Martensitic/Ferritic Super Heat-resistant 650°C Steels—Design and Testing of Model Alloys

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In the recent two decades advanced martensitic/ferritic 9–12 % Cr steels are recognized to be the most potential materials for 650°C Ultra Super Critical (USC) Power Plants. The critical issues are the improvement of long-term creep strength and corrosion resistance. The aim of the present research is to design new super heat-resistant 12 % Cr martensitic/ferritic steels using basic principles and concepts of physical metallurgy, to test and optimize model alloys and to investigate and clarify their behavior under long-term creep conditions with emphasis on microstructural stability and corrosion resistance.

Fine distributions of stable precipitates, which block the movement of subgrain boundaries (M23C6 carbides, Laves phase) and dislocations (MX carbonitrides) and delay coarsening of microstructure, are the key to high creep strength of this type of steels. Therefore, different carbide, nitride and Laves phase forming elements (Cr, W, Nb, V, Ta, Ti) have been used to provide precipitation hardening. Furthermore, the aim is to produce a sequence of precipitates with different kinetics, i.e. with precipitation of a new phase during coarsening of the prior one. Co has been used for obtaining 100% martensite initially and for slowing down diffusion processes and particle coarsening. The partial replacement of Co by Cu is also investigated to reduce costs.

The first results of mechanical tests of the studied model alloys have shown positive effects of the addition of W and Ta as Laves phase and MX forming elements, respectively, as well as of the addition of B. Alloying with Co has also shown beneficial effects on the creep strength.

KEY WORDS: ferritic heat-resistant 12 % Cr steels; Laves phase; microstructural stability; creep strength; corrosion resistance.

1. Introduction

The demands for reduction of monetary and environmental costs of electricity generation have resulted in the development of a new class of coal-fired plants—Ultra Super Critical (USC) Power Plants. The higher steam parameters (operating temperature and pressure) of the new plants require new materials with improved long-term high-temperature properties. This has resulted in intensive worldwide activities in research and development of new steels.1–3)

The new martensitic/ferritic super heat-resistant 9–12 % Cr steels (always mass%) have been recognized as an alternative for widely used high-strength austenitic stainless steels because of their favorable physical properties (thermal expansion and heat conductance) and lower price.4,5) The critical issues are the improvement of long-term creep strength, as well as oxidation and corrosion resistance.

As is well known, the increased temperature accelerates all degradation processes in steels, such as migration of atoms and dislocations, recovery and recrystallization, grain and subgrain coarsening, precipitation coarsening, corrosion etc. Therefore, under service conditions (elevated temperature and pressure) pronounced microstructural changes occur, leading to the degradation of long-term properties. Hence, improvement of microstructural stability is the key for decelerating degradation processes and obtaining excellent long-term creep strength. For this it is necessary to slow down the recovery of microstructure, provide enough solid solution and precipitation strengthening and slow down precipitation coarsening.

A new German project (within the frame of the MARCKO program) has been initiated to develop a new super heat-resistant 12 % Cr ferritic steel for application at 650°C and 300 bar in conventional power plants using basic principles and concepts of physical metallurgy, to test and optimize model alloys and to investigate and clarify their behavior under long-term creep conditions with emphasis on microstructural stability and corrosion resistance. The aim is to investigate the effect of different types of precipitates (M23C6, MX, Laves phase), which block the movement of subgrain boundaries and dislocations and delay coarsening of microstructure, as well as the effect of alloying elements on creep behavior. In particular, the Laves phase is studied, which precipitates during service and which is to strengthen the alloys when M23C6 precipitate particles, besides finely distributed other carbides and nitrides, become less effec-
The development is supported by theoretical calculations and simulations of the expected phase transformations and precipitation processes. The effects of various austenite-forming alloying elements are also studied. This paper describes the alloy design philosophy and the present state of development.

2. Experimental Procedure

Small laboratory casts (~0.5 kg mass) with systematically varied compositions with respect to relevant alloying elements are vacuum induction melted. Standard heat treatments, with austenitization at 1 070°C for 0.5 h, subsequent air-cooling and annealing for 2 h at 780°C with air-cooling, are used to achieve the initial microstructure of model alloys.

Yield strength, ultimate strength and fracture strain are determined in tension at room temperature whereas yield strength at 650°C is determined in compression. Screening creep tests are performed at temperatures between 600°C and 700°C with two regimes: in compression with stepwise loading and in tension with constant loading under stresses ranging from 40 to 240 MPa. The long-term tensile creep testing of selected model alloys up to 20 000 h has been started. The steam oxidation tests in a simulated service environment (Ar–50vol%H₂O) are carried out at temperatures ranging from 40 to 240°C.

The microstructures of the model alloys in the initial state and after mechanical and corrosion testing are qualitatively and quantitatively analysed by optical (OM), scanning electron (SEM) and transmission electron (TEM) microscopy. The crystal structure and the precipitates were identified by TEM (Philips CM200), operated at 200 kV and equipped with energy depressive X-ray spectroscopy (EDX), using thin foils and extraction replica samples. The thin foils were prepared by twin jet electropolishing in solution of perchloric acid + acetic acid (1 : 10 volume ratio) at 10°C and 20 V. Replicas were prepared by selective matrix etching in Vilella etchant to isolate the precipitates, deposition of carbon and separating the carbon film from the matrix in acid (volume ratio HNO₃ : HCl : H₂O = 10 : 1 : 10). The details about quantitative analyses are given elsewhere.

The microstructure observations are compared not only with the predictions of the empirical Schaeffler diagram, but also with theoretical simulations using the computer program Thermo-Calc.

3. Results

3.1. Design of Model Alloys

The most important design parameter is the 10⁵ h creep rupture strength of 100 MPa at 650°C, as well as sufficient corrosion resistance. Additionally, it is necessary to provide sufficient toughness, good weldability and sufficient hot workability.

The mechanical properties and their changes during service of ferritic high-Cr steels depend on chemical composition and initial microstructure as well as on service conditions. An advantageous initial microstructure of the 9–12% Cr steels is tempered martensite without δ-ferrite, formed during the final normalising and tempering heat treatment.

This microstructure consists of ferrite subgrains with a high dislocation density and evenly distributed more or less fine stable precipitates, which block the movement of subgrain boundaries (M₇C₃ carbides) and dislocations (MX carbonitrides). During exposure to elevated temperatures and creep stress, pronounced microstructure evolution occurs (recovery, and subgrain coarsening, precipitate coarsening), which deteriorate the mechanical properties. To achieve sufficient creep strength during the entire service life it is necessary to provide enough solid solution and precipitate strengthening and decelerate the microstructure coarsening, i.e., to slow down diffusion processes. In view of the minimization of the particle coarsening by Ostwald ripening, precipitation of coherent or semicoherent stable MX particles with low solubility in the matrix is strongly desirable. Precipitation of intermetallic phases (in particular Laves phase) during service, when the existing precipitate (M₇C₃) over ages, is to be used besides finely distributed carbides to provide enhanced creep resistance during entire high-temperature exposure. Therefore, relatively high amounts of carbide, nitride and Laves phase forming elements (Cr, W, Nb, Ta, Ti together with C and N) are added, but restricting C and N to retain weldability, Fig. 1. The effects of relevant alloying elements and different types of stable precipitates on the long-term deformation behaviour and on the oxidation resistance in steam are to be investigated systematically.

Precipitate forming elements are also ferrite-forming elements, but formation of δ-ferrite, as detrimental phase, in the final heat-treated microstructure should be avoided. The Ms temperature should be kept sufficiently high to provide a complete martensitic transformation, and a high A1 temperature is aimed at to raise the upper limit of the tempering temperature. The ability to form a fully austenitic and hot-workable microstructure during normalising depends on the proper balance of austenite and ferrite forming elements. In order to avoid δ-ferrite the alloy composition was selected such that the empirical relation Crₜₐₚ≥6.5 was fulfilled. The Cr equivalent, Crₑ𝑞ₚ, used for the present alloys was defined as:

\[ \text{Cr}_{\text{eq}} = \text{Cr} + 6\text{Si} + 4\text{Mo} + 1.5\text{W} + 11\text{V} + 5\text{Nb} + 12\text{Al} + 2.5\text{Ta} + 8\text{Ti} - 40\text{C} - 2\text{Mn} - 4\text{Ni} - 2\text{Co} - 30\text{N} - \text{Cu} \]
Thermo-Calc calculations were also used to check the presence of δ-ferrite. Co was added to balance the ferrite-forming elements, Fig. 1. It has almost no effect on the $A_c^1$ temperature, increases the $M_s$ temperature and Curie temperature and is expected to slow down diffusion processes and consequently coarsening of particles. Co shows high solubility in ferrite and almost no solubility in the Laves phase. The partial substitution of Co by various austenite-forming elements (C, Cu and Mn) is studied in view of cost reduction. For further improvement of creep properties, addition of B is to be used.

It was reported earlier that 9% Cr steels cannot be used in a temperature range above 625°C because of oxidation and corrosion problems and too high contents of Si have negative effects on creep properties. To obtain the necessary oxidation and corrosion resistance the contents of Cr and Si were fixed at 12% and 0.2%, respectively.

According to this concept three series of model alloys have been prepared to investigate the effects of different combinations of precipitate particles on the creep resistance, Tables 1–3. The first series is to reveal the effect of various Laves phase precipitates on strengthening after precipitation of $M_23C_6$, Table 1. Based on the alloy with 3% W from the first series and the experiences with the 9% Cr steels, which contain fine MX carbides and carbonitrides, the second series of alloys has been designed using V, Nb, Ti and Ta as MX forming elements to investigate effects of different types of carbonitrides on creep properties, Table 2.

The increased amount of W (4%) and Ti and Ta, which are the most promising MX forming elements in view of the high stability and the low solubility of the respective MX phases, with additional microalloying by B is the base for the design of the third series of alloys, Table 3.

Table 4 shows the designed chemical compositions of additional alloys in which Co in the alloy with 4% W is substituted partially by C, Cu and Mn in order to study the effect of different austenite-forming elements on creep. 3.2. Thermodynamic Computer Calculations of Phase Equilibrium and Precipitate Growth

The widely used simplified approach to predict the microstructure of steels using $C_{eq}$ and the empirical diagrams of Schaeffler and Schneider may be used as a guide line and gives preliminary information about the presence of δ-ferrite in the initial microstructure. For a more accurate evaluation of phase stability in the complex multi-component systems, such as the new ferritic steels, the computer program Thermo-Calc with a validated database of Gibbs free energies for the thermodynamic calculation of phase equilibrium has become a new, powerful tool. The thermodynamic data for Boron are incomplete and those for Ta are not yet implemented in the database SSOL, but preliminary calculations with a non-public database with Ta, obtained in cooperation with Dr. Ales Kroupa, could be performed.

The Laves phase is treated as a 2-sublattice phase (Cr, Fe)$_2$(Mo, Nb, Ta, Ti, W). The parameters of the phase description were obtained by a fit of the corresponding binary phase diagrams where Laves phase was observed. In the Cr–W and Cr–Mo systems where miscibility gaps and no Laves phase are observed the parameters were fixed such that Laves phase was not obtained in the corresponding calculated phase diagrams.

Figure 2 shows the calculated equilibrium mole fractions of coexisting phases as a function of temperature for four
model alloys. These alloys have been designed to be free of \(\delta\)-ferrite at about the austenitization temperature (right dotted line) and to show \(M_2\text{C}_6\) carbides, MX carbonitrides and Laves phase as stable phases in the ferritic matrix at the annealing temperature and at the service temperature of 650°C (left dotted line). The calculations have shown a strong dependence of the amount of \(M_2\text{C}_6\) carbides on carbon content, but a very small change with temperature. The amount of Laves phase increases with adding W, stabilising it to higher temperatures. MX carbonitrides are present in alloys with N. With the optimisation of the amounts of MX-forming elements it is possible to avoid formation of coarse particles from liquid phase and to provide precipitation mostly in low-temperature ferrite (arrows).

The microstructure after the heat treatment represents a metastable state, which tends to transform towards a more stable states. In Fig. 3 the result of a calculation of simultaneous growth of \(M_2\text{C}_6\) and Laves phase in a \(\text{Fe}–12\text{Cr}–3\text{W}–0.15\text{C}\) steel is shown. The calculations were performed with the software DICTRA. Local chemical equilibrium is assumed at the moving interfaces. It is assumed that the two particles grow in individual spherical cells of 5 \(\mu\text{m}\) radius. The two cells are coupled together by the condition of equal chemical potentials (\(\mu_i\)) of all diffusing components. The value of this surface potential is determined by the overall mass balance of the whole system composed of the two cells. The calculation corresponds to a heat treatment of ferrite at 780°C for 2 h, followed by a long-term annealing at 650°C corresponding to the service condition. It is seen that within the first 2 h \(M_2\text{C}_6\) grows fast, while the Laves phase particle is smaller by more than a factor of 10. The precipitation of \(M_2\text{C}_6\) has not yet come to completion after 2 h. The change in temperature to 650°C decreases the growth rate of \(M_2\text{C}_6\) considerably. After about 6 days the precipitation of \(M_2\text{C}_6\) is complete. The precipitation of Laves phase, on the contrary, takes more than 10 years to reach equilibrium.

3.3. Chemical Composition and Microstructure

The chemical analyses of the prepared model alloys have shown deviations from nominal compositions, in particular higher amounts of Cr and W and lower contents of C and N, which cause an increase of the \(\text{Cr}_{eq}\) values and enhance \(\delta\)-ferrite formation. This has been confirmed by thermodynamic calculations and the microscopic observations, but still fully or almost fully tempered martensitic microstructures have been obtained initially. Figs. 4 and 5. The martensite lath boundaries and martensite/\(\delta\)-ferrite bound-
aries are decorated by carbides, which have precipitated during heat treatment. The more detailed investigation of TEM foils (Fig. 5) reveals fine substructures of the martensitic matrix with high amount of low-angle and high-angle boundaries, very small subgrains with a high dislocation density and fine precipitates inside subgrains as well as on grain and interphase boundaries, indicating interactions between the precipitates and the dislocation substructure. The quantitative investigations of selected model alloys have shown a decrease of subgrain size in initial state with increase of W content, but subgrains are still distinctly coarser than in the commercial P92 alloy.\(^{16}\) Fig. 6(a). The subgrain size in alloy DT4-13 with 0.2Ta is of the same order as in P92. Significant growth of subgrains during creep has been detected. However, after creep, subgrains in alloy DT4-13 are still smallest.

Figure 7 shows the microstructure of alloys DT4-2 from the first series and DT4-13 from the second series of alloys in the heat-treated state and after creep. Different types of particles, precipitated on subgrain boundaries and inside subgrains, have been detected by EDX analyses in initial, heat-treated, and as-crept condition, Figs. 7 and 8 and Table 5. After tempering, all investigated alloys contain relatively coarse M\(_{23}C_6\)-precipitates, which are mainly located at grain and subgrain boundaries. A few coarse Laves phase particles have also been observed in alloy DT4-2 and fine, homogeneously distributed TiX and TaX particles have been precipitated inside subgrains in both DT4-9 and DT4-13, respectively. A distinct coarsening of M\(_{23}C_6\) carbides and a pronounced precipitation of Laves phase, raising its volume fraction to values equal to or even higher than the initial values for M\(_{23}C_6\), has been observed in all three alloys DT4-1, DT4-2, DT4-13 in as-crept microstructure, Figs. 6(b) and 6(c). Some of the large Laves phase particles (the similar size as M\(_{23}C_6\)) have precipitated in connection with M\(_{23}C_6\) carbides, indicating nucleation at the M\(_{23}C_6\)/ferrite interphase boundaries. The observation of a strong decrease of the volume fraction of M\(_{23}C_6\) together with a strong increase of the volume fraction of Laves phase may indicate growth of the Laves phase at the expense of M\(_{23}C_6\). Precipitation of Laves phase also causes desaturation of the matrix, reducing the excess solid solution strengthening down to the “solubility limit” solid solution strength. This was considered as detrimental by some authors.\(^{17}\) TaX particles in alloy DT4-13 have practically not changed their size, i.e. they grow very slowly, as was expected. The quantitative microstructural analysis of alloy DT4-9 is still in progress.

More work is needed to quantify the various hardening contributions under creep conditions when the dislocation density decreases and the particles coarsen.

3.4. Mechanical Properties

3.4.1. Yield and Ultimate Strength

The ultimate tensile strength at room temperature of all selected alloys from the three series, Fig. 9, are on the same level or higher than the minimum specified value for P92 (600 MPa\(^{18}\)). The increased amounts of W and C and addition of N and B on the one hand, and addition of MX forming elements on the other hand increase both yield strength and ultimate tensile strength by up to 35% and 39%, respectively. The ductility decreases, but the fracture strain is still of the order of 20%. Increasing the testing temperature from room temperature to 650°C lowers the strength, but again increases of W and C and addition of N and B lead to higher yield strengths at 650°C.

3.4.2. Impact Toughness

Results of impact tests for selected model alloys are shown in Fig. 10. The brittle-to-ductile transition temperature (temperature for medium energy between lower and upper level of impact energies) is about −35°C and −22°C for alloys DT4-7 and DT4-13, respectively, and about −20°C for the other 3 alloys. High impact energy values (77 J/cm\(^2\) and 74 J/cm\(^2\) for the first two alloys and about 60 J/cm\(^2\) for the last three alloys) are reached at 30°C and 60°C, respectively.
3.4.3. Creep

The secondary creep rates $\dot{\varepsilon}_{\text{min}}$, as determined by compression creep tests with stepwise loading, for higher stress levels at 650°C for selected alloys from series 1–3 are shown in Fig. 11. The base alloy DT4-1 (with 3% W) exhibits a stress dependence of the secondary creep rate similar to that of P92, tested under the same conditions. This is remarkable as the subgrains in DT4-1 are distinctly coarser ($\approx 700$ nm, Fig. 6(a)) compared to P92 ($\approx 300$ nm$^{19}$) so that there is less subgrain strengthening in DT4-1 in comparison to P92. Furthermore, the other alloys exhibit lower minimum creep rates than P92. The increased W content, balanced with Co for keeping the chromium equivalent constant, as well as addition of MX forming elements and B, lead to improved creep resistance. The addition of 0.2% Ta shifts the curve of DT4-13 to even higher stresses. The expected further increase of creep strength for alloy DT4-31 has not been obtained probably because of a possible deviation from nominal composition and presence of $\delta$-ferrite. The change in the slope of the $\sigma-\dot{\varepsilon}_{\text{min}}$ curves (i.e. the stress exponent $n$ in Norton’s power law equation $\dot{\varepsilon}_{\text{min}} = A\sigma^n$), from 16–20 in the high-stress region (above
rates in the initial stage of creep, whereas the primary creep of alloy DT4-2 extends to longer times than that of the alloy DT4-1, resulting in a lower minimum creep rate and longer rupture time. The longer duration of primary creep is believed to result from the higher amount of Laves phase precipitates on boundaries in alloy DT4-2. It should also be noted that at higher stresses (120–150 MPa) point of the minimum creep rate is observed for higher strain levels (for alloy DT4-1 in the strain range 0.015–0.02 and for alloy DT4-2–up to 0.05), Figs. 12(e) and 12(f). At lower stresses (60 to 100 MPa), however, point of the minimum creep rate is reached at small strains less than 0.01. Thus the transition from primary creep to tertiary creep occurs at relatively small strains compared with creep at higher stresses.

Addition of MX-forming elements reduces the creep rate in the primary stage and shifts the strain for minimum creep rate to lower values, although the effect on creep life, compared with base alloy DT4-1, is less pronounced, Figs. 13(a) and 13(b). Still alloy DT4-2 with increased amount of W exhibits the lowest creep rate and the longest creep life. The first results of series 3 alloys have shown a beneficial effect of the simultaneous increase of W content and addition of MX forming elements as well as addition of B, Figs. 14 and 15. The creep rate in the primary stage (650°C, 120 MPa) is significantly reduced and the resultant creep life is almost double that of alloy DT4-2. The improvement of creep life is evident at both testing temperatures, 650°C and 675°C, Fig. 15. Larson–Miller-type analyses, Fig. 16, have shown the same behavior for alloy DT4-2 as for previously reported alloys: in the short-term region the creep rupture strength changes are small, while in the long-term region strength rapidly decreases as a result of microstructural changes. Increasing W content and adding B shifts these curves towards higher creep strength.

According to first results at 650°C, substitution of a small part of Co by Cu can improve creep properties. 1% Cu in alloys with 4% W has nearly doubled creep life, Fig. 17, though there was a significant amount of d-ferrite in the initial microstructure (caused by loss of N).

All these results are used for the selection of model alloys for more detailed studies and long-term creep testing up to 20 000 h, which has been started. The long-term creep tests are to be performed with materials with three different heat-treatments in view of components in USC power plants, i.e. pipes and turbine rotors (core and surface). This research is in progress.

3.4.4. Corrosion

Steam-side corrosion may produce very thick oxide scales, which reduce the load-bearing capability, lead to overheating and may spall and cause failure of USC components. Figure 18 reports the first long-term corrosion test results for the selected model alloys under simulated service conditions. The new 12% Cr alloys exhibit an improved corrosion behaviour compared to the commercial
Fig. 13. Tensile creep rate vs. time curves for selected alloys at 650°C (stress level 100 MPa).

Fig. 14. Tensile creep rate vs. time and curves for selected alloys at 650°C (stress level 120 MPa).

Fig. 15. Creep rupture strength of model alloys DT4-2 and DT4-31 as a function of Larson–Miller parameter (with constant $C_{\text{H11005}}^2$ and rupture time $t_{\text{R}}$).

Fig. 16. Creep rupture strength of model alloys DT4-2, DT4-30 and DT4-31 as a function of Larson–Miller parameter (with constant $C_{\text{H11005}}^2$ and rupture time $t_{\text{R}}$).
9% Cr steel P92. Especially alloys with Nb and Ta have exhibited an extremely high corrosion resistance. The SEM-EDX analyses have revealed very thin and stable external oxide scale in alloy DT4-4 with 2% Ta, which prevented internal oxidation, Fig. 19.

4. Discussion

The present results for various 12% Cr model alloys have indicated a potential for reaching a sufficient creep and satisfying corrosion resistance at 650°C. In spite of the deviation from the nominal compositions and hence higher Cr eq than 6.5, the addition of Co to 12% Cr steels, which balances the effect of the ferrite-forming elements, indeed prevents δ-ferrite formation and produces martensitic microstructures without lowering the A_{C1} and M_{s} temperatures too much. The first results of the partial substitution of Co by Cu are rather promising. This is being studied in more detail with support by thermodynamic equilibrium calculations and microstructural investigations.

Alloying with MX forming elements and W has indeed produced precipitation of MX carbonitrides in the heat-treated initial microstructure and Laves phase during creep. The volume fraction of Laves phase seems to depend only on the W content. The amount of MX phase depends sensitively on the N content. The further work, supported by theoretical calculations of phase equilibrium and of the kinetics of phase transformations, is concentrated on the careful balance of alloying elements for producing a precipitation sequence of MX phase and Laves phase. The complex multicomponent alloys, which contain some non-typical alloying elements, require modifications of the original database with additional thermodynamic data, for example for systems containing Ta and B. It has also to be mentioned that the present kinetic calculations cannot yet reproduce the real situation correctly. The influence of temperature on kinetics is incorporated in the model, but not the possible strain effect. Further, the experimental data discussed above show that the M_{23}C_{6} nucleates preferentially at grain and subgrain boundaries. Laves phase nucleates preferentially at the surface of M_{23}C_{6} rather than homogeneously in the bulk. Therefore, growth is not only controlled by volume...
The composition of N and Co in selected alloys from series 1 and 2 and characteristics of MX particles (according to thermodynamic calculations).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>DT4-2</th>
<th>DT4-8</th>
<th>DT4-9</th>
<th>DT4-13</th>
<th>DT4-7</th>
<th>DT4-1</th>
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<tr>
<td>$\delta_\text{in}$</td>
<td>5.05 E-10</td>
<td>1.76 E-09</td>
<td>3.82 E-09</td>
<td>4.58 E-09</td>
<td>5.95 E-09</td>
<td>7.16 E-09</td>
</tr>
<tr>
<td>N content (wt.%)</td>
<td>-</td>
<td>0.0093</td>
<td>0.0210</td>
<td>0.0098</td>
<td>0.0015</td>
<td>-</td>
</tr>
<tr>
<td>Co content (wt.%)</td>
<td>5.6</td>
<td>3.9</td>
<td>2.5</td>
<td>2.05</td>
<td>3.6</td>
<td>4.8</td>
</tr>
<tr>
<td>Precipitation of MX</td>
<td>- in solid state</td>
<td>from liquid phase</td>
<td>in solid state</td>
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diffusion, but also by boundary diffusion. It is also to be expected that the Laves phase may grow much faster when in contact with an $\text{M}_2\text{C}_6$ particle by taking up Cr and W from the carbide rather than by slow volume diffusion. Such calculations are now in progress.

The results of mechanical short-term testing are promising. The ultimate tensile strength, yield strength and ductility at room temperature and at 650°C are on the same level or higher than for alloy P92\(^{18}\). Even toughness, which is usually the main problem of creep resistant steels, is still satisfying.

The present creep test results have shown positive effects of W and Laves phase precipitation on creep strengthening. The results of subgrain measurements (subgrain size of alloys DT4-1 and DT4-2 in comparison with P92, Fig. 6(a)), microstructure investigations (profuse Laves phase precipitation at grain and subgrain boundaries) and creep tests (Figs. 11 and 12) indicate a higher contribution of so-called "particle-stabilized subgrain hardening"\(^{20}\) than of the subgrain strengthening itself, in comparison to P92. The more detailed investigation is needed to understand the Laves phase contribution to hardening of this class of steels.

The addition of MX-forming elements and N to the second series of model alloys has not produced the expected positive effects, Fig. 13. The low N level in the studied model alloys is believed to be the reason for the still low strengthening effect of the MX precipitates in the present alloys, Table 6. The higher content of N and Co as well as precipitation of fine MX phase in the solid state obviously led to better creep properties, together with increased W content. The further optimization of the amount of the MX forming elements—in particular Ta (reported negligible content. The further optimization of the amount of the MX led to better creep properties, together with increased W content. The ultimate tensile strength, yield strength and ductility at room temperature and at 650°C are on the same level or higher than for alloy P92\(^{18}\). Even toughness, which is usually the main problem of creep resistant steels, is still satisfying.

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