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EDITOR-IN-CHIEF'S WORD

Dear readers,

Technical sciences are the foundation of our modern society, applied to solve practical problems, advance human knowledge, and built a better future to all. Croatian Academy of Engineering promotes and advances the field of engineering through research, education, and collaboration, and helps to develop and recognize the contributions of outstanding engineers. It serves as a platform for engineers to exchange ideas, address critical issues facing society, and provide guidance on important engineering-related policies and practices. This issue of Engineering power is dedicated to metallurgy. This field of engineering plays a crucial role in the development of new cutting-edge technologies, like renewable energy systems, electric vehicles, and advanced aerospace materials, which rely heavily on advanced metallurgical techniques and materials.

Editor-in-Chief
Vedran Mornar, President of the Croatian Academy of Engineering

EDITOR'S WORD

Dear readers,

it is our great pleasure to present to you the first issue of Engineering Power journal, published by the new editorial team. This issue was edited by Prof. Zdenka Zovko Brodarac, PhD, associate member of the HATZ Department of Mining and Metallurgy. With an overview of the scientific research potential of the Faculty of Metallurgy, University of Zagreb, you will have the opportunity to read review paper on the historical development of metallurgy, focusing on the discovery and use of aluminium, as well as original scientific article on the resistance of tool steels to local corrosion. Have a good time!

Editor
Bruno Zelić, Vice-President of the Croatian Academy of Engineering

FOREWORD

Visions of the professional development of scientists, as an integral part of the academic society, directly contribute to the development of the field of metallurgy both in the academic world and in the international community. At the same time, it is important to keep in mind the development and preservation of the primary role of the Faculty of Metallurgy in the education and training of highly qualified engineers in the field of metallurgy as an important part of the STEM field. The knowledge and technology transfer of the Faculty as a result of R&D should be evaluated as an indispensable factor for strengthening the economy, based on a 15.5% share of metallurgical production in Croatian industrial production, which is the result of the main subactivities in 2020.

The importance of the metallurgical profession and the influence of the Faculty is reflected as a triad of metallurgical competitiveness supported by state-of-the-art technology, efficient manufacturing processes and a skilled workforce. Since the metal production industry is extremely export-oriented, the scope of the production is also oriented to the needs of foreign manufacturers of end products. In the same 2020, this was supported by the high contribution of the metallurgical industry with 24% of the total merchandise exports of the Republic of Croatia. According to the economic analyzes Croatia should pursue its industrial development through the metal production industry, encouraging the development of SMEs´ with specific end products, starting up with relatively low investment and operating costs, all supported by quality education and knowledge and technology transfer relying on experts and resources of the Faculty of Metallurgy. Today, the Faculty's experts are currently working on cutting-edge metallurgy study subjects. Therefore, metallurgy is presented here with articles related to metallurgical development through scientific, research and professional results by enhancing the scientific research potential of the Faculty of Metallurgy through the implementation of infrastructure projects, the development of aluminum and its alloys through history, but also with a glimpse of future application followed by an example examining the local corrosion resistance of tool steel.

Guest-Editor
Zdenka Zovko Brodarac, University of Zagreb Faculty of Metallurgy

CONTENT

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Advancement of the scientific-research potential of the Faculty of Metallurgy through the implementation of infrastructure projects

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Abstract

Metallurgical production is considered as one of the drivers of the world economy. Metallurgy is a traditional, profitable and export-oriented industry branch in the Republic of Croatia. Excellence can be based on investment in highly sophisticated equipment as a potential for acquiring new and/or innovative knowledge, creativity and recognition on the European research map. The investment potential is based on the infrastructure projects Center for Founding - SIMET (KK.01.1.1.02.0020) of the Faculty of Metallurgy University of Zagreb in partnership with the Sisak-Moslavina County and VIRTULAB – Integrated laboratory for primary and secondary raw materials (KK.01.1.1.02.0022) in which the Faculty of Metallurgy is one of the partners. The projects were funded by the European Fund for Regional Development in the framework of Operational Program Competitiveness and Cohesion (2014-2020). Investment in equipment is not an end in itself! The created research potential forms the basis for investments in the knowledge, skills and competences of employees and students, while opening opportunities for economically targeted activities. Today, self-sustainability must be achieved by delivering excellent research results to stakeholders. Specific scientific research and professional projects as well as targeted education and training for critical and innovative thinking based on sophisticated equipment purchased through infrastructure projects will stimulate innovations in metallurgy. Raising the level of research quality with the motto "From idea to final product" will promote the competitiveness, recognition and general importance of ideas and innovations in metallurgy and metal industry as an important sector of the economic development of the Republic of Croatia.

Keywords: *metallurgy, foundry, raw materials, economy, scientific research and high education*

1. Introduction

The history of metallurgy dates back to 6000 BC, when man's first encounter with copper was recorded. Metallurgy (according to the Greek: μέταλουργεῖν: to dig ores) is an economic and scientific activity that deals with the production and application of metals and their alloys. It belongs to the field of technical sciences. It belongs to the field of technical sciences and includes the branches of process, mechanical and physical metallurgy. Process (extractive) metallurgy includes the reduction of metals from ores and their refining, i.e. separation, refining, alloying, casting, and other metal shaping processes in order to obtain semi-finished or finished products. Mechanical (processing) metallurgy deals with the shaping of metal in a plastic or solid state by technological procedures such as rolling, pressing, forging, bending and extrusion of metal. Physical metallurgy deals with determining the physical and chemical repeatability of the metal materials behavior during processing, shaping, testing and application. It includes crystallography, mechanical testing, determination of physical characteristics, metallography and other procedures for metal materials or end products testing to predict their quality, planning production processes and application conditions [1].

Founding is a scientific discipline which deals with the shaping processes of metallic materials in a liquid / molten state. Founding is the primary and most prosperous branch of production due to the exceptional flexibility of production and adaptation to competitive market conditions. It also enables the production of a whole range of metal materials, essential for everyday life. In addition, the application of modern casting technologies enables high productivity in qualitative and quantitative terms, which makes this industry extremely competitive.

Knowledge becomes an increasingly important resource for economic development. The Republic of Croatia is faced with the challenges of the world economy, according to which it must, among other things, meet certain requirements for the design of the education system. Ensuring the quality of the education system is one of the requirements that the Faculty of Metallurgy has set as a permanent mission. As the population's level of education affects economic progress, it is extremely important for the Republic of Croatia to increase the proportion of people with higher education in strategic field such as metallurgy as a part of technical sciences and STEM (science, technology, engineering and mathematics).

2. Infrastructure projects of the Faculty of Metallurgy

The University of Zagreb Faculty of Metallurgy is the only scientific and teaching institution in the Republic of Croatia that, respecting the culture of quality, provides higher education at the undergraduate, graduate, postgraduate and professional levels in the field of metallurgy with outcomes in metallurgical engineering and industrial ecology and also occupational safety, health and environment. The transfer of knowledge and technologies to students, academic society and economic entities in the metallurgical, metalworking, shipbuilding and foundry industries is done through conferences, seminars, workshops, public forums and lectures, are systematically conducted as part of a lifelong learning and training programme. The Faculty of Metallurgy bases its activities on high academic and ethical values, as well as on contribution and responsibility towards society as a whole [2,3].

Manufacturing activities and education form the basis of the development of every country, and the development strategy must rely precisely on excellent young people who, by acquiring knowledge and a research approach at the Faculty of Metallurgy, enrich the economy with specific knowledge, skills and competences. All of this is reflected in the strategic development directions Metallurgical Engineering and Industrial Ecology, Metal Materials and Occupational Safety, Health and Environment [4]. Excellence is based on investment in highly sophisticated equipment as a potential for new and/or innovative knowledge, creativity and visibility on the European research map. The investment potential is based on the infrastructure projects Center for Founding - SIMET (KK.01.1.1.02.0020) in partnership with Sisak-Moslavina County financed with 5.847.910,69 €. The other infrastructural project VIRTULAB – Integrated laboratory for primary and secondary raw materials (KK.01.1.1.02.0022) of the Faculty of Mining, Geology and Petroleum Engineering as a project leader, with 403.286,60 € for the Faculty of Metallurgy as a one of the partners. Both projects were financed by the European Fund for Regional Development, Operational Program of Competitiveness and Cohesion (2014-2020). Investment in equipment is not an end in itself! *The created research potential forms the basis for investments in the knowledge, skills and competences of employees and students, while opening opportunities for economically targeted activities* through the opening of spin-off companies as a way of achieving self-sufficiency. Targeted activities should open up lifelong learning opportunities for interested external stakeholders. These could create start-up companies through scientific research and professional projects as well as targeted education related to research opportunities and critical and innovative thinking training, according to the motto: *from the idea to the final product.*

In order to strengthen the competitiveness of economic stakeholders, smart specialization of production is necessary, i.e. sustainable high-quality production, cheap and environmentally friendly products. The global market requires optimization of existing technologies and the rationalization of production costs.

In recent years, a number of small companies have successfully developed (automotive industry parts, hospital chairs, profiled sheet metal, construction sheet metal) that successfully compete on the domestic and also global markets with innovations and high quality products. Given the growing demand for small series goods by global makers, it is assumed that they will establish a supplier network to which Croatian producers can contribute. Small series quantities are adequate to utilize their production capacities, and with qualified labor and new market possibilities, established businesses will expand, as will the establishment of new ones. By investing in sophisticated equipment and production certification, metal producers show their commitment to growth. The basic features of Croatian industry are consistent product quality and reliability in accordance with EU standards, while on the other hand it is important to invest in the available professional workforce, targeted support from academic and scientific institutions, and excellent production infrastructure with an emphasis on modern technologies and global transportation connections.

Since the Croatian market is too small for a significant increase in production, companies in the observed industry primarily direct their production capacities to countries in the European Union, which also means an increase in the level of productivity of assets and labor force, in order to compete with foreign competition. Competitiveness can be based solely on modern technology, efficient production procedures, but also on a highly qualified workforce. All of this requires investment in infrastructure and educational study programs that should strive to acquire, first of all, practical knowledge and skills with an emphasis on the development and application of modern materials and technologies in order to position the Republic of Croatia as an important production partner on the global market.

Therefore, the Faculty of Metallurgy University of Zagreb, recognized the necessity of influencing a transformative vision development of science, the teaching process and the economy by applying and implementing infrastructure project Center for Founding - SIMET, strategically important for the Faculty of Metallurgy, University of Zagreb as a whole, Sisak-Moslavina County and Republic of Croatia [5].

The problems faced by the Croatian metal industry are related to the unfavorable business environment, insufficiently developed entrepreneurial culture, lack of business investments and capital, and promotion measures of related institutions. In comparison to EU norms, the startup rate is extremely low. The number of small and medium-sized enterprises based on knowledge of metallurgy is insufficient. Furthermore, there is a lack of active cooperation between small and medium-sized enterprises in the field of metallurgy, the academic community and public authorities, as well as limited communication within the research community itself. Due to the lack of an inter- and multidisciplinary approach and the lack of suitable equipment, the cooperation of higher education institutions with small and medium-sized enterprises was limited.

The problem has been recognized precisely in the lack of capacity for the know-how concept of production. At this point, the Faculty of Metallurgy has identified a niche for its smart specialization, in which it will place itself as a provider of project ideas and advances, i.e. knowledge-based economic recovery. Therefore, a partnership between the Faculty of Metallurgy University of Zagreb and the Sisak-Moslavina County was established to create a favorable environment through the Center for Founding - SIMET, which would raise the level of technology transfer and research and development (R&D) results from of higher education institutions to economic entities.

The strategic goals on which the future development of the Faculty of Metallurgy in the area of scientific research is based include expanding the scope and increasing the quality of scientific research to a level that ensures the international recognition and competitiveness of the Faculty in the European research area; raising the quality of university postgraduate studies and the scientific advancement and employee training. The strategic goals of the Faculty of Metallurgy in the area of professional activity envisage professional advancement and competitiveness based on a strong connection of the Faculty of Metallurgy with leading economic entities in the Republic of Croatia, a strong alumni organization and recognizable lifelong learning and training programs; connecting with the economy, public and local community and improvement of professional work. An important segment is the transfer of knowledge and technology to students, the academic community and the economy.

The motivation for the initiation and implementation of projects Center for Founding – SIMET and VIRTULAB – Integrated laboratory of primary and secondary raw materials are defined by the general and specific goals of the project. The general goal of the projects was defined as follows:

- Investing in organizational reform and infrastructure in the research, development and innovation (RDI) sector aims to increase the sector's ability to conduct top-quality research and meet the needs of the economy, all of which contribute to economic strengthening applying research and innovation.
- By strengthening the capacity of investigation, research and innovation (IRI), the competencies of teaching staff and students will be improved. Therefore, the Faculty of Metallurgy and the metallurgical sector in general will be able to identify and activate their IRI potential.

In both infrastructure projects specific goals related to academic institutions are [6]:

1. Improving the accessibility of current instrumentation while introducing contemporary technology to improve the quality of scientific research.
2. Increasing productivity, i.e. the number of scientific research papers and the number of applications for competitive scientific and innovative projects.
3. Improving the quality of teaching while strengthening students' competencies and thus their competitiveness and employability on the labor market.
4. Transfer of knowledge and innovation to the economy.

The SIMET and VIRTULAB were established to connect necessary parties as a target group and enable the transfer of knowledge and skills in the function of research in the creation of materials and technologies to prospective users:

- scientific, teaching and professional staff and students and also,
- stakeholders from the economy sector.

through the design of innovative materials in response to market requirements and the creation of the final product, designing, characterization and reuse of primary and secondary raw materials, then product development using specific technologies (CAD/CAE technologies), computer-supported design of the product development process and construction, production preparation, but also through lifelong learning intended for students, business experts, etc.

The global market requires optimization of existing technologies and rationalization of production costs. The significance of the Center for Founding – SIMET and also the use of the VIRTULAB equipment will be represented in focused research in material development and technology transfers to partners from the real sector under the motto from idea to final product. The activities will be divided into three categories:

- designing of innovative materials for specific market requirements, i.e. the manufacturer, and the characterization of the synthesized or innovative material based on the specific improved and/or required properties of the final product,
- product development using sophisticated CAD/CAE technologies (CAD - Computer Aided Design, computer-supported design of the product development process and structural preparation of production and CAE - Computer Aided Engineering, casting and solidification process elaboration and prediction of potential errors). When developing products in addition to creating prototypes and tools, attention is paid innovation and optimization of production processes and procedures,
- lifelong learning (L3) – the goal is to bring sophisticated equipment and research and knowledge based on it to students, business experts and all interested stakeholders, allowing for the development of engineering skills, innovation, and inventiveness in solving project tasks, and thus launching globally com-

petent experts in the metal processing industry and employees of metallurgical companies.

- ➢ Designing and developing products as well as prototyping, emphasizes innovation and optimization of production processes and procedures with targeted research and development outcomes with carefully selected equipment unique in the Republic of Croatia, whose contribution to the development of materials and technologies is shown in a schematic representation of research methods and techniques connected to the Center for Founding – SIMET as shown in Figure 1.

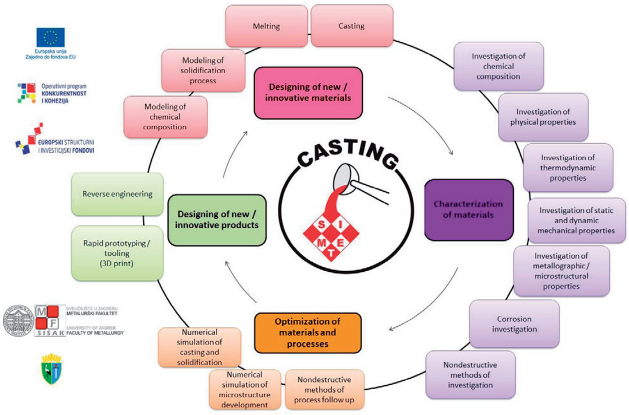

Fig. 1. Schematic representation of R&D outcomes within the infrastructure project Center for Founding – SIMET.

Finding, repurposing or reusing of raw materials is the driving force and link between the scientific community and the economy. The organization of VIRTULAB indicates the multiple analytical possibilities focusing on the life cycle of primary and secondary raw materials using areas of expertise of the involved laboratories and Faculties [6]. VIRTULAB has research capabilities that meet the needs of prospective research of primary and secondary raw materials, exploitations, refining, production processes, recycling, and finally finding substitute raw materials.

3. The impact of infrastructure projects on the development of scientific-research field of metallurgy

Nowadays, modern metallurgy is a specific discipline that deals with the design, development and characterization of everyday materials that surround us in our homes and workplaces, as well as materials with special requirements for specific purposes such as those for the automotive or space industries. At the same time, the right choice of production processes is also essential. The recovery of metal and disposal of waste materials from production is covered by industrial ecology in correlation with the management of materials and technologies.

Metallurgical production is considered one of the most important factors influencing the development of the world economy. It is profitable in the world, but a number of problems have been identified in the Republic of Croatia, such as a poor business environment, a lack of investment and poor communication between small and medium-sized entrepreneurs in the metal industry, scientific institutions, universities and local and regional authorities. The implementation of SIMET and VIRTULAB made it possible to change these conditions. In terms of theoretical knowledge, the metallurgical profession is highly dependent on the economy in mutual exchange of knowledge and experience. The already mentioned important segment of knowledge transfer, but also an important part of technology, will be reflected in the organization of many activities. Some of them have already been recognized, some are being targeted, and some will serve not only academic stakeholders, but also socially responsible businesses, such as Scientific and professional seminars, International Foundrymen Conference, Career Day, but also participation with innovations at international fairs / exhibitions innovation [5].

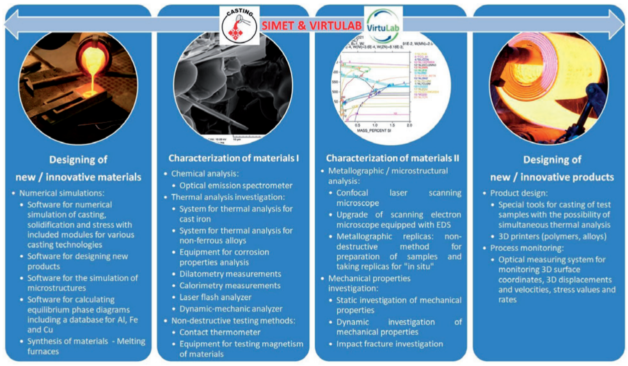

Fig. 2. Schematic representation of investigation methods and techniques within the infrastructure project Center for Founding – SIMET and VIRTULAB – Integrated laboratory of primary and secondary raw materials.

Within the framework of the Center for Founding – SIMET and VIRTULAB – Integrated laboratory of primary and secondary raw materials, the planned research and development activities, together with other activities related to the introduction of innovations in companies, are necessary for the positioning, recognition of the excellence of the Faculty of Metallurgy, recognition and visibility of the University of Zagreb, the recognition of Sisak and Sisak-Moslavina County as a center of attractive scientific excellence, knowledge and competence and therefore a niche for the development of the economy of the Republic of Croatia.

4. Conclusion

The metal industry in Croatia has a future, but it is necessary to concentrate on the trinity of the competitiveness of the metal industry using modern technology, an efficient production process and a highly qualified labor, to which the Center for Founding – SIMET and VIRTULAB – Integrated laboratory of primary and secondary raw materials directly contribute. For the development of the scientific, teaching and professional activities of the Faculty of Metallurgy University of Zagreb, as well as the development of the metal industry in the Republic of Croatia, a representative triangle of influential factors such as business sector, scientific research capacities and public policy plays a key role in the Triple Helix mode.

Through the implementation of the Center for Founding-SIMET and VIRTULAB – Integrated laboratory of primary and secondary raw materials projects, the Faculty of Metallurgy will strengthen its recognition as a place of continuous improvement of knowledge and its acquisition as well as competences in metallurgy and related STEM fields. With increasing opportunities for scientific and professional development and networking, the Faculty of Metallurgy will achieve the status of an integrative and competitive scientific and educational institution within the framework of European higher education and research. This strengthens its position as a socially responsible institution by raising the level of education, the expertise of outcome engineers in the technical field, and the development of economic branches related to metallurgy, materials, environmental protection, and occupational safety, health, and environment while adhering to academic ethical principles.

5. Acknowledgment

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Metallurgy development: Discovery and utilization of aluminum through history

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Abstract

Since the early human civilizations, the discovery and use of new materials and the development of new technologies have changed culture and influenced the development of the modern human environment. At the same time, innovations based on scientific discoveries and technological advances are connected to increasingly complex social and political structures and international relations, which have an impact on economic growth and social benefits. Unfortunately, the human capacity for technological and strategic innovation has most often been demonstrated under stressful conditions inspiring the phrase "necessity is the mother of invention". The goal of this review is to examine the necessity that compelled mankind to search for metals, primarily focusing on the discovery of aluminum and the challenges represented by the complex nature of its minerals. Although men's first contact with metal initiated with native copper and meteoritic iron, bronz was the first metallic material significantly impacting human society. The experiments with its chemical composition led to the development of metallurgical processes such as smelting, refining, and casting as well as mechanisms of economics and communication. The accidental discovery of iron in the process of copper ore refining gave mankind greater control over its environment, resulting in increased population and expanded settlements. Aluminum, as a brilliant white metal, was introduced to the world through the works of Wöhler and Deville. However, it became commercially available after electrolysis was discovered by Charles Martin Hall on February 23rd 1886 in a woodshed using home-made battery. A few months later, the similar results were obtained by Paul Louis Toussaint Héroult, so the process for electrolytic production of aluminum bears both of their names. As a symbol of modernity aluminum is used today in the automotive, aerospace, railway, marine, electric, and architectural applications. At the *end of this work, it is superfluous to ask whether humanity would have been able to explore the universe and reach the stars if it had been restricted by stone, bones and wood.*

Keywords: *history of metallurgy, human society, aluminum*

1. Introduction

Since the beginning of human civilization, the discovery of new materials and the development of new technologies have changed culture and influenced the development of the modern human environment [1]. In archeological studies this relationship is described by the term "*material of past cultures*" [2], referring to the materials that were produced, used, purchased or consumed [3]. This term is based on the fact that social conditions as well as the social status of an individual can be reflected in physical objects [4]. Given that innovation based on scientific discoveries and technological breakthroughs is a dynamic process, their impact on economic growth and social benefits is not surprising [5,6]. In historical context a general increase in technological complexity, diversity, and efficiency has been correlated with increasingly complex social and political units of organization [7]. However, the cross-cultural view shows that the changes in social values, social norms, patterns of organizational behavior as well as the power and authority have frequently ended in conflict or war [8]. As one of the causal variables, the conflict has inspired the idea that humans have an inherent capacity for technological and strategic innovation under stressful conditions. This view is summed up in the hopeful phrase "*Necessity is the mother of invention*" [9] and represents one of the earliest cultural models of evolution [7].

The purpose of this paper is to examine the need that forced mankind to search for metals, and the impact of metallurgy on the development of human society. The paper focuses primarily on the discovery of aluminum (Al) and the challenges posed by the complex nature of Al-containing minerals as well as the need for interdisciplinary approach to the development of an industrially sustainable Al production process.

2. The evolution of early metallurgy

The evolution of metallurgy (**Fig. 1.**) and material sciences in general includes an artistic, industrial, and scientific approach. The artistic notion was inspired by initial realization that different materials behave differently. The different types of industrial and social organizations at different times were sparked by the need for large-scale production due to the useful properties of the materials. Ultimately, the need to achieve an optimal balance between properties and application led to the development of a science that permitted the selection of chemical composition and the manipulation of structure at many levels - metallurgy [10]. The history of metallurgy was determined by the availability of metals. It started with the utilization of native metals and developed with the knowledge of how to create an environment with higher temperatures to enable the smelting of ores, melting, and alloying of metals [12]. Consequently, early metallurgy began with the use of native copper (Cu) and meteoritic iron (Fe). While the rarity of meteoritic iron (*amūtu* [13]) limited its application to ritualistic and embellishment purposes [14], the shaping and annealing of Cu represented the next step in the development of metallurgy (**Fig. 1.**) [14, 15]. The early use of native Cu

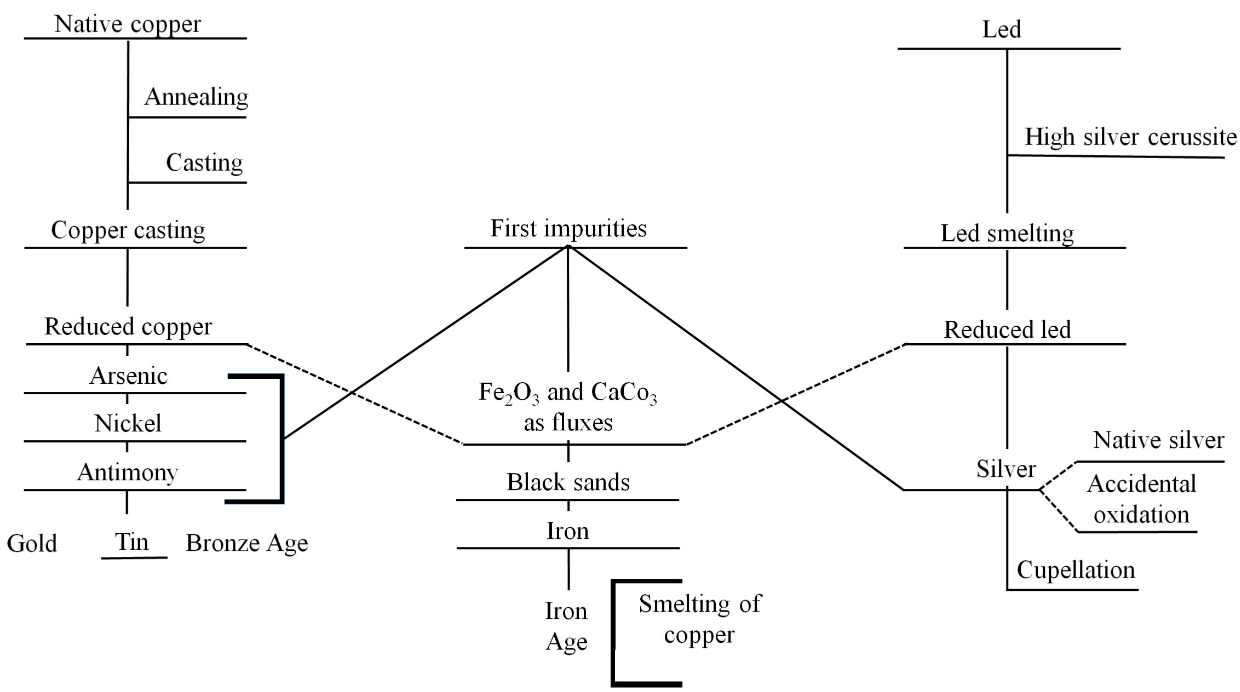
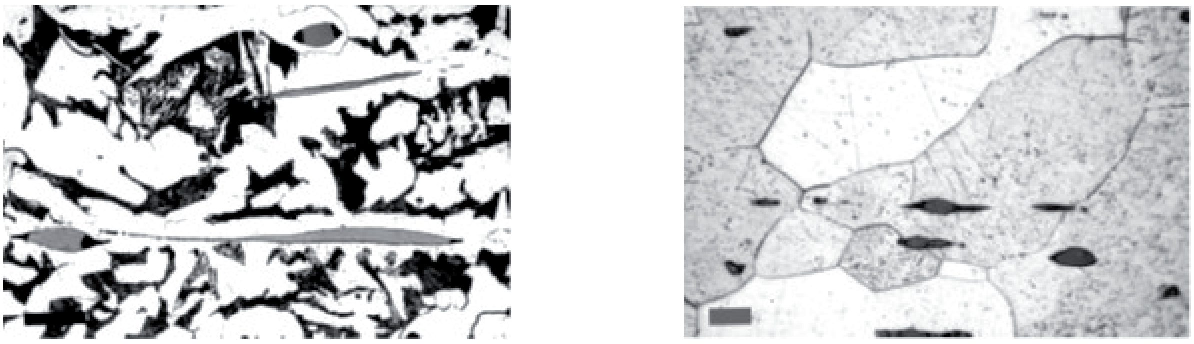


Fig. 1. Schematic tree of the development of metallurgy [11]

involved the use of an extremely limited Stone Age technique of cold forming to produce beads and possibly awls, pins, or hoops [17]. The complexity of the early design increased with the use of annealing. In this process, native Cu was exposed to a gentle heat that resulted in a softening of the material. The casting of native Cu occurred accidentally when it was exposed to temperatures over 1083 °C during annealing. The melted pieces of copper solidified in a single puddle (*puddle casting*), which allowed the reuse of the scrap and increased the availability of metal [18]. The appearance of *puddle casting* indicated that the early artisans almost simultaneously followed two important courses of discovery. The first course dealt with the shaping and melting of the native metals, At some unknown point in history, smiths realized that Cu, lead (Pb), silver (Ag) and zinc (Zn) can be found in sulfide ores developing techniques of roasting, matting and fire refining [19]. The first use of iron by pre-Hittite and Hittite people of Anatolia and Mesopotamia around 1500 BCE was the culminating moment in both pyrotechnological and early metallurgical processing [11]. Compared to modern pyrometallurgy, pyrotechnology involved the use of fire by humans to produce plasters, ceramic pots and bricks, glazes, glasses and metals in a temperature range between 100 °C to 1500 °C [20, 21, 22]. While the temperature of 100 °C was used for roasting gypsum to make plaster of paris [23], the temperature of 1100 °C was used to cast native Cu, extract most metals from ores, and vitrify pots to a kind of a glaze [18]. As shown in **Fig. 1.** the smelting of terrestrial Fe (*aši'u* [13]) was a derivative of large-scale smelting of Cu and Pb from sulfide ores using Fe-containing flux [24]. The smelting of Pb ores with the addition of hematite (Fe_2O_3) or gossan [25] fluxes sometimes yielded a mass of unfused Fe known as "*bear*" as a consequence of high heat and the excessive use of fluxes. Pure Fe was also yielded during the smelting of covellite (CuS) or chalcocite (Cu_2S) ore with a use of gossan flux [26, 27]. The early Turkish experiments showed that iron could be obtained in industrially usable form by carefully controlling smelting temperature in order to keep it in a spongy state [15]. The iron ore and wood were put into a furnace to burn. The reaction between carbon and the oxygen from the Fe ore enabled the reduction of Fe in the form of a spongy mass. This mass contained slag that was mostly removed by hammering to produce wrought Fe and shape it into a tool. While Turkish metallurgists were not able to generate enough heat to produce Fe castings [12], better furnaces and Fe ores with higher phosphorus content enabled the production of cast iron in China as early as 3rd century BCE [28]. The appearance of polymetallism and the awareness of the beneficial effect of alloying resulted from the development of smelting techniques. Early alloying systems were developed through the use of complex ores (especially sulfides and gossans), techniques of fluxing ores with each other and the discovery of active impurities during casting (native Cu) and smelting. As shown by the discovery of Fe, smelting did not begin with the reduction of a single metal from the ore, but with an attempt to reduce several metallic ores with one fluxing the other [11]. While Ag accidentally occurred as an impurity during Pb refining by cupellation [29], [30] (**Fig. 1.**), arsenic (As) was detected in the vicinity of Cu deposits. Consequently, it became known for its silvering effect observed in many Eurasian bronzes of the 3rd and early 2nd millennia [31]. In the rage of 0.25 % to 12.0 %, As seems to have been the most consistent impurity forcing early metallurgist to search for an adequate alloying element – tin (Sn). Considering that the origins of Sn in Anatolia, Mesopotamia, and Iran are still not completely clear, its use remains the mystery of bronze metallurgy (**Fig. 1.**) [11]. Today, it is assumed that Sn was supplied by two main routes. The first involved the trade of hundreds of kilograms of Sn moving from Aššur in Assyria to Kamiš in Anatolia, while the other progressed from Susa to a site identified as Crete by the way of Euphrates. This assumption is supported by philological analysis of documents containing the word *annaku* meaning tin [32, 33]. Up to this point, the social and cultural consequences of metallurgy development can be considered as minor. Since Cu was too soft a material to replace stone tools and weapons used in Neolithic times [34], its primary purpose was ornamental [17]. The first bronze, as an alloy produced by adding tin to copper, has a predecessor of approximately the same hardness and strength in the so-called arsenic or antimony copper, or as many consider arsenic/antimony bronze, which as a formation was created from a complex ore - tennantite ($(Cu,Fe)_{12}As4S_{13}$) and tetrahedrite ($(Cu,Fe)_{12}Sb_4S_{13}$). Furthermore, the experimentation with bronze chemical composition led to the development of metallurgical processes such as smelting, refining and casting as well as mechanisms of economics and communication [35]. The archeological discoveries in Kültape and its satrapies [36] represent the evidence of organized production of Cu from sulfide ores, the first large-scale trade in the rare metal Sn, the fabrication of bronze by industrial methods, the output of Ag, experimentation with Fe as well as the extensive use of mechanisms of economics such as banking, crediting and keeping of complex records [37, 38]. These documents describe the expansion of metal trading area deep into Europe and western Asia. In the middle of the 2nd century BC, the search for the most elusive and sought-after metal Sn led men as far as Cornwall in England [39]. The penetration of sulfide technology to Cu deposits of Cyprus and Pb deposits in Greece marked the beginning of mass production [40]. Consequently, the Cu billets of Cyprus in the shape of ox hide are considered to be the trademark of this period (**Fig. 2**) [41].

Fig. 2. Copper ox-hide ingot dating to the Late Bronze Age discovered at the Enkomi in Cyprus [41]

Thanks to the development of smelting techniques, Fe replaced bronze as a principal material in tool and weapon production. The utilization of iron gave mankind grater control of its environment leading to the increased population and larger settlements. It was not until the 14th century that iron smelting furnaces, known as blast furnaces, were built in Europe. The blast furnaces had water powered bellows that produced much higher temperatures allowing iron to absorb smaller quantities of carbon (C). Consequently, the *pig iron* could be obtained at a lower smelting temperature and directly poured into molds [42]. The substantial improvements to the blast furnaces referring to increased high stack due to the higher pressure of the blast, but also a change in stack geometry, enabled a continuous smelting process with increased efficiency and productivity. A further reduction in C content and the transition from *pig* to *wrought iron* was obtained in reverberatory furnaces through the works of Henry Cort and James Neilsen [43, 44]. *Wrought iron* was the principal material of Industrial Revolution until the second half of the 19th century when a process was invented to produce cheaper steel. The Bessemer process involved blowing air through the bottom of a vessel called converter containing liquid *pig iron* [45]. Oxygen (O_2) from the air combined with Fe to produce iron oxide (FeO) that reacted with C from the *pig iron* to produce carbon monoxide (CO). The reduction in C content is a consequence of the reaction between CO and C from pig iron. The remaining C is additionally removed when the O_2 from air is combined with silicone (Si) and manganese (Mn) to form slag. Since the resulting steel was brittle, the chemical composition needed to be amended with the addition of Mn and C [46]. An alternative method of making steel known as the *open-hearth process* was invented in 1864 by the William and Frederic Siemens and improved by the Pierre and Emile Martin. The furnace chambers known as regenerators were alternatively heated by the furnace gases leading to higher temperatures. Similar to the Bessemer process, FeO and CO were used to reduce C and remove impurities. Although it took longer to achieve better control over C content, open-hearth process enabled a reduction in phosphorus (P) content and decrease in non-metallic inclusion content. The optical micrographs of the steel produced by early Bessemer and *open-hearth process* are shown in **Fig. 3**.



a) b)

Fig. 3. The optical micrographs of:
a) Brooklyn Bridge steel showing manganese sulfide (MnS),
b) Springfield Barrel steel showing MnS inclusions with silicate ends [47]

The metallographic analysis performed on the Brooklyn Bridge steel produced by the early Bessemer process revealed the presence of large complex non-metallic inclusions consisting of MnS and manganese silicate (**Fig. 3. a**). The reduction in size and content of non-metallic inclusions in Springfield Barrel steel produced by *open-hearth process* (**Fig. 3. b**) was a consequence of the prolonged deoxidation time allowing impurities to form slag on the surface of the melt [47]. The Bessemer and *open-hearth* production processes reduced the price and increased the production of steel. Cheaper steel replaced iron in a variety of applications such as railway, shipyard, and bridge building [12].

The early models were classified as arc radiation or arc conduction furnaces. The Stassano furnace developed in Italy was one of the first models of arc radiation furnaces initially used in the experimental reduction of iron ores (**Fig. 4.**)

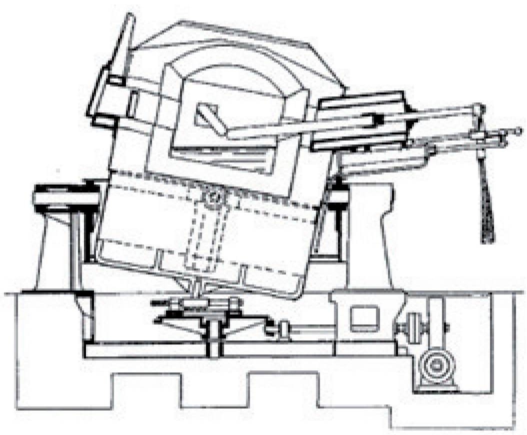


Fig. 4. Stassano furnace [48]

Its three electrodes slightly inclined at an angle of 120° enabled easy regulation and steady load even when using cold input materials. However, the utilization of Stassano furnace was limited by its low heat-efficiency and use of a tap-hole. The second type of electric arc furnace is considered more efficient because in addition to passing through the electrodes, the electrical energy also passed through the input material. However, one of the first models known as Héroult furnace exhibited significant surface instability of the melt preventing its use in the production of higher quality steel [48].

Despite being more expensive than Bessemer and *open-hearth procedure*, the electric arc furnace enabled better control of temperature and production of higher quality steel [12]. It was extensively used during World War One in the production of alloyed steels for ordinance purposes. In the post-war period, the arc technology allowed for quick rebuilding and revitalization of Europe. Mower, it enabled European manufactures to effectively compete with large steelworks of the United States in the production of cheap carbon steel [49]. Presently, it is commonly used for the production of stainless and manganese steel as well as a whole range of low alloy steels for the automotive and aircraft industry [50].

The further development of electric furnace technology enabled the large-scale production of metals such as tungsten (W), chromium (Cr) and Mn as well as the mass production of Al [46].

3. Discovery of aluminum

Although it is only one hundred and sixty years since Al was discovered in its elemental form, and only one hundred years since a viable manufacturing process was established, more Al is now produced annually than all other non-ferrous metals combined [51]. In 2021, 67,092 thousand metric tons of primary Al was produced with a daily average of 183.8 thousand metric tons. The leading producer of primary aluminum in 2021 was China with 38,837 thousand metric tons followed by Gulf Cooperation Council consisting of Bahrain, Oman, Qatar, Saudi Arabia, and United Arab Emirates with 5,889 thousand metric tons [52].

The scientific and technological application of Al and its alloys began during the Industrial Revolution in the late 19^{th} and early 20^{th} century with the development of automotive, railway and marine industries. However, the Al alloys had the greatest impact on the aerospace industry. Due to their low cost, easy fabrication, light weight and the high-strength levels achievable through the heat treatment, Al alloys become the main aircraft material since they started replacing wood in the late 1920s [53]. In order to meet the requirements of the contemporary aerospace industry low structural weight, higher damage tolerance, and higher durability, further improvements in fracture toughness, fatigue performance, formability and superplasticity [54] have been achieved [55]. Simultaneously, Al and Al alloys have found application in different branches of industry.

3.1. The main obstacles in the discovery of aluminum

Because it does not occur naturally in its native form, Al was discovered late. Instead, Al constitutes 8.2 % of the earth's crust in the form of Al-bearing ores such as alum (potassium aluminum sulfate), feldspars (sodium aluminum silicate), micas (aluminum silicates), clayey earths (aluminum silicates) and bauxite [56]. As a consequence, in their attempt to synthesize elemental Al, the first researchers were not only confronted with the complex nature of the Al-bearing minerals, but also with the need for interdisciplinary engineering and scientific approach to the development of industrially viable process for Al extraction, reduction and manufacturing [57]. Although the synthesis of elemental Al required a contemporary approach, the use of its minerals began in ancient times.

3.2. Ancient history

The concept that all mater is composed of particles too small to be seen was introduced in ancient Greece by Leucippus and Democritus. They assumed that atoms are homogeneous and completely solid with different sizes, shapes and weights [59]. Regardless of his aversion towards Leucippus and Democritus theory, their work allowed Aristotle to define the nature of the element [60]. His theory was important for understanding the results of experiments performed by the early metalworkers and craftsmen. They have learned that regardless of the extraction result, the process could be reversed without permanently affecting the basic element. To the ancient world that was aware of Ag, Au, Cu, C and S and was struggling to extract Pb, Sn, Hg and Fe, aluminum could be connected through the alum ($KAl(SO_4)_2$ $12H_2O$). When clay reacts with sulfuric acid from damp volcanic earth, alum is produced. Consequently, its deposits are located near the surface and easily mined. In the ancient civilizations of Mesopotamia, Sumeria, Egypt, Greece and Rome, alum was mainly used for medical purposes. Alum was also used by ancient metalworkers in Au purification, surface enrichment of Ag alloys and artificial patination process [61]. The Egyptian black-patinated statuette of a cat is shown in **Fig. 5**.

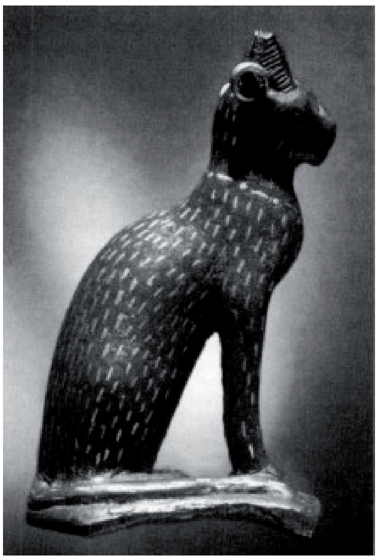


Fig. 5. The Egyptian black-patinated statuette of a cat exhibited in the Los Angeles County Museum of Art [61]

The statuette was made from Cu alloy containing approximately 1% Au and 1% Ag. The statuette was inlayed with Ag and patinated in the chemical bath composed of Cu salts, alum and vinegar [61]. The alum extraction process and its application are best described in the encyclopedic work of Pliny the Elder entitled *Naturalis Historia*. In the book 35 chapter 52 named *Alumen and the several varieties of it; Thirty eight remedies*, Pliny recalls the story of a strange, light, silvery metal obtained from plain clay, insinuating the possibility that Al may have been discovered by accident 2000 years ago. One day, a goldsmith in Rome was allowed to show the Emperor Tiberius a dinner plate that was very light and almost bright as silver. The goldsmith told Emperor Tiberius that only he and the gods knew how to produce this metal from clay. Tiberius was one of the Rome's great generals who conquered most of Europe and amassed a fortune in gold and silver. He was also a financial expert who knew that the value of his fortune would decline if people suddenly had access to a shiny new metal that was rarer than gold. So, instead of giving the goldsmith expected regard, the Emperor ordered his beheading [62]. Although the story is most likely a legend, it implies that other metals besides Pb, Sn, Hg, and Fe may have been reduced.

3.3. Alchemy and the Middle Ages

Craftsmanship and alchemy are considered to be the basis for scientific research and development that unknowingly depended on phenomena such as thermodynamics and diffusion. Alchemy, the early science of material transmutation with a purpose of evocating a valuable changes, provided some accurate explanations for chemical and physical reactions. Alchemists developed and carefully recorded processes that yielded the desired changes in material properties. However, when they found no obvious explanation, the magic was accredited [63]. Although it was practiced in China, Near East and Greece, alchemy is most often associated with the Egyptians who developed initial formulas in the 1st century AD. From there, alchemy spread to Western Europe and was practiced during the Middle Ages. Improvements of different alchemical recipes for similar engineering processes were made possible by cultural overlapping due to warfare, travel and trade. The cuneiform codex not only lists the formulas and processes, but it also shows the differences between the Babylonian and Egyptian approaches to alloying and coating. While Babylonian approach to transmutation involved heating the metal in the bath, Egyptian transmutation was performed by immersing previously heated metal in the mixture of chemicals [12]. Although alchemists failed to transmute Al, alum was extensively used. The military application of alum is mentioned during the First Mithridatic war when Greek general Archelaus realised that *alu*- based solution can be used to treat wood in order to make it partially flame resistant. Parallelly, his opponent Roman general Sulla used the same solution to protect the fleet from Archelaus attempts to set it on fire utilizing metallic mirrors [64]. The First Mithridatic War ended in Orchomenus where Sulla, using the terrains natural defences defeated Archelaus's more superior army [65]. In addition to its military purposes, alum was also used by tanners (lat. *alutarii*) to produce a special type of soft white leather (lat. *aluta*). The tanning effect was obtained through the weak reaction between alum salts and carboxyl groups in collagen proteins [66]. The Chinese alchemists used alum to make aqueous solutions used in metal surface processing. According to one of the recipes, to obtain a solution for surface treatment of Fe, it to mix transparent pieces of alum with horses' teeth in a green bamboo tube and add 4 measured of nitric acid. The opening is then tightly sealed, and a tube is immersed in vinegar for 30 days. Applying the obtained solution on the surface of Fe will result in the appearance of copper [67]. Besides metallurgical applications, alum is also mentioned in recipes concerning the elixir of life known as Golden flower. According to this recipe the cinnabar, mercury and alum are placed in the egg-shaped container made of silver. The container is heated in a mixture of Fe rust, Cu, S, realgar, saltpetre and honey. As expected, the procedure did not result in the elixir of life, but often resulted in serious hand and facial injuries as well as arson [68]. So it is not surprising that alchemy was considered tempering with Order of Creation and the attempt to conquer the Nature. This gave cautious and dangerous political and religious connotations leading to persecution. The religious persecution initiated in 3rd century when Roman Emperor Diocletian ordered the destruction of the alchemic texts and codex. This drove the alchemic practices into secrecy marking it as "The Dark Arts". Unfortunately, the dark connotation followed alchemy through Middle Ages associating it with evil, demonic, and occult practices. In this period the scientific work of all types that was not solely for medical purposes was considered heresy [69]. The believe that philosophical understanding or scientific approach were inspired by the devil ended in 15th century with the downing of the Renaissance. The beginnings of liberal thought and the development of new ideas are evident in the scientific theories and engineering innovations of Copernicus, Galileo, Leonardo da Vinci, Kepler, and Paracelsus. Fearing excommunication by the Catholic Church rather than execution, Renaissance scientists abandoned the Greek ideas of alchemy and concentrated on mathematics and the natural sciences. This new approach to intellectual freedom led to a scientific revolution [70]. The Georgiou Agricola's catalogue entitled *On the Nature of Metals* is considered to be one of the earliest Renaissance works representing the *state of the art* mining, refining and smelting. In his catalogue, Agricola describes alum production in 12th book together with salt, soda, vitriol, sulphur, bitumen, and glass. The alum, described as astringent and sharp solidified juice (*succi contracti*), was obtained from aluminous water or a solution containing "*kind of earth*", rocks, pyrites and other minerals using hydrometallurgy (**Fig. 6. a**) or pyrometallurgy (**Fig. 6. b**) [71].

Raw materials are placed in wooden tanks at the beginning of the hydrometallurgical process (**Fig. 6. a, A**) and mixed with water and urine. After the solution is mixed and stirred for several days (**Fig. 6. a, B**), the plugs (**Fig. 6. a, C**) are taken out and the solution is drawn into a wooden trough (**Fig. 6. a**, **D**). This alum-rich solution is transported into a reservoir (**Fig. 6. a, E**) and diluted with water and urine. After a few days of soaking the reservoirs are emptied using launders (**Fig. 6. a, F**) into a small led cauldron (**Fig. 6. a**, G). The solution is boiled until most of the water has evaporated. The obtained solution is full of meal consisting of fatty and aluminous matter as well as asbestos and gypsum impurities. Afterwards, the obtained solution can be cooled in a wooden tub (**Fig. 6. a, H**) or purified by running through the vats. The purification of the cooled solution containing alum is performed by running the solution through the vats containing twigs that enable alum crystallization (**Fig. 6. a, I**). At the end of the hydrometallurgical process, the small transparent white cubes of alum are placed in the hot rooms to dry. The pyrometallurgical process consists of roasting aluminous rocks in a furnace (**Fig. 6. b, A**) until they become red in color and desulfurized. After roasting and cooling, the desulfurized rocks are conveyed into an open space (**Fig. 6. b, B**) to be sprinkled with water for four days. After moisturizing for a given time, the aluminous rocks began to crumble (**Fig. 6. b, C**). The obtained material is transported using deep ladles (**Fig. 6. b,** *D*) into a copper cauldron (**Fig. 6. b,** *E*) containing boiling water. After the solution is sufficiently purified and ready to congeal, it is ladled trough the launders (**Fig. 6. b, F**) into the trough (**Fig. 6. b, G**). In wooden trough the solution congeals and condenses into the alum. When pyrites and other rock types are used, the alum is obtained pyrometallurgically after Au, Ag and Cu have been separated [71].

A – tanks, B – stirring poles, C – plug, D – trough, E – reservoir, F – launder, G – lead cauldron, H – wooden tubs sunk into the earth, I – vats in which twigs are fixed

a)

A – furnace, B – enclosed space, C – aluminous rock, D – deep ladle, E – caldron, F – launder, G - troughs

b)

Fig. 6. The alum extraction process by a) hydrometallurgy, b) pyrometallurgy [71]

3.4. The discovery of aluminum

As a part of his new theory of oxygen combustion, Lavoisier proposed the idea that alumina (Al_2O_3) was an oxide of a metal with a high affinity for oxygen [72]. Alessandro Volta, an Italian physicist and chemist, found in 1800 that an electric current is produced when two metal electrodes are separated by an electrolyte solution (**Fig. 7**). Soon after, the possibility of utilizing Volta's invention in metal synthesis was recognized. The first attempts to obtain pure Al were made in 1807 by Berzelius and Humphry Davy (**Fig. 7.**).

Berzelius attempted to decompose Al, boron (B) and silicone (Si) from aluminum fluoride (AlF_3) using potassium amalgam (KHg_2). Unfortunately, his approach to Al extraction was unsuccessful due to the high solubility of Al in caustic potassium (K) produced during electrolysis. Had he used the excess amount of AlF_3, Berzelius would be accredited for discovering Al. Thus, that merit belonged to his most famous student Friedrich Wöhler [73]. By introducing the molten compounds to an electric arch, Davy successfully produced pure K, sodium (Na), calcium (Ca), strontium (Sr), barium (Ba) and Mg. However, Davy was not able to synthesize pure Al. Instead, he synthesized Al-Fe alloy through electrochemical reactions in fluid alumina followed by carbon-based reduction. Although he used alumina in his experiments, Davy named this new element after alum, this "*precious*" and "*bitter*" white mineral [74]. First he spelled it *alumium*, latter changing it to *aluminum*, while finally settling on *aluminium* in 1812.

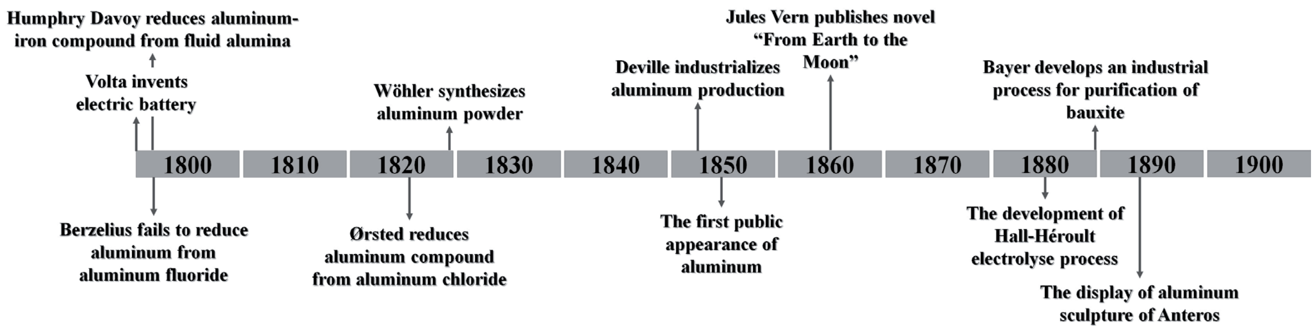


Fig. 7. The timeline of aluminum discovery, technological developments, and applications during 19th century [57]

While scientific community preferred aluminium due to its classical ring, the aluminum was adopted in the United States when metal begun to be widely available. The name aluminium was finally standardized in the 1990 by The International Union of Pure and Applied Chemistry [75].

In 1825 Hans Christian Ørsted started to investigate the chemical action of the voltaic current and tried to electrochemically isolate the metal believed to reside in alumina. Firstly, Ørsted prepared aluminum chloride ($AlCl_3$) by passing a flow of chlorine (Cl) over a mixture of charcoal and alumina preheated to redness (**Fig. 8.**).

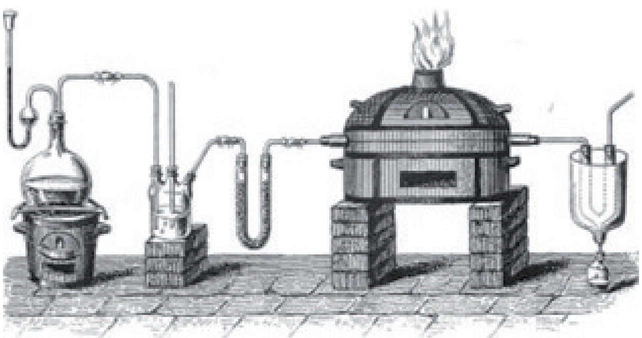


Fig. 8. Ørsted's apparatus for synthesis of dry aluminum chloride [76]

The obtained $AlCl_3$ was mixed and heated with KHg_2 producing potassium chloride (KCl) and aluminum amalgam (Al(Hg)). By distilling Al(Hg) in the inert atmosphere, he was able to obtain metal that looked like Sn. At the end of experiment, Ørsted reported:

"*This amalgam is very quickly decomposed in contact with the atmosphere. By distillation without contact with the atmosphere, it forms a lump of metal which in color and luster somewhat resembles tin. Moreover the author has found, both in the amalgam and the aluminum, remarkable properties which do not permit him to regard the experiments as complete, but show promising prospects of important results*" [74].

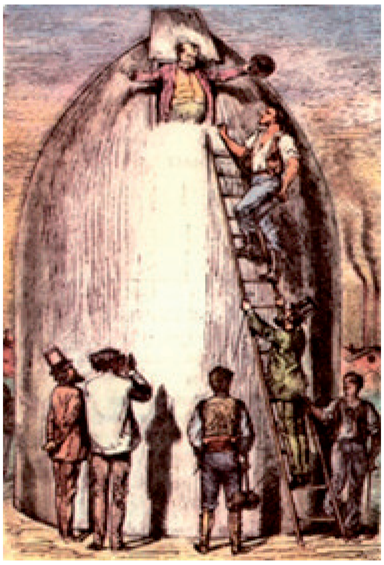
Although Ørsted's contribution to Al discovery was not recognized by the scientific community of that time, Wöhler's discovery was based on the results of his experiments. By repeating the Ørsted's experiment and reheating the synthesized mass, Friedrich Wöehler was able to indicate that the present impurities are mostly K-based originating from the reaction between diluted potassium amalgam and aluminum chloride [77]. Since Wöehler was not able to synthesize pure Al by relaying on the previously established method, he prepared the $AlCl_3$ as indicated by Ørsted, and devised a new plan to isolate pure Al. This new plan was based on the decomposition of $AlCl_3$ using K and the stability of Al in water. After adding the excess amount of hot potassium carbonate (K_2CO_3) to a boiling hot solution of alumina, Wöhler was able to precipitate aluminum hydroxide ($Al(OH)_3$). The precipitates were rinsed in water, dried and mixed with powder charcoal, sugar and oil into a thick paste. Upon heating this paste in the closed crucible and introducing dry Cl gas, Wöehler produced $AlCl_3$. Since the $AlCl_3$ decomposition is too volatile for glass crucible, Wöhler used platinum (Pt) crucible and crucible cover. Although only gentle heat was applied to start the process, the exothermic reaction caused significant heat release and enabled crucible attacks. After cooling, the crucible was plunged into water allowing for the pure Al to be separated as a gray powder. The obtained Al powder contained K, Pt and $AlCl_3$ impurities. In 1845 he was able to successfully melt the powder into s coherent metallic mass no larger than a pinhead (**Fig. 7.**). Wöehler was able to synthesize beryllium and yttrium in the same manner [74]. Since his process was not suitable for large-scale production, Al remained an expensive metal that cost more than gold [57]. Pure Al was first synthesized when Henri-Etienne Sainte-Claire Deville became interested in the possibility of obtaining a lower aluminum oxide by reducing $AlCl_3$ with metallic K (**Fig. 7.**). He was not able to obtain the aluminum oxide, but he did produce a mixture of $AlCl_3{\cdot}KCl$ containing voluminous globules of a "*brilliant white metal*" describing them as:

"*It is understandable that a metal white and unalterable like Ag, that does not blacken in air, that is fusible, malleable, ductile, and tough, and that presents the particular property of being lighter than glass (density = 2.56), how much useful such a metal would be if it would be possible to manufacture it easily. If in addition, we consider that this metal is abundantly present in nature, that its mineral is clay, it is desirable that it became common.*" [78]

Therefore, it is not surprising that after the initial success in Al synthesis, Sainte-Claire Deville set a goal to develop an industrial process for Al reduction. He was able to replace the K with cheaper Na and developed a process to reduce Al from less volatile solution of aluminum chloride and sodium chloride ($AlCl3 \cdot NaCl$) salts. Later, Sainte-Claire Deville used the same $AlCl3 \cdot NaCl$ salt to obtain the metallic Al by electrolysis. Although Deville's method enabled reduction of 200 metric tons of Al [79], synthesized metal was primarily used for jewelry and in ornamental purposes. Disillusioned by its luxurious application, Sainte-Claire Deville stated:

"*There is nothing harder than to make people use a new metal. Luxury items and ornaments cannot be the only sphere of its application. I hope the time will come when aluminium will serve to satisfy the daily needs*" [80].

The first book about Al was published in 1858 by Charles and Alexander Tissier. One year later in his science novel "*From the Earth to the Moon*" the French novelist Jules Vern used Al to construct his projectile Columbiad (**Fig. 9. a**) and shot it to the Moon (**Fig. 9. b**). In the 1867 Paris exhibition, Al sheet, foil, wire as well as helmets and telescopes were presented to the public [57]. One of the first architectural applications of Al was in 1884 when it was chosen to complete the Washington monument [80]. Base on his previous work on Al purification using sodium vapors, William Frishmuth was engaged. He was able to cast the largest piece of Al with a height of 20.23 cm and 2.83 kg in weight (**Fig. 10.**). Unfortunately, unlike his foundry skills, his business skills proved to be lacking. Before sending it to the Washington, Frishmuth displayed the cap in the Tiffany's jewelry store in New York City without permission.



a)

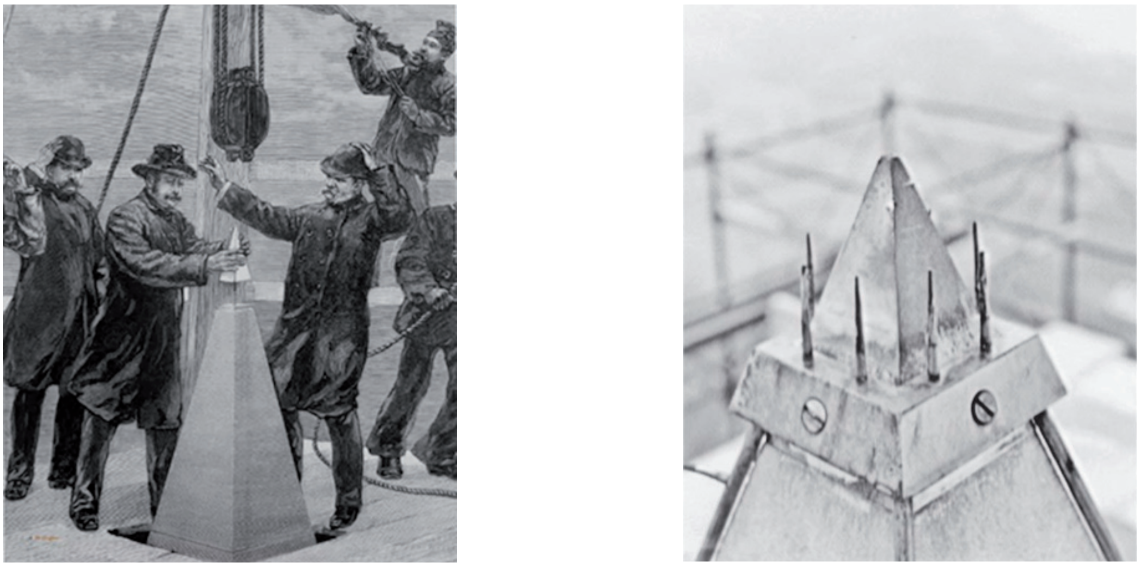
b)

Fig. 9. The illustrations of Jules Vern science novel "*From the Earth to the Moon*":
a) Columbiad, b) The firing of the Columbiad [81]

Moreover, instead of charging initial $100, he increased the price to $225. Two months after the cap was placed on top of the Monument (**Fig. 10. a**), Frishmuth found himself with additional Al left over from casting. By placing the advertisement in the journal Scientific American, he offered watch charms from pure Al for 75 cents, Al alloy charms for 20 cents or gilded Al alloy charms for 20 cents [82]. Like its creator's character, the purity of Al cap was also questionable. Investigations performed during its display in the jewelry store indicated that the cap was made of Al-1.70 wt.% Fe-0.55 wt.% Si alloy. Even after the cap was installed, Frishmuth was no prepared to part from his work. After a series of lightning strikes in 1885, Frishmuth offered to provide lightning-rod (**Fig. 10. b**). Frustrated by his previous behavior, the clients led by Thomas Lincoln Casey flatly rejected his proposal hiring his competitor, Joseph Neumann. Unfortunately, drama did not stop there. Two of his assistants were caught in an attempted theft, one of whom was arrested and convicted for stealing chemicals worth $2.50.

Looking back on the whole experience, Casey concluded that Al was not practical metal for widespread use just yet. Although Al did have its advantages, Casey emphasized the difficulty in getting even 100-ounce sample, finishing his account with words:

"*would seem to imply that Aluminium cannot yet be manufactured at such rates as to make it a commercial success*" [83].



a) b)

Fig. 10. Toping of the Washington Monument:
a) illustration of placing the cap [83], b) cast Al cap with lightning-rods [84]

Ironically, less than two years after the Washington Monument was completed, the process for making Al cheap and commercially available was discovered [85].

The time of Al widespread application came with the discovery of more cost-effective electrolytic method. The electrolytic reduction of Al was discovered by Charles Hall and Paul Héroult, independently and almost simultaneously. Charles Martin Hall found that the melting temperature of alumina (2050 °C) could be lowered by adding cryolite (Na_3AlF_6) [86]. He assumed that passing electric current through that mixture could lead to the reduction of Al. His assumption was confirmed on 23rd of February 1886 when Al was first electrolyzed in an improvised laboratory in the woodshed using home-made batteries. His first electrolyzed Al in the form of buttons is up to this day treasured by Aluminum Company of America and referred to as crown jewels (**Fig. 11**) [74]. Paul Louis Toussaint Héroult was second to electrolyze Al from the same electrolyte mixture on April 23rd 1886 [86]. Apart from the differences in the electrode number and Al electrolysis cells design, the main difference is that Héroult preferred aluminum bronze over pure Al. Since his first experiments resulted in Al absorption on the surface of Cu cathode and increased metal coalescence, Héroult became aware that it was easier to produce aluminum bronze. However, in order to remain competitive to Hall, Héroult had to introduce changes in the pot lining and electrode pitch decreasing the current efficiency [87].

Even though Hall and Héroult met only once in 1911, the process for electrolytical production of primary Al bears both their names. The industrial scale application of Hall-Héroult process was enabled by the developments in electrical current supply and alumina production. The Bayer process boosted yield and practicality of Hall-Héroult method by producing alumina from bauxite ($Al_2O_3 \cdot Fe_2O_3 \cdot SiO_2 \cdot TiO_2$) more efficiently [79]. The modern production of Al is based on both Bayer and Hall-Héroult processes (**Fig. 12.**). Since 1919 the increase in pot productivity, reduction in specific energy consumption, reduced environmental impact as well as decrease in investment and productivity cost were achieved through invention of Søderberg anode, introduction of pot computer control, pot feeding of alumina, polyvalent pot tending machines, pot hooding and gas dry scrubbing, mathematical modelling of pot thermo-electrical fields and magnetohydrodynamics [89]. Despite technological and process improvements the industrial production of primary Al still requires 14.21 MWh/tone energy intensity and accounts for approximately 3.5 % of direct global greenhouse gas emissions (GHG) in the industrial sector. This environment impact is a consequence of electricity use, anode consumption and anode effect [90].

Fig. 11. The crown jewels of Aluminum Company of America [88]

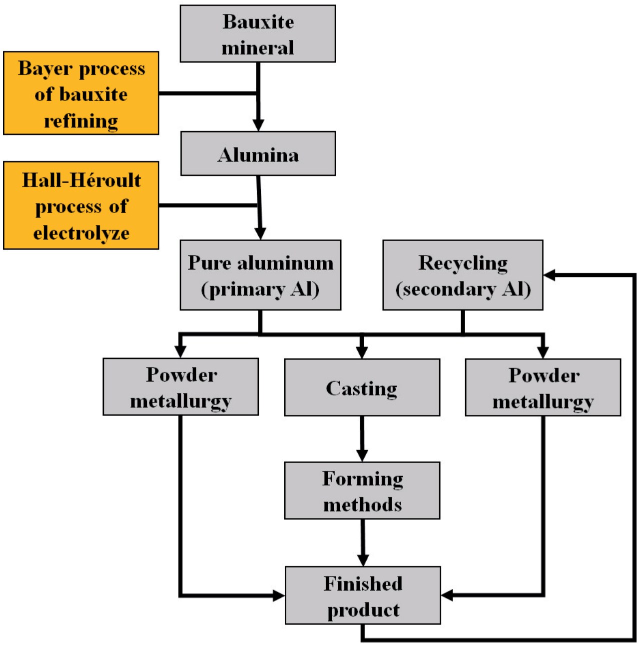


Fig.12. Flow chart of Al production process [57]

Recycling is considered an alternative to primary Al production. Compared to other high-volume production metals, such as Cu, Zn, and Mg, Al has the largest energy difference between primary and secondary production. Production of secondary Al through recycling allows for 95 % energy reduction and emits only 5 % of the GHG compared to primary Al reduction [58]. By producing 1 t of secondary Al, the 8 t of bauxite, 14 000 kWh of energy, 6300 l of oil and 7.6 m^3 of landfill are saved. However, assuring the required chemical composition remains the main obstacle to secondary Al production [91]. The first commercially available Al-Mg-Si alloy was developed in 1921, while the first heat-treatable Al alloy of the same type (AA 6061) was introduced in 1935. Due to good weldability and corrosion resistance, it was popular in early railroad and marine applications. From that moment Al became more just than a single material and developed into a diversity of alloys with different physical, chemical and mechanical properties [57]. Consequently, at the beginning of the 1960s Al became the most widely used non-ferrous metal in the world [92]. Today, Al is still considered an attractive material with many applications, including automotive, aerospace, railway, marine, electric, and architectural. The Al alloys continue to develop and slowly begin to include specific scientific and technological applications such as 3D printing and composite material industry. Based on the excellent properties of Al in combination with low price, significant scrap value and growing recycling market, the Al industry is expected to grow through the 21st century. Consequently, additional research and development efforts are needed to minimize the negative environmental impact associated with both primary Al production as well as industrialization of human society in general [92]. Therefore, it is not surprising that Alfred Gilbert decided to name his aluminum sculpture after the Greek god Anteros (**Fig. 13.**), who, unlike his brothers Eros and Cupid, reflects mature and selfless love. The sculpture was displayed at Piccadilly Circus in London as a memorial statue to the Earl of Shaftesbury [93].

Fig.13. Anteros toping the Shaftesbury Memorial Fountain at Piccadilly Circus in London, England [93]

4. Conclusions

This paper emphasizes the importance of metalworking and metallurgy through their impact on the development of human society with a focus being primary placed on the discovery of aluminum and the challenges represented by the complex nature of aluminum-containing minerals. Although man's first contact with native copper and meteoritic iron was mostly artistic resulting in ornaments and jewelry, the first practical application of metals began with the development of bronze. Due to its better properties and easier shaping in comparison to the stone and bone, bronze began to be used in tool making. The first bronze, as an alloy produced by adding tin to copper, has a predecessor of approximately the same hardness and strength in the so-called arsenic or antimony copper, or as many consider arsenic/antimony bronze, which as a formation was created from a complex ore - tennantite ($(Cu,Fe)_{12}As_4S_{13}$) and tetrahedrite ($(Cu,Fe)_{12}Sb_4S_{13}$). Furthermore, the experimentation with bronze chemical composition led to the development of metallurgical processes such as smelting, refining and casting as well as mechanisms of economics and communication. When smelting copper ore, iron ore was used as a fluxing material. The resulting slag contained spongy iron. That was one of the theories of iron discovery. Soon after iron replaced bronze as a principal metal inspiring Industrial Revolution. To the world struggling to produce cheap steel, aluminum came to be known through the works of Wöehler and Deville. However, this brilliant white metal was primarily used for jewelry and for ornamental purposes, till it was first electrolyzed in a woodshed using home-made batteries on February 23rd 1886 by Charles Martin Hall. Few munts later, the similar procedure was developed by Paul Louis Toussaint Héroult. Even though

Hall and Héroult met only once in 1911, the process for electrolytical production of primary Al bears both their names and is still used today. Due to its latte discovery as well as the necessity for interdisciplinary engineering and scientific approach to the development of industrially viable processes of extraction, reduction and manufacturing, aluminum is considered as a symbol of modernity. In today's society aluminum has many applications, including automotive, aerospace, railway, marine, electric, and architectural. This conclusion ends with a question as what if the early men did not have curiosity or necessity to discover metal? How would contemporary society look like if it was limited to stone, bone, and wood?

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Influence of microstructure on the resistance of tool steels to local corrosion in 3.5% NaCl medium

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Abstract

In this research, electrochemical and metallographic tests were carried out on tool steel for cold and hot work, as well as steel for cementation, with the goal to obtain corrosion parameters to determine which of the examined samples is more resistant to local pitting corrosion. Electrochemical tests were performed in a medium of 3.5% NaCl, and were based on conducting cyclic anodic polarization in the potential range from -2000 mV to 200 mV vs SCE and vice versa. The results of the research showed that all three samples are subject to pitting corrosion, but the worst was the cementing tool steel sample X19NiCrMo4, which had the lowest pitting potential. The W600 tool steel sample for hot work proved to be the best, with the highest pitting potential.

The results of the electrochemical tests coincide with the metallographic tests, because after corrosion in the chloride medium only the beginnings of pitting corrosion are visible on the surface of the W600 sample in the form of partial accumulations of corrosion products, while the X19NiCrMo4 cementing steel sample was completely covered with corrosion products, which means that of the three tested tool steels, cementing steel is the most susceptible to pitting corrosion and is not recommended for use in conditions where it comes into contact with chloride ions. The martensitic microstructure of cementing tool steel is responsible for the very low pitting potential and, consequently, pronounced pitting corrosion. On the other hand, the W600 tool steel showed better corrosion resistance due to its finer grain and uniform carbide distribution.

Keywords*: pitting corrosion, tool steels, cyclic anodic polarization, 3.5% NaCl, microstructure.*

1. Introduction

Corrosion is the destruction of the material and its critical characteristics during electrochemical, chemical and other reactions where the surface of the material is in contact with the environment [1,2]. Corrosion of metals and nonmetals occurs as an interaction with the environment on the surface of the material. It affects structures and objects of different materials, as well as the ambient air, which is loaded with moisture and oxygen, and can initiate the corrosion process, known as rusting [3,4].

Many factors affect material damage through corrosion. In the case of buried structures and pipelines, the rate of corrosion damage is determined by soil chemistry and moisture [5]. Acid fumes such as sulfuric acid and sodium hydroxide dust also accelerate corrosion. In the case of aluminum, the oxide film created by the initial corrosion attack protects the surface from further damage. In marine environments, where airborne salt crystals are deposited on ships, corrosion of submerged surfaces as well as floating surfaces occurs.

Corrosion affects the microstructure, mechanical properties and physical appearance of the material itself [1-4]. Rusting and other types of deterioration drastically reduce the capacity of pipelines and equipment, resulting in lost production and therefore lost equipment [5].

In the fight against corrosion damage of critical structures and equipment, anti-corrosion coatings are used [6]. Electric currents can produce passive films on metals that do not normally have them. Some metals are more stable in certain environments than others, and scientists have invented alloys like stainless steel to improve properties in certain conditions. Some metals can be treated with lasers to give them a non-crystalline structure, which is resistant to corrosion. During galvanizing, iron or steel is coated with more active zinc, a galvanic cell is created where zinc corrodes and iron does not. Other metals are protected by electroplating with an inert or passivating metal. Non-metallic coatings such as plastics, paints and oils can also prevent corrosion.

Tool steel refers to various carbon and alloy steels that are particularly suitable for tool making [7-9]. Their suitability is a result of their distinct hardness, resistance to wear and deformation and their ability to keep an edge at high temperatures. This makes tool steels suitable for use in shaping other materials. There are six groups of tool steel: water-hardening tool steel, cold-work tool steel, shock-resistant tool steel, high-speed steel, hot-work steel, and special-purpose tool steel (plastic molds) [7-9]. Group selection depends on cost, operating temperature, required surface hardness, strength, impact resistance and toughness requirements. The more difficult the working conditions (higher temperature, abrasiveness, corrosiveness, load), the greater the alloy content and consequently the amount of carbide needed for tool steel.

In this work, the resistance of three different types of tool steels (one for hot work, one for cold work and one for cementing) to local corrosion in a medium of 3.5% NaCl was tested. Electrochemical techniques were used to obtain corrosion parameters such as pitting potential, repassivation potential, and hysteresis potential, as indicators of the resistance of the tested tool steels to local corrosion. In addition, metallographic tests were performed on sample surfaces before and after corrosion in a specified medium, with the aim of finding out which of the specified tool steels is the most resistant to local corrosion in the chloride medium.

2. Experimental part

2.1. Samples

In the experimental part of this work, three samples of tool steels were tested: tool steel for cold and hot work and tool steel for cementing.

Cold work tool steels include a group of steels for shaping and processing at temperatures up to 200°C [7,8]. They can be unalloyed or low-alloyed. Cold working non-alloyed steels have a carbon content of 0.5-1.3%, less hardenability and better toughness than other tool steels, and are used to make tools with a smaller section and simpler shapes. Low-alloy steels for cold processing have significantly better properties, which are achieved by adding alloying elements: chromium, tungsten, vanadium and molybdenum. The purpose of alloying is to obtain refractory carbides that ensure good toughness, high hardness and dimensional stability at elevated operating temperatures [7,8,10]. This group of tool steels is used to produce tools that are prone to corrosion, and chromium fulfills the purpose of corrosion resistance. In addition to chromium, there are other alloying elements such as V, Mo and W. Cold work tool steels must be impact and wear resistant [7-10]. Table 1 shows the chemical composition of the tested cold work tool steel marked as K110.

Table 1. Chemical composition of K110 cold work tool steel (wt.%) [11,12]

C	1.55	**Ni**	-
Si	0.30	**V**	0.75
Mn	0.30	**W**	-
Cr	11.30	**Co**	-
Mo	0.75	**Fe**	balance

Among the supporting elements, the tested steel contains silicon and alloying elements: chromium, molybdenum and manganese. Chromium is added to steel because it increases its hardenability and lowers the martensite formation temperature. Molybdenum in combination with other alloying elements increases the hardenability and prevents brittleness when yielding. Manganese has a deoxidizing effect. In combination with chromium, molybdenum increases corrosion resistance [9]. The composition shown in the Table 1 meets the prescribed qualities related to production [11,12].

Hot work tool steels are used to make tools that are heated to a temperature higher than 200°C during operation [7,8]. The most essential attribute of this steel is its resistance to yielding. Resistance to yielding refers to occurrences that can occur when exposed to high temperatures (e.g. reduction of hardness, microstructural changes). In addition to resistance to yielding, tool steels must meet additional requirements such as resistance to [9]: appearance of plastic deformations, wear, high temperature corrosion, satisfactory impact load (toughness).

Favorable properties are achieved by alloying (e.g. carbide formers: W, Mo, Cr and V) and low carbon content. Nickel is added to increase toughness and hardenability, and silicon to improve dynamic durability. Table 2 shows the chemical composition of the tested hot work tool steel marked as W600 [12].

Table 2. Chemical composition of W600 hot work tool steel (wt.%) [12]

C	0.32
S	0.001
Si	0.12
Cr	0.11
Ni	2.1
V	0.01
W	1.9
Co	0.01
Al	0.009
Cu	0.01
Mn	0.23
Mo	3.2
P	0.005
Sn	0.005
Ti	0.01
Nb	0.01
B	0.001
N	0.008
Fe	balance

The tested steel includes silicon from the supporting elements, as well as phosphorus and sulfur from the undesirable elements, in small quantities that can never be fully removed. Alloying elements include chromium, nickel, aluminum, manganese and molybdenum. Hot work tool steels enable hot forming of work pieces made of iron and non-ferrous metals, as well as alloy derivatives at high temperatures. They are used in processes such as die casting, extrusion and forging, as well as in the production of pipes and glass [7,8,12]. Tools made of hot work tool steel are not only subject to constant high temperatures when in use, but also to fluctuating thermal loads that occur where the tool surfaces come into contact with the materials being worked. Combined with wear caused by abrasion or impact, thermal loads present very specific requirements for hot working tool steels. The key requirements are high tempering resistance, temperature strength, thermal shock resistance, high temperature resistance and wear resistance [7,8,12].

Cementing steels belong to the group of structural steels. With their help, the edge layer is carbonized after processing, separating the particles. After carburizing comes tempering, in order to increase the toughness of the non-carburized core and to obtain high wear resistance of the edge layers [12,13]. This type of tool steel contains 0.1-0.2% carbon before carburizing and can be low-alloyed or unalloyed. After carburizing, the edge layer contains 0.8 - 0.9% carbon, so its hardness is 61 - 64 HRC [7,8,13]. Table 3 shows the chemical composition of X19NiCrMo4 cementing tool steel.

Table 3. Chemical composition of X19NiCrMo4 cementing tool steel (wt.%) [12,13]

C	0.170
Si	0.27
Mn	0.41
P	0.009
S	0.002
Cr	1.18
Mo	0.19
Ni	3.90
Fe	balance

The tested steel contains silicon as a supporting element, and phosphorus and sulfur in permitted amounts as undesirable elements. The tested steel also contains alloying elements such as manganese, chromium, nickel and molybdenum. Nickel has good properties, so we add it to increase the toughness of steel and to increase corrosion resistance [7,8]. Chromium is added to steel because it increases its hardenability and lowers the martensite formation temperature. Molybdenum is added in combination with other alloying elements and increases the hardenability and prevents brittleness during yielding. Manganese has a deoxidizing effect. Molybdenum in combination with chromium increases corrosion resistance [7,9]. The chemical composition listed in the table satisfies the production's required quality standards. [12,13].

2.2. Media for conducting electrochemical tests

A 3.5% NaCl solution is employed as the medium for electrochemical testing of tool steel resistance to local corrosion. The 3.5% NaCl solution was chosen to simulate the application of tool steels in real conditions, i.e. conditions similar to seawater solution. A 3.5% NaCl solution was prepared by adding 8.75 g of NaCl to 250 ml of distilled water. The solution was stirred and allowed to stand. Using a laboratory pH-meter and a conductometer, the pH value was measured before and after electrochemical tests (Table 4).

Table 4. pH values of the medium before and after electrochemical tests

Sample	**pH (before the test)**	**pH (after the test)**
K110	6.80	6.96
W600	6.80	6.89
X19NiCrMo4	6.80	7.10

From the data in table 4, it can be seen that all three tested samples had the same pH value before the measurement, i.e. all three samples were neutral before the test. They continue to be in a neutral medium after the test, but the pH levels have slightly risen. The biggest difference in the pH value before and after the measurement was observed in the third sample. Its pH changed from 6.80 to 7.10.

2.3. Test methods

During this research, metallographic and electrochemical tests were used [11-13].

2.3.1. Metallographic tests

For easier handling of the samples, as well as for metallographic testing of the samples, two samples were cut from each tested tool steel. For this purpose, the samples were prepared by hot investment in conductive mass using a device for investment in carbon mass by hot pressing process (SimpliMet® 1000). After that, the samples were ground and polished on an automatic grinding and polishing device (Büehler) for 5 minutes at a force of 10 N [11-13].

Grinding was carried out using waterproof sandpaper with gradation Nos. 240, 400, 600 and 800 and polished on Microcloth felt using Al_2O_3 suspension in water. After polishing, the samples were washed in distilled water and degreased in ethanol. After the aforementioned sample preparation, one representative of each tool steel was used for electrochemical tests and observation of the surface of the samples after corrosion, and the other sample from each tool steel taken was intended for metallographic tests [11-13]. Metallographic tests were first carried out "on white" in order to observe the purity of the material itself, i.e. the presence of inclusions or cracks. After that, the samples were etched in 3% nital in order to highlight their microstructure. An optical microscope with an Olympus DP27 digital camera and an automated image processing system was used to record everything (Steram Motion) [12].

2.3.2. Electrochemical tests

Electrochemical tests were based on performing cyclic anodic polarization of the tested samples in the range from −2000 mV to 200 mV vs SCE and vice versa, with a potential rate of dE/dt = 5 mV s^{-1}. This test was performed in the three-electrode glass cell shown in Figure 1, at room temperature in a medium of 3.5% NaCl [12].

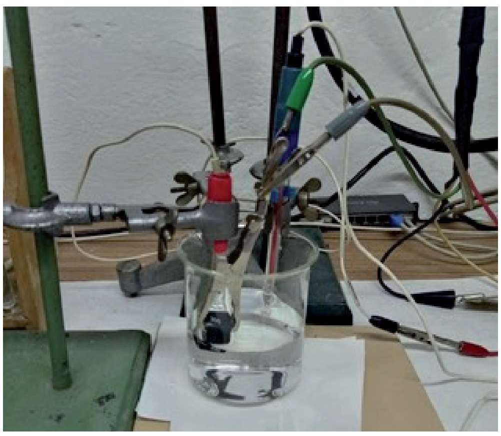


Fig. 1. Three-electrode glass cell for electrochemical tests [12]

The working electrode is the sample, the counter electrode is the Pt electrode, and the reference electrode is the saturated calomel electrode (SCE) [11-13]. The potential of the working electrode is measured using the reference electrode, and the Pt electrode is the conductor that closes the circuit [11-13]. The working surface of the tested samples is 0.98 cm^2, which was determined by measuring the sides a (1.4 cm) and b (0.7 cm) of the samples and multiplying them. The specific working surface of the samples is marked with a black strip [12].

The samples were degreased in ethanol and dried after metallographic preparation. First, the working medium is added to the glass (the glass represents the cell), then the reference electrode and the counter electrode are immersed, and finally the sample is immersed, in our case the working electrode up to the black strip. Measurement parameters are set on the computer. The electrodes are connected to a computer-controlled potentiostat/galvanostat [11-13].

During the measurement, the sample submerged in the medium must first be stabilized, which takes around 30 minutes or 1800 seconds. When the sample is in a stationary state, then the open circuit potential E_{ocp}, is read. This completes the first part of the measurement [11-13].

In the continuation of the measurement, cyclic anodic polarization of the samples was performed in the range −2000 mV to 200 mV in relation to the SCE and vice versa with the potential rate dE/dt = 5 mV s^{-1}. Potentiodynamic measurements were plotted on a two-coordinate plot on a computer using PowerCore™ software. After that, the corrosion parameters E_{corr}, E_{pitt}, E_{rep} and E_{hyst} were read from the polarization curves, which are indicators of the resistance of the tested tool steels to local corrosion [12,14]. Electrochemical tests were performed in 3.5% NaCl medium, at least twice for each sample. If two measures differed, a third measurement was taken to ensure that the results were reproducible.

3. Results and discussion

3.1. Results and discussion of electrochemical tests

Anodic and cathodic processes occurred throughout the test. The anodic process occurs at the tested sample, during which the metal dissolves and electrons are generated. The cathodic process is the depolarization of hydrogen or oxygen, and this depends on the medium in which the measurement is performed. The purpose of conducting electrochemical tests is to obtain the following parameters of resistance to local corrosion [12,14]:

- E_{corr} - corrosion potential,
- E_{pitt} - pitting potential,
- E_{rep} - repassivation potential and
- E_{hyst} - hysteresis potential.

The corrosion potential, E_{corr}, of the open circuit is read after the sample immersed in the medium (electrolyte) is stabilized. The stabilization time lasted 30 minutes. The pitting potential together with the repassivation potential is used to evaluate the resistance of metals to pitting corrosion [1-3,12,15]. The pitting potential, E_{pitt}, can be read by drawing tangents on both parts of the starting curve and reading the value on the x-axis at their intersection, i.e. the pitting potential is determined according to the criterion of a marked increase in current on the initial polarization curves [1-3,12]. The pitting potential is actually the critical potential at which the passive electrode surface is activated and the breakdown of the passive layer occurs. The lower the E_{pitt}, i.e. more negative, the material is more susceptible to local corrosion, i.e. pitting corrosion. The repassivation potential, E_{rep}, can be read at the first intersection of the initial and return curves, i.e. at the point where the anode hysteresis loop closes.

The hysteresis potential, E_{hyst}, is then calculated according to the equation [1-3,12]:

$$E_{hyst}=E_{pitt}-E_{rep} \tag{1}$$

Figure 2 shows the diagram of the time dependence of the open circuit potential of the tested samples of tool steels in a medium of 3.5% NaCl.

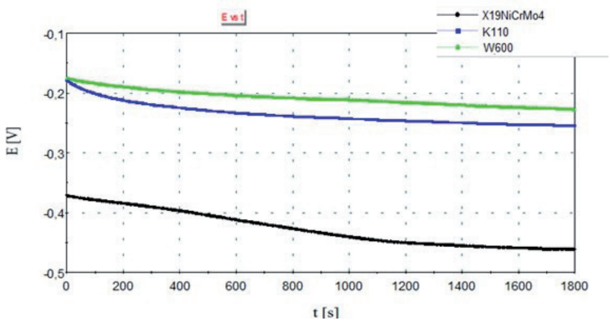


Fig. 2. Diagram comparing the time dependency of the open circuit potential of the tested tool samples in a 3.5% NaCl medium

The tool steels W600 and K110 attain their open circuit potential in 1150 seconds in the 3.5% NaCl medium, as shown in the diagram. The potential tends to a more positive value of the open circuit potential. In contrast to them, the corrosion potential of X19NiCrMo4 steel tends to a more negative value, which points to the dissolution of the sample. Figures 3 to 5 show cyclic voltammograms of tested samples in 3.5% NaCl medium. The peak indicating pitting can be seen in the tested chloride medium, which means that pitting corrosion can be observed in the chloride medium in all three of the tested tool steel samples, according to the presented voltammograms.

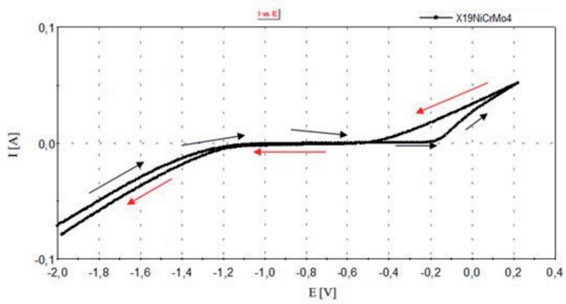


Fig. 3. Cyclic voltammogram of X19NiCrMo4 sample in 3.5% NaCl medium

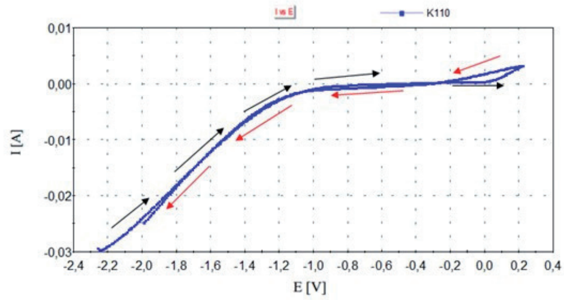


Fig. 4. Cyclic voltammogram of K110 sample in 3.5% NaCl medium

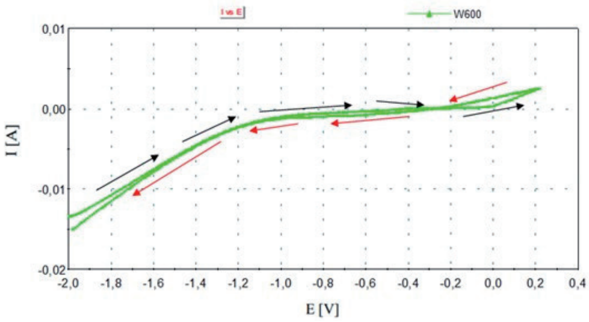


Fig. 5. Cyclic voltammogram of W600 sample in 3.5% NaCl medium

Table 5 shows the corrosion parameters obtained for steels X19NiCrMo4, K110 and W600 in 3.5% NaCl medium. If the corrosion potential value is negative, this indicates a more pronounced dissolution process, i.e. stronger corrosion in chloride media tested [1-3, 12, 15].

Table 5 shows that the value of the corrosion potential is the lowest for X19NiCrMo4 steel, and the highest for W600 steel. As for the value of the pitting potential, it is the lowest (most negative) for X19NiCrMo4 steel, and the highest (most positive) for W600 steel, which points to the fact that W600 steel is the most resistant to local corrosion in the tested chloride medium. On the other hand, it is significant to note that there aren't many differences between the pitting potentials of the K110 and W600 samples, which means that the K110 steel is roughly equivalent to the W600 steel in its ability to fend off local corrosion in the chloride medium. If we look at the repassivation potential values, we see that the K110 and W600 steels do not differ much, but that is why the X19NiCrMo4 steel has a significantly lower repassivation potential.

Table 5. Corrosion parameters of X19NiCrMo4, K110 and W600 steel in 3.5% NaCl medium

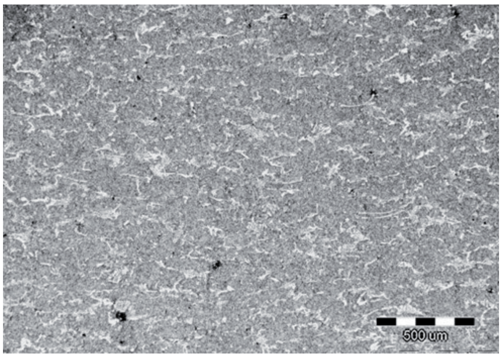
Steel	**E_{corr} vs SCE [mV]**	**E_{pitt} vs SCE [mV]**	**E_{rep} vs SCE [mV]**	**E_{hyst} vs SCE [mV]**
X19NiCrMo4	- 461	-180	- 500	320
K110	- 254	50	- 280	330
W600	- 227	60	- 260	320

In terms of hysteresis potential, steel with a narrower hysteresis loop is generally more resistant to local corrosion [1-3,12]. However, a more relevant parameter for determining corrosion resistance is the pitting potential.

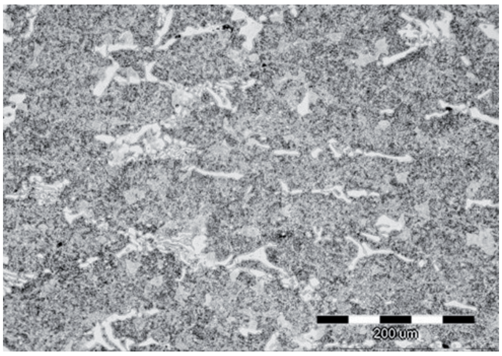
3.2. Results and discussion of metallographic tests

Figure 6 shows metallographic images of K110 cold work tool steel after etching in nital.

Figure 6 shows that the primary structure of K110 cold work steel is ledeburite, which after hardening and low yielding achieves the structure of martensite + secondary carbides [11,12,16]. The steel matrix is dark in the image and the carbides stand out in white.



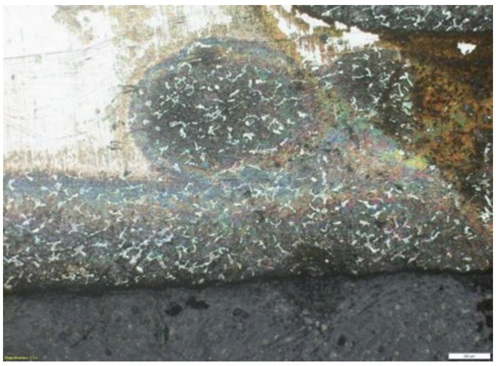
a)



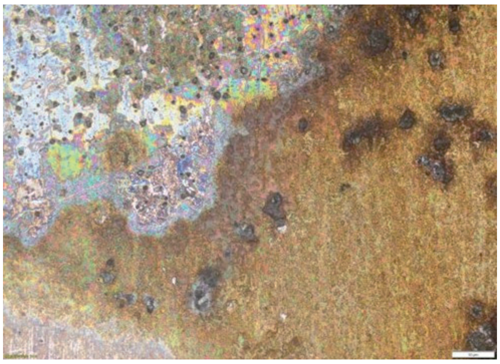
b)

Fig. 6. Microstructure of K110 sample after etching in nital: a) magnification 50x; b) magnification 200x

Figure 7 shows metallographic images of the tested K110 cold work tool steel following electrochemical tests in 3.5% NaCl medium.



a)



b)

Fig. 7. Metallographic image of K110 sample after electrochemical tests in 3.5% NaCl medium:

a) magnification 50x; b) magnification 200x

This type of steel belongs to the group of semi-stainless tool steels. It contains a significant amount of carbon and chromium. Due to its very good properties, such as extraordinary hardness and strength and wear resistance, it is used to make hand tools and blades [9,11,12].

After conducting electrochemical tests in a solution containing 3.5% NaCl, we can see that the tested steel's surface is partially covered in corrosion products, primarily on the edges of the sample. It was also discovered that chloride ions attack the steel matrix more aggressively than precipitated carbides.

Figure 8 shows metallographic images of W600 hot work tool steel after etching in nital.

a)

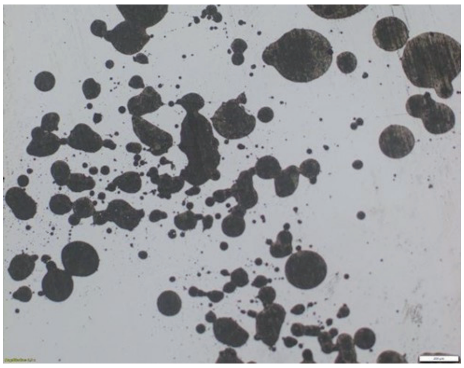
b)

Fig. 8. Microstructure of W600 sample after etching in nital: a) magnification 50x; b) magnification 200x

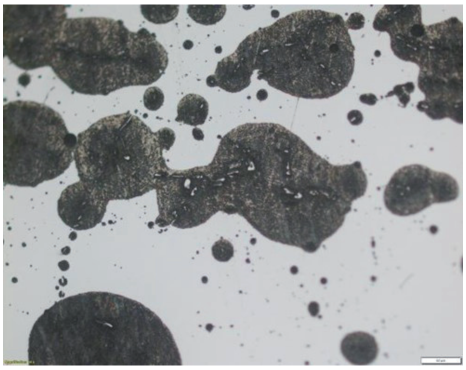
Figure 8 shows that the microstructure of W600 hot work tool steel is martensitic, but the structure is fine-grained with a uniform distribution of carbides [12,16].

Figure 9 shows metallographic images of W600 hot work tool steel after electrochemical tests in 3.5% NaCl.

Figure 9 shows that the surface of the sample exposed in a medium of 3.5% NaCl is not completely but only partially covered by the corrosion product. The W600 sample turned out to be the best, because there are dotted black spots visible on the surface, which indicates the beginning of pitting corrosion [12]. It most often occurs where the passive coating layer is physically damaged or chemically attacked. In particular, when the sample was reground, the corrosion products from the surface were easily removed, indicating that the corrosion damage was not deep [12]. The tested tool steel includes a significant quantity of nickel and hence has strong corrosion resistance, making it the best of the three tested steels. Additionally, its fine-grained microstructure and uniform carbide distribution significantly increased its resistance to pitting corrosion [12].



a)

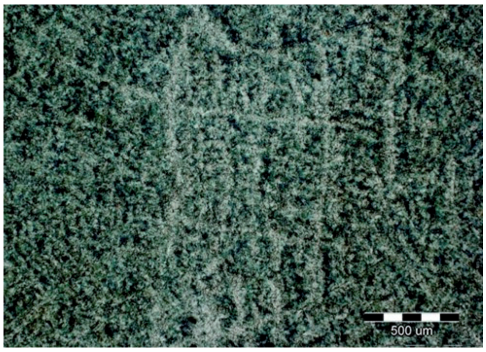


b)

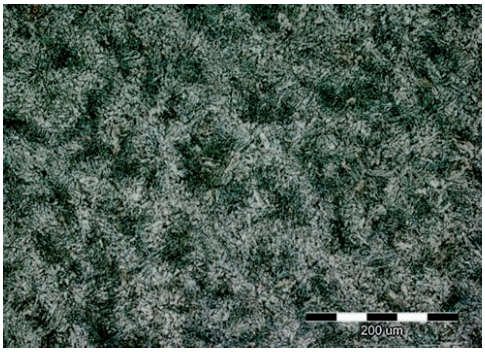
Fig. 9. Metallographic image of W600 sample after electrochemical tests in 3.5% NaCl medium:

a) magnification 50x; b) magnification 200x

Figure 10 shows metallographic images of X19NiCrMo4 cementing steel after etching in nital.



a)

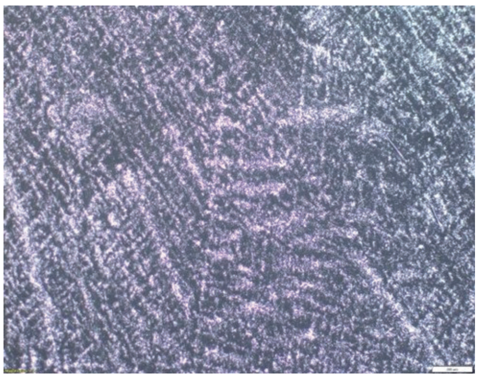


b)

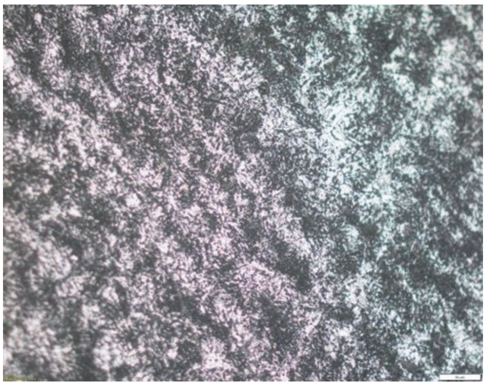
Fig. 10. Microstructure of X19NiCrMo4 sample after etching in nital: a) magnification 50x; b) magnification 200x

Figure 10 shows the martensitic structure of X19NiCrMo4 cementing tool steel [12,13,16]. Martensite is formed by transformation of austenite during rapid cooling below the temperature at which martensite begins to form. It can also be produced as low-carbon steel laths, though plates are the most common form [12,13,16]. The martensite microstructure is particularly unfavorable in terms of corrosion resistance due to its characteristics, as shown in the present research. X19NiCrMo4 in the chloride medium showed a very low, i.e. the most negative, pitting potential among the tested tool steels [12,13].

After conducting electrochemical tests on the X19NiCrMo4 steel in a chloride medium, we can see that the corrosion progressed very quickly and that the tested steel was completely covered with corrosion products (Figure 11). This surface condition corresponds to the obtained corrosion parameters, so the tested cementing tool steel cannot be recommended for use in contact with chloride ions [12,13].



a)



b)

Fig. 11. Metallographic image of X19NiCrMo4 cementing tool steel after electrochemical tests in 3.5% NaCl medium: a) magnification 50x; b) magnification 100x;

4. Conclusion

At the end of the test carried out, the following can be concluded:

- The resistance to local corrosion of K110 and W600 tool steels for cold and hot work and X19NiCrMo4 cementing steel was tested using metallographic and electrochemical methods.

- Cyclic anodic polarization of the mentioned steels in a 3.5% NaCl medium in the potential range of −2000 mV to 200 mV vs SCE and vice versa was carried out, all with the aim of collecting corrosion parameters as an indicator of the resistance of the tested samples to local corrosion.

- Resistance to local corrosion is determined using the pitting potential parameter E_{pitt}. Since the pitting potential was recorded in all three tested samples, it is evident that all three tool steel samples are subject to pitting corrosion in a chloride medium. The lowest E_{pitt} was obtained for the X19NiCrMo4 steel sample, while the highest E_{pitt} was recorded for the W600 steel, indicating that the W600 hot work tool steel is the most resistant to local corrosion among the tested steels. However, due to the very small difference in potential levels of pitting, K110 cold work tool steel can be considered equally resistant.

- Metallographic tests confirmed the results of electrochemical measurements, showing that the surface after corrosion was completely covered by corrosion products on the X19NiCrMo4 cementing tool steel sample, and that the martensitic microstructure of the tested steel was responsible for such the rapid propagation of pitting corrosion.

- Unlike the X19NiCrMo4 sample, the W600 sample was partially covered by corrosion products after corrosion in a chloride medium, and the fine-grained martensitic microstructure and the uniform distribution of carbides were the reason for the lower susceptibility to pitting corrosion.

- Finally, it can be concluded that although they are susceptible to pitting corrosion, the durability of the tested steels in the chloride medium can increased to some extent by an adequate choice of anti-corrosion protection.

5. Acknowledgments

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Engineers' Day in the Republic of Croatia 2023

On March 2, 2023, the Croatian Engineering Association celebrated Engineers' Day of the Republic of Croatia in the Old Town Hall. The event was organized in cooperation with the Croatian Academy of Engineering, and under the auspices of the Ministry of Construction, Spatial Planning and State Property of the Republic of Croatia. The theme of this year's Engineers' Day in the Republic of Croatia was "Urban Planning and Architecture – Drivers of Sustainable Development in Croatia" in an effort to draw public attention to contemporary issues. The meeting was attended by scientists and experts from universities, academies, institutes, representatives of chambers, industries and entrepreneurs. Exchange of experience and implementation of engineering solutions in the form of lectures is the most effective way to transfer new knowledge, new ideas and technologies in the service of engineering and the development of economy.

"In the year that marks 145 years since the establishment of the then association, which is now the Croatian Engineering Association, our attention is focused on space as a national asset that requires special care in its use and development planning, but unfortunately it is not systematically implemented. The profession of architecture and urban planning has a duty and obligation to ensure its preservation and improvement", said Mr. Zdravko Jurcec, President of the Croatian Engineering Association. "Today we officially have 16 areas of science and technology, covering all technical disciplines in education, science and economy. However, in today's complex world, it is necessary to develop as much as possible, particularly in education and science, multidisciplinarity, and interdisciplinarity, so that our engineers can monitor and develop all areas of human activity," said Mr. Vladimir Androcec, Member of the Governing Board of the Croatian Academy of Engineering.

The attendees were also addressed by the president of the Croatian Academy of Engineering, Mr. Vedran Mornar, rector of the University of Zagreb, Mr. Stjepan Lakušić, delegate of the President of the City Assembly of the City of Zagreb, city representative Mr. Robert Faber, Deputy Mayor of the City of Zagreb, Mr. Luka Korlaet, envoy of Minister Nina Obuljen Koržinek, Mr. Davor Trupković, Chief Conservator of the Ministry of Culture and Media, and the representative of the Deputy Prime Minister of the Republic of Croatia, Minister Branko Bačić, Mr. Željko Uhlir, State Secretary of the Ministry of Construction, Spatial Planning and State Property.

The Croatian Engineering Association expressed its acknowledgement and gratitude.

This year, HIS presented the Certificate of Acknowledgement for Financial Support from the Ministry of Culture and Media of the Republic of Croatia, which was received by the president of the *Croatian Association* of Nature and *Environmental Experts* Mr. Nenad Mikulić and the Acknowledgement for financial support to the Ministry of Culture and Media which was received by the envoy of the Minister Nina Obuljen Koržinek, Mr Davor Trupković, Chief Conservator of the Ministry of Culture and Media.

The following lectures on the conference topic "Urban Planning and Architecture - Driving Forces of Sustainable Development in Croatia" were delivered as part of the Engineers' Day 2023.

Prof. Emeritus Tihomir Jukić, PhD: "Why urbanism and how to proceed?"

Nikša Božić, Bachelor of Architecture: "Existing legal framework and its adaptation"

Assistant Professor Lea Pelivan, Bachelor of Architecture: "Sustainability and Circular Economy"

Prof. Sanja Gašparović, PhD: "Towards the Challenges of the City of the Future"

The lectures emphasized that space, as a national asset, needs particular attention in its use and planning development. The profession of architecture and urban planning has a duty and obligation to ensure its preservation and improvement".

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