

HISTORY OF SCIENCE

DOI: 10.32703/2415-7422-2023-13-2-243-262

UDC 669

Maryna Gutnyk

National Technical University “Kharkiv Polytechnic Institute”

2, Kurpuchova Street, Kharkiv, Ukraine, 61002

E-mail: maryna.gutnyk@khpi.edu.ua

<https://orcid.org/0000-0002-2723-2755>

Florian Nürnberger

Institute of Materials Science Leibniz University Hannover

An der Universität 2, Garbsen, Germany, 30823

E-mail: nuernberger@iw.uni-hannover.de

<https://orcid.org/0000-0002-7824-0675>

The Fe-C diagram – History of its evolution

Abstract. *The evolution of concepts and methods of physical and chemical science that contributed to the formation of the Fe-C diagram during the previous centuries is considered. Despite the classical knowledge, there are still differences in the representation of the Fe-C diagram by scientists from different countries, in particular, the data of scientists from Germany, Poland, Ukraine, the USA, and Australia are somewhat mismatched. The authors tried to understand the reasons for this discrepancy. To conduct the research, general scientific methods of cognition were used: comparative analysis and synthesis, as well as a chronological one. It is claimed that the first studies of carbon content in steel were carried out in 1802. Further research development began in 1827–1829 when it was established that graphite is pure carbon. It is emphasized that further studies of carbon content in steel and cast iron are connected with attempts to create the first graphs of dependence on content and temperature. This, in turn, contributed to the development of the industrial revolution. It is believed that the first complete diagram was presented in 1897 by Roberts-Austen. Later, with the use of X-ray methods and microscopy, the Fe-C diagram gradually took on a new form. At the beginning of the 20th century, scientists actively proposed their phase diagrams. Studies conducted by scientists of different countries during 1909–1911 gained a consolidation, which was produced at the 6th Congress of the International Association for testing materials meeting into the unification of the names of phase transformations. Further research until the beginning of the Second World War was aimed at the creation of “pure” steel, that is, without*



harmful impurities, and clarifying the transformation temperatures. The period of the Great Depression in the USA and the war in Europe did not contribute to scientific research. At the same time, for the mass production of steel and cast iron, errors in critical points of a few degrees did not have a significant impact, that is, refining the temperatures of phase transformations were not considered appropriate. Today's trend in scientific research is aimed at solving environmental problems caused by the industrial revolution.

Keywords: *Fe-C diagram; unification of transformation modes in Fe-C binary alloys; consolidation of science; material science*

Introduction.

The development of a post-industrial society could not have been achieved without the application of structural materials, the main of which remain steel and cast iron. The dominant components of these alloys are iron and carbon. The type of alloy that can be obtained in the final result depends on the percentage content of the component, the temperature, as well as the emergence of carbon e.g. in the form of graphite and in a certain morphology. While working on a joint study (Nürnberg, Frolov, Grydin, Gutnyk, & Blank, 2022), the authors saw a discrepancy between the diagrams in the percentage of graphite included in the composition of the steel. If Ukrainian scientists take 2.14 % as the maximum content (Timofeeva & Komarova, 2013, p. 50; Bobrova, 2016, p. 18), Polish scientists – 2.11 % (Hucińska, 1995, p. 86; Pawłowski, 2012, p. 2; Pawłowski, 2017, p. 146), then in Germany in general – 2.03% or 2.06% (Eckstein, 1969, p. 53; Horstmann, 1985, p. 117; Läßle, 2022, p. 56). Moreover, the carbon content in cast iron is the same in all countries. It turns out that each country has its own knowledge, of the apparently “classic” Fe-C diagram. The most complete publication that today gives the history of iron-carbon alloy research is the monograph of Eugeniusz Tyrkiel (Tyrkiel, 1963), although it is limited to data up to 1955 and unfortunately does not reveal the development of research including modern knowledge.

The purpose of the article: is to trace the origins of knowledge in materials science, namely the creation of the main “points” on the Iron-Carbon diagram. To reveal which knowledge preceded the study of the physical state of steel and cast iron at different percentage ratios and different melting temperatures. To evaluate from the point of view of modern knowledge of materials science, the development of knowledge about the percentage ratio of iron and carbon.

Methods: general scientific methods of cognition were used: comparative analysis and synthesis, as well as a chronological one. This made it possible to carry out a comprehensive study of the stated topic, to present how the concept about the percentage of carbon and iron were formed during the melting of steel and cast iron, to follow how knowledge and discoveries in the field of physics and chemistry contributed to the formation of the equilibrium system in the Fe-C diagram and transformation of temperatures.

Results and Discussions.

The first attempts to establish mass production of steel and cast iron in the 19th century contributed to the accelerated development of research in this direction. Among the harmful impurities in the production of the mentioned alloys, sulfur, and phosphorus were the most difficult to eliminate. Though in laboratory conditions the steel turned out to be of good quality, the finished castings suffered from redness due to the industrial scale of its smelting and cold brittleness. On the one hand this is caused by sulfur forming a chemical compound FeS with iron, which with iron in steels forms a eutectic with a melting temperature of 985 °C. This eutectic melts at certain comparatively low temperatures and as a result the connection between the grains is lost and cracks are formed. In addition, sulfur reduces the plasticity and strength of the steel, its resistance to abrasion and its corrosion resistance. A fragility at low temperatures on the other hand is a result by the fact that phosphorus causes strong internal crystal liquefaction (Fedirko et al., 2017, p. 74).

Back in 1802, the Englishman David Mushet (Mushet, 1802) conducted a large-scale study to determine the carbon content in certain types of iron-carbon alloys. Starting with Swedish iron and varying amounts of charcoal, he prepared alloys in both open and tightly closed melting pots. By carefully weighing the materials used to cast the alloy and the final products (iron or steel and other carbon), he tried to determine the amount of carbon in % corresponding to different types of alloys. And so, for example, he obtained values from about 0.8 % (soft) to 2 % (very hard) for steel, about 4 % for white cast iron and 5 % for cast iron ingot, and for gray iron more than 6 %. Robert Forester, David Muschet's son, performed more than ten thousand experiments on the influence of impurities on the quality of steel. It was he who invented a method with the addition of manganese to avoid sulfur in the melt (Gutnyk, 2012, p. 254). Significant discoveries and successes in chemistry in the first decades of the 19th century greatly influenced the further development of views on iron-carbon alloys. In particular, one of the main laws of chemistry – the law of constancy of the composition of chemical compounds (“the law of constant ratios”) was formulated by the French chemist Joseph Louis Proust. The German scientist Jeremias Benjamin Richter initiated the study of the quantitative side of chemical reactions and founded a new branch of chemistry – stoichiometry.

The Englishman John Dalton established the law of simple and multiple ratios and created the modern atomic theory. Swedish chemist Jöns Jakob Berzelius introduced chemical symbols and formulas, and determined the atomic mass of many elements (Mourelo, 1916; Ostwald, 1974; Rocke, 2005; Berzelius, 1841).

In 1816, the German metallurgist Carl Johann Bernhard Karsten published a handbook on metal structures (Karsten, 1816). The scientist devoted his extensive research to determine the form which carbon can acquire in alloys with iron. Extensive studies of the essence of graphite conducted by the Swedish chemist Nils Gabriel Sefström during 1827–1829 (Sefström, 1828; Sefström, 1829), confirmed Karsten's thesis that graphite is pure carbon. Karsten's works represent to some extent a turning point in the development of views on iron-carbon alloys.

The use of a scientific approach in the development of research on mass steel production became the impetus for the presentation of the first graphs of the dependence of the concentration of carbon and iron. For example, Reinhard Mannesmann, was one of the 4 brothers who ran one of the first steel company in Germany – the Mannesmann company. Most of the commercially successful projects in the development of the company are related to him. The Mannesmann company also produced crucible steel, which was new at the time and had good quality indicators. Mannesmann products received the highest awards at all world exhibitions in the 19th century. The jury of the 1867 exhibition in Paris also suggested awarding Reinhard Mannesmann with the Legion of Honor. Emperor Napoleon III ordered that naval arsenals should be primarily equipped with Mannesmann products. In 1879, the entrepreneur presented the first graph of the dependence of the concentration of carbon and iron depending on the temperature. This graph was quite primitive and far from modern ideas about critical points because at that time it was not possible to measure the temperature physically accurately in the melt (Wessel, 2009).

In 1886, Floris Osmond published the publication “On the phenomena that occur during the heating and cooling of molten steel” where he listed several critical melting points of steel, and also in 1906 on the crystallography of iron (Osmond, 1886; Osmond & Cartaud, 1906).

In 1897, William Chandler Roberts-Austen presented the first complete temperature-concentration diagram (Fig. 1) for the iron-carbon system (Roberts-Austen, 1897), which the Dutchman Hendrik Willem Bakhuis Roozeboom converted into his phase diagram (Fig. 2) (Wisniak, 2003, p. 429). The face-centered cubic form of iron, *Austenite*, is named after Roberts-Austen (Kayser & Patterson, 1998). *Austenite* denotes the soft non-magnetic part of the alloy in which iron takes the form of an allotropic gamma modification, stable at high temperatures. As for other names of different chemical states in iron-carbon compounds, *martensite* should not be overlooked. It should be noted that this name was proposed by Floris Osmond in honor of the German metallurgist Adolf Martens (1850–1914). This is a needle-like structure characteristic for quench-hardened iron-carbon steels (the hard magnetic part of the alloy). It is noteworthy that these assumptions were confirmed only after the application of X-ray diffraction methods. A. Martens was one of the founders of materials testing research in Germany. He was one of the pioneers in using the light microscope as a tool for analyzing metal structures. For many years, the scientist headed the metallographic laboratory. During 1880–1882, A. Martens determined the three main structural components of cast iron: *graphite*, *free iron*, and *bound iron* and he showed that these components (today the latter are called *ferrite* and secondary *cementite*) are easy to recognize when etched with chemical reagents. In 1899, he published a textbook on materials science, which was highly evaluated at the time (Pfender, 1990).

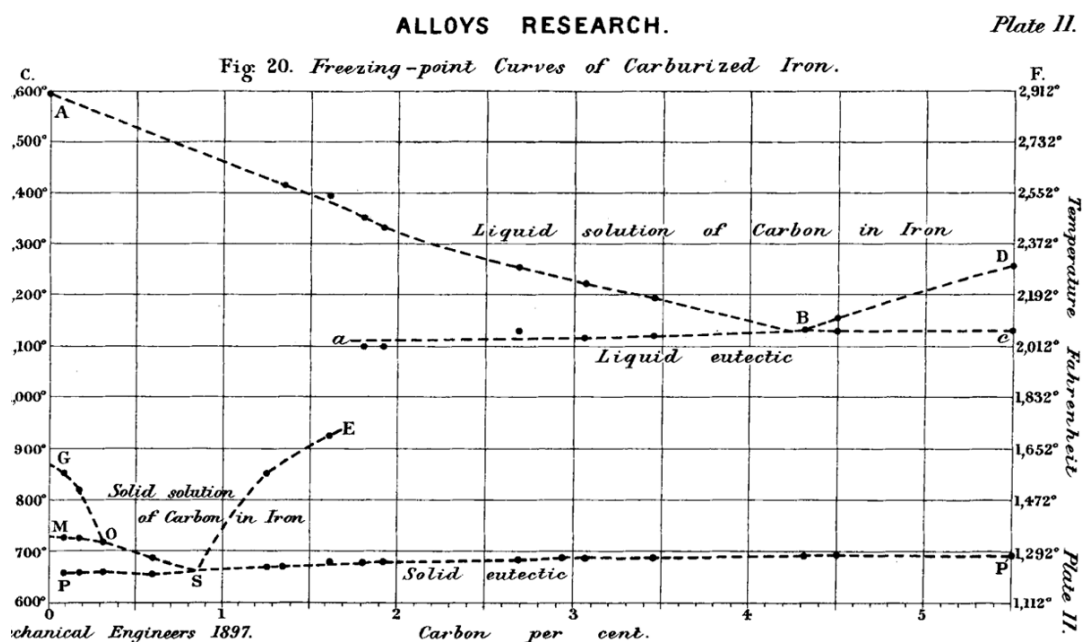


Figure 1. The Fe-C diagram by W. Roberts-Austen (Roberts-Austen, 1897).

To create his diagram, W. Roberts-Austen used a rhodium thermocouple developed by Henri Louis Le Chatelier, which he connected to a self-designed device that recorded the temperature as a function of time. Thus, this diagram is the first for the iron-carbon system.

The work by H. Roozeboom was based on the previous studies of Josiah Willard Gibbs and the diagram was built following the J. Gibbs' phase rule. The diagram already featured closed fields to which certain phases or complexes of phases correspond; all boundary lines create a continuous grid; the solidus temperature of eutectic aBC and the solid eutectic line PSK (eutectoid) do not depend on the carbon content and are horizontal lines; the solidus line showing the carbon content in *austenite* was presented. Since graphite is a more stable modification of carbon than carbides, and its solubility in iron is lower than in the form of carbides, the difference between these two Fe-C systems was also presented: stable (iron-graphite) and unstable (iron-iron carbide) (Wisniak, 2003, p. 428).

In 1888, A. Ledebur, professor of metallurgy at the Berg-Academy in Freiberg, Saxony, proposed to use four forms of carbon and to recognize technical iron. He distinguished between *bound carbon*, *free carbon*, *hardened carbon*, and *graphite* (Ledebur, 1888). This classification became generally accepted in Germany and in a significant part of foreign special literature. It remained valid for about 20 years until it was given a new designation.

According to the state of scientific research at that time, A. Ledebur's views were based on the knowledge of the formation of *hardened carbon* and *carbon carbide* as follows: *bound carbon* in iron-carbon alloys at normal temperatures is usually found in the form of *iron carbide (cementite)*; this chemical compound with the chemical composition Fe_3C contains 93.33 % of iron and 6.66 % of carbon. When heated above 700 °C, *iron carbide* begins to partially dissolve in the iron-carbon alloy, but its state remains solid. This so-called solid solution contains *solid carbon* (Ledebur, 1906).

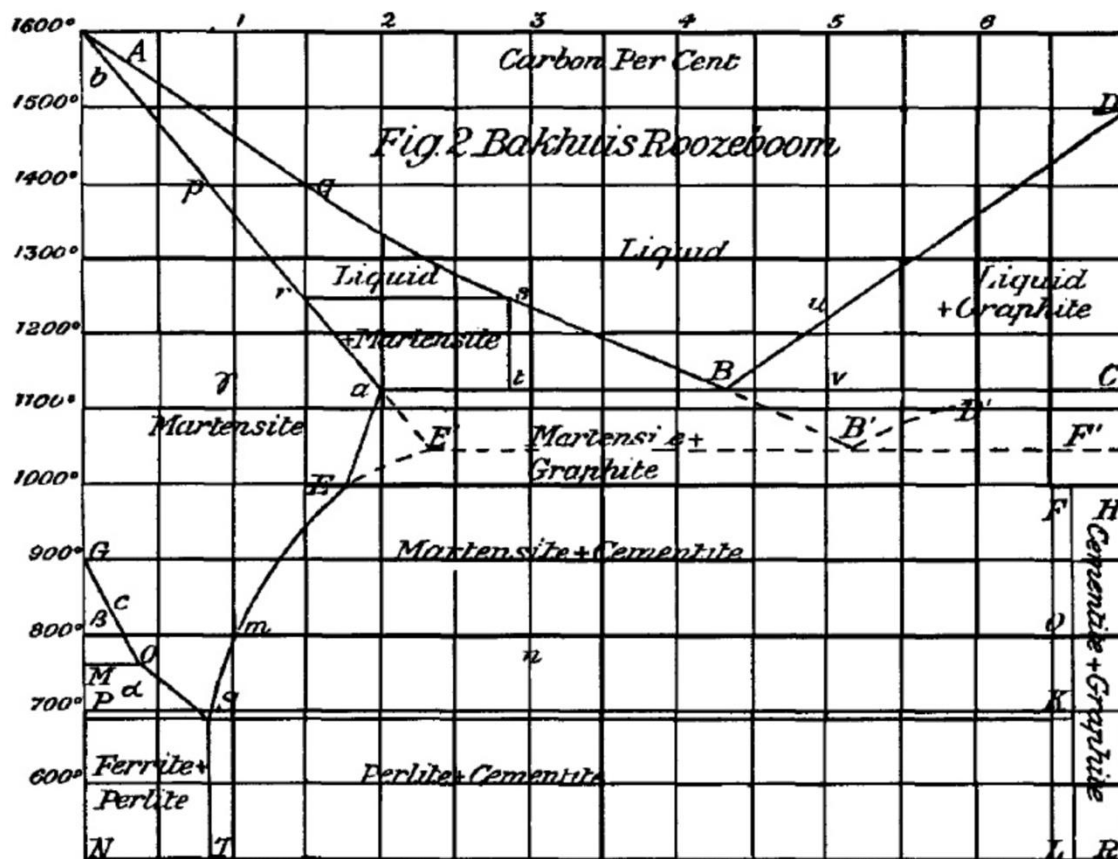


Figure 2. The diagram by H. Roozeboom, 1900 (Wisniak, 2003, p. 429).

As Dr.-Ing. Carl Geiger noted, carbon influenced the properties of industrial cast iron to such an extent that cast iron types were divided into two big groups based on the carbon content: high-carbon cast iron and low-carbon forgeable cast iron. He also assumed that the lower limit of carbon content in cast iron is approximately 2 %. At the same time, the professor indicated that the alloy, which contained approximately 1.5 to 2.5 % carbon in the presence of moderate amounts of other particles, was badly forged and cast. And, “such types of cast iron” (although this content today is attributed to steel) are used only in special cases. It is not possible to change the shape of cast iron in a cold or heated but unmolten state by pressure or tension. This can only be achieved by casting after melting. If cast iron (with a composition close to the eutectic point) is heated to the melting temperature (1100–1300 °C), it suddenly changes from a solid state to a liquid state without previously becoming pasty (Geiger, 1925, p. 1–2).

The rapid development of metallurgy at the end of the 19th century, especially in England and France, was based on an organized form of the scientific study of metals and the introduction of microscopic analysis. Thus, in England in 1889, the Society of Mechanical Engineers (Institution of Mechanical Engineers) formed the Alloys Research Committee; soon a similar research center (Commission des Alliages) was organized in France by the Society for the Encouragement of Domestic Industry (Société d’Encouragement pour l’Industrie Nationale). These centers, which had significant material resources, began an extensive study of metals and alloys, primarily

the study of the influence of alloying elements on the properties of metals. Among the activities of such centers was extensive research of alloys by methods of thermal and microscopic analysis, due to which in the last decade of the XIX century numerous phase diagrams considering temperature and chemical composition of binary and even ternary alloys appeared. In the following years, studies of the Fe-C diagram were mainly concerned with clarifying the position of individual lines (peritectic part, solubility of carbon in iron, graphite eutectoid).

At the beginning of the new century, European scientific studies of metals and alloys spread to America. Thus, in September 1912, the 6th Congress of the International Association for Testing Materials was held in New York, USA, which was the first congress of this Association to be held in America. The work of the 6th congress may be concisely summarized by the high number of publications of 153, roughly twice as much as the preceding congress and in the results of the work of technical committees it was at least equal to any of the previous congresses. The first official act of the congress was to elect Acting President Henry M. Howe as the president of the association, an act which was beyond the constitutional power of the governing council, after the death of the regularly elected president Dr. C. B. Dudley. The congress accepted the invitation of the Tsar of Russia to hold the next congress in 1915 at St. Petersburg and elected Dr. Nikolai Belebubskyi, St. Petersburg, president of the association for the next three years. Professor H. M. Howe was made a life member of the council. The secretary of the association was Ernst Reitler, Vienna, Austria (The engineering and mining journal, 1912, p. 484).

Among the landmark reports at this congress, it is necessary to note the proposal of the president of the association H. M. Howe, and professor of metallurgy Albert Sauveur on the definition of the names of microscopic substances and structures of steel (Howe & Sauveur, 1912) (Fig. 3). Thus, the names of the structures in the iron-carbon system were defined:

“...*Graphite*, definite metal (now we use the word “metal”). *Definition*: the free elemental carbon which occurs in iron and steel. *Composition*: probably pure carbon, identical to native graphite. *Genesis*: derived in large part, from the decomposition of solid *cementite*. Others hold that its formation as kish may be from solution in the molten metal, and that part of the formation of temper graphite may be from elemental carbon dissolved in *austenite*. It is the stable form of carbon in all parts of the diagram. *Occurrence*: 1. as kish, flakes which rise to the surface of molten cast iron and usually escape thence; 2. as thin plates, usually curved, e. g. in gray cast iron, representing carbon which has separated during great mobility, i.e., near the melting range; 3. as temper graphite pulverulent carbon which separates from *cementite* and *austenite*, especially in the annealing process for making malleablized castings.

Austenite (up to the year 1900 often called martensite, and wrongly sometimes still called so). The metal of variable composition. *Definition*: the iron-carbon solid solution as it exists above the transformation range or as preserved with but moderate transformation at lower temperatures, e.g., by rapid cooling, or

by the presence of retarding elements, (Mn, Ni, etc.), as in 12 % manganese steel and 25 % nickel steel.

Martensite, metal. Its nature is in dispute. *Definition*: the early stage in the transformation of austenite characterized by needle structure and great hardness, as in hardened high-carbon steel.

Ferrite, definite metal. *Definition*: free alpha-iron. *Composition*: nearly pure iron. It may contain a little phosphorus and silicon, but its carbon content if any is always small, at the most not more than 0.05 %, and perhaps never as much as 0.02 %.

Pearlite. *Definition*: the iron-carbon eutectoid, consisting of alternate masses of ferrite and cementite. *Constitution and Composition*. A conglomerate of about 6 parts of ferrite to 1 of cementite.

Ferronite (today ferrite), hypothetical definite metal. *Definition*: solid solution of about 0.27% of carbon in beta iron.

Hardenite. *Definition*: Collective name for austenite and martensite of eutectoid composition.

Troostite. *Definition*: in the transformation of austenite, the stage following martensite and preceding sorbite (and Osmondite if this stage is recognized).

Sorbite. *Definition*: in the transformation of austenite, the stage following Troostite and Osmondite, if this stage is recognized, and preceding pearlite...”

In addition, definitions for *Ferrous Sulphide, Cementite, and Osmondite...*” were given (Howe & Sauveur, 1912).

Among the reports, the analysis conducted by Professor E. Heyn was also quite interesting. The scientist presented an iron-carbon diagram with different critical points of states proposed by various researchers, including William Chandler Roberts-Austen, Heinrich Hanemann, Nikolai V. Gutovskiy et al. (Fig. 4).

Thus, in the late 1910s, there was still a difference of opinion about the positions of the critical points, and also about the use of the term “steel”. In everyday life, the term “steel” was used for any higher-quality material, without understanding that it is an alloy and how it differs from pure iron. Later, the following definition of the term was given: “steel is an alloy of iron that is hardened during hardening.” But such a definition remained vague, since there was no clear hardenability limit, and the methods of determining hardness also differed for different alloys. The carbon content started at 0.5 %, but it was not yet possible to calculate extraneous impurities that affected the hardening of steel and, accordingly, its hardness at that time. At the time in European shipbuilding, unhardened ductile iron was almost always called as steel. The Prussian Railway Administration used tensile strength in 1889 and determined that all materials with a strength greater than 50 kg/mm² could be described as steel. Regarding tensile strength as a distinguishing feature, professor A. Ledebur has already emphasized that the same wrought iron can show quite different strengths, depending on whether it is tested on thin or thick pieces, or whether it has previously undergone more or less intensive processing. Nevertheless, in 1905 the committee of the German Association for the Testing of Materials in Technology (*Deutscher Verbund für die Materialprüfungen der Technik*) proposed to define the difference between steel and

iron as subdivisions of liquid processed iron such as by the Thomas or Bessemer process (“Flusseisen”), on the one hand, and weld metal, on the other hand, that iron is called steel, regardless of its composition and regardless of whether it can be hardened and which has a hardness subsequent to the liquid state after annealing of 50 kg or more per square millimeter, and in a pasty state after puddling of 42 kg or more per square millimeter (Industrienormen Deutsche, 1922, p. 19).

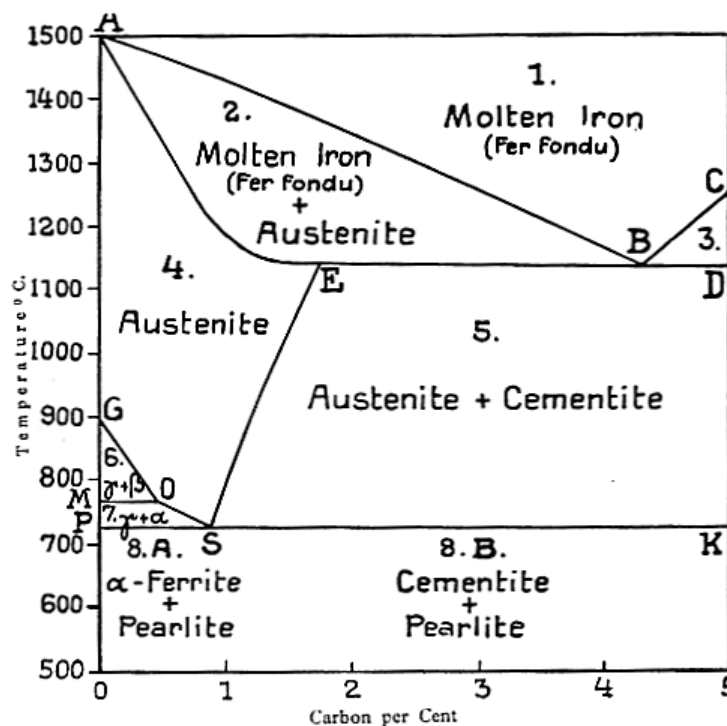


Figure 3. The diagram of different states in the iron-carbon system: the line PSK was often called “A1”. The Line GOS is often called “A3”, and this name was sometimes applied to the line SE (Howe & Sauveur, 1912).

Finally, in 1919, the German Industrial Standards proposed that in the future for wrought iron and steel, the material obtained in the pasty state should be called “iron” and the material produced in the liquid state – “steel”. Several participants objected to the proposal, referring to trade. Such a renaming seemed very complicated and questionable from a commercial point of view. Misunderstandings in the iron trade, for example with bar iron (*Stabeisen*), were inevitable. After several years of negotiations, at the end of 1923, it was agreed that the term “steel” should be defined for all industrially produced iron except pig iron and cast iron (*Roheisen und Gußeisen*) namely “mild steel” for material, obtained in a liquid state and subjected to forging without further processing, welding, etc. “Puddling steel” – for that obtained in a pasty state. The word “iron” itself should be reserved for the element iron. However, this principled decision should not affect commercial names, such as bar and shaped iron, universal iron, sheet iron, etc. (Geiger, 1925, p. 6).

The double diagram of iron-carbon alloys.

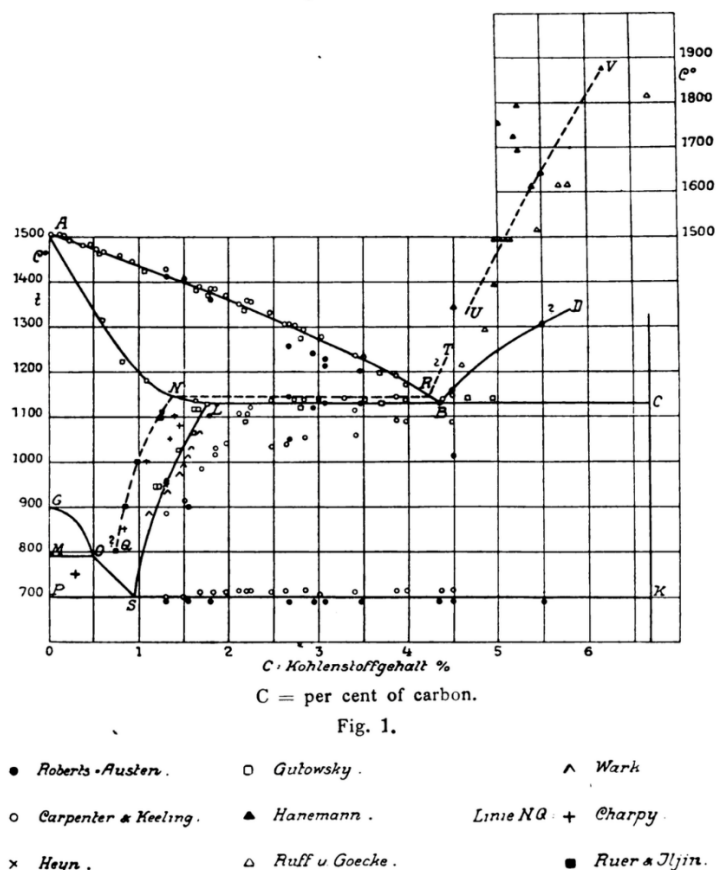


Figure 4. Critical points of states proposed by various researchers before 1911 (Heyn, 1912).

The names of iron processed into objects of everyday use by casting have also been a highly controversial area for a long time. The German Industrial Standards Committee provides the following definitions of terms:

1. Cast iron is melted and cast into molds separately or with iron scrap, steel scrap, and other smelting additives, but is not subjected to processing for the purpose of forging. Depending on the amount of precipitated graphite, the following are distinguished: a) gray cast iron with abundant graphite allocation, b) semi-gray cast iron with a small graphite allocation, c) white cast iron with no graphite or only traces of graphite release, d) chilled cast iron with a white outer zone and a gray core.

2. Malleable iron is cast as cast iron, namely from white iron, and then refined or forged by annealing with a decarbonizing agent.

3. Cast steel is made from steel produced in a crucible, Siemens-Martin, electric furnace, or in a pear-shaped converter without further processing by forging. Therefore, cast steel is already a finished product and the material is formed in the final form (Geiger, 1925, p. 6).

Later, with the development of new material research methods, the location of critical points on the Fe–C diagram gradually normalized. Thus, the first large-scale X-ray studies of cast iron and some steels were conducted in 1921 by Swedish researchers Arne Westgren and Axel E. Lindh (Westgren & Lindh, 1921, p. 184) according to a slightly modified Debye–Scherrer method (Debye & Scherrer, 1916, p. 4–8). Based on

the assumption that metals are usually a conglomerate of very large numbers of very small crystals, these authors concluded that the Debye-Scherrer method can be applied to non-powdery metal preparations. The experiment has confirmed this assumption, it turned out that this method can be successfully tested on metals in the form of thin rods or wire without the need for additional powder coating. From the X-ray pattern obtained by scientists, it turned out that β -iron, like α -iron, has a spatially centric cubic lattice (Fig. 5, a). Further research by Arne Westgren and Axel E. Lindh conclusively demonstrated that γ -iron (Fig. 5, b) is fundamentally different from α -iron in crystallography, while β - is identical in this characteristic to α -iron (Authier, 2013, p. 144). It should be noted that the γ - to α -transformation is accompanied by an atomic volume change of approximately 1%, which can lead to the generation of internal stresses during transformation (Bhadeshia & Honeycombe, 2006, p. 4).

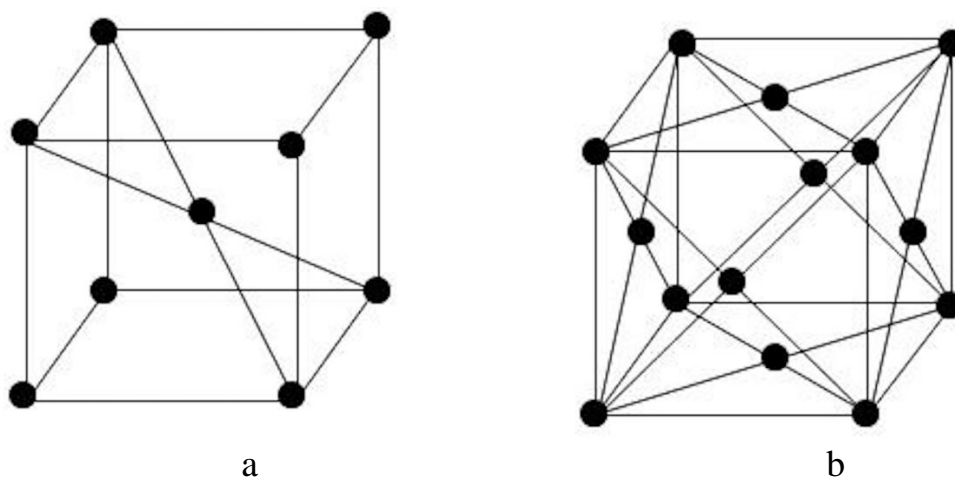


Figure 5. α -iron (a) and γ -iron (b) structure.

The majority of researchers who began to use X-rays for the study of metals concluded that due to the allotropy of crystalline bodies with β -polymorphism, iron cannot be considered as a separate allotrope. In 1922, Arne Westgren and Gösta Phragmen (Westgren & Phragmen, 1922) conducted an X-ray diffraction study of electrolytic iron melted in a vacuum, as a result of which they found that δ -iron, like β -iron, crystallizes in the same order as α -iron and that it is spatially centric (today it is called body-centered cubic or bcc). Thus, these studies showed that the transformation of one structure into another is a reverse process. That is, at very high temperatures, iron returns to a form with properties similar to those it had in its original form (Westgren & Phragmen, 1922).

In the 1920s, several works devoted to X-ray studies of both carbon and alloy steels were published. In particular, this was the work by Nikolai Seljakov, Georgii Kurdjumov, and Nikolai Goodtzov (Seljakow, Kurdjumow & Goodtzow, 1927), which also included the results of G. Kurdjumov's thesis, where the crystallographic structure of *martensite* was indicated, and the mechanism of martensitic transformation was recognized. Further research conducted by G. Kurdjumov at the Institute of Metals Research in Berlin on *austenite* single crystals together with Goldman Sachs led to the creation of a scheme for the rearrangement of *austenite* crystal lattices into *martensite*

lattices through two shifts. The mutual orientation of *austenite* and *martensite* crystals that occurs in this case was called the Kurdjumov-Sachs orientation (Lee & Han, 2012).

The period of 1930 to the 1940s was not marked by significant discoveries in the development of physical and chemical science that would affect the formation of the lines of the iron-carbon diagram. This was primarily related to the economic and political situations in the world. Repression and famine in the Soviet Union, the stock market crash, and, of course, the Second World War. In addition, it was not considered applicable to repeat the research to clarify the temperatures of phase transformations, instead, the researchers switched to experiments to create alloys devoid of impurities, that is, of much higher purity.

In 1941–1942, the American Bureau of Standards conducted an extensive study on the properties of pure iron, and Wm. F. Roeser and H. T. Wensel (Roeser & Wensel, 1941) were concerned only with determining the melting temperature of iron, and Harold E. Cleaves and John M. Hiegel (Cleaves & Hiegel, 1942) studied various physical properties of iron, including the A_3 transformation temperature, i.e., the lower temperatures of the γ -iron formation. During determining the iron melting points, scientists critically reviewed all previous studies in this direction and came to the conclusion that the melting point has not yet been unambiguously determined for the following reasons: 1) the researchers were mainly interested in determining the equilibrium diagram, rather than the exact determination of the melting point of iron; 2) the number of impurities in the studied samples were generally high and so different that individual results cannot be considered as referring to the same material; 3) the analysis did not take into account the content of gases that have a significant effect on the melting temperature; 4) iron was exposed to pollution, especially by gases, during the test; 5) the basis of marking of temperature measuring devices by individual researchers was not identical (Roeser & Wensel, 1941, p. 275). Roeser and Wensel used iron with a high degree of purity (total impurities below 0.01 %), obtained by reducing pure iron oxide to sponge iron (cast iron) and then remelting it twice – one time in an atmosphere of hydrogen, the second time in a vacuum. The tests were performed in a helium atmosphere, and the samples were melted in a high-frequency induction furnace in a beryllium oxide crucible. The temperature was measured using an optical pyrometer directed on a crucible with molten cast iron. As a result of these studies, the melting point (solidification point) of pure iron (99.99 % Fe) was determined at 1539 ± 1 °C. Before, the temperature of 1528 °C (determined in 1914 by R. Ruer and R. Klesper (Ruer & Klesper, 1914, p. 260), was most often indicated on the iron-carbon equilibrium diagrams.

In 1948, in the *Metals Handbook*, John B. Austin published what is now considered the classic American diagram, where he indicated that the solubility of carbon in γ -iron in the presence of *cementite* is about 2 %, and not about 1.7 %, as previously reported (Austin, 1948, p. 1182) (Fig. 6).

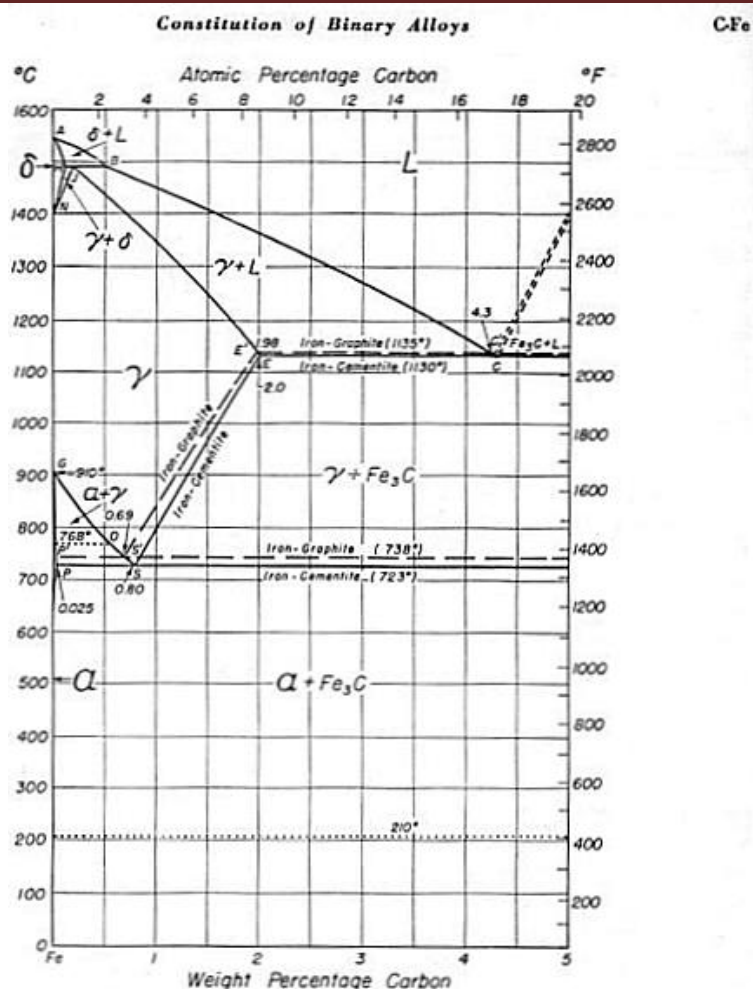


Figure 6. Diagram Fe-C by Austin (Austin, 1948, p. 1182).

In the middle of the 1970s American scientists continued their experiments with carbon steels (now known as Ultrahigh carbon steels – UHCS). That study had its origin in the development of superplastic behavior in steels and the recognition that increasing the carbon content was of importance in developing that property. The scientists summarised that the maximum solubility of carbon in Austenite is 2,1% C (Wadsworth & Sherby, 1997, p. 11). In 1978 it was determined that carbon contents beyond UCS, containing 2.1 and 2.3 % C, show superplasticity (Wadsworth & Sherby, 1997, p. 14).

In the early 1980s, Australian researchers conducted experiments on the Fe-C composition in the range from 1.5 to 4.42 % C. The possibility of a certain modification of the γ -solidus was also proposed, and a refined phase diagram was presented (Chicco & Thorpe, 1982, 1983).

The subsequent period of scientific research did not bring any new data that would significantly affect the critical points of the Fe-C diagram. At the beginning of the new millennium, there is still a difference of opinion among scientists about the carbon content in the steel. The authors of this research consider that this is related to anomalies in the plasticity of iron at certain temperatures, in particular as it was investigated in (Shakhnazarov & Pryakhin, 2016). Today’s steel making research is concerned with environmental issues, in particular with the transformation of

technological processes towards CO₂-reduced or -free production of steels and cast iron due to the occurring climate challenges and the global goals for a sustainable development (Ito, Langefeld, & Götz, 2020; Vercammen, 2022; Kueppers, Hodgson, Levi, Vass & Lechtenbohmer, 2022). We should add, that today, the use of hydrogen (H₂) or ammonia (NH₃) in metallurgy has the potential to become an important and promising direction of development (Ma et al., 2023). Hydrogen cannot only be used as an alternative fuel for mobility or other combustion processes to reduce greenhouse gas emissions but to improve steel production. One of the possible applications of hydrogen is its use in the production of iron and steel. Hydrogen can serve as a substitute for carbon in the direct iron reduction. Instead of carbon, which is used in traditional iron production processes, hydrogen can be used as a reducing agent to extract iron from ore, significantly reducing CO₂ emissions (Ma et al., 2023); e.g., Thyssenkrupp as only one of the steel manufacturer in Germany produces about 2.5 % of Germany's total CO₂ emissions. (Kleier & Hansmann, 2023; Leitprojekt Dekarbonisierung, 2023, p. 16–17). Currently, huge investments such as by Thyssenkrupp and Salzgitter AG (Finanzierung des SALCOS®-Programms gesichert, 2023; Hartbrich, 2023) are started to build new direct reduction process plants as well as to provide new hydrogen pipelines in Europe to the participating steel mills or to connect already existing pipeline networks.

Conclusions.

As can be seen from the iron-carbon phase diagram, since its initial presentation in the late 19th century, it has actively evolved until the mid-20th century. Initially, scientists tried to determine the different forms in which graphite exists when combined with iron at different temperatures. Such research was simultaneously conducted in England, Sweden, France, and Germany. Even the definition of what steel or iron is undergoing lengthy discussions.

It is considered that the first representation of the Fe-C dependence in the form of a diagram was presented by William Roberts-Austen, and then the search for names for different states followed. It should be noted that all of these states were named after well-known metallurgists, such as Martensite, Austenite, Ledeburite, and others. The evolution of the iron-carbon diagram is directly related to discoveries and methods in the field of physics and chemistry. With the gradual use of microscopes and X-ray diffraction methods, critical points were especially intensively explored in the interwar period.

While the maximum carbon content in cast iron of 6.67% does not raise any objections among scientists from all countries, there are different opinions regarding the maximum carbon content in steel. Furthermore, modern textbooks repeat the information from the second half of the 20th century and do not enrich the understanding of the actual maximum carbon content in steel. Even if we assume that there was no exchange of scientific information between American and Soviet scientists (including Ukrainian scientists for a considerable period of time), it remains a mystery why different data exist among scientists from Germany, Poland, and Australia.

Despite the so-called “age of polymers” in which we live now, steel and cast iron remain the most important basic materials in mechanical and civil engineering. The basis for the development of materials science is the knowledge of metallurgy, and the Fe-C diagram is the basis for the study of phase transformations occurring in alloys.

During the 1880s and 1980s, scientists from many countries in Europe and North America, as well as Australia, actively studied phase transformations in the iron-carbon system. Today, the direction of research has shifted due to new challenges of the 21st century. Hence, in most countries, there is still no consistent definition of the percentage of carbon content in the steel.

Conflicts of interest.

The authors declare no conflict of interest

Acknowledgments.

The authors thank the German Academic Exchange Service (DAAD) for funding within the project "OER with Ukraine" (Ukraine digital: Ensuring academic success in times of crisis, duration 01.06–31.12.2022).

References

- Austin, J. B. (1948). C-Fe Carbon-Iron. In T. Lyman (Ed.), *Metals Handbook* (pp. 1181–1182). Cleveland: American Society for metals.
- Authier, A. (2013). *Early Days of X-ray Crystallography*. Oxford: Oxford University Press. <https://doi.org/10.1093/acprof:oso/9780199659845.001.0001>
- Berzelius, J. J. (1841). *Jahresbericht über die Fortschritte der Physischen Wissenschaften*, 20. Tübingen: Heinrich Laupp. Retrieved from <https://www.digitale-sammlungen.de/de/view/bsb10130758?q=%28Jahresbericht+%C3%BCber+die+Fortschritte+der+physischen+Wissenschaften+1841%29&page=30,31> [in German].
- Bhadeshia, H. K. D. H., & Honeycombe, R. (2006). Iron and its interstitial solid solutions. In *Steels: Microstructure and Properties* (3rd ed.) (pp. 1–16). Oxford: Butterworth-Heinemann. <http://dx.doi.org/10.1016/B978-075068084-4/50003-0>
- Bobrova, T. B. (2016). *Osnovy materialoznavstva. Navchalnyi posibnyk – [Basics of materials science. Tutorial]*. Kyiv: GURT Resource Center. Retrieved from <https://www.gurt.org.ua/uploads/news/files/2016-8/Матеріалознавство-min.pdf> [in Ukrainian].
- Chicco, B., & Thorpe, W. R. (1982). Experimental determination of the austenite + liquid phase boundaries of the Fe-C system. *Metallurgical and Materials Transactions A*, 13, 1293–1297. <https://doi.org/10.1007/BF02645513>
- Chicco, B., & Thorpe, W. R. (1983). A further determination of the austenite solidus of the Fe-C system. *Metallurgical and Materials Transactions A*, 14, 312–314. <https://doi.org/10.1007/BF02651629>

- Cleaves, H. E., & Hiegel, J. M. (1942). Properties of high purity iron. *Journal of Research of the National Bureau of Standards*, 28(5), 643–669. <http://dx.doi.org/10.6028/jres.028.027>
- Debye, P., & Scherrer, P. (1916). Interferenzen an regellos orientierten Teilchen im Röntgenlicht. I. In *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse, 1916* (pp. 1–15). Berlin: Weidmannsche Buchhandlung. Retrieved from https://gdz.sub.uni-goettingen.de/id/PPN252457811_1916?tify=%7B%22view%22:%22info%22,%22pages%22:%5B%5D%7D [in German].
- Eckstein, H.-J. (1969). *Wärmebehandlung von Stahl: Metallkundliche Grundlagen*. Leipzig: Deutscher Verlag für Grundstoffindustrie VEB [in German].
- Fedirko, P. Krol, V., Hutsol, T., ... & Dziedzic, B. (2017). *Materialoznavstvo i sliusarna sprava – [Materials science and metalworking]*. Krakow, Kamianets-Podilskyi: Traicon. Retrieved from <https://depot.ceon.pl/bitstream/handle/123456789/13411/MATERIALS%20SCIENCE%20AND%20METALWORKING.pdf?sequence=1&isAllowed=y> [in Ukrainian].
- Finanzierung des SALCOS®-Programms gesichert (2023). *Stahl und Technik*, (3), 30–31. Retrieved from <https://www.stahl-und-technik.de/artikel/finanzierung-des-salzgitter-salcos-programms-gesichert> [in German].
- Geiger, C. (1925). Die Begriffe “Eisen” und “Stahl”. In C. Geiger, (Ed.), *Handbuch der Eisen- und Stahlgießerei*. (pp. 1–7). Berlin, Heidelberg: Springer. https://doi.org/10.1007/978-3-642-90865-1_1 [in German].
- Gutnyk, M. (2012). Robert Forester Miushet – liudyna, yaka nadala formu suchasnomu svitu [Robert Forester Mushet – the man who gave a shape to the modern world]. *Materialy 11-yi Vseukrainskoi naukovoï konferentsii «Aktualni pytannia istorii nauky i tekhniki» [Materials of the 11th All-Ukrainian Scientific Conference “Current Issues in the History of Science and Technology”]*, Kyiv, October 4–6, 2012, (pp. 253–255). Kyiv: Center for Monument Studies of the National Academy of Sciences of Ukraine and UTOPIK [in Ukrainian].
- Hartbrich, I. (2023, June 19). Thyssenkrupp und Zweiter Kohleausstieg an der Ruhr. *VDI Nachrichten*. Retrieved from <https://www.vdi-nachrichten.com/technik/werkstoffe/thyssenkrupp-und-der-zweite-kohleausstieg-an-der-ruhr/> [in German].
- Heyn, E. (1912). Report on the progress of metallography since the commencement of the year 1909 to the end of the year 1911. In *Sixth congress of the International Association for Testing Materials, held in New York, September 3–7, 1912, Vol. 1, Part II(1)*. New York: McGraw-Hill. Retrieved from <https://babel.hathitrust.org/cgi/pt?id=coo.31924004059048&seq=105>
- Horstmann, D. (1985). Das Zustandsschaubild Eisen-Kohlenstoff und die Grundlagen der Wärmebehandlung der Eisen-Kohlenstoff-Legierungen. Düsseldorf: Verlag Stahleisen [in German].
- Howe, H. M., & Sauveur, A. (1912) The Nomenclature of the Microscopic Substances and Structures of Steel. In *Sixth congress of the International Association for*

- Testing Materials, held in New York, September 3–7, 1912, Vol. 1, Part II(7).* New York: McGraw-Hill. Retrieved from <https://babel.hathitrust.org/cgi/pt?id=coo.31924004059048&seq=246>
- Hucińska, J. (1995). *Metaloznawstwo materiały do ćwiczeń laboratoryjnych*. Gdansk: Wydawnictwo Politechniki Gdańskiej. Retrieved from <https://pbc.gda.pl/dlibra/publication/edition/4096/content> [in Polish].
- Industrienormen Deutsche (1922). *Werkstoffnormen für Eisen und Stahl, herausgegeben vom Normenausschuß der Deutschen Industrie*. Berlin: Selbstverlag des Normenausschusses [in German].
- Ito, A., Langefeld, B., & Götz, N. (2020). *The Future of Steel making – How the European Steel Industry Can Achieve Carbon Neutrality*. Munich: Roland Berger GMBH. Retrieved from https://www.rolandberger.com/publications/publication_pdf/roland_berger_future_of_steelmaking.pdf
- Karsten, C. J. B. (1816). *Handbuch der Eisenhüttenkunde. Vol. 1: Die Eigenschaften des Eisens*. Halle: Curt. Retrieved from <https://www.digitale-sammlungen.de/de/view/bsb10706033?page=,1> [in German].
- Kayser, F. X., & Patterson, J. W. (1998). Sir William Chandler Roberts-Austen – His role in the development of binary diagrams and modern physical metallurgy. *Journal of Phase Equilibria*, 19, 11–18. <https://doi.org/10.1007/BF02904718>
- Kleier, T., & Hansmann, Th. (2023). Maßgeschneiderte Dekarbonisierung. *Stahl und Eisen*, 06, 16–17 [in German].
- Kueppers, M., Hodgson, D., Levi, P., Vass, T., & Lechtenbohmer, T. (2022). Iron and Steel. *International Energy Agency*. Retrieved from <https://www.iea.org/reports/iron-and-steel>
- Läpple, V. (2022). *Wärmebehandlung des Stahls*. Haan-Gruiten: Europa-Lehrmittel [in German].
- Ledebur, A. (1888). Über die Benennung der verschiedenen Kohlenstoffformen im Eisen. *Stahleisen*, 742 [in German].
- Ledebur, A. (1906). *Handbuch der Eisenhüttenkunde, Vol. 1: Für den Gebrauch im Betriebe wie zur Benutzung Beim Unterrichte Bearbeitet; Einführung in die Eisenhüttenkunde (Classic Reprint)*. Leipzig: Arthur Felix [in German].
- Lee, D. N., & Han, H. N. (2012). Directed growth of ferrite in austenite and Kurdjumov-Sachs orientation relationship. *Materials Science Forum*, 715–716, 128–133. <https://doi.org/10.4028/www.scientific.net/MSF.715-716.128>
- Leitprojekt Dekarbonisierung. (2023). *Stahl und Eisen*, 03, 16–17 [in German].
- Ma, Y., Bae, J. W., Kim, S.-H., Jovičević-Klug, M., Li, K., Vogel, D., ... & Raabe, D. (2023). Reducing iron oxide with ammonia: A sustainable path to green steel. *Advanced Science*, 10, 2300111. <https://doi.org/10.1002/advs.202300111>
- Mourelou, J. R. (1916). L'oeuvre de Proust en Espagne. *Revue scientifique*, 54, 257–266 [in French].
- Mushet, D. (1802). XXIV. On the different proportions of carbon which constitute the various qualities of Crude iron and steel. *Philosophical Magazine*, 13(50), 142–149. <https://doi.org/10.1080/14786440208676104>

- Nürnberg, F., Frolov, I., Grydin, O., Gutnyk, M., & Blank, T. (2022). *Materials Testing*. Hannover. <https://doi.org/10.57961/5fbf-7745>
- Osmond, F. (1886). Sur les phénomènes qui se produisent pendant le chauffage et le refroidissement de l'acier fondu. *Comptes rendus*, 103, 743–746; 1135–1137 [in French].
- Osmond, F., & Cartaud, G. (1906). Die Kristallographie des Eisens. *Metallurgie*, 3, 522 [in German].
- Ostwald, W. (1974). J. B. Richter. In *Günther Bugge: Das Buch der grossen Chemiker, Vol. 1* (p. 375). New York, Weinheim: Verlag Chemie [in German].
- Pawłowski, B. (2012). Temperatura przemiany magnetycznej cementytu, *XL Szkoła Inżynierii Materiałowej, 24–27 IX 2012* (pp. 1–5). Kraków: Akademia Górniczo-Hutnicza im. Stanisława Staszica w Krakowie. Retrieved from https://www.researchgate.net/profile/Bogdan-Pawlowski/publication/251880650_Temperatur_a_przemiany_magnetycznej_cementytu/links/0c96051f247cc3500e000000/Temperatur_a_przemiany_magnetycznej_cementytu.pdf [in Polish].
- Pawłowski, B. (2017). 8. Obróbka cieplna i cieplno-chemiczna stali. In *Wydział Chemiczny Technologia Chemiczna* (pp. 144–167). Retrieved from <https://www.studocu.com/pl/document/politechnika-slaska-w-gliwicach/wydzial-chemiczny-technologie-chemiczna/dr-inz-bogdan-pawlowski-obrobka-cieplna-i-cieplno-chemiczna-stali/31346752> [in Polish].
- Pfender, M. (1990). Martens Adolf. In *Neue Deutsche Biographie (NDB)*, 16, (pp. 266–273). Berlin: Band Duncker & Humblot. Retrieved from <https://www.deutsche-biographie.de/pnd116800453.html#ndbcontentCC-BY-NC-SA> [in German].
- Roberts-Austen, W. C. (1897). Fourth report to the alloys research committee. *Proceedings of the Institution of Mechanical Engineers*, 52(1), 31–100. https://doi.org/10.1243/PIME_PROC_1897_052_009_02
- Rocke, A. J. (2005). In search of El Dorado: John Dalton and the origins of the atomic theory. *Social Research: An International Quarterly*, 72(1), 125–158. <https://doi.org/10.1353/sor.2005.0003>
- Roeser, Wm. F., & Wensel, H. T. (1941). Freezing temperatures of high purity iron and some steels. *Journal of Research of the National Bureau of Standards*, 26(4), 273–287. <https://doi.org/10.6028/jres.026.015>
- Roozeboom, H. W. B. (1900). *The Metallurgist*, 3, 293–300.
- Ruer, R., & Klesper, R. (1914). Die γ - δ -Umwandlung des reinen Eisens und ihre Beeinflussung durch Kohlenstoff, Silizium, Kobalt und Kupfer. *Ferrum*, 11, 257–261 [in German].
- Sefström, N. G. (1828). Berättelser rörande göromalen vid Bergsskolan år 1827. *Jern-Kontorets Annaler*, 12, 145 [in German].
- Sefström, N. G. (1829). Versuche zur Ausmittlung der Natur des Graphits. *Annalen der Physik*, 16, 168 [in German].
- Seljakow, N., Kurdjumow, G., & Goodtzow, N. (1927). Eine röntgenografische Untersuchung der Struktur des Kohlenstoffstahls. *Zeitschrift für Physik*, 45, 384–408. <https://doi.org/10.1007/BF01343061> [in German].

- Shakhnazarov, K., & Pryakhin, E. (2016). Plasticity anomaly of iron as a result of transformation at ~650°C. *Journal of Mining Institute*, 217, 150–154. Retrieved from <https://pmi.spmi.ru/pmi/article/view/5093/2958> [in Russian].
- The engineering and mining journal*. (1912, September 14). *The engineering and mining journal*, 94(11), 484.
- Timofeeva, L., & Komarova, G. (2013). *Materialoznavstvo ta tekhnolohiia konstruktsiinykh materialiv. Chastyna 1 [Materials science and technology of structural materials: Lecture notes. Part 1]*. Kharkiv: UkrDAZT. Retrieved from <http://lib.kart.edu.ua/handle/123456789/6702> [in Ukrainian].
- Tyrkiel, E. (1963). *Wykres zelazo-węgiel w rozwoju historycznym*. Wrocław-Warszawa-Kraków: Wydawnictwo Polskiej Akademii Nauk [in Polish].
- Vercammen, S. (2022, August 1). Steel. Transition to net zero, *McKinsey Quarterly*. Retrieved from <https://www.mckinsey.com/capabilities/sustainability/our-insights/spotting-green-business-opportunities-in-a-surg-ing-net-zero-world/transition-to-net-zero/steel>
- Wadsworth, J., & Sherby, O. D. (1997). The History of ultrahigh carbon steels. *The Metallurgical Society 1997 Materials week, Indianapolis, IN (United States), September 14–17, 1997*, (pp. 1–42). Retrieved from <https://www.osti.gov/servlets/purl/611842>
- Wessel, H. A. (2009). Globale Unternehmensaktivitäten im Spannungsfeld von unternehmerischem Gestaltungswillen und (wirtschafts-) politischen Realitäten. Das Beispiel der Familie Mannesmann aus Remscheid. In *Hilger, Susanne/Soénius, Ulrich S. (Hg.), Familienunternehmen im Rheinland im 19. und 20. Jahrhundert*, (pp. 66–102). Köln: Stiftung Rheinisch-Westfälisches Wirtschaftsarchiv [in German].
- Westgren, A., & Lindh, A. E. (1921). Zum Kristallbau des Eisens und Stahl. *Zeitschrift fuer Physikalische Chemie*, 98(1), 181–210. <https://doi.org/10.1515/zpch-1921-9815> [in German].
- Westgren, A., & Phragmen, G. (1922). X-rays studies on the crystal structure of steel. *Journal of the Iron and Steel Institute*, 105, 241–273.
- Wisniak, J. (2003). Hendrik-Willem Bakhuis Roozeboom: Equilibrium and Phase Topology. *Journal of Phase Equilibria*, 24, 422–430. <https://doi.org/10.1361/105497103770330073>

Марина Гутник

Національний технічний університет «Харківський політехнічний інститут»,
Харків, Україна

Флоріан Нюрнбергер

Інститут матеріалознавства Ганноверського університету імені Лейбніца,
Гарбзен, Німеччина

Діаграма Fe-C – Історія її еволюції

Анотація. Розглядається еволюція концепцій і методів фізичних та хімічних наук, що сприяли формуванню діаграми Fe-C протягом минулих століть. Незважаючи на класичні знання, існують відмінності у представленні діаграми Fe-C ученими з різних країн, зокрема дані науковців з Німеччини, Польщі, України, США та Австралії децю не збігаються. Автори намагалися розібратися у причинах цієї розбіжності. Для проведення дослідження використовувалися загальні наукові методи пізнання: порівняльний аналіз і синтез, а також хронологічний підхід. Зазначається, що перші дослідження вмісту вуглецю у сталі були проведені в 1802 році. Подальший розвиток дослідження розпочався у 1827–1829 роках, коли було встановлено, що графіт – це чистий вуглець. Наголошується, що наступні дослідження вмісту вуглецю в сталі та чавуні пов'язані зі спробами створити перші графіки залежності вмісту вуглецю і температури. Це, в свою чергу, сприяло розвитку промислової революції. Вважається, що першу повну діаграму представив у 1897 році Робертс-Аустен. Пізніше, із використанням рентгенівських методів та мікроскопії, діаграма Fe-C поступово набула нового вигляду. На початку 20-го століття учені активно пропонували свої фазові діаграми. Дослідження, проведені науковцями з різних країн впродовж 1909–1911 років, були об'єднані, це відбулося на 6-му Конгресі Міжнародної асоціації для випробування матеріалів, що призвело до уніфікації назв фазових перетворень. Подальші дослідження до початку Другої світової війни були спрямовані на створення «чистої» сталі, тобто без шкідливих домішок, та уточнення температур фазових перетворень. Період Великої Депресії в США та війни в Європі не сприяли науковим експериментам. У той самий час для масового виробництва сталі та чавуну похибки в критичних точках на декілька градусів не мали суттєвого впливу, тобто уточнення температур фазових перетворень не вважали доцільним. Сучасна тенденція у наукових дослідженнях спрямована на вирішення екологічних проблем, спричинених промисловою революцією.

Ключові слова: діаграма Fe-C; уніфікація режимів перетворення в бінарних сплавах Fe-C; консолідація науки; матеріалознавство

Received 07.07.2023

Received in revised form 10.09.2023

Accepted 15.09.2023