



Overview of Major Steels

4. Scientific Steels

General Remarks

Advanced

When I was born in 1949 steelmakers and related scientists knew very well how a "plain" carbon steel, always containing some manganese and silicon from the "killing", would behave "strength-wise" after some thermal treatment. They got that knowledge from scores of measurements. They also had all kinds of scientific tools like phase diagrams, diffusion constants, temperature-time-transformation (TTT) diagrams and much other paraphilia of the trade. Some of that stuff they could even calculate, at least in principle.

Nevertheless, there were white spots on the steel map. The exact structure of "bainite", for example, wasn't clear; even today (2013) not all question to this topic have been answered. The concept of plastic deformation by [dislocation movement](#) and how it affected the mechanical properties was clear in principle to scientists but it had not yet trickled down to steelmakers. The inner working of things like [creep](#) and [fatigue](#), while known phenomena, was not really clear to anybody.

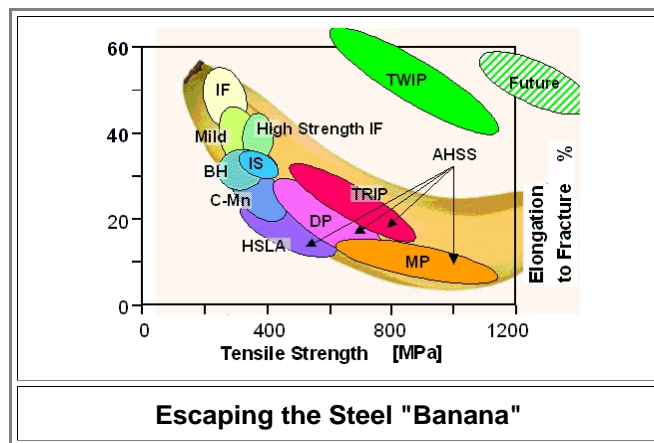
That changed bit by bit in the second half of the 20th century. Most everything became clear *in principle*. It even became clear how one could "calculate" steel (and everything else). That means that one could write down the relevant equations. The problem was in solving those equations. You just couldn't do that with paper and pencil within a reasonable time. You only could do that with computers.

Well, we did invent computers and a lot could now be done by using them - even with the early ones. The first big science job that involved computer work was the making of the atomic bomb around 1943. Atomic bombs, however, are extremely simple things compared to steel. In terms of number-crunching power modern computers compare to the 1950 ones like the heat of an atomic bomb to that of a match - but it is still insufficient power to calculate something as simple as the melting point of iron with sufficient precision. I guess if we silicon guys continue to work as well as we did in the last 40 years, it won't take much longer before we get that covered, too.

Be that as it may, computing power in the last 20 years was already good enough to trigger another revolution in steel making. Let me illustrate this with a quote. In 2004, Georg **Frommeyer** from the German Max-Planck-Institute for Iron Research, one of the pioneers of "science" steels, said:

*"A few years ago, the steel insiders assumed that the properties of steel had all been pretty much optimized by existing alloying technique. However, **based on theory**, our group was convinced that one could go much further".*

That's what they did. They went much further and developed "**Twinning Induced Plasticity**" or **TWIP** steels, belonging to what is now called **HSD** or **High strength and ductility** steel. And it isn't over yet.



All steels until let's say 1980 were either very ductile or very hard but never both. Plotting [ductility](#) (measured as maximal elongation before fracture) versus [yield strength](#) (or [hardness](#)) gives the **steel "banana"**. No matter how much tricky engineering you put into your steel, if it was hard it wasn't very ductile - and that includes the highly sophisticated steels developed not so long ago dealt with in the preceding modules.

Now look at TWIP steels! For the same hardness as any of the "banana" steels, it's ductility is about three times as large. Considering that there are hundreds if not thousands of different steel types in the banana, and that large numbers of smart people have tried to get out of the banana for 100 years or longer, HSD steel is quite an achievement.

- What's more, it is not the end of new "scientific" steels, but the beginning. Ultrahard steels with ductilities beating those of soft iron or gold are just around the corner. Think of it this way: A sword made from that kind of steel is harder in all of its body than the cutting edge of the best katanas or wootz blades. It is incredibly elastic: Not only can you bend it into a semicircle without breaking it, you can make a complete circle. And when you keep bending, it still won't break but wind into a spiral by plastic deformation.

So what is the scientific principle behind those HSD or "super steels"? Read on.

Transformation-Induced Plasticity (TRIP) Steels

The first "scientific" steels starting the *High strength and ductility* class were the TRIP steels. They consist of "many" or complex "phases": ferrite, retained austenite, bainite and martensite. Some people actually count TRIP steel among the dual phase or complex phase steels.

TRIP steels are generally low carbon steels containing some γ stabilizers like nickel (Ni), manganese (Mn) and cobalt (Co) that lower the $\gamma \Rightarrow \alpha$ temperature (**A₁**) and thus enable to keep some austenite stable down to room temperature,

- The TRIP trick, however, is produced by adding sizeable amounts of (cheap) silicon (Si) and aluminum (Al). These elements cause and control the *transformation-induced plasticity* by enabling *strain*-induced martensite formation. This is a different thing from *stress*-induced martensite formation that you get by quenching. It is a kind of new work-hardening effect and indeed, TRIP steels may get much harder upon deformation.
- Of course, making TRIP steel demands precise processing. Similar to the principles of dual phase steel you might start with intercritical annealing to provide for a well-developed ferrite / austenite structure. Then you cool with a (relatively large) rate to a temperature that leads to bainite formation and stay there a while, doing "austempering". Then quench to room temperature but without forming much martensite. Of course, as soon as this works, you try to get the proper structure in easier and cheaper ways.

You notice that I was avoiding the big why question so far: 1. *Why* does this structure work so well? 2. *Why* does *strain* induce martensite formation?

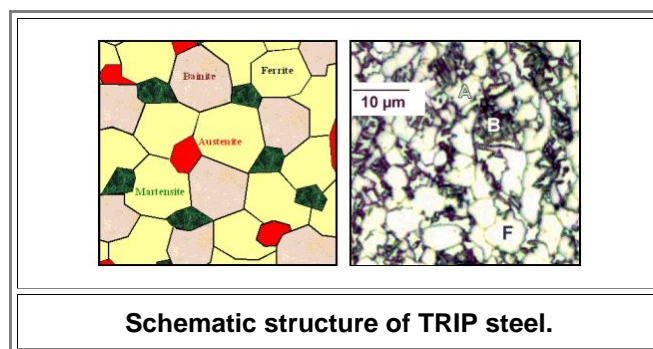
- The answer to the *first* question is: Look up dual phase steel and why they work so well. The same basic principles you find there also apply to TRIP steel - except that the amount of martensite increases with deformation, leading to more pronounced work hardening, and that the bainite and the small carbides / nitrides that are also in there provide for some additional hardness right away. Look at the comparison of stress-strain curves to see the point.

The answer to the second question is simple: I don't know. Martensite formation is a tricky business in just "plain carbon" steel, and under what kind of conditions it might occur in complex structures is not something explained in a few lines.

Let me just give you some ideas about what all those alloy elements do:

- Manganese (Mn), Nickel (Ni), cobalt (Co), and others stabilize the austenite so retained austenite can be formed.
- Carbon is used in somewhat higher quantities than in **DP** steels to enable the retained austenite to transform to martensite during deformation. The level of carbon determines if the transformation starts at small strains (low level) or high strains (higher level).
- Relatively high concentrations of silicon and/or aluminium accelerate the ferrite formation and retard cementite formation in the "bainite". This forces the carbon into the still present austenite and keeps it there.

- What the structure of TRIP steels might look like is shown below. On the left is a schematic structure after some deformation and thus martensite formation; on the right a real structure before deformation is shown..



Schematic structure of TRIP steel.

- By now there is a large variety of TRIP steels with a broad range of compositions. Typically, the concentration of alloying elements is low with a sum total of no more than around 3.5 %. Here is an example:

C	Mn	Si	P	S	Cr	Ni	Cu	Al	Si	Nb	Ti
0.19	1.45	1.9	0.02	0.07	0.07	0.03	0.04	0.02	0.003		
0.55	0.59	1.35	0.015	0.010	0.59	0.07	0.13	0.027	1.35		
0.24	1.55	0.87	0.010	0.004						0.034	0.023

Randomly collected compositions of some TRIP steels.

● The carbon concentration is critical; it determines to some extent the concentration of the other elements and how to process the mess. As much carbon as possible should remain in the austenite. While higher concentrations - up to and exceeding 0.4 % - might be good for mechanical properties, they are bad for [weldability](#) and that's why commercial TRIP steels usually employ carbon concentrations around 0.20 % – 0.25 wt.% or less.

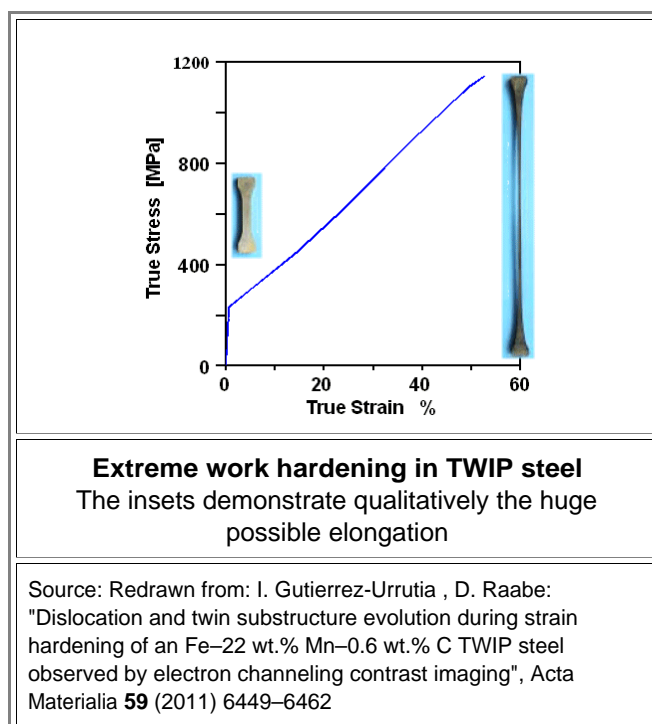
▸ All things considered, one conclusion is now unavoidable: When you go into TRIP steels, you definitely need to know what you are doing. You are well on the way to making **scientific steels!**

"Twinning Induced Plasticity" or TWIP Steels

▸ While TRIP steels might be seen by the sceptics as just a somewhat improved dual phase steel, TWIP steels are not. They are unique. They are definitely scientific steels from the very beginning (see above) *and* they are not just evolutionary improvements of existing steels but stick out from the crowd like a physicist in his normal attire from a gaggle of fashion models.

The big trick for making extremely hard *and* extremely ductile TWIP steel is to provide for **twinning** as the major mode of deformation. I have dealt with [twinning as a deformation mode](#) before; it can be seen as somewhere between the normal deformation via dislocations and violent deformation by martensite formation.

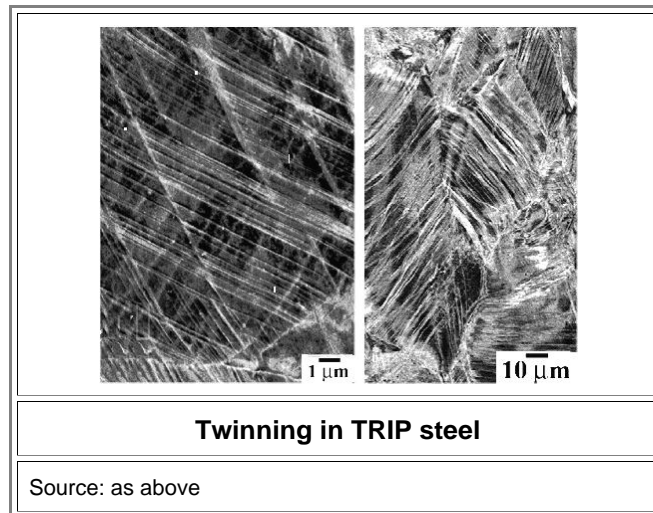
What it does is to provide for more grain boundaries as the deformation proceeds. Essentially low-energy [twin boundaries](#), but grain boundaries nonetheless. And more grain boundaries make deformation more difficult - we have [grain-size hardening](#). So, as in TRIP steel, we may have substantial work-hardening as we deform the steel, just more so:



● This is just one example. You also can get flatter curves, starting at higher yield strengths or hardness.

▸ TWIP steels are always austenitic [high alloy steels](#) with lots of manganese as major alloying element. The steel in the figure above, for example, essentially contains 22 wt.% Mn and 0.6 wt.% C. One could argue that good old [Hadfield's steel](#) was a precursor to TWIP steels. But there are many special and optimized TWIP compositions, containing, e.g., in addition to the manganese some % of silicon and substantial amounts of aluminum.

- Things are not quite that easy, however. There is a continuous transition from TRIP to TWIP as you alloy more and more manganese, it seems. Since manganese is a [γ stabilizer](#), with increasing Manganese concentration you get more and more retained austenite until eventually all is austenite. Then you run into a kind of double-TRIP behavior, where two kinds of martensites are formed: first a new hexagonal kind, and then the normal cubic / tetragonal one. Twinning as deformation mechanism comes next, followed eventually by the formation of what is called "micro-banding", something related to the much coarser [Lüders band](#) formation. A decisive role is played by our old and long since forgotten friend, the [stacking fault](#). The stacking fault *energy* changes with alloying, and its value determines to some amount which deformation mechanisms are prevalent. Here are two pictures demonstrating the heavy twinning you find in TWIP steels:



- We are looking with a [scanning electron microscope](#) on, and in particular *below*, the surface of the steel (very tricky; you don't want to know about how this is done). The bright lines denote twinning. The vague cloudy structures in the background of the left-hand picture, all extending from the lower left to the upper right, result from bunched-up dislocations.

So why? Why is all this happening and why does it allow such amazingly large deformations? Well - I don't know. You must go far deeper into steel science than I intend to do at this point. I've stated that *scientists* almost understand the science of steel by now. I haven't said this includes *me* or that it would be easy!

- In very simple terms, the trick is to have more than one deformation mechanism. When dislocations are finally stuck and no more plastic deformation would be possible, twinning takes over, and so on. But that is just a hand-waving argument. If you need to know more, read the article!

[Article Link](#)

**TWIP
Steel**

The Future

What kinds of steel will the future bring? Who knows. It is rather likely, however, that we will get more "super" steels and more steels that are precision-tailored to the needs of some specific applications. After all, we have hardly scratched the surface of what is possible when you alloy 4, 5, 6, .. elements to iron in some specific concentrations followed by some specific processing. The number of possible variants is not far from infinity. Once more the [first law of practical science](#) applies!

- For a taste treat of what might be around the corner, I give you the ([augmented](#)) abstracts of three papers I happened to run across:

Concept for the design of Maraging-TRIP steels

Prof. Dr. D. Raabe

Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Advanced high strength steels can be designed via stimulating athermal transformations during deformation such as martensite formation or twinning in unstable austenite, or, alternatively, by introducing nanoscale precipitates. The first types of steels are referred to as TRIP and TWIP steels and the latter ones as maraging or nano-precipitate steels (TRIP: transformation-induced plasticity; TWIP: twinning-induced plasticity; maraging: martensite aging through thermally stimulated precipitation of particles).

In an effort to exploit both effects for obtaining improved strain hardening, namely, athermal transformations and precipitates, we *designed* a novel class of materials that we call *maraging-TRIP steels*. These are precipitation-hardened ductile high-strength austenitic-martensitic TRIP steels with up to *1.5 GPa* strength and total elongations between *15% and 20%*. The alloys have a low carbon content (0.01 wt.% C), (9-15) wt.% Mn for designing different levels of retained austenite volume fraction and stability, and minor additions of Ni, Al, Ti, and /

or Mo (1wt.% -2 wt.%). The latter elements are used to create precipitates in the martensite during aging. The nanostructure design of the material proceeds by homogenization in the austenitic phase followed by quenching. Depending on the Mn and Ni content the resulting microstructure is either fully martensitic (as in [conventional maraging steels](#)) or martensitic with some fraction of retained austenite. After quenching the material is heat treated at a temperature 100 K -150 K below the bulk re-austenitization temperature to create nanoparticles in the martensite (usually at 450°C).

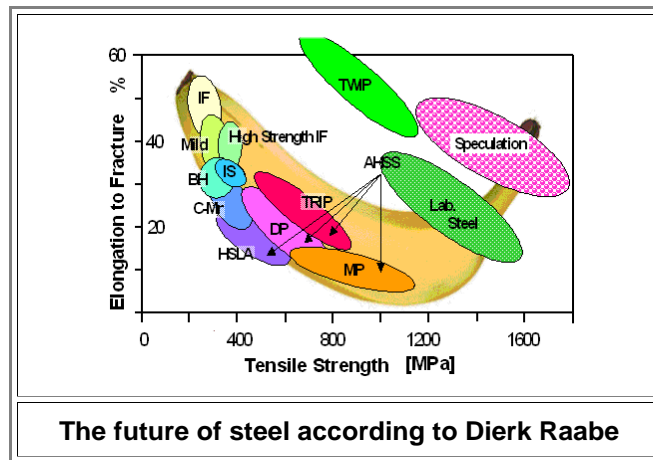
Upon loading, strain hardening in these materials is realized by combining the TRIP effect (of the unstable austenite) with particle hardening (of the martensite). More specific, the TRIP mechanism is here based on the deformation-stimulated athermal transformation of metastable austenite into nearly cubic martensite and the resulting matrix and martensite plasticity required for accommodating this transformation misfit. The maraging treatment is based on the hardening of the quenched-in martensite through the formation of small intermetallic precipitates [5-8]. The size of these particles is of the order of several nanometers as revealed by atom probe tomography, Fig. 1.

Interestingly, the atom probe analysis of retained austenite-to-martensite interfaces and also of Mn-decorated martensite grain boundaries revealed, that pronounced austenite reversion can take place during aging (e.g. at 450°C, 48 h for the specimen shown in Fig.1), i.e. far below bulk re-transformation to austenite. This means that during the martensite aging heat treatment both, precipitation in the martensite and austenite reversion take place. It is worth noting that the occurrence of two types of austenite with different stability (retained, reversed) leads to a broader deformation regime where the TRIP effect occurs. This mechanism seems to promote ductility. Hence, the combination of the various mechanisms pointed out above in the form of Fe-Mn maraging TRIP steels, namely, the precipitation hardening of martensite and the transformation-induced formation of martensite in both, retained and reversed austenite opens a novel and lean alloy path to the development of ultrahigh strength steels .

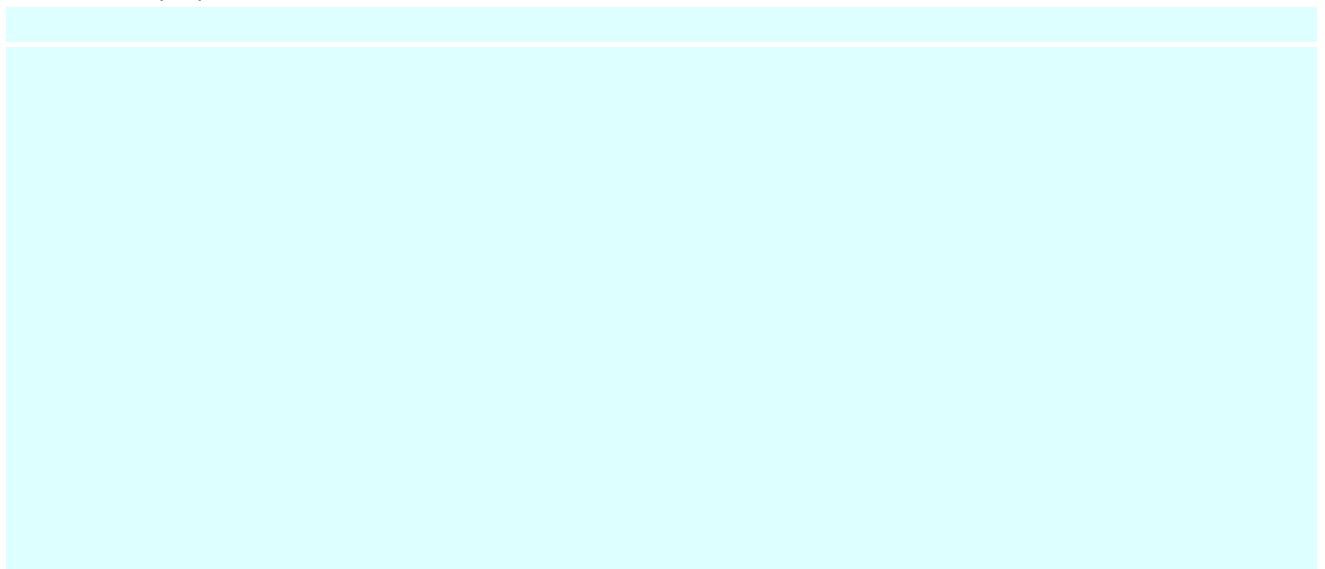
My colleague **Dierk Raabe** is a world-renowned expert for iron and steel (in contrast to me), and his [private website](#) is full of first-rate information, mostly in an easy-to-understand level.

Here is his view on the future of steel, distilled from the article above. I have drawn it into the [banana figure from above](#). Note the change in scale!

The "Lab Steel" denotes what he and his group have already made in the laboratory, the "Speculation Steel" is what they are going for.



Here is the abstract of a paper published in Nature Materials in 2002 (underlining by me) that shows that researchers start to calculate properties from scratch.



Letter abstract

Nature Materials 2, 25 - 28 (2003)
Published online: 15 December 2002 | doi:10.1038/nmat790

Subject Categories: [Metals and alloys](#) | [Computation, modelling and theory](#)

Stainless steel optimization from quantum mechanical calculations

Levente Vitos^{1,2}, Pavel A. Korzhavyi¹ & Börje Johansson^{1,3}

Alloy steel design has always faced a central problem: designing for a specific property very rarely produces a simultaneous significant improvement in other properties^{1,2}. For instance, it is difficult to design a material that combines high values of two of the most important mechanical characteristics of metals, hardness and ductility. Here we use the most recent quantum theories of random alloys³ to address a similar problem in the design of austenitic stainless steels, namely, to combine high mechanical characteristics with good resistance against localized corrosion. We show that an optimal combination of these basic properties can be achieved in alloys within the compositional range of commercial stainless steels. We predict, first, that Fe₅₃Cr₁₈Ni₂₄ alloys possess an intermediate hardness combined with improved ductility and excellent corrosion resistance, and, second, that osmium and iridium alloying additions will further improve the basic properties of this outstanding class of alloy steels.

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● Note that they suggest new kinds of alloying elements: Osmium (Os) and Iridium (Ir) - rather expensive stuff!

▀ A last one, showing that even "graph theory", not much used in Materials Science so far, may be able to make important contributions:

Graph theory and the passivity of binary alloys

E. McCafferty

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Corrosion Science, Volume 42, Issue 11, November 2000, Pages 1993–2011

Abstract

The passivity of a binary alloy is considered in terms of a network of –M–O–M– bridges in the oxide film, where M is the component of the binary alloy having the oxide of the lower free energy of formation. The structure of the oxide is represented by a mathematical graph, and graph theory is used to calculate the connectivity of the oxide, given by the product of the number of edges in the graph and the Randic index. A stochastic calculation is employed to insert ions of the second metal into the oxide film so as to disrupt the connectivity of the –M–O–M– network. This disruption occurs at a critical ionic concentration of the oxide film, which is then related to the concentration of alloying element in the metal alloy by means of experimental surface analysis data. The results of this analysis for Fe–Cr, Ni–Cr, Cu–Ni, and Fe–Si are each in good agreement with experimental observations.

▀ I rest my case.

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