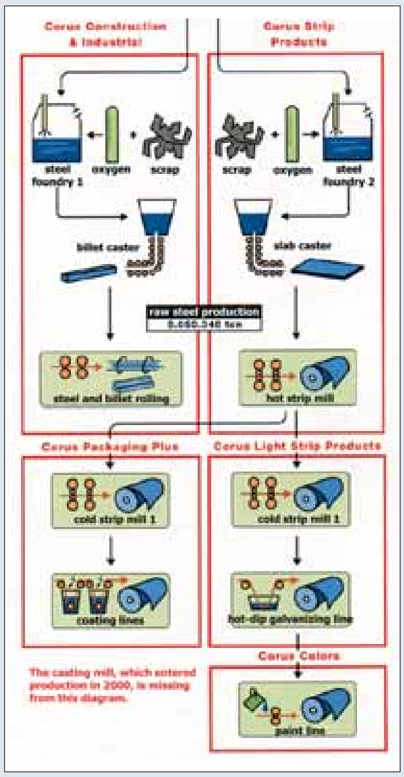
A ‘living’ material that does not easily reveal its secrets.

X-ray view of steel

At the Corus IJmuiden mills, steel at 1200 °C is rolled at high speed to the desired thickness in a number of steps, then cooled with water.

by ARNO SCHRAUWERS

Steel is a difficult material, or rather, it tends to guard its secrets jealously. At the Interfaculty Reactor Institute (IRI) and the subfaculty of Materials Science and Engineering at TU Delft, Dr. ir. Erik Offerman is doing his utmost to get to the bottom of this enigma. His endeavours even required the support of the synchrotron of the European Synchrotron Radiation Facility (ESRF) at Grenoble in France. Using an X-ray beam from this electron accelerator – which is about a billion times as strong as the types used in medical X-ray equipment – he managed to become the first person to actually observe the changes in steel as they took place, an achievement that got him into *Science* magazine. In the mean time, Offerman has developed a model that will enable him to explain the observations made at the synchrotron in Grenoble.



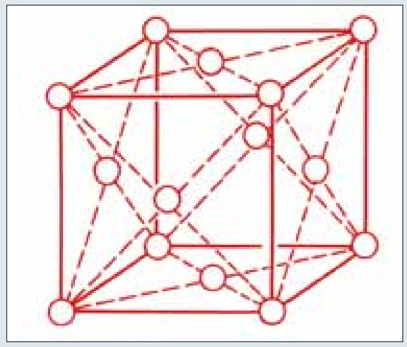
Schematic diagram of the steel production process at Corus IJmuiden that processes scrap metal into a range of end products.

Steel remains the most widely used structural material, with properties that make it a clear favourite for a wide range of applications. However, steel is also a difficult material. The reason for this is that steel is an alloy, an amalgam of various elements, with iron and carbon forming the basic ingredients. To a large extent, the properties of a steel alloy are determined by its microstructure, i.e. the way in which various crystals that make up the solid material are shaped and connected. These crystals can be seen through a microscope, where they present a rather complicated view. The size of each crystal depends on the alloy components and, more importantly, on the way the steel is cooled after the rolling process at high temperature. The components making up a steel alloy vary and can include manganese, silicon, aluminium, chromium, nickel, molybdenum, and phosphorous.

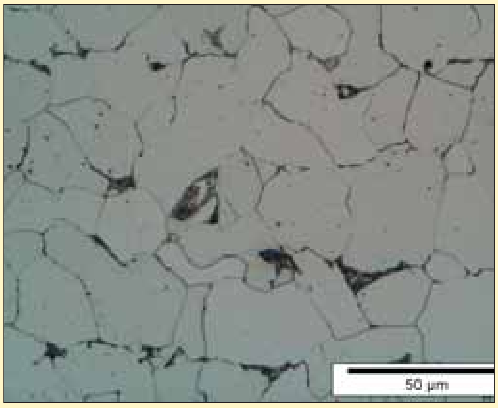
The microscopic structure of steel can occur in a number of different crystalline forms, the most important of which are austenite and ferrite, both of which are ductile. In addition there is pearlite, which is layered but strong, the needle-structured bainite, of intermediate hardness, and the strong but brittle phase called martensite. Not to worry, we are not about to embark on a course in crystallography. This is just a basic introduction to make Offerman's story easier to follow and to help you understand why the various forms of crystals in steel ultimately determine its uses.


(PHOTO: ERIK PEEKSTOK, DELFT)

Microscope view of austenite in pure iron. The image was obtained using a laser-scanning confocal microscope at a temperature of 1000 °C.

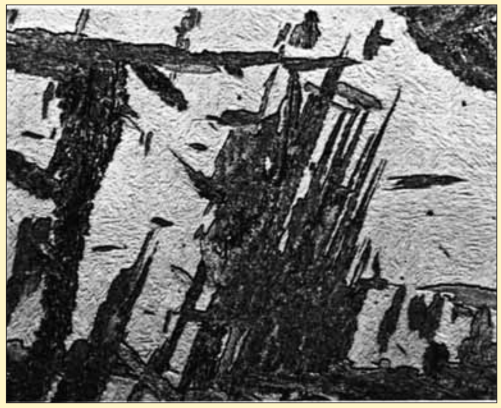


Crystal structure of austenite in pure iron. Austenite is stable at temperatures over 912 °C. The iron atoms are arranged in a regular pattern at the vertices and in the centres of the six surfaces of an imaginary cube. The structure is known as face-centred cubic.

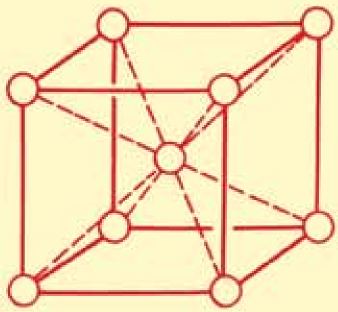


Optical microscope image of carbon steel at room temperature. The pale grey areas in the microstructure are ferrite crystals separated by crystal boundaries (the black lines). The large black areas are colonies of pearlite. The small black dots are impurities that are always present in commercial steel.


(PHOTO: TON DE HAAN, DELFT)



Optical microscope image of bainite (dark areas) at room temperature. Like pearlite, bainite is a composite of ferrite and cementite, but it has a totally different microstructure. Bainite consists of ferrite needles interspersed with cementite.

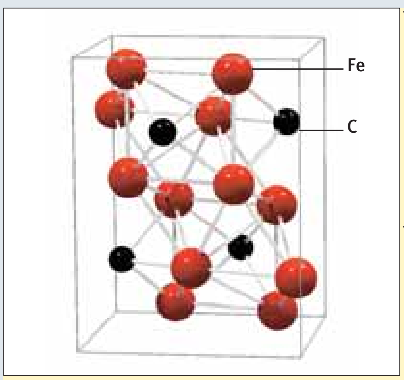


Crystal structure of ferrite. The iron atoms are arranged in a regular fashion at the vertices and at the centre of an imaginary cube. The structure is also referred to as body-centred cubic.

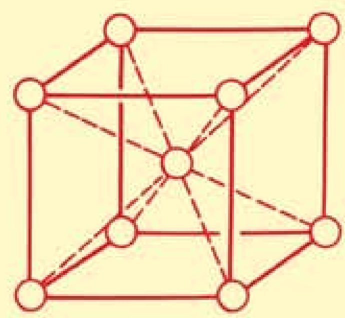
(middle above) Optical microscope image of practically pure perlitic steel at room temperature. The Pearlite structure consists of alternating layers of ferrite and cementite (Fe_3C).

BMW ¶ 'There is a trend towards producing types of steel that combine high strength with a high degree of formability,' says Offerman, who recently gained his doctorate with professor Dr. ir. Sybrand van der Zwaag, 'and in order to be able to control the manufacturing process, you need to know exactly how the crystals grow. The most important process in the production of steel is the transformation of austenite into ferrite, and to a lesser extent, into pearlite. At high temperatures, austenite takes the upper hand, but at room temperature you tend to get ferrite. The formation of new ferrite grains from existing austenite grains was the basis of my research project at ESRF. Steel with a high ferrite fraction forms the basis of most types of steel used in applications requiring high strength and formability, such as sheet metal for car bodies. In addition, there is austenitic steel, in which the austenite is stable at room temperature.'

The advantage of this is that austenite produces extremely strong yet highly formable types of steel. On the other hand, austenitic steel types are expensive because they require relatively large quantities of high-cost alloy elements. The industry is currently working on a cheaper alternative, TrIP steel (in which TrIP stands for Transformation Induced Plasticity). The composition of this type of steel is very similar to that of the cheapest carbon steel types, but special



(IMAGE: MARNIX WAGEMAKER, DELFT)



A colony of pearlite consists of two interwoven crystals, cementite (left) and ferrite.

heat treatments and the addition of aluminium, silicon, and phosphorous result in a special microstructure containing about 10 percent of residual austenite. The moment a piece of TrIP steel is deformed, the residual austenite is instantly transformed into martensite which increases the strength of the material and failure is delayed.

Offerman: 'This type of steel is of interest to upmarket car manufacturers, such as BMW. TrIP steel is first subjected to a special heat treatment in which the steel is heated to 800 °C, a temperature at which both austenite and ferrite co-exist. The material is then rapidly cooled to 400 °C, causing part of the austenite to be converted into bainite, while the rest of the austenite remains intact, even after cooling down to room temperature. The hard X-ray technique I have used to look at steel is eminently suitable for observing such processes as they take place. While my research so far has focused on the transition from austenite to ferrite, plans exist to take a look at bainite as well. The ultimate goal is to produce tailor made steel .'

Gun target ¶ So what about the actual research? During his research for his doctorate, Offerman looked at steel samples at various temperatures using X-rays from a synchrotron, which is a particle accelerator that can supply very high-intensity, very high-energy X-rays. Bombarding a steel sample with these hard type of X-rays from the synchrotron produces a plot – a spectrum – that looks like a target at a gun range. In this case the dots on the target aren't bullet holes, but provide information about the crystals that make up the steel sample. By zooming in on these holes, you can see the crystals grow and decay as it were. Once you really get to know the differences between austenite and ferrite, the method enables you to follow the nucleation and growth of ferrite crystals and the disappearance of the austenite crystals.

Put like this it all seems very simple, but Offerman and his fellow team members were the first people to ever observe these processes live. It has to be said though, that in order to be able to do so, Offerman worked in close cooperation with Dr. Henning Poulsen, Dr. Erik Lauridsen, Dr. Larry Margulies and Dr. Stephan Grigull, all staff at the Danish Risø National Laboratory research centre at Roskilde. They were the ones to develop the beam line of the synchrotron that Offerman used for his measurements. They also wrote many of the computer programs that process the experimental data into bite-size units.

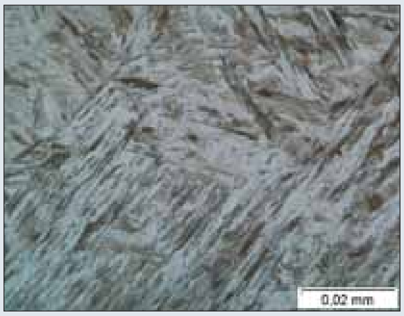
Models ¶ Yet another bit of theory about steel: in order to understand the transition from austenite into ferrite, it is essential to know that ferrite can contain less carbon than austenite. In other words, the crystal lattice of austenite offers a hundred times as much room for carbon as does the ferrite crystal. This is why, when ferrite is formed, carbon gets ejected from the ferrite grains, which is the preferred term among the researchers when they mean crystals.

Offerman distinguished four types of growth for the ferrite crystals, the occurrence of which depends to a large extent on the amount of ferrite already formed in the parent austenitic environment. The first type of growth is called as the Zener growth, named after professor Zener who as early as 1949 had indicated how the crystals grow as the temperature changes.

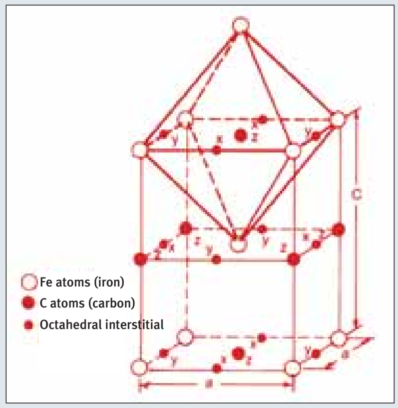
'In fact,' Offerman says, 'this type of growth occurs only in cases where no ferrite grains have formed in the direct vicinity. The second type of growth is one in which at one point ferrite grows on to become pearlite, which has a lamellar structure. We were the first group to make a live observation of this type of growth in three dimensions. The third type of growth is what we have named «retarded growth». The deviation from Zener's prediction is caused by the vicinity of other ferrite grains, all of which are trying to release their carbon. This slows down the nucleation of new ferrite grains.'

The fourth type of growth is what Offerman for want of a better word has named complex growth. In this process, the ferrite grains both grow and shrink. The live observations last year resulted in a publication in *Science* magazine.

Offerman: 'Even so, at the time we did not understand why these types of growth do not follow Zener's theory. We have now got to the stage where we have come up with suitable explanations for these phenomena. I have created a model that describes three of the four growth types. The most important aspect of the model is that there is a transition from non-overlapping to overlapping carbon fronts. This means that at the interface between austenite and ferrite, a carbon front is created on the austenite side, which is pushed forward like a snow shovel. When such carbon fronts meet, the growth of ferrite is

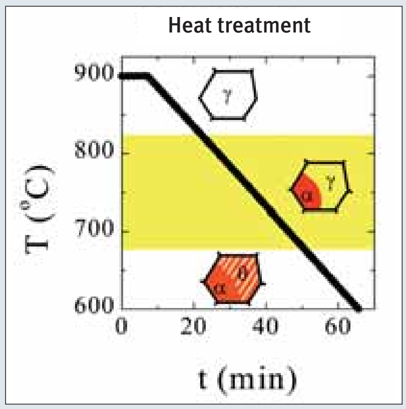


Optical microscope view of martensite at room temperature.



The crystal structure of martensite is very similar to that of ferrite. The difference is that the C-axis of the martensite crystal structure is elongated relative to the base plane (the A-axis) due to the formation process in the presence of carbon, which is frozen in the spaces between the relatively large iron atoms.

The production of steel wire at Fundia Nedsteel, Alblasserdam, in the vicinity of Rottrerdam



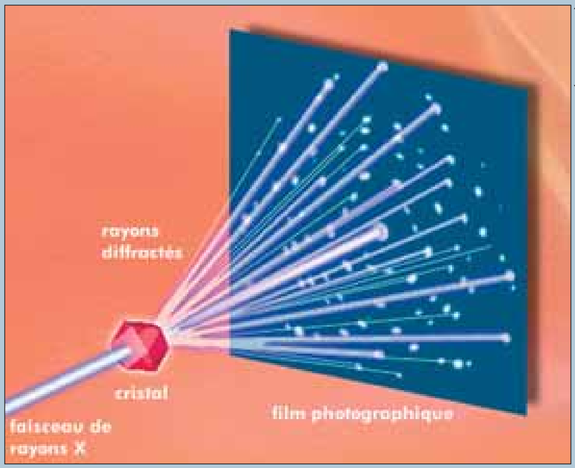
The cooling path of the carbon steel used for gathering the experimental data. The stable crystal phases have been schematically indicated as a function of the temperature. From high to low temperature the following crystal structures are stable: face-centred cubic austenite (γ), cubic-spatial-centred ferrite (α), and orthorhombic cementite (θ). At low cooling rates, ferrite and pearlite are formed, at higher cooling rates bainite forms, and even higher cooling rates produce martensite.

Setup at the European Synchrotron Radiation Facility (ESRF) at Grenoble

(IMAGE: ESRF)

ESRF is located on a stretch of land encircled by the rivers Isère (left) and Drac (right). In the foreground is the circular synchrotron Offerman used for his experiments on red-hot steel.

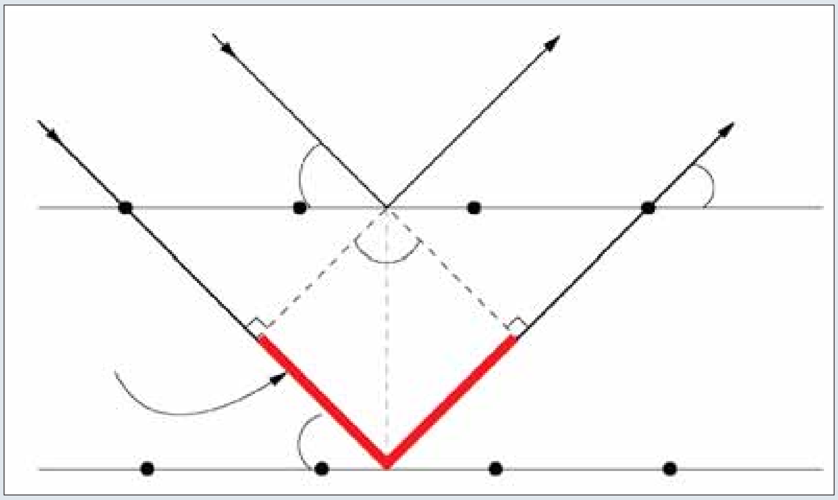
Schematic diagram of an X-ray diffraction experiment on a crystal. Radiation from a synchrotron (high-intensity X-ray radiation) strikes a crystal and becomes diffracted. The diffracted radiation is collected on a detector (a CCD camera) as a pattern of dots which is made visible on a PC display.



(IMAGE: ESRF)

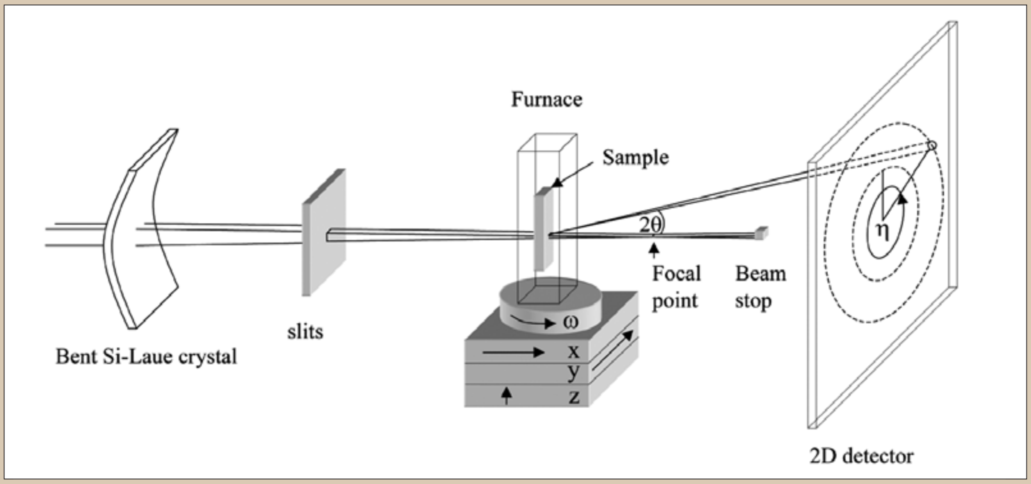
retarded. At that point, the process deviates from Zener's theory. By the way, the fourth type of growth also deviates from Zener's theory.'
This was something he did not find out until he returned from Grenoble to process the experimental data at the IRI.
Offerman: 'During the experiments at the ESRF institute we were unable to see that the cooling phase between 800 °C and 600 °C showed an oscillation in the growth of some ferrite grains. This was something I did not find out until I looked at the data back at the IRI. There are two possible explanations. The oscillation either is the result of local retransformations into austenite caused by temperature fluctuations, or it is caused by the increasing number of ferrite grains competing for the same space, a process in which the surface tension of the colliding ferrite particles plays a major role. The latter explanation would seem to be a better fit with what is actually happening, for we also looked into the disappearance of the austenite grains. We saw that the first three types of ferrite growth also occur in austenite; the fourth type does not. This makes the second theory, the one with the competing ferrite grains, more likely. The great thing about the model we are using is that we can model both the disappearance of austenite and the growth of the first three types of ferrite.'

Modified models ¶ The Delft researcher has not reached the end of the road yet. Far from it.
Offerman: 'The traditional models describe the average transformation behaviour, whereas a realistic model includes the local conditions. The growth behaviour of the ferrite turns out to be strongly dependent on the local carbon



Schematic diagram of the principle of X-ray diffraction on a crystal. At the atomic level, a crystal consists of a regular arrangement of atoms (represented here by spheres). As the X-rays (the arrows) enter the crystal and are reflected at various depths inside the crystal by the crystal planes, constructive interference of the X-rays occurs if the differences in the length travelled by the rays (red) is equal to a full number of wavelengths of the X-ray radiation.

Schematic diagram of the three-dimensional X-ray diffraction microscope used for the experiments at the ESRF. A 'white' beam of X-rays from the synchrotron, comprising a wide spectrum of wavelengths, strikes a curved silicon Laue crystal. This selects the desired 0.0155 nm wavelength and focuses the X-ray beam. A diaphragm then sets the beam size of 0.1 x 0.1 mm. The steel sample is in a furnace. To prevent detector burn-in, the centre beam is stopped by a piece of lead. The diffracted radiation is collected by a 2-D detector (a CCD camera). To date, this is the only method that has allowed the inner workings of steel at high temperatures to be observed *live*.



concentration and the number of neighbouring ferrite nuclei. If the local carbon concentration is low, with only a few ferrite nuclei nearby, the ferrite grain will be able to grow rapidly because the carbon fronts take longer to meet up.
Most models start with a single austenite grain, and assume that the carbon remains inside it during the transformation to ferrite. We have now seen that in fact this is not the case. In order to obtain a realistic description of the development of the microstructure during the transformation, the models will have to be modified. My experimental data also show that the austenite crystals tend to be rather unstable during the cooling process. It turned out that right up to the transformation to ferrite some austenite grains will increase in size while others decrease. This knowledge should also be included in the further development of models. As it happens, I am writing a paper on the subject.'

Buttons ¶ And so life as a researcher continues, with Offerman having processed only about 5% of his 100 GB of data. Even so, the processing of his data has gained momentum by now.
'I have set up a framework to process the data, and this allows me to process the data much faster than I could at the start.'
So what is the practical application of this knowledge? Where are the buttons that steel manufacturers can push to have the mills turn out the right type of steel without too much alchemy and experimentation? Isn't that what this is all about?
Offerman reassures us: 'I'm working on making these buttons as we speak. Corus, Fundia Nedsteel, SKF, and STW are paying for my first year as a postdoc to further analyse the data. During my doctorate research I had to report to my backers a couple of times a year, and they were very interested. Of course, having an article published in *Science* magazine is fantastic, but in my opinion the real proof of research is to have the results applied in the real world. The models I have developed will be particularly helpful in getting a better grip on the production process.'
As part of the Veni, Vidi, Vinci programme of the Dutch research council NWO, Offerman has been offered a Veni grant to continue his efforts to unravel even more of the steel enigma. n

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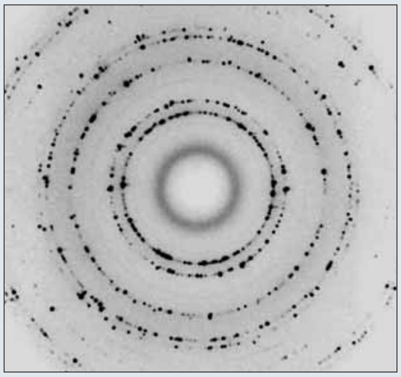
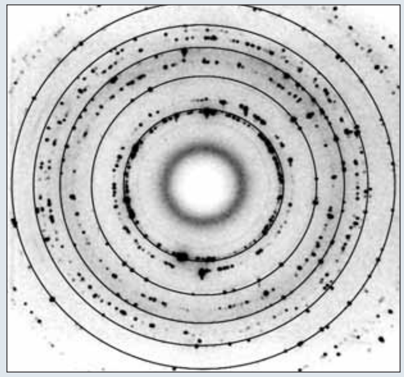
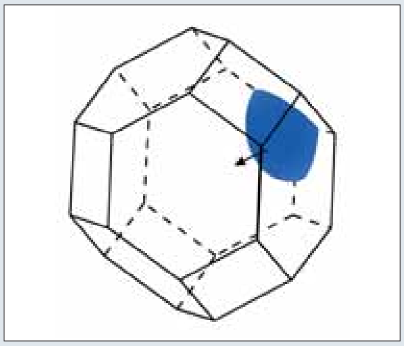


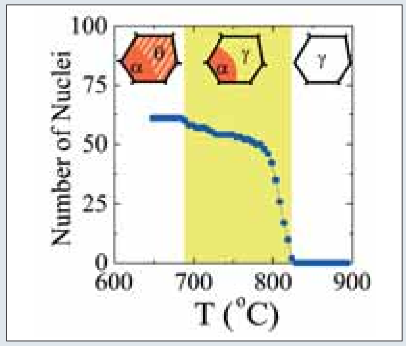
Diffraction pattern of austenite. At temperatures around 900 °C, austenite is the stable phase in the carbon steel used. The dots on the detector are all the result of the diffraction of the X-rays by individual austenite crystals within the steel sample. The size of an individual crystal can be deduced from the intensity of the dots, since a large crystal will diffract more X-rays and thus produce a higher intensity.



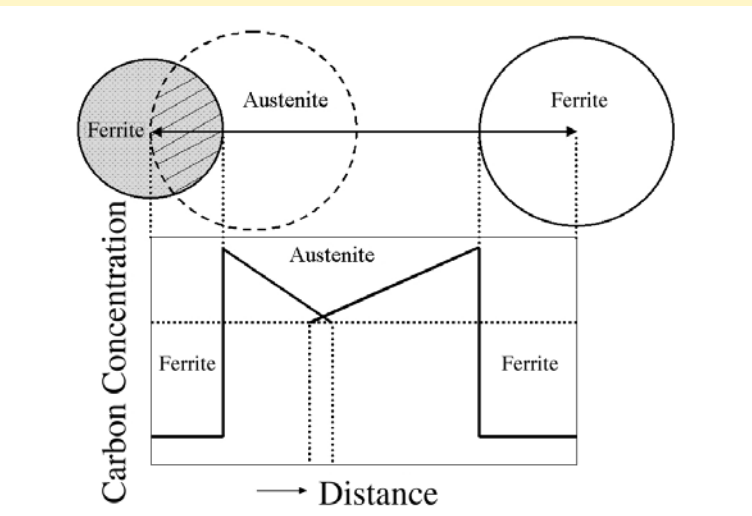
Diffraction pattern of austenite and ferrite. As the steel sample cools, the austenite crystal structure is transformed into ferrite, causing additional dots to appear on the detector (the dots on the circles). This enables the observer to see live when a crystal of the new ferrite phase is being produced. The growth of the crystal can subsequently be determined by making a film of a large number of diffraction patterns and converting the intensity of a dot into crystal size.



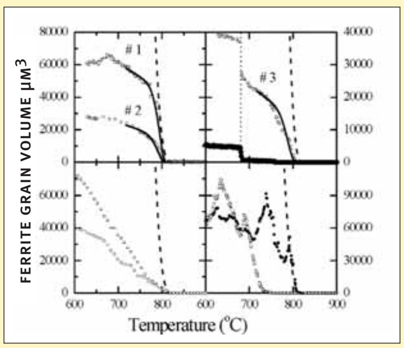
Schematic diagram of an austenite crystal with a ferrite crystal growing inside it. By preference, the crystal will start to grow on one of the corners of the austenite crystal, since that is the optimum location energy-wise.



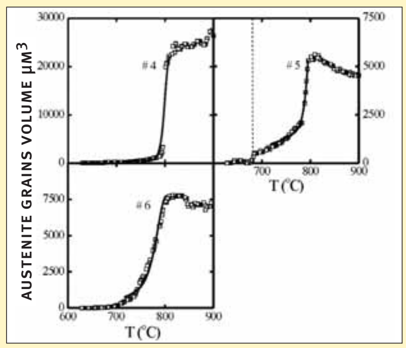
The number of ferrite nuclei measured in carbon steel that was cooled in one hour from 900 °C down to 600 °C. Offerman's measurements show that the activation energy required to produce ferrite crystals is at least a hundred times less than previously assumed. This knowledge is of crucial importance for modelling phase transformations in steel.



Schematic representation of the model used by Offerman to predict the growth of ferrite in austenite. Austenite can contain up to 2% carbon, whereas ferrite can contain only 0.02 %, one hundred times less. Therefore, as the ferrite grows, the carbon has to be pushed out in front of the ferrite crystals, which slows down the rate of growth. The growth is retarded even more by the presence of nearby ferrite grains that also try to get rid of their carbon. At a certain point, a situation occurs in which the carbon fields start to overlap.



The volume of individual ferrite crystals as a function of the temperature during the cooling process. Four types of ferrite are distinguished, the last two of which were discovered by Offerman: growth in which a transition takes place from isolated carbon fields to overlapping carbon fields, growth in which the ferrite continues to grow into pearlite at 685 °C, retarded ferrite growth due to the direct overlap of carbon fields, and oscillating ferrite growth. The broken line indicates Zener's classic growth theory, while the solid lines show the new model.



The disappearance of individual austenite crystals. Inevitably, the growth of ferrite causes the disappearance of austenite crystals. Within the disappearing austenite, although the first three types of ferrite growth (see previous illustration) can be detected, the fourth type cannot. The disappearance of the austenite leads to the conclusion that carbon atoms are being exchanged between different austenite crystals.