P23 AND P24 FOR POWER GENERATION AND HYDROGEN SERVICE
- ARE THEY FIT FOR THESE APPLICATIONS? -

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ABSTRACT

Within the Netherlands a Joint Industrial Programme is almost finished to assess the workability and operating window of P23 and P24 pipe materials, both for power generation and hot hydrogen service. It includes the effect of welding processes, consumables selection and PWHT conditions on toughness, creep and (hot) hydrogen behaviour. The programme was launched because P23 and P24 can be cost effective alternatives compared to P22 and even compared to P91/ P92 and E911. It showed that P23 and P24 welded joints can not be used in "as welded" condition, a PWHT is necessary to obtain sufficient toughness. The actual creep strength of the welded joints in P23 and P24 is on the lower bound for base metal, but far above that of welded joints in P22 base metal. However, when for welds in P24 consumables with a low amount of Ti are used, the creep strength is far below the lower bound of the base metal. The hot hydrogen resistance of P23 and P24 is far superior to that of P22. Under severe conditions no Nelson attack was assessed while the P22 welded joints showed macro cracks. However, there are still remaining uncertainties which have to be solved before these materials will be widely accepted for power generation and hydrogen service.

INTRODUCTION

During the last 2 decades quite an effort has been put into the introduction of the 9% Cr materials P91/P92 and E911 as cost effective alternatives for the existing work horses 10CrMo910 (P22) and X20. Within research programmes the comparisons were mainly based on severe operating conditions, that is temperatures above 580°C in combination with high pressures. However, quit a lot of equipment is operating at temperatures below 580°C. Those used for hydrogen service are mainly operating in the plastic regime, where Re/Rm is the determined factor. P23 and P24 , which are modifications of P22, can be a cost effective alternative for the materials P91/P92/ E911 and certainly for the work horse P22. In **Table 1** the chemical composition of P22, P23, P24, P91 and X20 and some relevant creep code data are presented.

Table 1 Chemical composition (weight %) and creep rupture strength of T23 and T24 compared to P22, P91 and X20.

Steel grade	C	Cr	Mo	V	W	Ti	Nb	B	N	σ 10^5h/ 550°C (MPa)	σ 10^5h/ 580°C (MPa)
T22 *(10CrMo910)*	max. .15	1.9 2.6	.90 1.20	---	---	---	---	---	---	68	44
T23 *(HCM 2S)*	**.04** **.10**	1.9 2.6	**.05** **.30**	**.20** **.30**	**1.45** **1.75**	---	**.02** **.08**	**.0005** **.0006**	**max** **.030**	***126***	***98***
T24 *(7CrMoVTi10-10)*	**.05** **.10**	2.2 2.6	.90 1.10	**.20** **.30**	---	**.05** **.10**	---	**.0015** **.0070**	**max** **..012**	***152***	***99***
X20 *(X20CrMoV121)*	.17 .23	10 12	.80 1.20	.25 .35	---	---	---	---	---	128	82
P91 *(X10CrMoVNb9-1)*	.08 .12	8 9.5	.85 1.05	.18 .25	---	---	.06 .10	---	.030 .070	162	115

The main differences in chemical composition between P22, P23 and P24 are:

- In P24 small amounts of Titanium, Vanadium, Boron and Nitrogen are added. Chromium and Molybdenum are comparable to P22 and carbon is lower.
- in P23 a significant amount of Tungsten is added and small amounts of Vanadium, Niobium, Boron and Nitrogen, while Carbon and Molybdenum is reduced.

These small differences in chemical composition has a significant effect on the mechanical properties:

- The (hot) yield strength of the mod. 2.25Cr-1Mo steels P23 and P24 is much higher than for P22, **Figure 1.**
- The creep strength is significantly higher and closer to that of the 9%Cr steel P91, **Figure 1.**

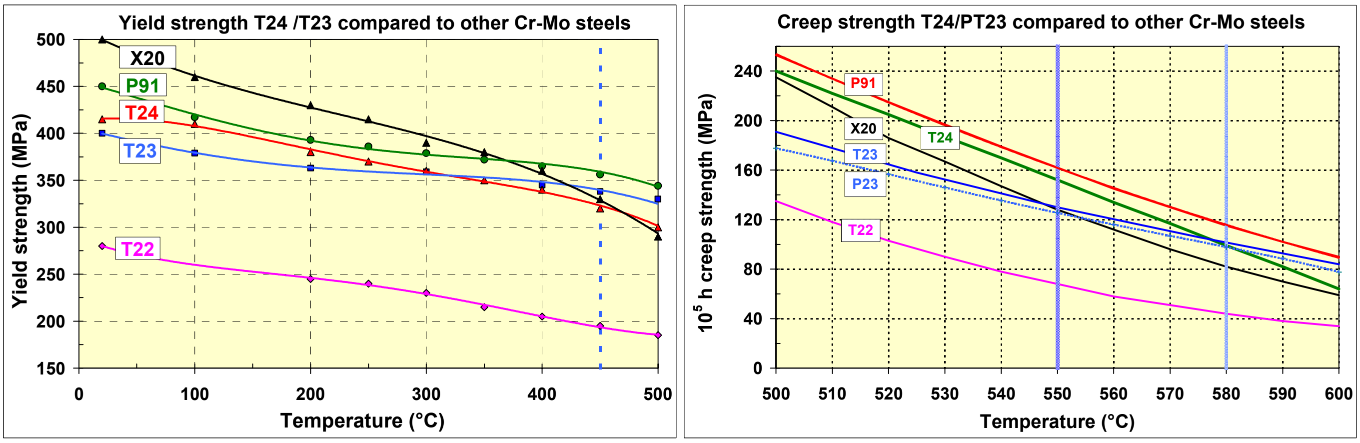

Figure 1. Yield strength (left hand) and creep rupture strength (right hand) of P24/P23 materials compared to the common Cr-Mo materials P22, X20 and P91.

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Potential advantages for the selection of P23/P24 are:

- Compared to P22 the wall thickness can significantly be reduced, without using the expensive new 9%Cr materials. This will result in both a reduction of material and manufacturing (welding) costs, **Figure 2.**

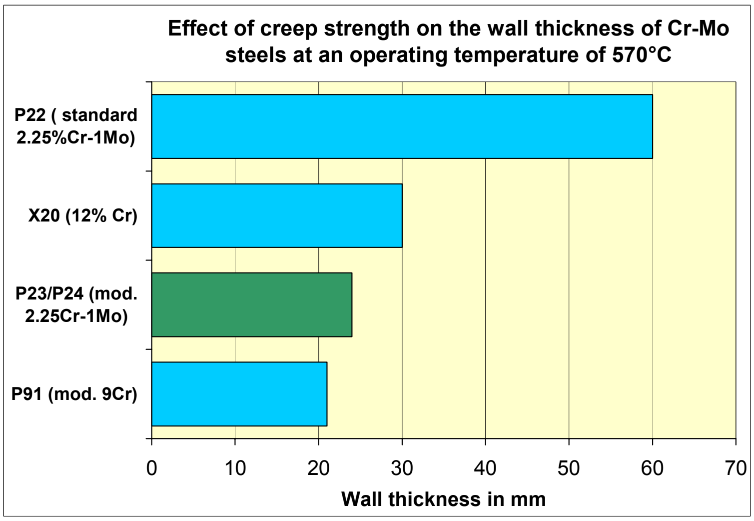

Figure 2. Effect of creep strength on wall thickness. In this case the wall thickness of P22 is fixed at 60 mm and a design temperature of 550°C was selected. For a P23/P24 design the wall thickness is reduced from 60 down to < 25 mm.

- Better behaviour in hot hydrogen. Due to the micro alloying elements in P23 and P24 these 2 materials are probably more resistant to Nelson attack and less susceptible for disbanding during shut down operation.

Possible applications are for instance:

- New steam lines.
- Replacements of existing P11, P22 and14MoV63 steam lines, headers etc.

However, there are also uncertainties:

- P23 and P24 have different chemical compositions and does that result in a different behaviour after manufacturing processes?
- Hardly data are available concerning the creep behaviour of these pipe materials in especially welded condition.
- No data at all are available for the (hot) hydrogen performance.

No end user will take the risk to install these materials without reliable data (proven technology).

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1. OBJECTIVES

Because of the promising economical benefits of P23/P24 a programme was launched in the Netherlands with 15 partners, including steel and consumable suppliers, engineering companies, equipment manufacturers and end users in the field of petrol-chemical industry and power generation. The programme was initiated and co-ordinated by TNO Science and Industry.

The main objectives of the programme were:

- Assessment of the workability and operating window of these materials for:
  - power generation up to 580°C (creep regime),
  - hot hydrogen service up to 485°C (plastic regime).
- The set up of a Recommended Practice both for power generation as for hydrogen service.

2. EXTENT OF THE PROGRAMME

Within the programme the effect has been assessed of:

- Base material selection (P23 versus P24),
- Welding processes and consumables, both for similar and dissimilar welded joints
- PWHT conditions,

on:

- Charpy-V toughness and hardness,
- Creep behaviour,
- Hydrogen resistance,
- Temper embrittlement behaviour.

The base materials and welded joints involved within the programme are presented in **Table 2.**

Table 2: Matrix of the base materials and weld metal combinations.

Base metals→ ↓	**P23**	**P24**	**14MoV63**	**P91**	**Alloy 800H**
P23 219 * 30 mm	**SA weld SMA weld**	---	**SA weld: with P23 cons.**	---	---
P24 380 * 40 mm	---	**SA weld with - low Ti - high Ti SMA weld with - low Ti - P91 cons.**	---	**SA weld: - P24 cons. SMA weld: - P91 cons.**	**SA weld: Ni base cons.**

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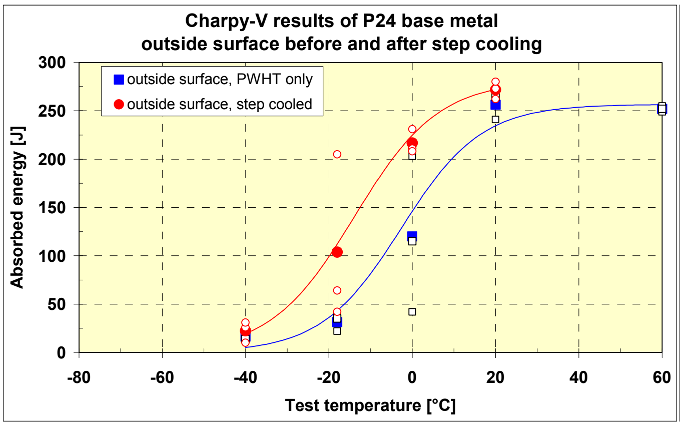
3. OVERVIEW OF THE RESULTS

Charpy-V toughness base materials

The transition curves of the P23 and P24 base materials in simulated PWHT condition are presented in **Figure 3.** It also includes transition curves after a step cool heat treatment. With this heat treatment the resistance to temper embrittlement can be assessed. In simulated PWHT condition the transition curve for P23 base metal is 25 °C lower than for the P24 material. The OT_{54J} temperature for P24 base metal is –15°C and for P23 base metal -55°C. P23 base metal met the acceptance criterion for hydrogen service of >54J at -18°C and P24 not.

After a step cooling heat treatment the transition curve of P24 does not shift to a higher temperature. P24 base metal is not susceptible for temper embrittlement. For P23 the shift in transition curve is + 40°C. The P23 material is susceptible for temper embrittlement and does not met the acceptance criterion for hydrogen service of CvTr40 + 2.5DCvTr40 = ≤ 10°C (API 934). After step cooling the OT_{54J} temperature for P24 is –30°C and for P23 – 20°C.



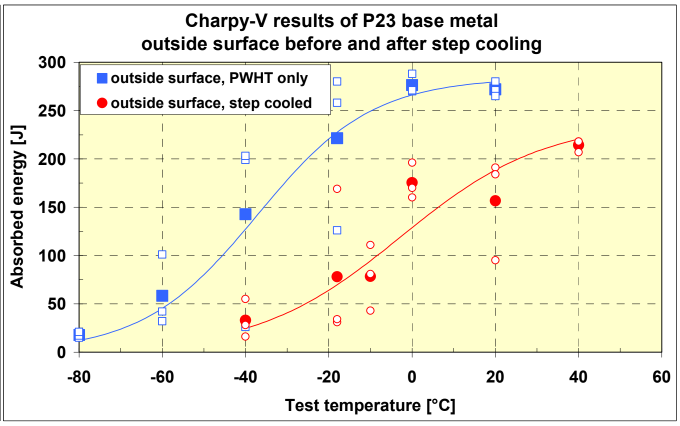


Figure 3. Effect of a step cooling heat treatment on the shift in transition temperature for P24 base metal (left hand) and P23 base metal (right hand).

Charpy-V toughness welded joints

The transition curves of a SA weld in both P23 and P24 base metal are presented in **Figure 4.** It also includes transition curves after a step cool heat treatment. After PWHT the transition curve for P23 weld metal is approximately 20°C lower than for the P24 weld metal. The OT_{54J} temperature for P24 is +25°C and for P23 –5°C. These values does not met the acceptance criterion for hydrogen service of >54J at -18°C. Compared to the base materials the toughness of the weld metals is significantly lower and the toughness of P23 is better than for P24, compare **Figure 3** to **Figure 4**.

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After step cooling the transition curves of both weld metals do not shift, the P24 and P23 weld metals are not susceptible for temper embritllement.

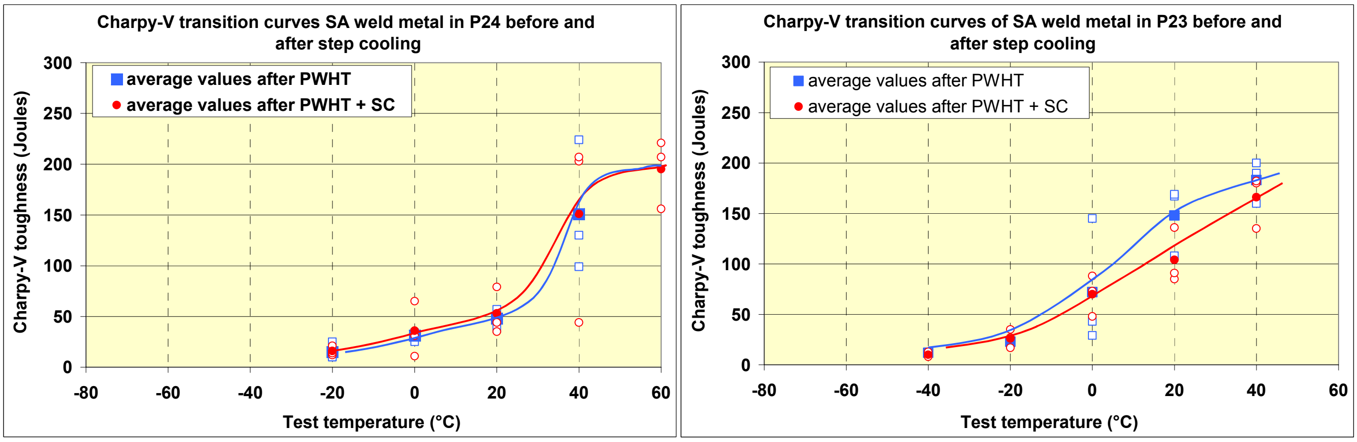

Figure 4. Effect of a step cooling heat treatment on the shift in transition temperature for SA weld metal in P24 (left hand) and SA weld metal in P23 (right hand).

Effect of PWHT conditions on toughness of the weld metals.

Within the programme a wide variety of Postweld heat treatments have been performed on many welded joints. A typical example for the effect of PWHT on toughness of P23 and P24 weld metal is presented in **Figure 5.**

- Proper toughness values of weld metal can not be achieved when a PWHT is omitted.
- For P23 weld metal the PWHT temperature must be >720°C and for P24 >700°C.

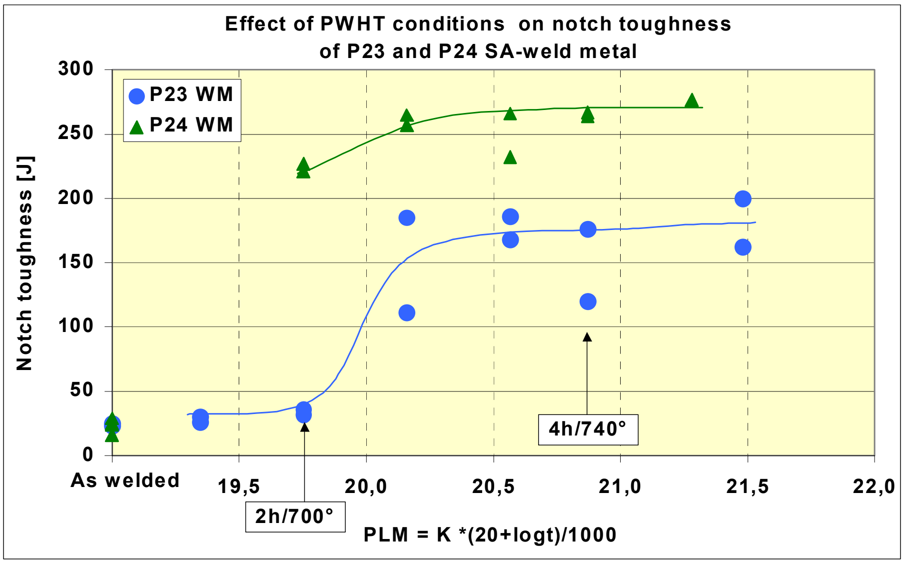

Figure 5. Example of the effect of PWHT conditions on Charpy-V toughness of P23 and P24 weld metal.

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Effect of PWHT conditions on hardness.

For hydrogen service the hardness should always be < 248 HV. For power generation applications different criteria are used. Most common are values <350 HV or <300 HV. In **Figure 6** typical hardness values of coarse grained heat affected zone and weld metal in P23 /P24 are shown as function of the PWHT conditions.

- For P24 material higher PLM values are needed to decrease the hardness to a level of >300 or > 248 HV than for P23. This accounts both for the weld metal as for the coarse grained heat affected zone (CGHAZ).
- For both materials the CGHAZ is the critical location concerning hardness criteria.

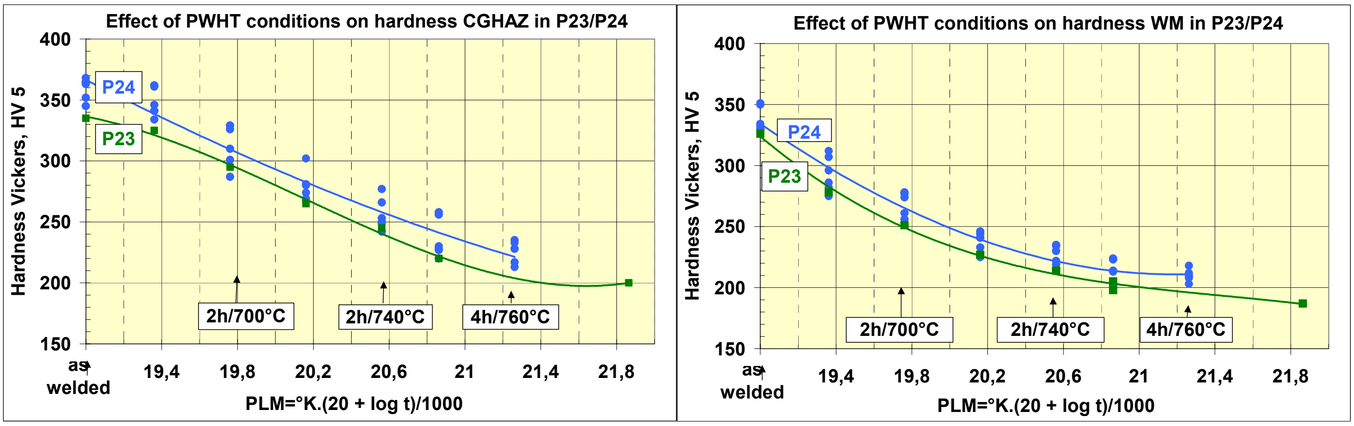

Figure 6. The effect of PWHT conditions on hardness in coarse grained heat affected zone (left hand) and weld metal (right hand) in P23 and P24 base material.

Creep behaviour P23 base metal and welded joints.

A number of **i**sostress creep tests have been performed with the 10^5 h creep strength values of ASME code case 2199 values at 550 and 580°C respectively.

In **Figure 7** some of the results are compared to ASME. All specimens fractured in the fine grained heat affected zone (FGHAZ) close to the base metal.

- The extrapolated creep lifetime at 550°C is approximately 20.000h, while the expected lifetime of the base metal is 100.000h. This welded joint is at 550°C just on the lower bound of the scatterband for base metal

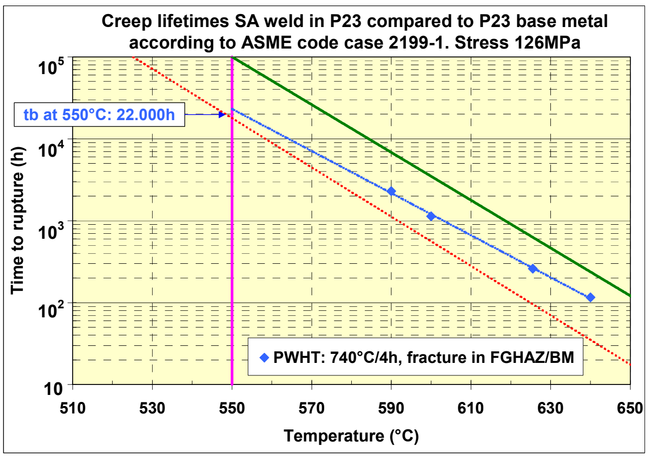

Figure 7. Some results of crossweld creep tests on a SA weld in P23. The stress level was 126 MPa (=10^5h/550°C). Fracture was in the FGHAZ close to the base metal.

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Creep behaviour P24 base metal and welded joints.

A number of isostress creep tests have been performed with the 10^5 h creep strength values of VdTÜV 533 at 550 and 580°C respectively. Some results of the creep tests with a stress level of 152 MPa are presented in **Figure 8.**

In first instance the tests were performed on SA and SMA welded joints, welded with consumables with a low amount of Ti.

All those specimens fractured in the weld metal and the lifetimes were dramatically low. The extrapolated lifetime at 580°C was 3.500h instead of 100.000h. It was decided to stop further testing on welded joints with a low amount of Ti. New welded joints have been produced:

- A SA weld with a high amount of Ti
- A SMA weld, using P91 consumables. This can be an intermediate option for the welding of p24 base materials.

The creep rupture lifetimes of the tests on welded joints with a high Ti amount are significantly better. The extrapolated lifetime at 550°C is >18.000h instead of 3.500h for the one with low Ti. This 18.000h is just below the lower bound of the scatterband of VdTÜV 533 seems that the actual

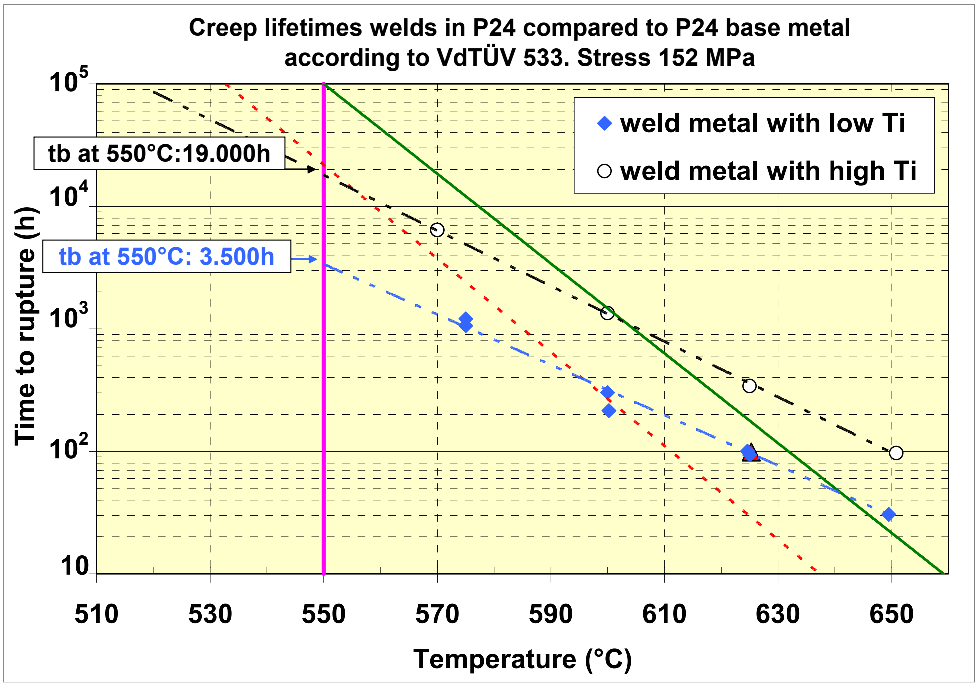

Figure 8. Some results of creep tests welded joints in P24 both with a low and high Ti content of the P24 weld metal. The stress level was 152 MPa (=10^5h/550°C). Fracture was in the weld metal (low Ti) or in the fine grained heat affected zone (high Ti).

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Creep behaviour dissimilar welded joints.

The creep tests on dissimilar welded joints are still ongoing, so it is for the creep tests on P24 material welded with P91 consumables. The data are not evaluated yet.

Hot hydrogen behaviour.

The hot hydrogen behaviour of the welded joints included 2 items:

- Hot hydrogen (Nelson attack) by which the carbides in the material can be attacked by H_2, forming methane → cavities → cracks.
- Effect of the combination of creep and hot hydrogen (still ongoing).

Nelson attack. The Nelson attack experiments were performed in autoclaves at 625 and 650°C with a hydrogen pressure of 18 MPa. Within the experiments also standard P22 (2.25Cr –1Mo) welded joints were exposed. The total test duration was 4.000h with intervals after 500,1.000 and 2.000h. The results were compared with an existing data base of TNO and the so-called Nelson curves.

- The standard 2.25Cr-1Mo showed already after 500h exposure Nelson attack. After 4.000h exposure at 625°C even micro-macro cracks were addressed, especially in the FGHAZ.
- The P23 and P24 welded joints with high Ti did not show any Nelson attack, up to 4.000h exposure at 600 and 625°C.

4. DISCUSSION

The research so far showed that the modified 2.25Cr-1Mo materials P23 and P24 can be attractive alternatives for the standard 2.25Cr-1Mo material P22 and the modified 9% Cr materials as P91. This accounts both for hydrogen service (plastic regime) and power generation (creep regime up to 580°C).

However, the research also showed that there are still important uncertainties which have to be solved before these materials can widely be introduced.

The main uncertainties are:

- The availability of these materials as pipes and the status of European and American code approvals.
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With respect to creep service the most important uncertainties are:

- Up till now all the data for the welded joints are at or below the lower bound of the codes for base materials. Do we need stress reduction factors for fully loaded welded joints and if so, what is the stress reduction factor?
- How to control the Ti content in P24 weld metal or do we need another type of consumables for the welding of p24 base materials?

With respect to hot hydrogen operating conditions the most important uncertainties are:

- The high Charpy-V transition temperature of P23 base material after step cooling. In this condition the material do not met the acceptance criteria of API 934.

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- The high Charpy-V transition temperature of the weld metals in P23 and P24. The weld metals do not fulfil the acceptance criterion of >54Joules at –18°C. The transition curves should be shifted to lower temperatures.

5. CONCLUSIONS

Power generation:

- The P23 and P24 pipe materials have a significantly higher creep strength than the standard P22 material.
- For P24 welded joints it is necessary that sufficient Ti is present in the weld metal. When Ti containing consumables are used it is essential that after welding the amount of Ti in the weld metal is not reduced.
- P23/P24 materials can not be used in "as welded condition". The Charpy-V toughness is in that condition not acceptable. In field repair without PWHT is not a realistic option.
- A hardness of <350HV is not a good criterion, but <300HV is, to obtain a sufficient toughness.
- The creep strength of the welded joints in P23 and P24 are at or below the lower bound of the codes and as expected the fine grained HAZ is the weakest location.

Hydrogen service:

- Hardness values of <248 HV can only be obtained with PWHT conditions (PLm values) far beyond those of power generation service. In other words the PWHT conditions for hydrogen service and power generation are different.
- The hot hydrogen resistance of P23 and P24 welded joints are far superior compared to that for the standard P22 material. No hydrogen attack at all was assessed in the P23 and P24 welded joints, while in the P22 welded joint severe cracking was addressed.
- The P24 base metal and P23 and P24 weld metals do not show susceptibility for temper embrittlement, but the P23 base material do.
- The Charpy-V transition curves of P23 and P24 are a matter of concern. For code approval they have to be shifted to lower temperatures.

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