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Design of new Fe-9CrWV reduced-activation martensitic steels for creep properties at 650°C

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Abstract

New low-activation martensitic steels for creep resistance between 600 and 700°C were designed using thermodynamic, kinetic and neural network modelling tools. Suitable compositions for a matrix stabilised by vanadium nitride (VN) particles were firstly suggested on the basis of phase stability calculations using the thermodynamic software MTDATA. A neural network method was then used to predict the creep rupture stress of the possible compositions. It was predicted that a creep rupture stress close to 100 MPa for 100,000 hours at 650°C could be achievable. Finally, the precipitation and growth kinetics of VN were calculated using an existing kinetic model. These calculations suggested that a fine (nanometre-scale) and homogeneous distribution of particles could be obtained using a high nucleation site density. This could, in principle, be achieved using thermomechanical treatments and should be even better than alloys produced using the classical normalisation and tempering route.

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Keywords

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K0100	Kinetics
L0400	Low Activation Materials
P1100	Precipitates and Precipitation

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1. Introduction

Ferritic-martensitic steels are known to perform well under irradiation, with a high resistance to radiation-induced swelling (see [1] for a complete review on martensitic steels for nuclear applications). The alloys are consequently candidate structural-materials for the international fusion reactor programmes. One of the difficulties with these steels is that they can exhibit brittle behaviour at low temperatures. The transition between the ductile and brittle behaviour is often characterised by the ductile-brittle transition temperature (DBTT) measured using Charpy impact tests. When irradiated at a temperature below 400°C, the DBTT shifts to higher temperatures. This could potentially compromise the structural integrity of the reactor, so over the last few years, attempts have been made to optimise the toughness of reduced-activation steels. It now appears that ferritic-martensitic steels could be used at even higher temperatures, up to 600°C or 650°C. In this case, the critical property would not be the toughness but the creep and hot-corrosion resistance during long-term service, therefore new reduced activation (RA) martensitic steels have to be designed to be consistent with these requirements. The purpose of the work presented here was to use thermodynamic, kinetic and property models to identify new alloys and fabrication routes for creep-resistant martensitic steels.

2. Design-rule for new Fe-9CrWV reduced activation martensitic steels

The concept of RA steels was introduced for materials which offer benefits for maintenance operations and waste management [2,3,4,5].

For martensitic/ferritic steels, the main alloying elements such as molybdenum, niobium and nickel present in ordinary commercial steels are substituted by elements such as tungsten, vanadium and tantalum. These elements have a similar influence on the processing and the structure, but exhibit a lower radiological impact. The development process for the RA alloys can benefit from the many years of experience on power plant materials even though the use of boron or cobalt is not permitted in fusion reactors. The design procedure used is based essentially on the following rules and assumptions:

- Eliminate the use of boron, cobalt, niobium and molybdenum which are present in conventional creep-resistant steels.

- Increase the amount of W as much as possible for solid solution strengthening.
- The creep resistance of martensitic steels is enhanced by a fine dispersion of non-shearable particles which are resistant to coarsening [6]. Vanadium nitrides are good in this context. It would be reasonable to assume that the creep properties improve as the fraction of second-phase particles increases.
- A fine dispersion of vanadium nitride particles can, however, only be achieved if they all dissolve at the austenitisation temperature, which in the industrial context must be 1200°C or below.
- The balance between austenite and ferrite stabilising elements has to be controlled to avoid the formation of δ ferrite at the solutionizing temperature 1200°C-1250°C.

With these criteria, the list of solutes permitted becomes limited to the following elements: Cr, W, V, Ni, Si, Mn, N and C.

3. Neural networks and thermodynamics in alloy optimisation

A first set of chemical compositions corresponding to the above criteria was selected using the phase stability calculations implicit in MTDATA associated with the SGTE substance database and the NPL solution database based on this [7]. The dissolution temperature for vanadium nitrides and the $\gamma/\gamma+\delta$ boundary were obtained in this way. Figure 1 illustrates the equilibrium phase fractions for a steel, V1 (Fe-9Cr1.5W0.32V0.1C0.085N wt%), with appropriate phase stability ranges for a VN-strengthened microstructure.

Based on past experience, MTDATA underestimates the $\gamma/\gamma+\delta$ transformation temperature by 40-50°C. However, this can be approximately allowed for by taking the transition temperature $\gamma/\gamma+\delta$ as 1300°C rather than 1260°C for steel V1.

Following the thermodynamic analysis, neural networks (NN) were used to adjust the chemical composition on the basis of the predicted creep rupture strength.

NN modelling is now widely used in science for the understanding of complex properties. The method is capable of dealing with nonlinear relationships of considerable complexity. Introductory papers on the neural network method in the context of materials science can be found elsewhere [8,9]. NN models have been developed at the University of Cambridge to estimate the creep rupture strength of martensitic/ferritic steels [10, 11]. In this work we have used the latest [12] which has been trained on more than 2000 creep data, to assess different hypotheses concerning the effect of each solute on the creep rupture strength. According to this analysis, low concentrations of Mn, Si and Ni are recommended to improve the creep rupture strength (figure 2). This is consistent with the good creep behavior noted in steels NF616 (Fe-9Cr-0.04Si-0.06Ni wt. %) and B2 (Fe-9Cr-0.07Si-0.06Mn wt. %) [13,14]. It was therefore decided to fix the Ni, Mn, and Si content of our steels at 0.05 wt%.

From thermodynamic calculations, the volume fraction of vanadium nitride (with complete dissolution in the γ domain at 1200°C) is a maximum if the V content is equal to 0.32 wt.% and the N content is 0.085 wt.%. A first optimised composition, steel V1 (table 1), was therefore proposed using these concentrations and Cr and W contents chosen to respect the balance between austenite- and ferrite-stabilising elements. A second optimisation was carried out by using the neural network to find the V/N ratio giving the greatest creep strength (inputs in table 1). The resulting steel V2 (table 1) has a composition V: 0.35, N: 0.07 W:2.5 and Cr: 8 wt% (table 1 steel V2). The NN predictions of creep rupture strength for the steels V1 and V2 are presented in figure 3. According to the NN used, a creep rupture strength close to 100 MPa at 650°C and after 100 000 h could be expected from V2. This compares with a value of 35 MPa calculated using the same neural network for Eurofer steel.

It is emphasised that the description of vanadium nitride in the databases used is simplistic because the phase is modelled as a compound of fixed composition VN. In practice, these precipitates are often described in the literature as M_4X_3, with M=V, Nb or Ta and Cr and X=C and/or N [15], and there is evidence that they undergo composition changes during precipitation [16]. According to the NN model, the optimum V/N atom-ratio is 1.37, which is close to the “ideal” ratio 1.33 corresponding to the stoichiometry V_4N_3. It is encouraging to see that the optimum V/N ratio found by NN is consistent with experimental observations.

4. Optimization of the heat treatment parameters.

As mentioned in part 2, the design of these alloys assumes that the creep resistance is enhanced by a fine distribution of vanadium nitride particles. Under standard conditions of normalisation and tempering, such as those considered in the NN calculation, nitrides mainly precipitate during service. However, this precipitation could be induced in the γ domain before the quench. A model [17,18] based on classical nucleation and growth theory was used to calculate the kinetics of vanadium nitride precipitation. Consider the nucleation of θ (spherical particles, interfacial energy $\sigma_{\gamma\theta}$) from γ. The nucleation rate is :

$$I = N \exp(-\frac{G^*}{RT}) \nu \exp(-\frac{G_t^*}{RT})$$

where N is the number density of nucleation sites, ν is the attempt frequency (often taken as kT/h), G^* is the activation energy which corresponds to the formation of the critical nucleus and G^*_t is the activation energy for transfer of atoms across the γ/θ interface. In this model, G^*_t is the activation energy for diffusion of vanadium atoms and

$$G^* = \frac{16\pi}{3} \frac{\sigma_{\gamma\theta}^3}{\Delta G_v^2}$$

with ΔG_v the variation of Gibbs energy per unit volume.

ΔG_v can be calculated with MTDATA (for more details see [17, 19]), as can the nucleation rate.

The growth rate is controlled by diffusion so local equilibrium between the precipitate and the matrix can be assumed during growth. At each time calculation step, the correct tie-line between the matrix and the precipitate is determined using MTDATA. The diffusion of species from the matrix to the interface is controlled by their composition gradient and the velocity of the interface is calculated [17]. The input parameters to determine the overall transformation kinetics are the number density of nucleation sites, the interfacial energy and the diffusion coefficients for the vanadium and the nitrogen. In the temperature range chosen for calculations, the only equilibrium phases present according to MTDATA are γ and VN. It is reasonable therefore to assume only one precipitating phase. The population distribution of VN for different temperatures, site densities and interfacial energies were calculated. Figure 4 presents a simulated time-temperature-precipitation diagram, assuming an arbitrary detection threshold of 0.025 volume % VN.

The temperature of the precipitation nose was found to be close to 950°C. At this temperature, the size distribution after the complete precipitation of VN particles with an interfacial energy of 0.21 J m^{-2} is plotted in figure 5, for a variety of number densities of nucleation sites. As expected, an increase in the nucleation site density results in finer (nanometre-scale) particles. The site density can be increased using thermo-mechanical processing in the γ domain. Buck and Garrison [6] obtained a uniform dispersion of titanium carbides with an average size of 6.5 nm in a Fe-9.5Cr martensitic steel after austenitisation at 1300°C, plastic deformation at 700°C and isothermal treatment at 675°C; they claimed excellent creep properties. Similar thermo-mechanical treatments could be proposed for our steels reinforced by vanadium nitrides.

The fabrication route could be an important issue. Homogenisation at high temperature (1200°C) appears necessary to obtain a fine and homogeneous distribution of vanadium nitride particles in the matrix. At this temperature, the austenite grain size will probably be over 100 μm. Tantalum is known to restrain the grain size at high temperatures but tantalum nitride is thought to be detrimental to the impact properties at high nitrogen contents. Instead, it is hoped to refine the austenite grain size after elevated temperature heat-treatment by cold rolling followed by a standard normalisation at low temperature (just above Ac3) and a classical tempering.

5. Conclusions

This work has shown how thermodynamic calculations, kinetic theory and property models (neural networks) can be used to design martensitic steels which should have improved creep properties for fusion-reactor applications. Two alloys have been proposed, both with optimised vanadium and nitrogen contents and low Ni, Mn and Si concentrations. With these specifications, the neural network predicts a creep rupture stress close to 100 MPa for 100 000 hours at 650°C. This value appears ambitious and the transposition of theory into practice could present problems not yet identified. This work gives several useful trends which could be followed to optimise creep properties of martensitic steels for fusion applications. A similar approach with steels stabilised with other elements such as titanium or zirconium could also be attempted.

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Steel	V1	V2
Normalising temperature (°C) (1 hour followed by air quench)	1200	1200
Tempering temperature (°C) (1 hour followed by air quench)	750	750
C (wt.%)	0.1	0.1
Si	0.05	0.05
Mn	0.05	0.05
P	0.008	0.008
S	0.001	0.001
Cr	9	8
Mo	0	0
W	1.5	2.5
Ni	0.05	0.05
Cu	0	0
V	0.32	0.35
Nb	0	0
N	0.085	0.07
Al	0.007	0.007
B	0	0
Co	0	0
Ta	0	0
O	0.005	0.005
Re	0	0

Table 1: Set of input parameters in the neural network model of creep rupture strength.

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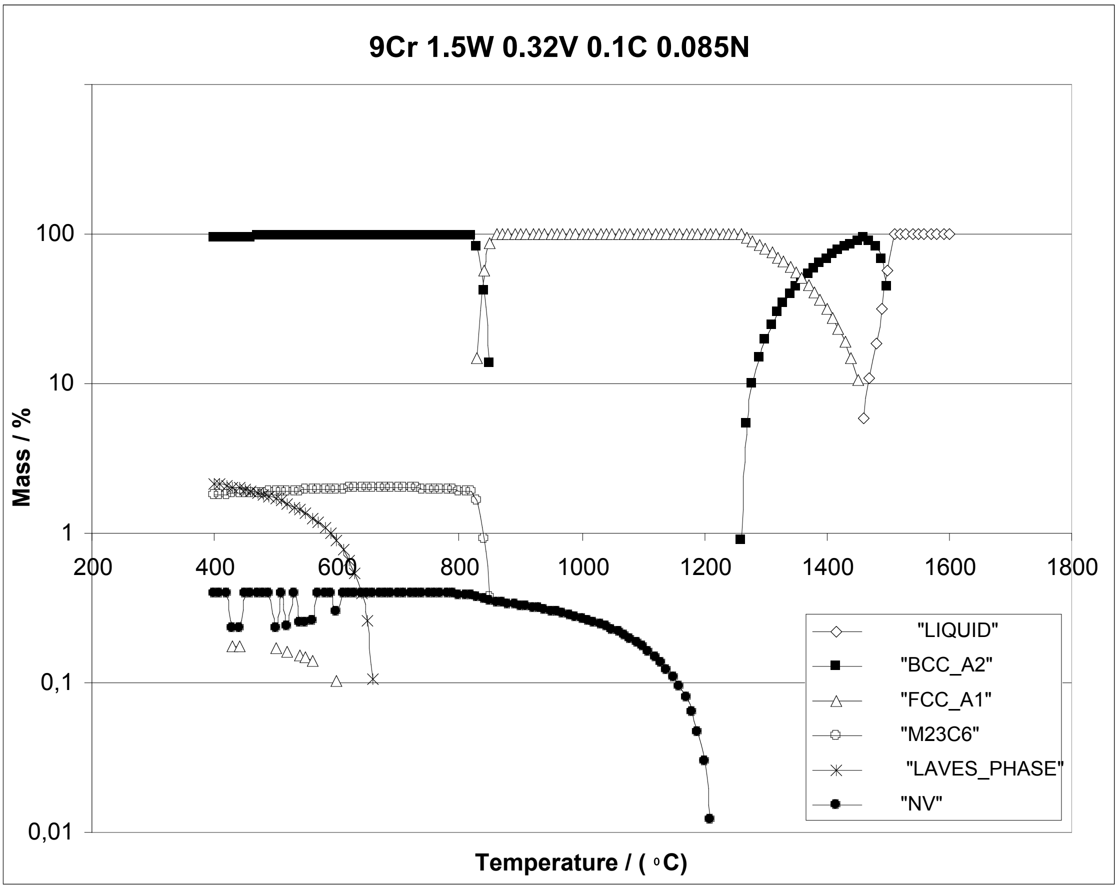

Figure 1 : Calculated equilibrium phase fractions for steel V1.

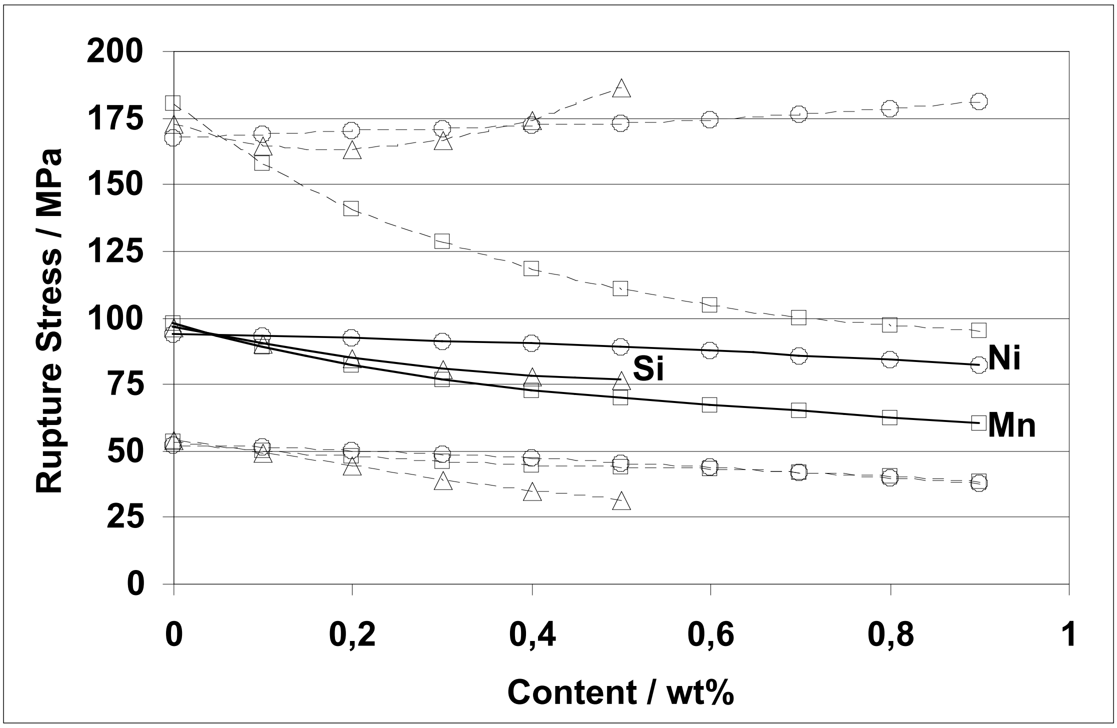

Figure 2: Effects of nickel, silicon and manganese on the calculated creep rupture strength of steel V2 at 650°C after 100 000 h. Solid lines represent the predictions and the error ranges are indicated by dashed lines with the same symbol.

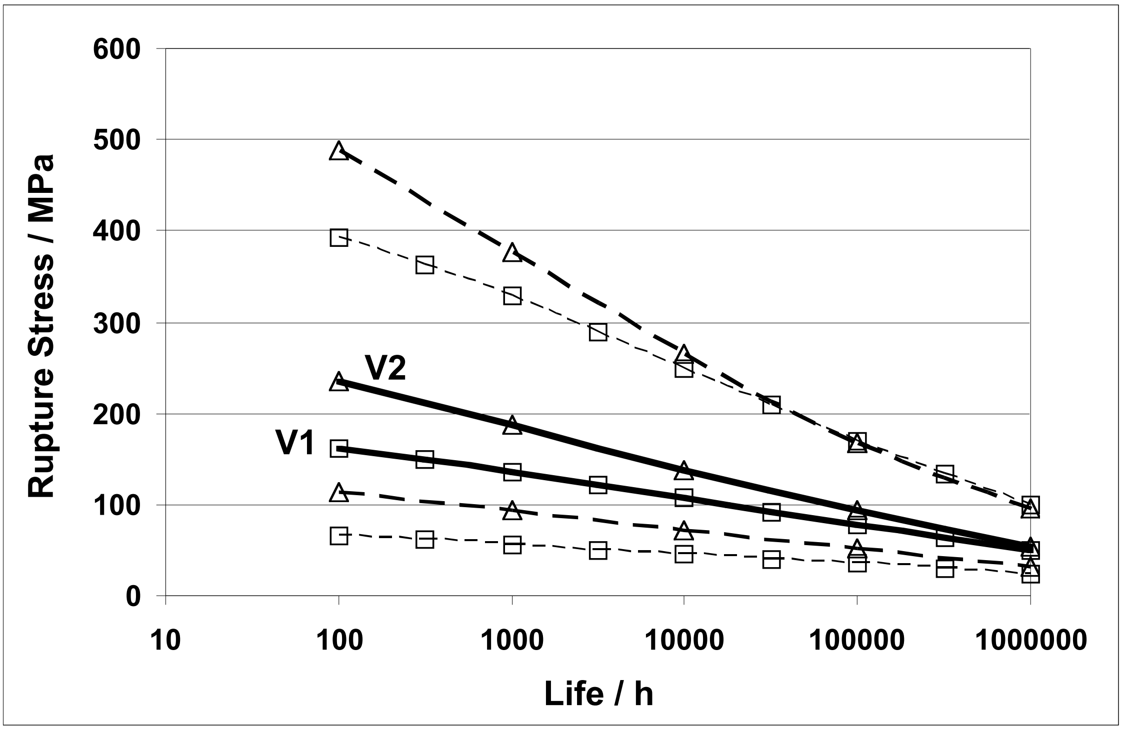

Figure 3: Predicted creep rupture strength of alloys V1 and V2 at 650°C.
The solid and dashed lines have the same meaning as in figure 2.

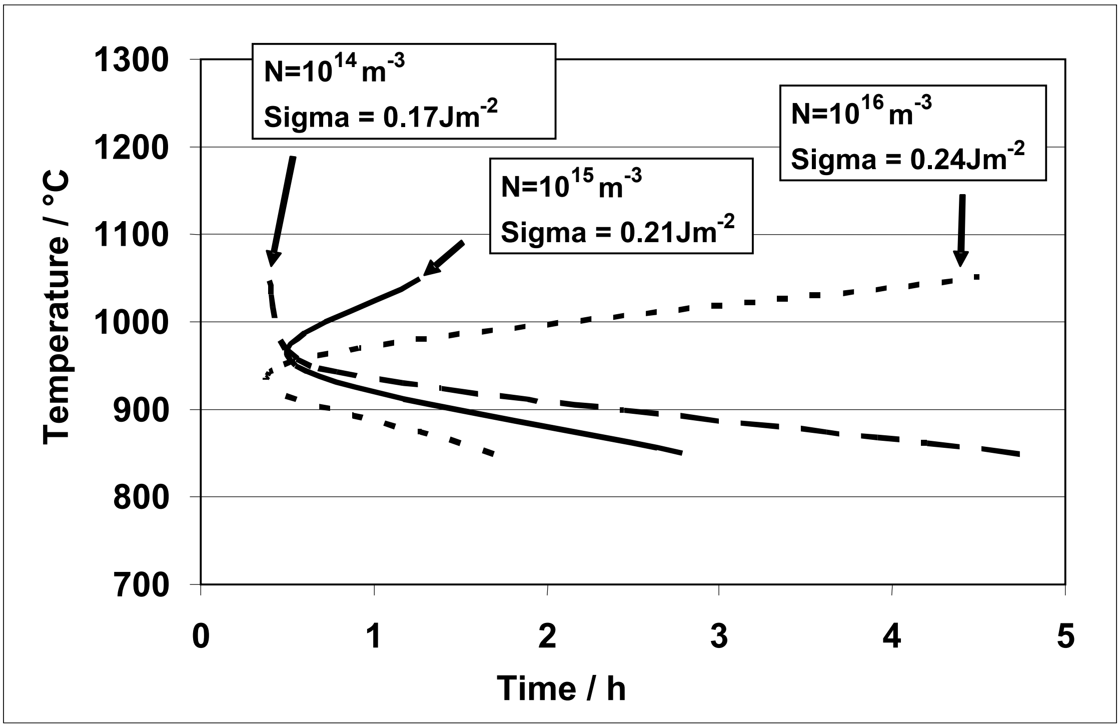

Figure 4: Calculated time-temperature-precipitation diagram for VN particles in V1 steel.

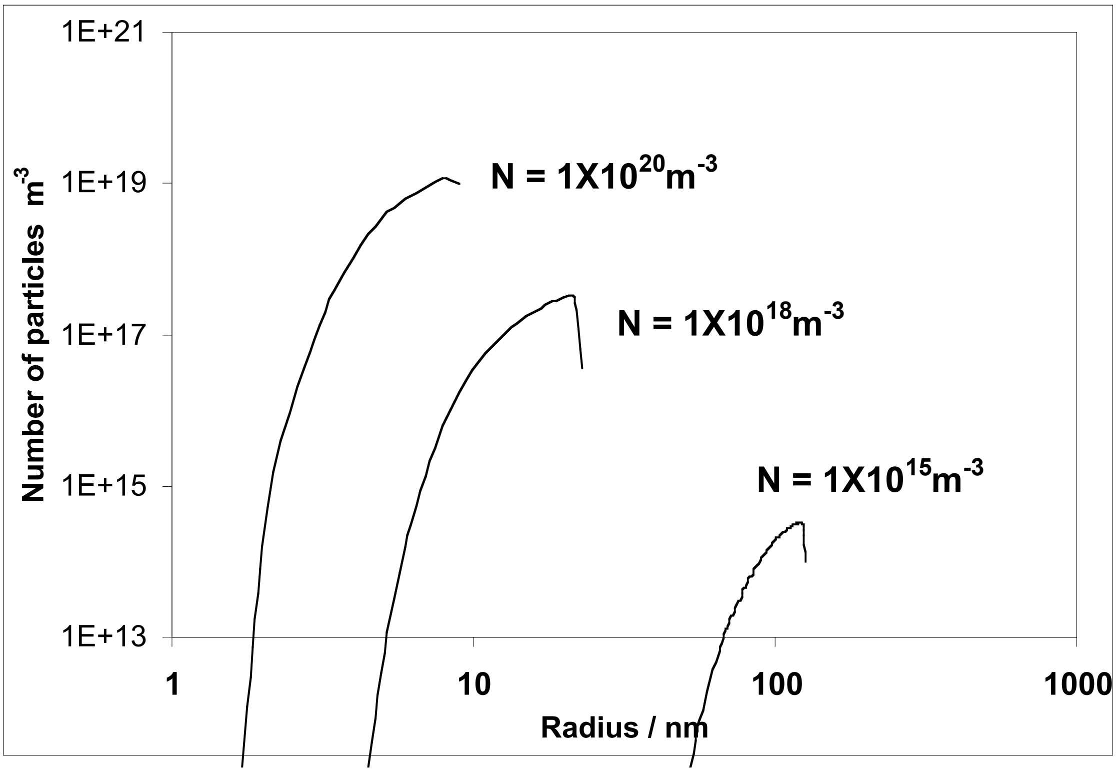

Figure 5: Calculated size distribution at 950°C of VN particles in V1 steel with various nucleation site densities. The interfacial energy used was 0.21 J m^{-3}.