1. Introduction

Since the 50’s the materials for large components in fossil fired power plants have been 9–12% chromium steels.\(^1\) The development of these steels, by alloying with new elements and improved heat treatment, has led to a large increase in creep strength.\(^2\) One of the most recent improvements has been achieved by cobalt alloying.\(^2–4\) A long time ago Speich et al.\(^5\) found that Co addition to a high Ni steel remarkably increased the resistance to tempering. The direct solution hardening effect of Co is probably small but Co is the only alloying element in steel that increases the Curie-temperature (\(T_C\)). It is well known that the ferromagnetic ordering of iron below \(T_C\) has a strong retarding effect of all diffusion processes.

In this report it is hypothesised that the improved tempering resistance caused by a Co addition stems from the increased ferromagnetic ordering yielding more sluggish diffusion. The purpose of the present work is to investigate this hypothesis further by simulations. All thermodynamical calculations are performed with Thermo-Calc\(^6\) and the SSOL\(^7\) database. The diffusion calculations are performed with DICTRA\(^8\) and the MOB2\(^9\) database.

The steel P92 is used to investigate the effect of Co and the effect both on tempering and under service conditions. This steel will probably not be alloyed with Co, but the steel is well known and the results will be representative for Cr steels. The steel P92 has the composition shown in Table 1. The microstructure of the steel consists of tempered lath martensite with precipitates both in the lath-boundaries and inside the laths. In the tempered condition \(\text{M}_{23}\text{C}_6\) (mainly \(\text{Cr}_{23}\text{C}_6\)) and MX (mainly VN) are present. The \(\text{M}_{23}\text{C}_6\)-particles are mostly in the lath-boundaries whereas the MX-particles are mostly inside the laths. At the service temperature large particles of Laves phase are also present.\(^10\)

2. The Curie-temperature

Close to and under the Curie-temperature the diffusion becomes more sluggish than if the material is paramagnetic. The effect yields a non-Arrhenian temperature dependence and the activation energy will vary with temperature. In Fig. 1 the activation energy for self-diffusion of iron in ferrite has been plotted as a function of inverse temperature. If the behaviour was Arrhenian the activation energy

Table 1. Chemical composition of the investigated steel P92 (mass%).

|   | Fe | Cr | Mn | Ni | Mo | W | V | Nb | C | B | N | Si | P |
|---|----|----|----|----|----|---|---|----|---|---|---|----|---|
| bal. | 8.96 | 0.46 | 0.06 | 0.47 | 1.84 | 0.20 | 0.07 | 0.11 | 0.001 | 0.05 | 0.04 | 0.008 |

Fig. 1. Activation energy, \(Q\), for Fe self-diffusion in pure Fe ferrite as a function of inverse temperature. Calculated from data in Ref. 11.)
would have been constant. The activation energy is almost two times larger at the Curie-temperature than in the paramagnetic state at high temperatures.\(^{11}\)

In order to investigate the effect of Co on the diffusion processes, the coarsening of M\(_{23}\)C\(_6\) in P92 will now be considered. Coarsening of M\(_{23}\)C\(_6\) and MX at 600°C and 650°C have been studied in Ref. 12). The experimental work involved energy filtered transmission electron microscopy (EFTEM) measurements.

The Curie-temperature of the ferritic matrix varies with its composition. All alloying elements except Co lower \(T_C\). In Fig. 2 \(T_C\) as a function of the Co content is shown both for the binary Fe–Co case and also for P92, equilibrated at two temperatures i.e. 600 and 770°C. At the lower temperature, where \(\text{M}_{23}\text{C}_6\), MX and Laves phase are stable, the amount of secondary phases is higher than at the higher temperature, where the Laves phase is not stable. Therefore, the amount of alloying elements in the ferrite is lower at 600°C yielding a higher \(T_C\). The Co content in the secondary phases is very low, e.g. for \(\text{M}_{23}\text{C}_6\) the calculated Co content is on the ppm level.

The direct effect of a Co addition on diffusion is shown in Fig. 3, where the calculated tracer diffusion coefficient of Cr and W in P92 has been plotted as a function of a Co addition. The tracer diffusion coefficient \((D^*\)\) is directly proportional to the mobility \((M)\) of the element A by means of Einstein relation, \(i.e.\)

\[
D^*_A = \frac{RTM_A}{\pi} \tag{1}
\]

From Fig. 3 it is evident that the tracer diffusion of Cr decreases with a factor two when the Co increases from 0 to 10 mass%. In Fig. 4 the tracer diffusion coefficient for Cr is plotted as function of temperature for P92 and with a Co addition of 10%. In the figure it can be noticed that the difference in diffusion coefficient with and without Co is largest close to \(T_C\). The largest effect of adding Co should thus be if the steel should be used just under \(T_C\).

### 3. Coarsening Simulations

The coarsening simulations were performed with the DICTRA\(^{8}\) software, which takes into account the full thermodynamic behaviour as well as the diffusional effects. The code is based on a numerical solution of the diffusion equations adopting local equilibrium at the phase interfaces. The coarsening model is based on the results of the Lifshitz and Slyozov\(^{13,14}\) and Wagner's\(^{15}\) theory that the largest particle is always 1.5 times the average particle size. The coarsening model together with comparison with experimental data for several different materials is described in Refs. 16 and 17).

For the conditions investigated so far, the model yields the same form of the evolution law as the classical treatment, \(i.e.\)

\[
r^3 - r_0^3 = kt \tag{2}
\]

where \(r_0\) is the mean initial particle radius and \(r\) the mean particle radius after \(t\) sec. The parameter \(k\) will hereafter be called the coarsening rate and given in \(m^3/s\).
The coarsening simulations for $\text{M}_2\text{C}_6$ were made taking the most important elements: Fe, C, Cr, Mo, W and Co into account. As already mentioned, the thermodynamic database SSOL and the mobility database MOB2 were used in all simulations. The mobility of Mo in Fe was, however, adjusted by help from Engström. The corrections were made because the coarsening rate for $\text{M}_2\text{C}_6$ was too large compared to experimental data in Ref. 12). In the simulations the matrix of tempered martensite will be approximated as ferrite. This assumption is however reasonable especially in the later stages of tempering. The uncertainty in the simulations essentially stems from deficiencies in the databases, both the thermodynamic and the mobility database. The accuracy of composition and temperature in the thermodynamic database is difficult to estimate and it depends on the range considered. The accuracy is probably lower in the mobility database due to the larger scatter in the original experimental data, which the database is based on. The uncertainty of diffusion coefficients could very well be as large as a factor 2.

4. Results and Discussion

Coarsening of $\text{M}_2\text{C}_6$ was simulated in Ref. 12) and compared with experimental data at 600 and 650°C for P92. That steel is not alloyed with Co. In order to investigate the influence of a Co addition coarsening during the tempering is also interesting. The investigated samples in Ref. 12) were tempered for 2 h at 770°C, but a common tempering temperature is also 750°C and thus simulations were also performed at that temperature.

The study in Ref. 12) was made on a tempered steel that was heat-treated at service temperatures. The first measurements were made after the tempering i.e. after 2 h at 770°C. To obtain a value on the initial radius for simulation of the coarsening process during tempering some different starting radii were tested in order to obtain a final radius after tempering of 46 nm. A value of the average initial radius of 27 nm gave a final radius after tempering close to the measured one and the value of the interfacial energy was chosen 0.5 J/m² in accordance with the same reference.

Simulations of coarsening of $\text{M}_2\text{C}_6$ were performed for 4 temperatures: 600, 650, 750 and 750°C with Co additions of 1, 2, 5 and 10 mass%. The simulations at 600 and 650°C were performed under the conditions that equilibrium amount of Laves phase has already formed and does not participate in the coarsening of $\text{M}_2\text{C}_6$. The same assumptions were made in Ref. 12) and there it was found that the difference compared with the simulations when Laves phase was not allowed to form was small. The calculated final average radius of $\text{M}_2\text{C}_6$ particles after 30 000 h at 650°C was 132 nm when the amount of Laves phase had formed to the equilibrium extent and only 7 nm larger when the Laves phase was not allowed to form. The value of the interfacial energy was set to 0.5 J/m². The simulations show that the difference is even lower at lower temperatures. In reality, the $\text{M}_2\text{C}_6$ coarsening should follow the curve when the Laves phase is not allowed to form in the early stages. Later, when more Laves phase forms, the coarsening rate will approach the curve assuming the equilibrium amount of Laves phase has formed. The Laves phase is fully precipitated after ca. 10 000 h according to Hätestrand and Andrén. At 740°C or higher temperatures the Laves phase is not stable and will not form.

In Fig. 5 and Table 2 the result of the simulations is shown as the coarsening rate, i.e. $k$ in Eq. (2). The difference in coarsening rate between P92 without Co and with the highest addition of 10% Co was close to a factor 2 at 600°C, 2.5 at 650°C and 3.7 at 750 and 770°C. An addition of only 1 mass% Co gives at all temperatures a difference in final particle radius of 10%.

The samples of the investigated steel were tempered for 2 h at 770°C but if the tempering temperature was 20°C lower, it would take close to 5 h to reach the same particle radius.

Another way to describe the result is to calculate the final radius of the $\text{M}_2\text{C}_6$ particles after long time use and take into account the coarsening at tempering. In Fig. 6 the final radius after 2 h at 770°C and 30 000 h (nearly 3.5 years) at 600 or 650°C is plotted. The final radius goes from 60 nm without Co down to 45 nm with an addition of 10% Co at 600°C. For 650°C the radius decreases from slightly over 130 nm down to just under 100 nm.

One way of visualising the strengthening effect caused by the particles is to consider the Orowan stress. The Orowan stress ($\tau$) is often written as:

$$\tau = \frac{Gb}{2\pi} \sqrt{I}$$

(3)
where $G$ is the shear modulus, $b$ is the Burger’s vector, $r$ the particle radius and $f$ the volume fraction of the secondary phase. In this case, where just Co is added, the shear modulus, Burger’s vector and the phase fraction could be regarded as almost constant and the Orowan stress is thus proportional to the inverse of the radius. In Fig. 7 the increase in Orowan stress after 30,000 h for P92 at 600 and 650°C respectively. The symbols show calculations and the dashed lines are drawn by hand.

There is also another effect to consider: according to Abe,\textsuperscript{21} the $M_23C_6$ retards the coarsening of the martensite lath structure. The growth of these laths or subgrains would be retarded by particles in the same way as grain growth is retarded by particles by Zener pinning.\textsuperscript{22} Written as an equation after Ref. 22), grain growth would stop when the average grain diameter, $D_m$, approaches:

$$D_m = \frac{8r}{9f} \text{.....................................(4)}$$

where $r$ is the particle radius and $f$ the volume fraction of the particles. Inserted in the Petch–Hall equation\textsuperscript{19)}

$$\tau = \tau_0 + \frac{c}{\sqrt{D_m}} \text{.............................(5)}$$

where $c$ is a constant, a decrease in particle radius of 30% would lead to a 20% increase in the last term of Eq. (5). It should be mentioned here, that the Petch–Hall equation is strictly valid for grain-boundary hardening and is here applied in martensite laths mainly because of its simplicity.

It thus seems likely that the combined effect of increased Orowan and Petch–Hall stresses due to more sluggish coarsening upon Co alloying could be of considerable technological importance.

There appears to be no direct experimental confirmation of the effect of Co on the rate of carbide coarsening. However, Speich \textit{et al.}\textsuperscript{4} reported that Co increases the tempering resistance in a steel with 10\% Ni, 2\% Cr, 1\% Mo and 0.12\% C. In that steel the yield strength after 1 h at room temperature was 1 100 MPa. Tempering during 1 h at 500°C caused alloy carbide precipitation and a secondary hardening effect resulting in a hardness which is higher the higher the Co content is. From their experimental data it is clear that the main effect of Co is to delay the drop in yield stress upon tempering. In the Co free steel 1 h tempering, right below the temperature where the secondary hardening effect becomes important, causes a 100 MPa drop in yield stress. The alloy with 8\% Co shows no drop at all after 1 h tempering at the same temperature. On the other hand, the secondary hardening effect does not depend very much on the Co addition. The reason is probably that at 500°C the coarsening is very slow even without Co and thus the drop in particle strengthening effect due to coarsening should be very small anyhow.

5. Conclusions

A possible effect of an addition of cobalt on particle coarsening and strength of a ferritic steel has been demonstrated with simulations with the DICTRA software. The simulations indicate that the effect should be important for Co-additions in the range of 10\% where the Orowan stress would increase with 30\%.

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