ON THE THEORETICAL DEVELOPMENT OF NEW CREEP RESISTANT ALLOYS AND THEIR EMPIRICAL VALIDATION.

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Abstract

In anticipation to the present revival of nuclear power, and to obtain more efficient, secure and environmentally-friendly power plants, new families of high temperature resistant, low activation materials are under development. This work presents an example of work performed at CEA during the development of novel ferrito-martensitic reduced activation alloys for Generation IV and Fusion applications.

In the past, the process of designing a new material was mostly heuristic, requiring repeated experimental trial and error, but nowadays, synergies between the accuracy of current scientific knowledge in thermodynamics and transformation kinetics and increased computer capacity enables us to design successful new alloys using minimal empirical feedback. This work presents this comprehensive and multi-model approach to alloy and microstructure design. The CALPHAD method, thermo-kinetic modelling of precipitation reactions and artificial neural network analysis are combined in the development of new alloys having their compositions and microstructures optimised for maximum creep resistance.

To complete this work, a selection of the alloys designed have been cast and the results obtained during alloy design and the modelling of various heat treatments have been verified. Optical and electronic microscopy have been used to characterise the microstructure. Uniaxial tensile tests have been used to measure the mechanical performance of the alloys presented at room, service and higher temperatures. The characterisation of the behaviour of the material in service conditions is underway with relaxation and creep tests.

Introduction

The development of new and improved alloys for critical applications had been hitherto (and in a great measure still is) a lengthy and expensive process, requiring multiple iterations of alloy

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design, casting and testing. However, the present level of scientific knowledge and the use of modern computational methods permit to ease and reduce this process substantially. One of the fields can benefit the most of the improved methods and the shorten development time is, undoubtedly, the power generation industry.

In order to satisfy more demanding efficiency requirements and to achieve better environmental and economic performance, modern power generation industry requires a continuous process of improvement. New materials able to outperform present ones in safety, mechanical properties and service temperature are a continuous need in this process. In order to achieve these goals better materials are needed, which enable to work under more demanding requirements of service temperature, life length, and creep resistance. In particular, in the case of nuclear power generation, critical components are required to withstand their service conditions for the complete operation life of the power plant, sometimes up to 50 or 60 years. In cases like that, it is also important to be able to predict accurately the evolution of the microstructure during and to the end of the service life of each component. Obviously, it is not practical to perform life tests of all possible conditions, and specially tests of the duration of the real working life of the component.

The work presented here exemplifies the use of various thermodynamic and statistic tools in the design of new creep resistant alloys for the nuclear industry, and the prediction of their micro-structural evolution during service life. The design process is still iterative, each stage leading to a more refined definition of the final alloy. The difference with the traditional approach is that most of the work is performed theoretically or computationally, involving the production of only a few essential experimental casts to corroborate the suitability of the final composition and thermo-mechanical treatments required to obtain an optimal performance.

Design methodology

Description of the method

The design method starts by a stage of exploration of the scientific literature and the industrial *expertise* in order to delimit the choices of composition and microstructure that will be analysed and optimised later on.

In order to narrow the range of composition and heat treatment for the alloy to obtain good creep resistance, an advanced statistical method has been used, an artificial neural network. By using this type of multi-dimensional non-linear regression method, it was possible to analyse a large quantity of data on creep resistance of many alloys and to obtain guidelines as to design an improved material.

After a narrow composition has been selected, CALPHAD-based thermodynamic models like ThermoCalc, MTDATA or MatCalc were used to ascertain whether a suitable microstructure could be obtained. Finally thermo-kinetic model like MatCalc, which is able to calculate the kinetics of multiple simultaneous precipitation reactions in multi-component alloys, was used to

find the heat treatment necessary to obtain the optimal microstructure (*i.e.* the finest precipitate distribution).

Comprehensive validation of the alloys developed must follow the theoretical design, starting with the static mechanical properties at room temperature and high temperatures, and high temperature relaxation and creep tests.

Step 1: General composition and microstructure

To illustrate the potential of modern materials design methods, a new family of alloys for the nuclear power industry has been developed. Ferritic-martensitic steels are known to perform well as low-activation materials, due to their low swelling under radiation and long service life at high temperature and even moderate corrosion resistance, therefore they have the potential to become optimal candidates for various critical applications in the thermal and nuclear power generation and petrochemical industries[1, 2, 3]. A Fe8-12Cr ferritico-martensitic alloy has been selected as base material.

Some elements commonly used in the power generation industry and other high temperature applications like Mo, Ni, Nb, Si, Mn, Co and B need to be reduced or even excluded and are commonly substituted by W, V and Ta in alloys that need to work under radiation [1, 2, 3]. Thermodynamic software packages like MTDATA and Thermocalc were used to perform the necessary calculations on the thermodynamic stability of the phases of interest [3, 4].

One effective method to enhance the creep resistance of an alloy is by producing a fine precipitate distribution that minimizes the deformation mechanisms at service temperature. MX precipitates like TiC, TiN, VN are especially suitable for this task, due to their morphology, homogeneous distribution and their slow coarsening (especially in comparison with $M_{23}C_6$-type carbides). Moreover, and VN precipitates are stable at higher temperatures than $M_{23}C_6$ precipitates, allowing an increase in the working temperature of the alloy. Nevertheless, an alloy with high nitrogen content could present some problems, including the formation of porosity during manufacturing [5].

A general range of possible compositions including the elements Fe, Cr, W, V, N, and C but with limited content of Ni, Si, Mn or B was therefore selected following the above criteria.

Step 2: Main target property: Creep resistance

The main mechanical property that had to be optimised was creep resistance. The physical phenomena governing creep behaviour of metals is extremely complex, but ultimately related to the composition, precise microstructure and service conditions of the alloy. Present physical models for creep phenomena are either simple empirical models or physical models of particular creep mechanisms very limited in application [2, 6], and therefore, an advanced statistical method, an artificial neural network model has been used to narrow the range of compositions to be considered [7, 5]. A Bayesian-based neural network has been used to perform non-linear regression analysis on a large database of creep data with multiple input parameters [8, 9]. The database used includes information on over 2000 datapoints of creep resistant alloys, each

of them described in terms of composition, heat treatment and creep life, creep test temperature and creep fracture stress [7]. This model is publicly available at the Materials Algorithms Project website [10]. With this tool the effect of variations in composition on the creep rupture strength after 100,000 hours was analysed and a well defined composition was defined that would potentially maximise creep resistance.

Figures 1 and 2 show just two examples of the analysis performed using the neural network model to study the effect of small changes in composition, corresponding to the effect in the predicted rupture time of tungsten and nitrogen respectively [7, 5]. The predictions for each set of conditions are plotted in solid lines and surrounded by dashed lines representing the *errorbar* or confidence estimation of the prediction [8, 9].

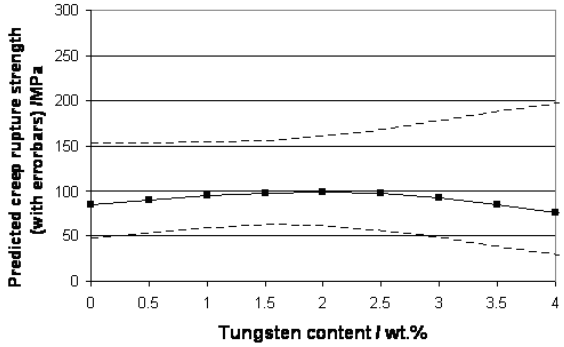

Figure 1: Creep rupture strength predicted using a neural network as a function of tungsten content.

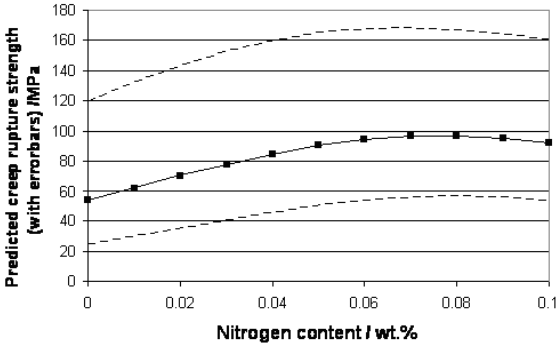

Figure 2: Creep rupture strength predicted using a neural network as a function of nitrogen content.

From the neural network analysis [7, 5] it was found that for some elements there was an optimal composition range (represented as a maximum in the predicted creep rupture strength at 10,000 hours), like is the case of tungsten around 2 wt.% (Figure 1).

Other elements, for instance carbon, which produces a strong solid strengthening effect, present a creep rupture strength that increases monotonically with the element content of the alloy. However, this type of trend needs to be taken cautiously, and it would be unwise to extrapolate too far. Using again the case of carbon, not all of it stays in solid solution but it tends to precipitate as $M_{23}C_6$. $M_{23}C_6$ precipitates have rapid coarsening kinetics and therefore produce little improvement in the mechanical properties, and on the other hand steal Cr from the matrix of the alloy, reducing its oxidation resistance.

In the case of nitrogen, the predictions of the neural network suggest that the optimal nitrogen content lies around 0.07wt.%, as shown in Figure 2. This amount will need to be matched stoichiometrically with that of vanadium for instance, to form the reinforcing MX precipitates. Moreover, an excessive N content could lead to porosity in the cast [4, 11].

Finally, the neural network analysis shows that the predicted creep rupture strength increases with boron content. It has been known that even small additions of boron have important influence on creep behaviour of Cr-steels [12, 13]. Boron is an element that, on its natural form

is deleterious in alloys exposed to radiation. However, if only small amounts are needed, isotope B^{11} could be used, which does not form helium under radiation like B^{10}, and still be able to benefit from the effect of boron [5].

As shown, it is possible to interrogate the neural network model to obtain a narrower definition of composition and heat treatments needed. To conclude, after examining the related literature and analysing the possible compositions with the help of advanced statistical methods, an alloy composition optimised to maximise the creep rupture strength and presenting good oxidation properties was chosen. One of the proposed composition, referred to as *Alloy VY2* is approximately (all compositions are in wt.%) Fe 9.0Cr 0.1C 2.0W 0.35V with up to 0.07N and with the possibility of small (less than 0.1 wt.%) additions of B^{11}. The limit on nitrogen was found as a compromise between the reinforcing role of nitrogent by the formation of nitrures and by solid solution on one hand and on the other hand, the need to be able to keep all nitrogen in solution during manufacturing (i.e. to avoid the occurrence of porosity), as it will be described in a later section.

Step 3: Microstructure and heat treatments

Once the composition of the alloy has been selected, the heat treatment to obtain the desired microstructure need to be carefully designed. In order to obtain the fine precipitation of vanadium nitrides the alloy needs to be austenitised to dissolve completely all existing precipitates. Subsequent quench to transform the austenite matrix in martensite and a temper to release internal stresses and to precipitate MX and $M_{23}C_6$ and therefore to stabilise the microstructure will finish the treatment. Using a thermo-mechanical treatment would also be feasible, adding stages of hot rolling prior to annealing to increase the density of precipitate nucleation sites and hence, accelerate the precipitation reaction and reduce the average size of the precipitate distribution. The optimisation of the heat treatment parameters (temperature and duration of each stage of the heat treatment) is possible using a thermodynamics and precipitation kinetics package like MatCalc, using the database "IWS_Steel", both developed at TU Graz [14, 15, 16].

A package like MatCalc, combines the equilibrium phase stability calculations with calculations on the kinetics of precipitation, (nucleation, growth and coalescence of precipitates), and the prediction of the size distribution obtained with each set of conditions [14, 15, 16].

Figure 3 shows the calculated phase stability diagram as a function of temperature for steel VY2. Using this diagram we can define the temperatures different stages of the heat treatment to obtain the optimal microstructure.

Using Figure 3 as a reference we can define the austenitisation temperature at 1200°C, and then a subsequent quench in oil. Then two different heat treatments have been considered. the first one (*Standard*) consists in a single overaging annealling at 720°C. The second one (*Optimised*) consists in a double annealling treatment, at 600 and 720°C for one hour each, to promote a finer distribution of reinforcing phases and to avoid exessive overaging of the microstructure.

Using a software package that includes at the same time thermodynamics and precipitation and coarsening kinetics simplifies considerably the selection the optimal heat treatment

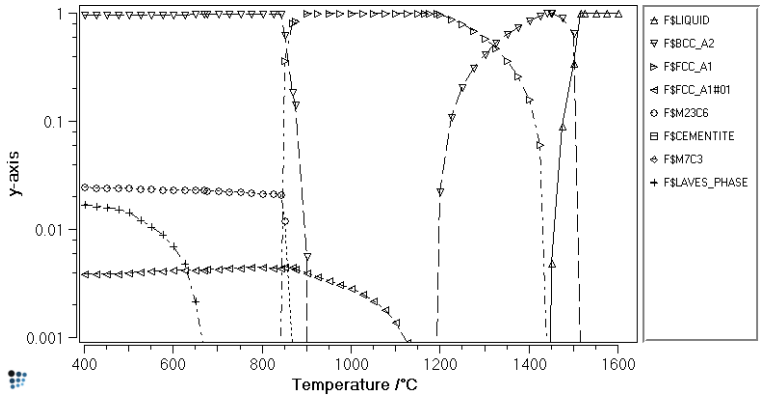

Figure 3: Phase distribution as function of temperature for designed alloy. Diagram calculated using MatCalc.

conditions to obtain the desired microstructure, precipitate distribution, avoiding incomplete precipitation reactions or excessive precipitate coarsening. This procedure has been used to determine the evolution of the precipitate distribution during the two heat treatments considered, as shown in Figures 4 and 5.

Moreover, a similar calculation could be performed to study the evolution of the microstructure during service conditions, for instance to predict the degree of coarsening of the reinforcing phases during long thermal aging.

Experimental assessment

After the theoretical design of the alloy, a careful experimental assessment is necessary. The main points of the assessment are to make sure that the phase stability and kinetics calculations predict the correct phases in the real material, and that the microstructure obtained lead to the expected optimised mechanical behaviour.

Undesirable phase: Nitrogen gas

In this section, a example of an unexpected (and undesirable) phase found in some of the alloys designed is shown.

As the nitrogen content of the alloy is increased to produce a larger extent of precipitation of the reinforcing phase VN, there is an increased risk that the matrix of the alloy will not be able to keep in solution all the nitrogen and some will be released as gas, producing a degree of porosity. Several parameters influence the possibility of formation of porosity in high nitrogen content alloys, some thermodynamic, like the sequence of phases forming during solidification (as each phase presents a different nitrogen solubility curve, as shown in Figure 6) and others more of a technological character [5]. In some alloys the porosity could even appear macroscopically, like it is shown in Figure 7. The nitrogent content of the alloy shown in Figure 7 is 0.073wt.% ,

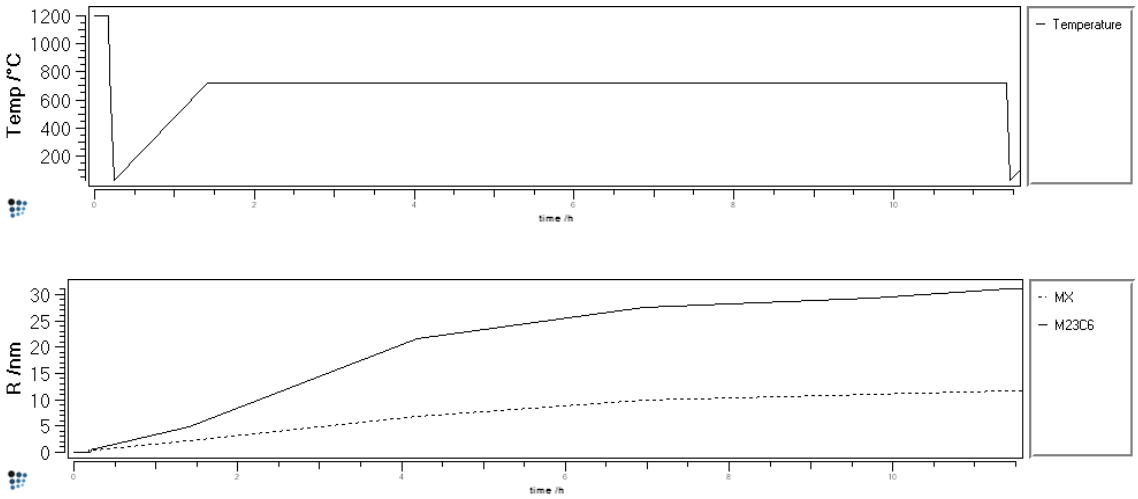

Figure 4: Simulation of the evolution of the average radius of MX and $M_{23}C_6$ precipitates on the designed alloy during the *Standard* heat treatment).

which is not far from the composition of the alloy designed in this work. The nitrogen content of the designed alloy has been kept at 0.04wt.% [5].

Mechanical properties

Tensile properties

A program of tensile tests has been planned to characterise the tensile behaviour at room temperature and at high temperatures of the alloy under consideration. As high temperatures, two characteristic temperatures have been chosen, 650°C, which is the contemplated service temperature, and 820°C, indispensable to be able to predict the behaviour of the material in the event of *extraordinary* service conditions.

The tests have been performed on an INSTRON machine with a load capacity of 200kN. The geometry of the specimens used is detailed below. The loading rate used in all cases was 0.84 mm/min. which is = $4{,}7.10^{-4}$ s^{-1}.

Figure 8 shows the comparison of the two different heat treatments considered with a PM2000 ODS steel (Oxide Dispersion Strengthening) with different grain sizes. This Figure shows the substantial improvement in yield stress obtained at all temperatures by using an *optimised* heat treatment consistent in a double precipitation annealling instead of a single long overaging annealling. The yield strength obtained in both cases is of the same order of magnitude as that obtained in ODS steels, without the need of the complex manufacturing process needed for such type of materials.

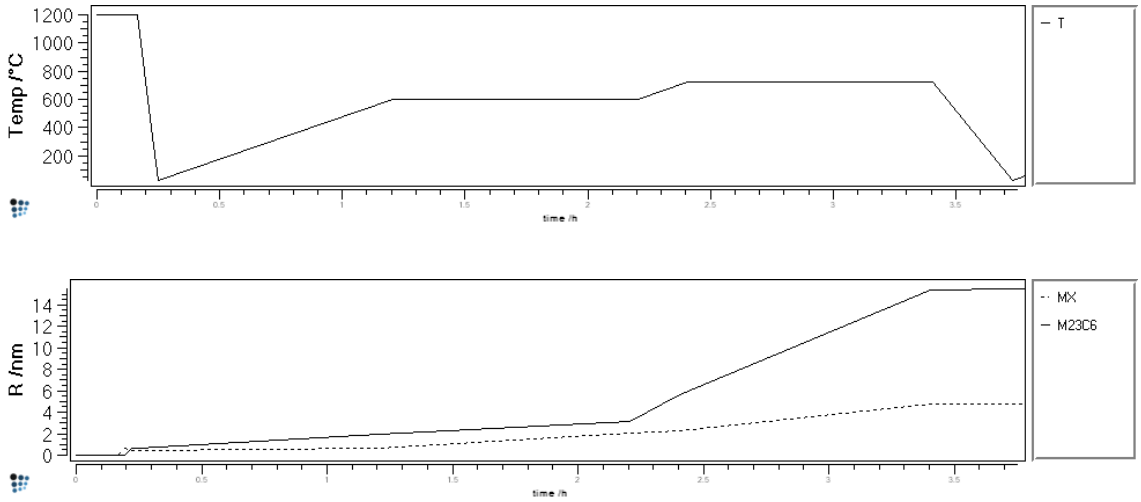

Figure 5: Simulation of the evolution of the average radius of MX and $M_{23}C_6$ precipitates on the designed alloy during the *Optimised* heat treatment).

Relaxation and creep properties

As a first approach to the long term behaviour of the alloy under consideration, a relaxation test has been used to compare its behaviour with that of a T91 alloy (Fe-9Cr-1Mo-V-Nb). Although it is possible to extrapolate the results from a relaxation test to obtain the same type of information that would be obtained from full time creep tests [**?**], a program of creep tests is under way. Figure 9 shows the comparison between the relaxation tests results for a T91 steel and VY2 alloy in the *Standard* condition.

It is encouraging to see that the newly developed alloy, even in the *Standard* condition behaves as well as a traditional alloy with good creep resistance. It is therefore expected that the creep tests on VY2 alloy in the *Optimised* condition will present improved creep resistance in the same way as it presents improved static mechanical properties.

A comprehensive characterisation of high temperature creep behaviour of alloy VY2 in both conditions *Standard* and *Optimised* is at present under way in CEA Saclay.

Microstructure stability

The microstructure and carbide distribution in a commercial creep resistant, low activation alloy (F82H) has been simulated using a thermo-kinetic model package, MatCalc. The microstructure after long thermal aging treatments (13,500 hours) at various temperatures, comparable to service conditions, have been considered. In all cases, the calculated carbide distributions describe with remarkable accuracy experimental measurements (Figure 10), showing that it is possible to describe and predict accurately the evolution of the microstructure and carbide distribution even for long heat treatments, at temperatures comparable to service conditions found in power plant applications [17].

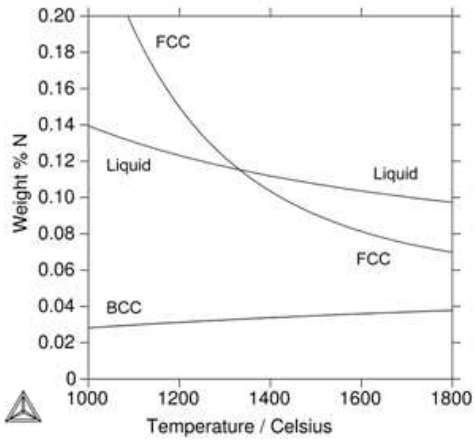

Figure 6: Nitrogen solubility limit for liquid, δ-ferrite, and austenite equilibrium with nitrogen gas,calculated using Thermocalc.

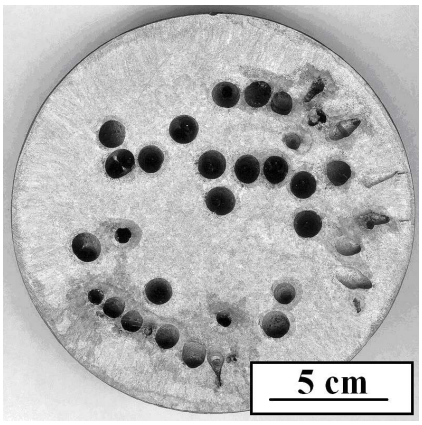

Figure 7: A2 steel presenting nitrogen caused porosity (in wt.% Fe 7.9Cr 0.1C 2.5W 0.3V 0.005Nb 0.073N).

With this confidence, a similar calculation was performed for the designed alloy, obtaining that the $M_{23}C_6$ carbide distribution (shown in Figure 11), has an average radius just under 100 nm after 10,000 hours.

Conclusions

The work presented here is a case study on how the present accuracy of thermodynamics and kinetics calculations allow to design new alloys responding to demanding solicitations and avoiding most of the experimental trial and error needed in the past. Software tools based on the CALPHAD-method and various kinetics models are available that allow to predict not only the feasibility of some target microstructure but its evolution during various heat treatments.

The microstructural and mechanical characterisation of the alloy designed is presently under way, and preliminary results have been presented in this work.

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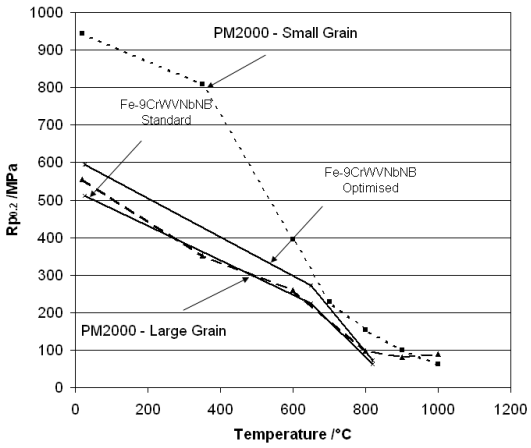

Figure 8: Comparison mechanical behaviour of alloy VY2 in two conditions with an ODS PM2000 alloy during uniaxial tensile tests between room temperature and 820°C.

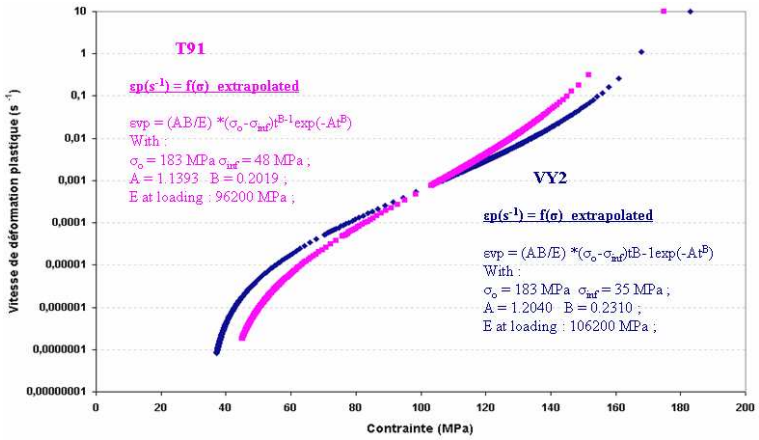

Figure 9: Comparison mechanical behaviour of alloy VY2 in the *Standard* condition with T91 steel during stress relaxation test at 650°C.

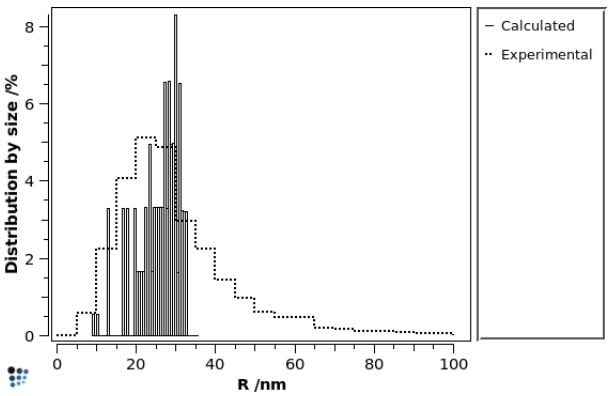

Figure 10: Comparison of the predicted carbide distribution with experimental measurements in a F82H steel thermally aged at 550°C for 13500 hours.

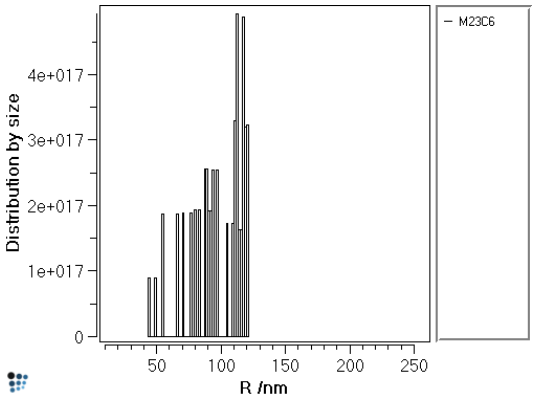

Figure 11: Predicted carbide distribution of VY2 steel thermally aged at 650°C for 10000 hours.

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