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HISTORY OF THE HARDENING OF STEEL : SCIENCE AND TECHNOLOGY

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Abstract. - The knowledge of the hardening phenomenon was achieved through a very cumulative process without any discontinuity or 'scientific crisis'. The history of the hardening shows a definite interrelationship between technological approach (or the application-side) and academic science.

The hardening of steel appears to have been an operation in common use among the early Greeks. The Greek and Roman smiths knew, from experience, how to control the final properties of the steel by quenching. The lack of fundamental knowledge of the phenomenon did not prevent the artisans to test different quenching conditions and quenching agents. Quenching temperatures were derived from visual control of the surface colours, a method still in use during the first half of our century (1). During the Middle Ages and even thereafter there seems to have been a preference for using urine and biological liquids as quenching agents. Some of them contained nitrogen compounds (e.g. blood, excrements, urine) to improve the heat flow during the sudden cooling. Other organic nostrums such as mustard, vinegar, resin, honey and juice of leaves, might cause transitory deposits on the surface of the hot steel and thus delay cooling enough in order to avoid cracks. A lot of magic was involved in the quenching practice maybe in order to 'protect' the smith's profession. This explains the preference for using exotic nostrums as quenching agents such as dew of a May morning, juice from worms or snails, human blood, dragon's blood a.o. (2).

Older theories. - Academic science was not dealing with the hardening until the end of the 16th century. From then on there was a cumulative and continuous progression of the scientific knowledge of the quench-hardening.

At first hardening was attributed to a shrinkage (or a narrowing) of the pores of the metal because some 'heat' was driven out during the sudden cooling or because of the 'antipathy' of the iron in regard to the cold water. This statement was completed by René Descartes (1639) who introduced the particle-concept. Since red-hot steel was filled up with particles from the fire, those particles had to be replaced by others during cooling. On air-cooling they were replaced by identical particles of the air while on quenching water-particles, which were much smaller, took the positions of the fire-particles. Since the former were too small to fill up the pores entirely, the pores narrowed during quenching while the steel became harder (3). Jacques Rohault, who was a follower of Descartes, used the particle-concept of the latter to introduce a 'freezing' model (1671). On heating the particles of the metal were put in motion while the distance between two nearest particles was decreasing. A sudden cooling prevented them to go back to their original positions i.e. they became 'frozen in', forming a denser and tighter metal. The final result of the whole process, however, did not differ from the former

shrinkage models . The narrowing of the pores was just attributed to another cause (4) .

In 1680 Charles Perrault, the famous architect of the Louvre, recorded an increase in volume of the steel on quenching . This observation obviously rejected the shrinkage-models . René Antoine de Réaumur, who was profoundly influenced by Rohault, was rethinking the freezing-model of the latter in order to explain the recent observations . Maintaining the particle-concept of Descartes, Réaumur believed iron to consist of two kinds of particles : the iron particles and some 'sulfurs and salts' which could diffuse among the former ones . Fire would drive the 'sulfurs and salts' out of the molecules while quenching prevented them to reenter the molecules (freezing) . On quenching the intervals between the molecules became filled up with the 'sulfurs and salts' which were frozen in so the steel became harder (1722) . According to Réaumur 'freezing' no longer stood for a narrowing of the pores, but, on the contrary, the rearrangement of the molecules of iron and 'sulfurs and salts' led to an increase of the volume which was in good agreement with the experimental observations . Réaumur, however, never defined the nature of his 'sulfurs and salts' neither he was able to discuss in terms of the different particle-content in iron and steel, the difference in hardening-capacity of those metals (5) . Later on the 'sulfurs and salts' were renamed as phlogiston according to the current chemical theories of that time (18th century) (6) . During the second half of the 18th century efforts were made to solve the problem of the 'sulfurs and salts' (or the phlogiston) by a chemical analysis of the metals which was the current research-technique at that time . The Swedish chemist Sven Rinman outlined the role, in iron and steel, of a certain substance which he called plumbago(1774). Plumbago (which we know today to be just carbon) was, at first, considered as a special kind of phlogiston in agreement with the current opinions . Another Swedish chemist Torbern Bergman succeeded in determining the exact plumbago-content in cast iron, wrought iron and steel . He accepted the Réaumur-freezing-model to explain the quench-hardening but, he too, was not able to discuss the difference in hardening between steel and iron in terms of the observed difference of the plumbago-content in both metals (7) . About 1800 plumbago was christened as carbon (8) . The models from the 17th and 18th century were purely academic and, in fact, useless for practice . None of these models could account for the relation between the final quenching product and the quenching temperatures, the various quenching agents a.o. The models were largely qualitative in nature and of unlimited flexibility so no quantitative use or verification was possible (9) .

The iron-carbon system. - The older models had finally focussed the attention on the specific role of the carbon in regard to the quench-hardening . Yet there was no clarity concerning the complex manifestations of the element . This was mainly because of the impossibility to detect the basic and allotropic forms of carbon by chemical analysis alone . A structural approach of the problem was thought to be indispensable by most of the investigators of the 19th century who believed hardening had to do 'something' with a specific structure of the carbon in the metal (10) .

From the 1860's on measurements of physical properties and observations of structural effects were introduced to investigate metals behaviour, including the hardening on quenching . About 1866-1868 Dimitri Chernov (or Tschernoff) discovered the critical temperatures at which transformations in steel occurred, as a function of the carbon content . One of these points was defined as the temperature below which steel did not harden (this point is now designated as A_1) . He graphically represented the influence of carbon on the position of the critical points by making the first

rough sketch of the most-important lines of the iron-carbon diagram . In 1869 G.Gore observed the momentary elongation of iron at a critical temperature on cooling while W.Barrett found (1873) this to be accompanied, in steel, by a sudden increase in temperature (11) . These changes were then attributed to allotropy which meant, at that time, only a molecular change without regard to the stacking of the atoms in the crystal (12) . By 1890 Floris Osmond recognized three modifications of iron : alfa, beta and gamma . Critical points, as a function of composition, were determined in various alloys by dilatation measurements, resistance measurements, thermocouples, photometrical methods, spectroscopy and calorimetry during the last decades of the 19th century (13) . About 1870 microscopical techniques became a very important complement to the physical methods as for the structural study of metals . These techniques were mainly developed by Henri Sorby and Adolf Martens . Microstructures of metals and alloys were related to the freezing point curves . By 1900 a range of structures had been observed in many alloys and cataloged in relation to composition and heat treatment (14) .

On the theoretical side, the application of Josiah Gibbs' principles of phase equilibria (1878) to metallic systems was suggested and effectively demonstrated by Hendrik Roozeboom in a famous paper in 1900 . Most of the observations on the range of existence of micro-constituents as a function of temperature and composition were suddenly reduced to order (15) . In the same year Roozeboom was able to give a full representation of the iron-carbon equilibrium diagram according to the phase rule (16) . Very soon this diagram and the critical points were used in order to discuss the hardening . Meanwhile, experience remained the only basis on which practical knowledge on quenching could be acquired by the artisan . The age-old method of visual control of the quenching and tempering temperatures remained in common use . Different agents were used and tried out by the craftsman who considered them as a 'commercial secret' of the production (17) .

Modern theories based on the iron-carbon diagram. - At first hardening was explained by the existence, above the A₁ temperature, of a hard compound of iron and carbon (hardinite) which was retained (or frozen in) on quenching . About 1900 Osmond believed beta-iron was the cause of the hardening since the normal transformation to alfa-iron was prevented by the sudden cooling . In 1895 both theories were reconciled by Henri Howe : the hardinite was thought to predominate in high-carbon steels while the allotropic effect (transformation from beta to alfa) predominated in low-carbon steels . Howe used the term martensite instead of hardinite, as suggested by Osmond in honour of the pioneering metallographer Adolf Martens . At that time martensite was thus considered to be a high-temperature phase which could be retained on sudden cooling . But one remained uneasy about the fact that steel was nonmagnetic at the customary hardening temperatures, whereas the quenched steel was strongly magnetic . How could this magnetic change be reconciled if quenching preserved the nonmagnetic beta or the high-temperature martensite at room temperature ? (18) . To solve this problem Albert Sauveur, a co-worker of Howe (19) regarded the high-temperature phase no longer as a compound but more as a solid solution . This solid solution was thought to decompose during quenching to an aggregate of finely dispersed carbides embedded in a matrix of ferrite, the latter being strongly magnetic . This final structure was also called martensite . The quenched structure was no longer considered as a retained high-temperature phase but as a result of the decomposition of it . In 1903 Howe adopted the name austenite, as proposed by Osmond, for the solid solution of carbon in iron and recognized that the allotropic form of iron dissolving the carbon was gamma-

iron rather than beta-iron . This made it possible to reserve the term martensite for the strong constituent in hardened steel and paved the way for accepting such martensite as a transformation product of a high-temperature phase (20) . About 1910 carbon was believed to act as a brake, on sudden cooling, to retard the normal decomposition of austenite into ferrite and cementite . Martensite was then a product of an incomplete transformation of austenite, mainly consisting of retained beta-iron (21) .

In spite of the differences between the successive hardening-models, all of them had, at least, one thing in common : the 'freezing' of Rohault remained essential in order to explain the final quenched structure . Modern theories considered the freezing first as a simple retention of a high-temperature phase and later on this concept was used to indicate a retardation of the transformation of that high-temperature phase (22) .

Nevertheless much confusion was still present in regard to the right terminology . Austenite of eutectoid composition was still called hardenite i.e. a high-temperature compound . In 1911 E. Heyn described the quenched structure of steel as hard cementite particles embedded in martensite while the latter was thought to consist of hard needles embedded in a soft matrix . For sake of simplicity Heyn preferred the term martensite to indicate the high-temperature phase although he was aware of the term austenite (23) . This confusion was not very beneficial for the practitioner as stated already by Howe in 1893 (24) . Judging from the textbooks for quenching-practitioners there was no influence from the recent academic theories on the quenching practice. The whole quenching-process was still based on empirical studies since the conventional equilibrium phase diagram was not very useful for non-equilibrium processes, although it could give some information about the quenching temperatures (25) .

On the whole the modern theories proposed a largely quantitative picture since they could, for the first time, account for the different hardening capacity of steel and iron .

A new impetus. - In 1926 Sauveur noted that most of the models which were valid at that time were already in existence in 1896 . No new explanations emerged and it seems that the main reason for this was the misunderstanding of the nature of allotropy which was still interpreted as a molecular change (26) . One had to wait for X-ray diffraction studies during the 1920's and thereafter (and later on the electronmicroscopy) to understand allotropy was in fact a crystallographical change . It was found that beta-iron had the same structure as alpha-iron and that iron in martensite was in the alpha-modification . Decisive experimental proofs that martensite was a solid solution of carbon in alpha-iron had been the discovery of the body centred tetragonal lattice of martensite in 1926-27 (27) . During the thirties it was found that transformations having kinetics and mechanism like the martensite transformation in steel occurred also in some non-ferrous alloys . This was, as for the knowledge of the hardening phenomenon, a real milestone since the martensitic transformation in these alloys was accompanied with very interesting features (such as e.g. the memory effect) which acted, because of potential industrial applications, as a stimulus for further research (28) . The reversibility of the memory effect was a stimulus for rethinking transformation mechanisms. As for the methodological approach recent research is still based on the 19th century tradition i.e. a structural approach (microscope, X-rays and electronmicroscope) combined with physical measurements (acoustics, calorimetrics, ultrasonics e.o.) .

About 1930 isothermal transformation diagrams and continuous cooling diagrams were determined to study the transformation of austenite under non-equilibrium conditions . These diagrams can be considered

as the first contribution of academic science to practice . They were a basis for some new heat treatments such as martempering, isothermal annealing and austempering . The non-equilibrium diagrams proved to be very useful as well to thermomechanic treatments (29) .

Conclusion. - Many of the scientists we have mentioned in this review were, in one way or another, influenced by the craftman's knowledge and technology or were stimulated by -potential or current- industrial applications (e.g. Descartes, Réaumur, the Swedish workers, Chernov, Sauveur, the memory-workers) . History shows a definite interrelationship between technology and academic science . At first this relation was almost unilateral but, from the end of last century on, it became more or less mutual . About the turn of the century a new type of scientist appeared, the chemical or physical metallurgist who had to bridge both the application-side and the academic science by interpreting the various results of several sub-disciplines and making them available for practical application (30) . As for the hardening phenomenon, however, academic research was, as yet, not very contributing to the application side, except in the case of the non-equilibrium diagrams . In some cases the academic theories were even confusing the practitioner(31), rather than helping him . Although one can not claim that potential applicability has to be a criterion for scientific value or that all academic and fundamental research has to show an immediate applicability, it is good to be aware of the damage that can be done to the practice by a too liberal and often unnecessary use of hypothetical models and concepts and an over-exploitation of a theoretical terminology (32) .

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- (1) T.A.WERTIME, The coming of the age of steel, Leiden, 1961, p. 9 and 19 ; P.JACQUEMART et J.-F.BOIS, Notions de Technologie, Paris, 1920, p. 38 .
- (2) J.E.GORDON, The new science of strong materials, Pelican book, 1974, p. 211-212 ; Sources for the history of the science of steel 1532-1786, ed. C.S.SMITH, Cambridge, Massachusetts and London, England, 1968, p. 4-5, 9-12 and 37 ; A history of technology, ed. Ch.SINGER, volume III, Oxford, 1957, p. 36 .
- (3) A history of technology, p. 33-36 ; Sources ..., p. 25 and 35 ; DESCARTES, "Lettre au père Mersenne, 9 janvier 1639", Les principes de la philosophie, Oeuvres philosophiques III, ed. F. ALQUIE, Paris, 1973, t. II, p. 118-120 .
- (4) C.S.SMITH, "The development of ideas on the structure of metals", Critical problems in the history of science, ed. M.CLAGETT, London, 1969, p. 478-479 .
Another freezing model was that of N.Hartsoeker (1696) according to which particles of steel were put in motion and disarranged by the fire, quenching giving a hard metal because the particles did not have time to rearrange themselves ; Id., p. 476 .
Worth mentioning is the theory of R.Hooke (1665) who believed hardening of steel arose from varying amounts of vitrified substance interspersed through it, a view remarkably prescient of the amorphous metal theory of nearly three centuries later, but, for that time of no practical use : A history of technology, p. 37 .
- (5) C.S.SMITH (1969), p. 483-484 ; T.A.WERTIME (1961), p. 38-40, 193 and 208-211 ; Sources ..., p. 65-68 en 171 .
- (6) T.A.WERTIME (1961), p. 40 .
- (7) Sources ..., p. 228-231 and 236-240 ; T.A.WERTIME (1961), p. 152 .
- (8) T.A.WERTIME (1961), p. 158-159 .

- (9) The qualitative models, however, were not completely without any experimental foundation. Rohault observed the fracture of hard and soft steel and saw the finer 'parts' (which today we call grains) in a quenched metal. This proved, according to Rohault, the pores to be smaller in quenched steel. Hooke observed, by microscope, the vitrification of the sparks struck by flint from steel and suggested steel was partly vitreous: C.S.SMITH (1969), p. 479 and 481.
- (10) "Que cette manière de voir soit exacte ou non, il est certain que l'acier dur et l'acier doux diffèrent essentiellement quant au mode d'existence du carbone dans la masse" : J.PERCY, Traité complet de métallurgie, t. IV, Paris/Liège, 1867, p. 304.
- (11) C.C.GILLISPIE e.a., Dictionary of scientific biography, New York, 1976, see: Chernov; C.S.SMITH (1969), p. 492.
- (12) C.S.SMITH (1969), p. 497.
 "Les effets de la trempe se manifestent par une modification moléculaire du métal et du carbone qui est combiné au fer" : H. PECHEUX, Précis de métallurgie, Paris, 1915, p. 261.
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- (13) C.C.GILLISPIE (1976), see: Osmond, Sorby and Roberts-Austen; H.PECHEUX (1915), p. 250-255; C.S.SMITH (1969), p. 491 and 494; E.HEYN, Handbuch der Materialienkunde für den Maschinenbau, zweiter Teil, Berlin, 1912, p. IX, X, 120 and 127; J.H.WESTBROOK, Met.Trans., 8A (1977), 1327, p. 1340-1341.
 In the neighbourhood of 768°C and up to 790°C there is, in iron and steel, a gradual magnetic change, ferrite being ferromagnetic below this temperature range and paramagnetic above. This change is also accompanied by a heat effect. It has since been found that the behaviour at this temperature does not involve a phase change, but Osmond thought not so and believed there was a specific phase involved which he called beta.
- (14) C.S.SMITH (1969), p. 490-491 and 494.
- (15) C.C.GILLISPIE (1976), see: Roozeboom and Le Châtelier; J.H.WESTBROOK (1977), p. 1342.
- (16) E.HEYN und O.BAUER, Metallographie, II; Berlin/Leipzig, 1926, p. 101; Id., Metallographie, II, Berlin/Leipzig, 1913, p. 103.
- (17) "Le degré mitoyen de chaleur ne peut s'acquérir que par la pratique" : Encyclopédie ou dictionnaire universel raisonné des connoissances humaines mis en ordre par M.DE FELICE, Yverdon, 1770- , see: Tremper les aiguilles.
 "C'est à la suite d'observations attentives et par une longue pratique seulement que les ouvriers chargés du recuit et de la trempe parviennent à déterminer exactement les températures les plus convenables pour la trempe des divers aciers du commerce: ils suppléent par coup d'oeil aux instruments thermométriques": J.PERCY (1867), p. 295.
 "Ces couleurs rendent par conséquent inutile l'usage d'instruments thermométriques" : Id., p. 289.
 "Ces pratiques particulières sont la base de plusieurs secrets qu'on a dans différentes manufactures" : Encyclopédie ou dictionnaire ... : see: Acier.
 "Et de nos jours plusieurs fabricants d'acier affectent une très-grande réserve à ce sujet (= les liquides employés dans la trempe)" : J.PERCY (1867), p. 296.
- (18) M.COHEN, Trans.AIME, 224 (1962), 638, p. 639-640.
- (19) Albert SAUVEUR (b. Louvain, Belgium, 1863; d. Cambridge, Massachusetts, 1939). Educated at the Ecole des Mines in Liège. Came to the United States in 1887. He was the first in the United States effectively to study the microscopy of steel. In an 1896 paper Sauveur critically summarized all the diverse current

theories of steel-hardening mechanisms .

- (20) M.COHEN (1962), p. 640 .
- (21) Encyclopaedia Britannica, 11th edition, New York, 1910, see: Iron and steel , 12, 13, 14 and 28 .
- (22) "... the carbon present seems to act as a brake to retard the change . Beta-iron may be preserved incompletely as in the 'hardening of steel' which consists in heating the steel into the austenitic state and then cooling it so rapidly, e.g. by quenching it in cold water, that, for lack of the time needed for the completion of the change from austenite into ferrite and cementite, much of the iron is caught in transit in the beta state . Martensite, very hard because of its large content of beta-iron, is characteristic of hardened steel": Id., 12, 13 and 14 .
- This finally led to the modern definition of a diffusionless, i.e. a more correct description of the 'freezing' or the retardation, transformation of the high-temperature phase .
- (23) E.HEYN (1913), p. 177 ; Encyclopaedia Britannica, see: Iron and steel , 12 and 22 ; E.HEYN und O.BAUER (1913), p. 80-81 ; Id., (1926), p. 83-85 .
- Some authors believed martensite to be composed of graphite and alpha iron (PECHEUX (1915), p. 129-130) while others thought martensite mainly contained beta-iron (Encyclopaedia Britannica, see : Iron and steel, 14 and M.COHEN (1962), p. 641) . Quibbling continued for many years, even after 1926, on whether the solute in gamma iron existed as carbon or as Fe_3C : M.COHEN (1962), p. 641 .
- (24) "How often does the investigator greatly reduce the debt which the practitioner owes him for his investigations, by publishing prematurely theories which, by their number and instability, confuse the beneficiary" : H.M.HOWE, The Heat-treatment of steel, Trans.AIME, 23, (1893), 522 .
- (25) E.g. P.JACQUEMART et J.-F.BOIS (1920), p. 37-38 ; O.MOENS, Grondstoffleer . Aanvankelijk handboek voor den metaalbewerker, Gent, 1926, p. 104-106 .
- None of the current practitioner-textbooks used, before 1930, the 'scientific terminology' (austenite, martensite e.a.) to describe the hardening .
- (26) M.COHEN (1962), p. 641 .
- (27) G.V.KURDJUMOV, "Mechanism of austenite-martensite transformation and behaviour of carbon atoms in martensite", Proceedings of the first JIM international symposium on new aspects of martensitic transformations, Kobe, 10-12 May 1976, p. 9 .
- (28) Id., p. 10 .
- "Over the past decade a considerable amount of interest has developed concerning the martensitic transformation in the inter-metallic compound TiNi, principally because of the potentially useful shape-memory effect associated with the transformation" : R.F.HEHEMANN and G.D.SANDROCK, Scripta Met., 5 (1971), 801 .
- "The lively interest in this effect (= shape memory), as evidenced by the ever growing number of scientific papers dealing with the subject, is not only caused by the wide range of potential applications which in some cases seem to belong to the realm of science fiction, but must also ascribed to the many questions that are raised concerning the martensite transformation" : H.TAS, L.DELAEY and A.DERUYTTERE, J.Less-Common Met., 28 (1972), 141 .
- "Much recent attention has been devoted to this phenomenon (= shape memory) not only for academic curiosity, but also because it represents, potentially, many new applications of the martensite transformation in non-ferrous alloys" : C.M.WAYMAN, "Some recent developments in martensitic transformations" : Pro-

