quite important. Manoir has obtained from a notified body a PMA (Pressure vessels European Directive) achievement.

This alloy has since gained market acceptance nearby users and engineering companies and several orders have been booked, been installed, or are under manufacturing.

Autors

Benjamin Fournier, R&D/Metallurgy & QC Senior VP, *internal and collaborative research programs coordinator focused on the development of high added value products, also in charge of the Quality Control Department to ensure the full compliance of strictly controlled components exposed to extreme conditions in service. His expertise in Metallurgy is a key component of customer support services through failure analysis, remaining lifetime estimates, technical marketting, etc...*

Antonin Steckmeyer, *a metallurgical engineer in the R&D department of Manoir Petrochem & Nuclear is in charge of the development of new alloys, both for enhanced creep and anticoking performances, and of casting and solidification simulations. He worked previously on nanostructured steels designed for nuclear reactors cladding, for which he obtained a PhD from Ecole des Mines Paris.*

Hugues Chasselin, *graduated from the French Foundry Engineering School, joined Manoir Industries 23 years ago to run their US production at that time.. Back to France, he has spent his last 20 years in manufacturing, sales, and technical interface with customers, visiting ethylene and reforming furnaces around the world. He's currently the senior V.P. for technical support and services, being in front of the customers technically to understand their needs and market Manoir's latest products, technologies, and plants. He also runs a team of project managers..*