

NIOBIUM IN CENTRIFUGALLY CAST TUBES FOR PETROCHEMICAL APPLICATIONS

Rolf Kirchheiner and Peter Woelpert

Schmidt + Clemens GmbH + Co. (S + C)
51779 Lindlar, Germany

Abstract

Niobium has been used in centrifugally cast tubes since about 1970 as a eutectic carbide forming element to increase creep strength and creep ductility, as well as carburization resistance. For a long time, the 35Ni-25Cr-Nb or HP Mod.Nb material dominated the market for steam reformer and steam cracker furnace tubes. In the mid eighties, the so called micro alloys were introduced in which other carbide forming elements like titanium, zirconium and Rare Earths (RE) were added to niobium to increase these effects. For increased corrosion resistance, particularly against fuel ash corrosion, the 50Ni-50Cr-Nb was created. It is used in static castings such as tube support plates in the convection section and tube hangers in the radiant section of petrochemical furnaces.

Introduction

When petrochemical furnaces were developed to produce hydrogen rich synthesis gases from naphtha or natural gas, and ethylene from n-paraffins instead of acetylene, the tubes in which the reaction took place [at temperatures of about 850 °C (1562 °F)] were made from ACI grade HK40 (25Cr-20Ni-0.4C). This was the only available material with reasonable creep strength up to 1000 °C (1832 °F).

However, this material suffered severe embrittlement in service due to precipitation of secondary M_7C_3 chromium-carbides along the grain and cell boundaries of the columnar structure of the centrifugally cast tubes.

The first improvement was made by modification of the cooling rates in the metallic moulds to create an equiaxed structure in about 30% of the wall thickness from the inner diameter, together with inside machining to reduce crack initiation in the tubes under inside pressure. Inside machining also reduced the inner surface through which carbon could diffuse into the material under carburizing conditions.

Metallurgical Development

A: 24Ni-24Cr+Nb

Based on the tradition in American metallurgy of stainless steel production to use niobium for the stable absorption of carbon, and to increase heat resistance (European metallurgy mainly used titanium), the second step in the early seventies was the addition of niobium to a modified HK 40, developed by International Nickel Ltd. under the name IN 519 (1, 2).

The formation of eutectic niobium-carbides combined with an increased nickel-content and slightly reduced chromium-content had two effects: First, it increased the creep rupture strength with even lower carbon contents of 0.3 to 0.35% and second, it reduced the volume fraction of the chromium-carbides. The result was a material with about 25% higher creep strength at 1000 °C and creep ductility of 8 to 10% after 10,000 hrs at 900 °C, compared to 3% after 10,000 hrs for HK 40. This improvement was achieved with an “optimum” addition of 1.2 to 1.5% niobium which resulted from experimental tests made by several manufacturers of centrifugally cast tubes.

S.R. Keown and F.B. Pickering found the same range when they examined the effect of niobium and carbon contents in stainless steels (4). They reported that maximum creep rupture strength occurred at around the stoichiometric Nb/C ratio and only undissolved or precipitated NbC affected creep strength.

Literature (7) concerning investigations of niobium containing centrifugally and static cast materials report that the 24-24-niobium material has been used for tubes in reformer furnaces since 1973. Worldwide, more than fifty furnaces with a total of more than 1,000 catalyst tubes have been installed and most of them are still in service after more than 100,000 hrs calculated lifetime. Some tubes are still in service after more than 150,000 hrs.

This long lifetime is caused not only by the better material, which allowed reductions in wall thickness compared to HK 40, but also by the inside machining of these tubes which eliminates crack initiating pores at the inside diameter. Another important fact was that operators could stabilize the process conditions. Multiple stop and go periods during plant start-ups which drastically reduced the lifetime of the tubes could be eliminated, as well as annual shut downs for catalyst replacement. Today, operating conditions are fairly uniform with shut downs every three years for change of catalyst. Precise temperature control is maintained by the use of top

or bottom burners instead of batteries of side wall burners, as well as better control of the equipment upstream and downstream of the reformer furnace such as compressors, waste heat boilers etc.

B: 35Ni-25Cr+Nb

With further increasing demands from the chemical industry, the metallurgy moved to the HP-grades with 35% Ni and 25% Cr. As the straight HP 40 had creep strengths below that of IN 519, producers immediately introduced the niobium modified alloy.

This HP 40 Mod.Nb has been the workhorse in petrochemical furnaces for many years as it provided a remarkable increase in creep strength as well as better carburization resistance than the 25Cr-20Ni –alloy group in the temperature range up to 1050 °C (1922 °F).

The adjacent diagram (figure 1) illustrates the ranking in creep resistance (average values) and the effect of niobium as an alloying element for various heat resistant alloys. For example, HP 40 with 15 % more nickel content shows a lower increase in creep strength than the 24-24 Nb alloy with only 4 % more nickel but with 1.2 to 1.5 % Nb (10).

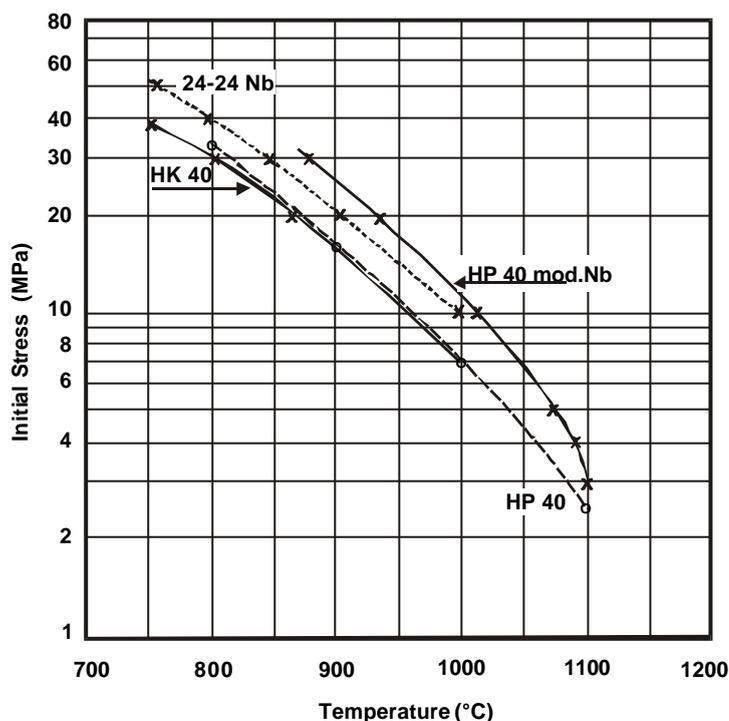


Figure 1: Ranking in creep resistance up to 1000°C.

This effect is caused by precipitation of eutectic niobium-carbides which predominantly appear on the grain boundaries of the columnar and equiaxed structure, as well as on the cell boundaries within the columnar grains, between the chromium carbides.

The niobium-carbides with their high melting point, remain in their positions with the same crystalline volume during exposure to high temperatures, while at the same time coagulation of the chromium carbides occurs. In nickel-chromium-alloys without any additions, these coagulated carbides cause formation of creep voids between the carbides which reduces the

creep resistance and consequently, the lifetime of such materials. Alloys with niobium-carbides remaining in place on the grain or cell boundaries therefore need longer times or higher stresses and/or higher temperatures to form such creep voids. As an example: The wall thickness of reformer tubes could be reduced from 18 mm with the 24-24-Nb material to 12 mm with the HP 40 Mod.Nb. (35Ni-25Cr-Nb) material.

However, initial creep tests revealed that the niobium and silicon contents had to be checked carefully for their effect on creep strength and creep ductility. It turned out that silicon reduced the creep strength of HP 40 Mod.Nb. At the same time, it reduced creep elongation in the 24-24-Nb alloy.

The niobium content had little influence on the creep ductility of 24-24-Nb but creep tests on the 35-25 material revealed that niobium contents of 1.2 to 1.5 % resulted in very high creep elongation, but drastically reduced creep rupture times.

A niobium content had to be found that gave the highest possible creep strength and at the same time a creep elongation higher than that of straight HP 40, which was unacceptably low at 2 to 3%.

Shibasaki et.al. (7) presented results of creep tests on niobium alloyed materials. The influence of niobium on the creep properties of HP 40 Mod.Nb is shown in figure 2:

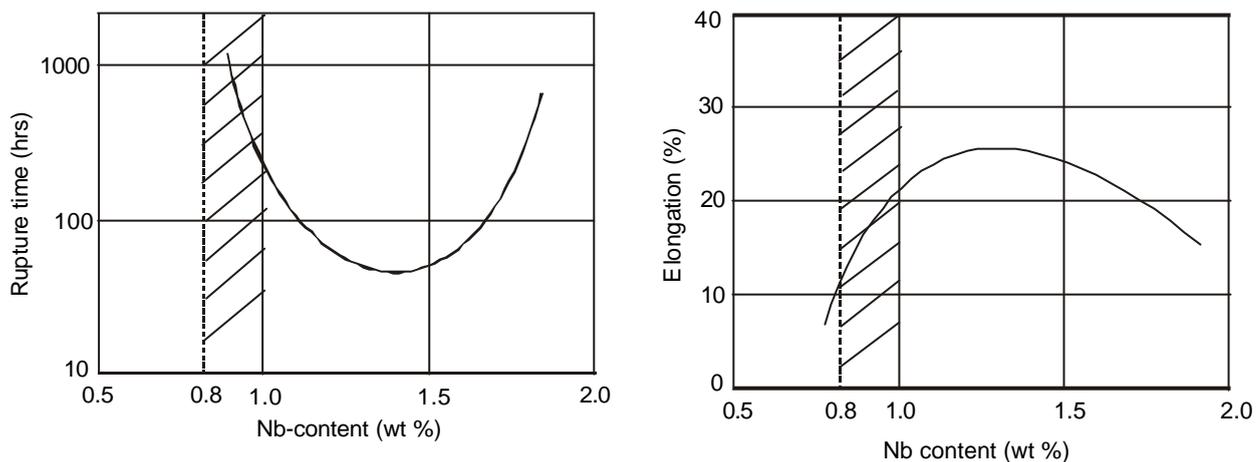


Figure 2: Influence of the niobium content on the creep properties of HP 40 Mod.Nb alloy.

The best compromise of creep strength and creep elongation was found in the range of 0.8 to 1.0 % Nb with creep elongation above 10% (3).

This low niobium content also means a reduced presence of eutectic carbides which are used to strengthen the material. The reason is most probably the increased nickel content (35%) which forms fewer stacking faults or other dislocations compared to the 24% nickel material. Stacking faults and dislocations are the preferred place for niobium carbide nucleation in austenitic structures according to Keown and Pickering (3).

The HP 40 Mod.Nb alloy is equivalent to GX40NiCrSiNb35-25 or Mat. No. 1.4852 according to DIN 17465. Because of the fast cooling rate in metallic moulds, the structure of centrifugally cast tubes in the outer wall area is columnar, and that the inner part is equiaxed

due to a reduced cooling rate. Some of today's specifications call for a minimum of 30% equiaxed structure from inside (Figure 3).

Creep damage normally starts in the inner third section of the wall thickness where thermal and hoop stresses have a combined peak. Crack propagation in an equiaxed structure is slower than in a columnar structure.

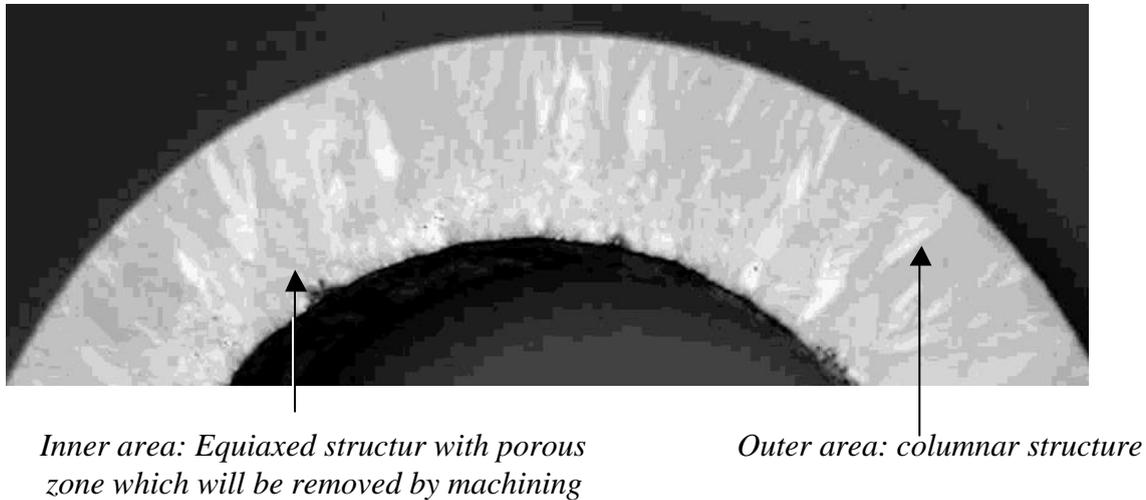
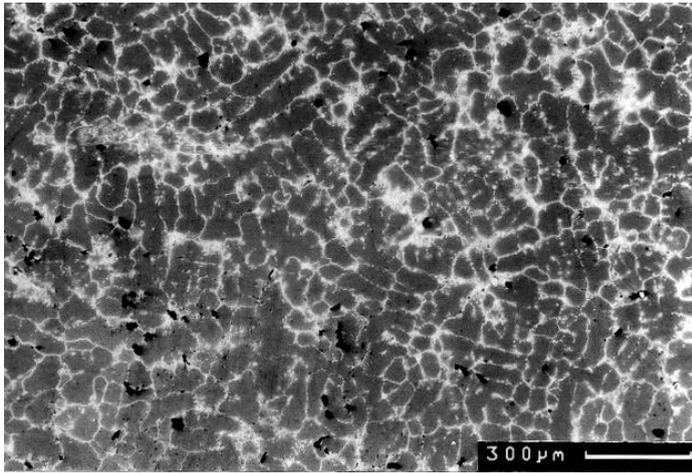


Figure 3: Macro-etched ring section of a centrifugally cast tube.

The cell size of the dendrites in the columnar region (figure 4) is about half that in the equiaxed region (figure 5). The columnar structure is therefore more dense and all impurities are separated by the centrifugal forces (up to 120 g) to the inner wall, as they are of lower density than the liquid melt. Carbide formation in this “as cast” alloy is mainly of the M_2C_6 form (the majority of M is chromium) alternating with niobium-carbides (NbC) along the grain- (or cell-) boundaries with some niobium-carbides finely dispersed in the matrix.



Figure 4: Columnar part of the structure (50X) of 1.4852.



*This porous area
will be removed
by machining.*

Figure 5: Equiaxed part of the structure (50X) of 1.4852.

The microstructure of the columnar area is shown in Figure 6, etched for carbide identification. The elemental distribution in the microstructures is shown in the X-ray mapping Figure 7 for chromium and in Figure 8 for niobium.

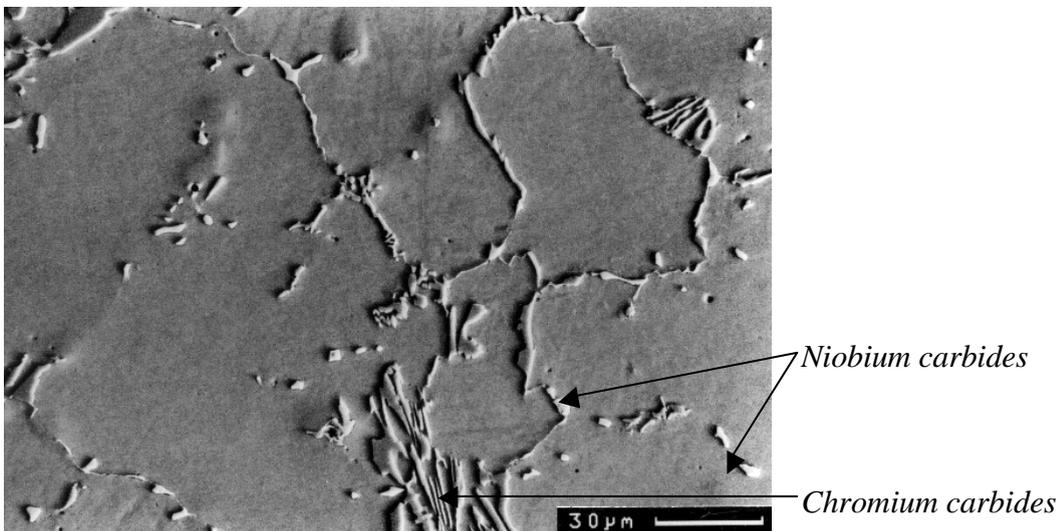


Figure 6: Microstructure of the columnar part (500X) of 1.4852.

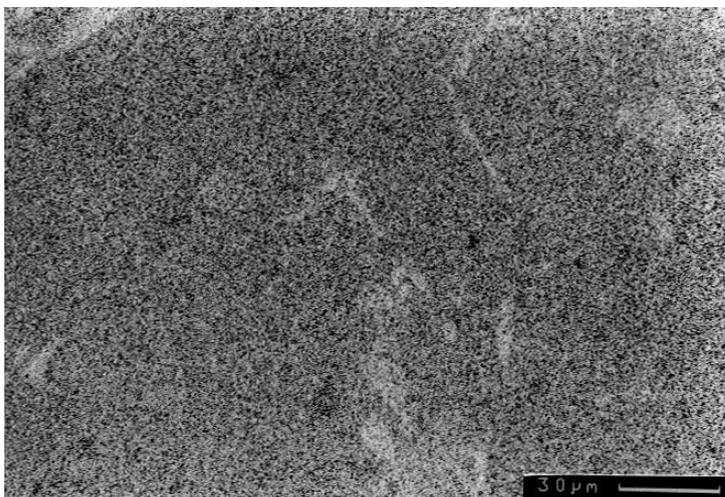


Figure 7: X-ray mapping of chromium in figure 6.

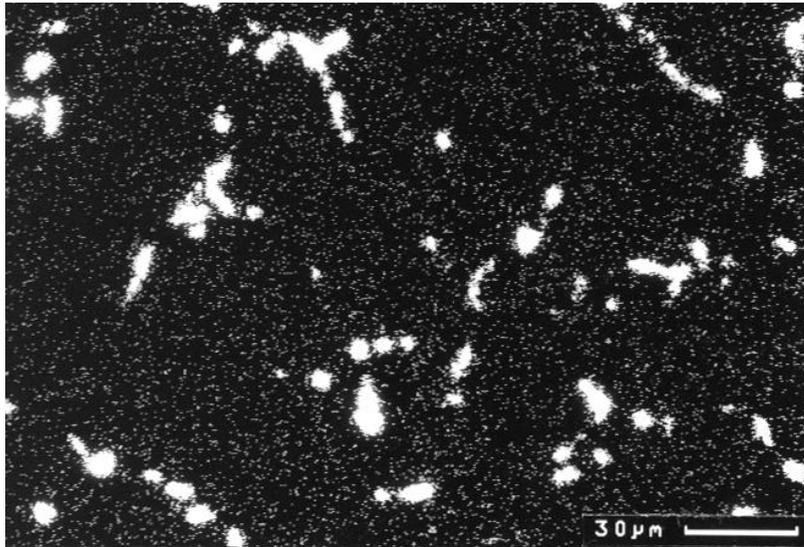


Figure 8: X-ray mapping of niobium in figure 6.

C: 32Ni-20Cr+Nb.

Another niobium-only alloyed material produced today as centrifugally cast tubes is DIN 1.4859 (11) which is a 32Ni-20Cr-Nb composition and is a modified cast version of Alloys 800 and 800HT, which cannot be produced by other casting methods because of their aluminum and titanium contents. It took a lot of effort to convince users to install this niobium-alloyed cast material in areas of petrochemical furnaces outside of the radiant section for pigtails, manifolds or transfer lines where high ductility and stress relaxation after aging is required.

The most important difference of this low carbon (0.08%) grade compared to HP 40 Mod.Nb (with C = 0.43%) is the formation of very fine carbides along the cell- and grain boundaries (Figure 9).

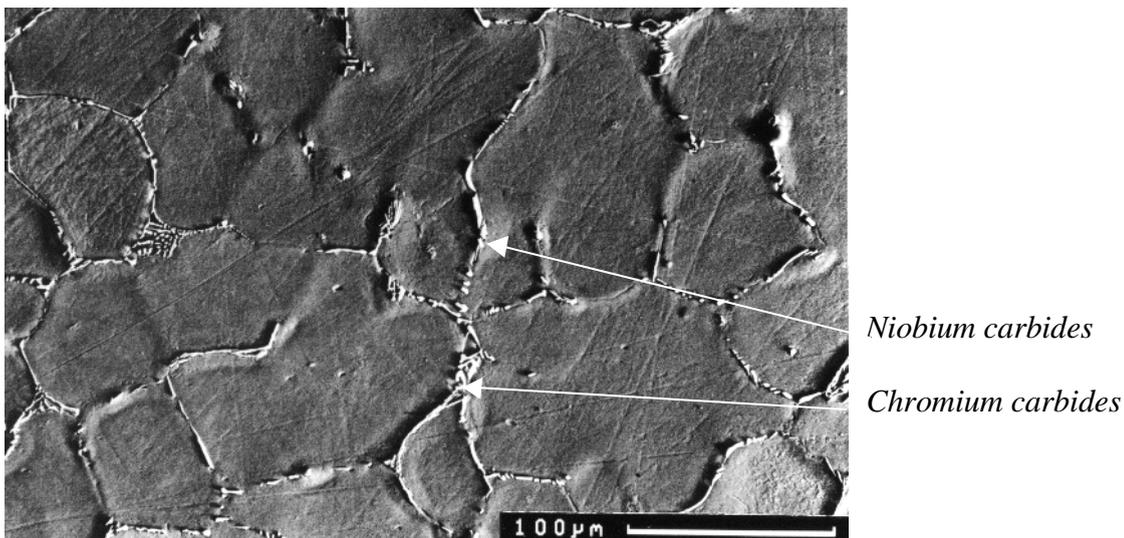


Figure 9: Microstructure of 1.4859 (250X).

The X-Ray mappings in Figures 10 and 11 show that there is only a small amount of chromium-carbide where grain boundaries meet, whereas niobium-carbides are precipitated along the grain boundaries. This is very important for the properties of this material even in comparison to Alloys 800 and 800HT.

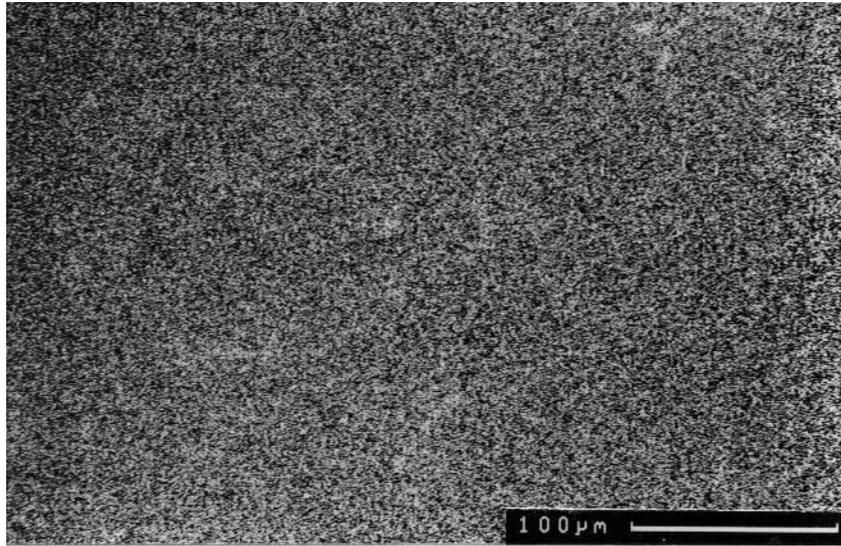


Figure 10: X-Ray mapping of chromium in Figure 9.

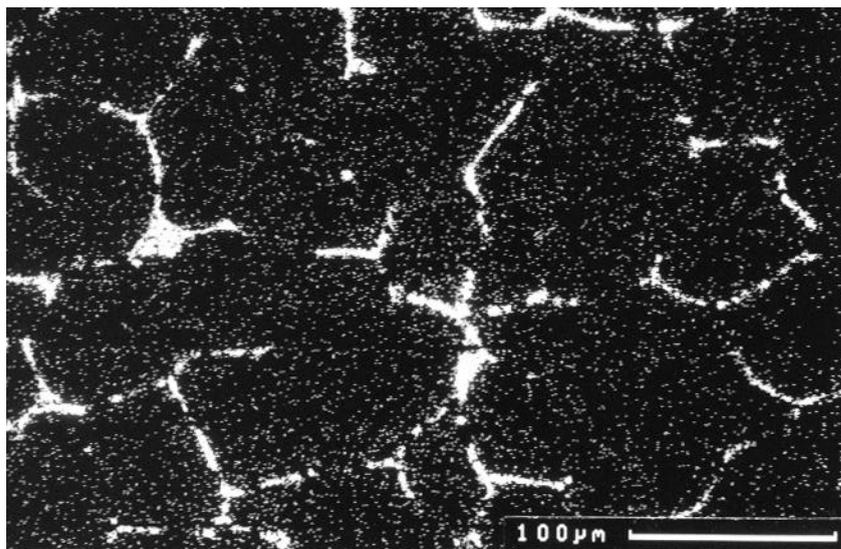


Figure 11: X-Ray mapping of niobium in Figure 9

As mentioned previously, niobium-carbides remain in place and do not change their volume. In the 1.4859 alloy they act like a glue between the grains. This is proven by thermal cracking tests on a triangular sample with sharp edges. One of the edges is induction heated and undergoes rapid temperature changes between room temperature and 800°C (1472°F) by water cooling of the sample through inside bores. It takes a very long time for cracks to develop from this edge and the cracks are all trans-granular, not inter-granular (10).

In addition, the 100,000 hrs. average creep strength of the niobium-alloyed cast material is much higher with 12 MPa at 900°C (12) than that of the Al+Ti alloyed wrought material 1.4959

with 9.4 Mpa (13). This higher strength allows for a reduction of the wall thickness of the pieces concerned which is another example of the versatility of these parts.

D: Micro Alloys

D1: HP-Micro (35Ni+25Cr+Nb+Ti+Add). As described above, the HP 40 Mod.Nb allows only the addition of 0.8 to 1.0 % niobium which does not produce as much carbide strengthening in the alloy as expected by extrapolation with data from the 24Ni-24Cr-Nb material.

In 1985, Hou Wen-Tai and R.W.K. Honeycombe (5) described the evolution from HK 40 and IN 519, to IN 519Z (with addition of zirconium) and IN 519TZ (with addition of titanium and zirconium)(6).

Following this experience, investigations were made to add these elements to HP 40 Mod.Nb combined with Rare Earths (RE) as additional carbide forming and refining elements. Cerium Mischmetal (Ce+La+Hf) was found to be the most effective and economic addition.

Through improvement in the alloying procedures, the HP-Micro alloy was developed, which showed the highest creep strength of this alloy group up to temperatures of 1100°C (2012°F), as shown in figure 12. Due to a very subtle carbide distribution, niobium-carbides mixed with chromium-carbides along the grain boundaries, titanium-, zirconium- and RE-carbides mainly dispersed in the matrix, not only was the creep strength increased but also the carburization resistance and the creep ductility. This material quickly replaced the HP 40 Mod.Nb grade. With experience gained in the melting procedure, mass production of the HP-Micro grade became no more expensive than the HP 40 Mod.Nb grade.

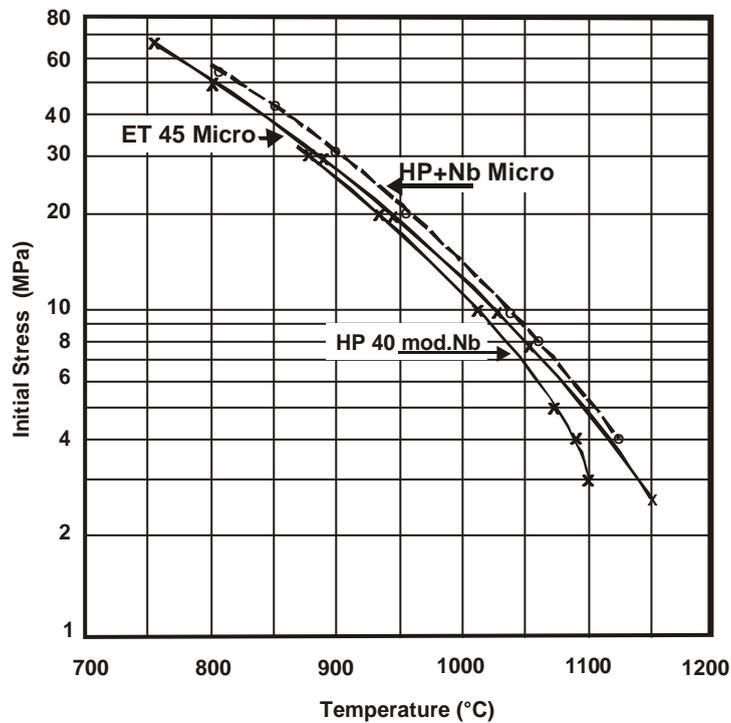


Figure 12: Ranking in creep resistance of micro alloyed materials.

This diagram shows the advantage in creep strength of the micro-alloys over HP 40 Mod.Nb, particularly at temperatures above 1000°C (1832°F) - Average creep strength as a function of temperature (10).

D2: ET45-Micro (45Ni+35Cr+Nb+Ti+Add). Even though the carburization resistance of HP-Micro was much better than that of the alloys used before, the change in design of ethylene units to shorter residence times increased tube wall temperatures up to 1150°C (2102°F) which was too high for the HP-Micro grade.

In 1984, metallurgists experimented with higher nickel grades like 48Ni-28Cr-5W (2.4879) (11) but also with the optimized stoichiometric ratio of 45% Ni and 35%Cr. The alloy ET 45 Micro (DIN GX45NiCrSiNb45-35) turned out to be oxidation resistant up to 1150°C (2102°F) with sufficient creep strength for ethylene tubes.

Based on the experience with HP-Micro, the metallurgy of this alloy family went immediately to the micro-alloyed version, using the same elemental additions. Intense testing in carburizing atmospheres showed that this alloy was very resistant to carbon diffusion. The reason was the formation of a tight surface layer of chromium-oxides and an inner layer of silicon-oxides, both stabilized by the carbide forming elements.

Research performed on materials resistant to metal dusting confirms that a minimum 28% chromium is required to form a stable, continuous layer of oxides to prevent carburization as well as metal dusting. This is also the reason why the HP-Micro grades with only 25% chromium are limited in carburization resistance.

As representative images for the oxide and carbide formation in micro-alloys, Figure 13 shows the inner wall area of an ET 45 Micro ethylene tube after three years of service. The continuous oxide layer is clearly visible, together with secondary carbide formation behind the decarburized zone. Figure 14 shows the X-ray mapping of niobium and figure 15 shows the X-Ray mapping of titanium in this carbide formation. Niobium again appears more frequently on the grain boundaries.

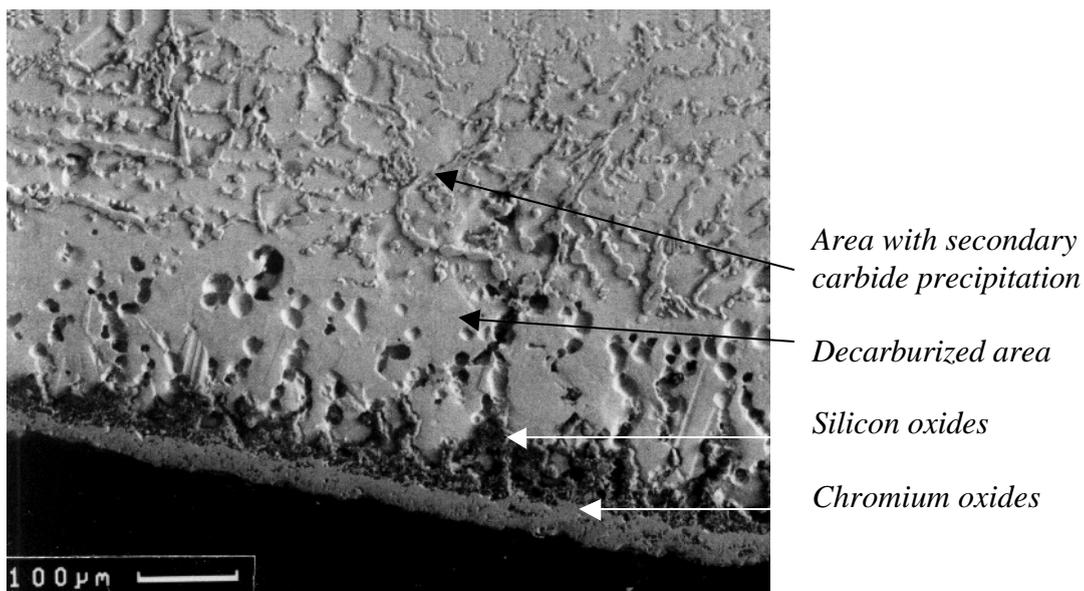


Figure 13: Inner surface of ET 45 Micro (100X).

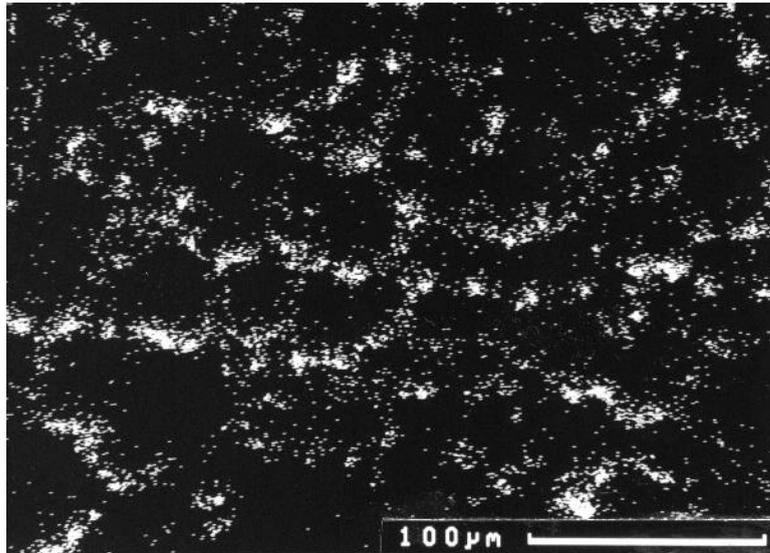


Figure 14: X-Ray mapping of niobium in the area with secondary carbide precipitation in figure 13.

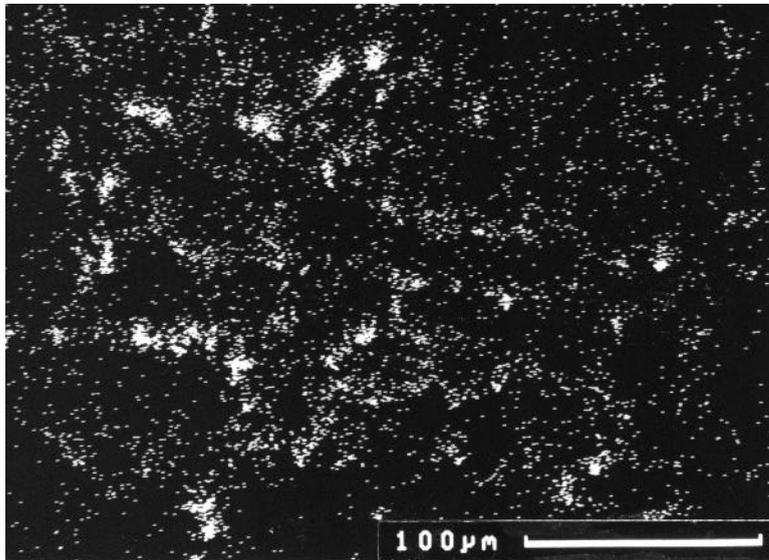


Figure 15: (250X) X-Ray mapping of titanium in the area with secondary carbide precipitation in figure 13.

Investigation of the carbides revealed that there was no carbon diffusion from the process. The carbides are formed only with the carbon content of 0.45%, initially available in the metal.

Due to the specific operating conditions of such tubes during start-up, the oxygen partial pressure is very high which in turn leads to chromium and silicon oxidation on the grain boundaries and in the matrix as well as a significant surface decarburisation.

In diffusing to the surface, both chromium and silicon are oxidized, and other carbide-forming alloying (mainly niobium) and microalloying elements will occupy the vacant sites within the lattice of the decarburized zone. Therefore, sub-surface grain boundaries, to a depth of roughly 0.3 mm, can disappear, leaving behind voids and a uniform matrix that is saturated by carbide forming elements like niobium (figure 16).

This structure changing process stops when the chromium and silicon oxides have formed a compact surface layer blocking all further diffusion reactions between the transported medium and the tube material.

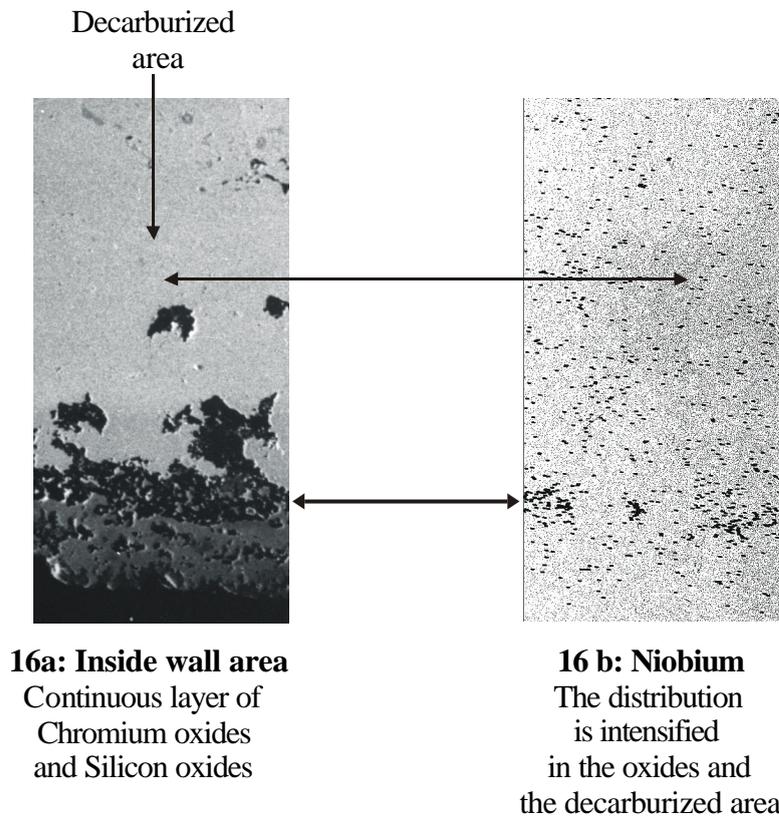


Figure 16: Section of the ET 45 Micro inner wall with inverted x-ray mapping of niobium.

Summary

Apart from the base elements nickel and chromium, niobium is the most important alloying element in all heat resistant materials, produced as centrifugally cast tubes.

Under strain or during aging, primary chromium-carbides tend to coalesce and transform into secondary M_7C_3 -carbides, particularly when carbon is diffusing into the materials as happens in steam cracking services. As stated before, this transformation reduces the volume of the carbides and creates creep voids. However, niobium-carbides remain in their original composition and volume. Therefore, materials having niobium-carbides precipitated along the grain- or cell-boundaries and fine dispersed in the matrix are more resistant to deformation by strain and this causes higher creep strength in the niobium-alloyed materials.

In materials with nickel contents above 40% (Nickel Base Alloys), NbC was found combined with Nb_2C , whereas in stainless steel grades the Nb_4C_3 was also detected in combination with NbN, which cannot occur in materials used for centrifugally cast tubes, due to their extremely low nitrogen content.

The main material used today in centrifugally cast tubes for reformer furnaces is the HP- Micro alloy, as it provides the highest creep strength at tube wall temperatures up to 1050°C (1922°F), and inside pressures up to 40 bar. For lower pressures, the 24Ni-24Cr-Nb alloy is sometimes used.

The main materials used today in centrifugally cast tubes for steam cracker furnaces are the alloys HP-Micro and ET 45 Micro (45Ni-35Cr-Nb+Add) for the hot outlet tubes, sometimes combined with HP 40 Mod.Nb or even HK 40 for the colder inlet tubes.

The standard material for pigtails, manifolds and transfer lines is the 32Ni-20Cr-Nb grade 1.4859 used in centrifugally cast tubes, as well as in static cast parts or vertically spun parts like T-pieces and cones.

References

- (1) International Nickel Limited: Reformer Tube Research (4356/577).
- (2) International Nickel Ltd, W. Herda, "Nickel-containing materials for high temperature applications in petrochemical processes and refinery furnaces", (4355/577).
- (3) S. R. Keown and F. R. Pickering: Niobium in Stainless Steel Niobium Conference, Nov. 1981.
- (4) S. R. Keown and F. R. Pickering, "Effect of Niobium Carbide on the Creep-Rupture Properties of Austenitic Stainless Steels Creep Strength in Steel and High Temp." Alloys, Metals Society, (London, 1974).
- (5) Hou Wen-Tai and R.W.K. Honeycombe, "Structure of centrifugally cast austenitic stainless steels Part 1: HK 40 as cast and after creep between 750 and 1000 °C," Mat. Science Technology, 1 (5) (1985).
- (6) Hou Wen-Tai and R.W.K. Honeycombe, "Structure of centrifugally cast austenitic stainless steels Part 2: Effects of Nb, Ti and Zr."
- (7) Toshikazu Shibasaki et. al., "Experiences of Niobium containing alloys for steam reformers.", AIChE Symposium, Ammonia Safety, August 1986.
- (8) Peter Woelpert, "Properties of recently developed materials for steam cracker furnaces". MICMEP - 99, Baroda, India.
- (9) S + C, R. Kirchheiner, P.Woelpert. Gusswerkstoffe für korrosive Belastungen bei hohen Temperaturen, Eigenschaften – Anwendungen Dresdener Korrosionsschutztag, April 2001.
- (10) Schmidt + Clemens: Material data sheets, Internal documents - test results.
- (11) German Standard: DIN 17465, Heat Resistant Cast Steels.
- (12) German Standard: VdTÜV Blatt 471, 03.97 for Mat. No. 1.4859.

(13) German Standard: Stahlschlüssel, Sect. 11a, High-temperature resisting steels and alloys \equiv DIN 17459.