MEMORANDUM ON THE OCCASION OF THE 55TH JUBILEE OF CZECH METALLIC SCANDIUM PREPARATION

POZNÁMKA K 55. VÝROČÍ PŘÍPRAVY ČESKÉHO KOVOVÉHO SKANDIA

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Abstract

In 1956, in the former Czechoslovakia, metallic scandium was prepared for the first time from Ore Mountain (Krušné Hory) wolframites processed to scandium concentrates at Spolchemie Ústí nad Labem. In connection with so called Geneva Protocol from 1955, After the release of information on processing of uranium and of a spent nuclear fuel, the interest in rare earth elements as well as in scandium and yttrium grew. The amount of a scandium concentrate available in Czechoslovakia was enormous, given the circumstances. However, after the monetary reform in 1953, the concentrate was sold in order to obtain foreign currency. Despite this fact, the researchers of the Institute of Chemical Technology, Prague, in competition with many renowned research facilities in the USA and France, succeeded in preparing metallic scandium and published the results on July 3, 1956 – three weeks before the similar results were published by CNRS in Paris. More than 50 papers on Czech scandium were published in many renowned journals since then. However, scandium was not used by the Czech industry, although it was used in the former USSR (MIG-29 and aerospace projects) to enhance properties of Al-Mg or Al-Mg-Li alloys, or in the USA in the illuminating engineering. This paper reviews the Czech research of metallic scandium, its alloys and compounds.

Key words: scandium; scandium compounds; scandium alloys; wolframite; zinnwaldite.

1. INTRODUCTION

In a very brief introduction, we can only summarize generally known facts about scandium. The existence of the element scandium 21Sc was predicted in 1871 by D. I. Mendeleiev, who named it eka-boron. Six years later, the element was found in gadolinite by L. P. Nilson, who named it scandium in honour to Scandinavia. Till the end of World War II, only few researchers were interested in scandium and its importance was minimal. For example, in 1937 B. Fischer published a work about electrolytic reduction during which he obtained metallic scandium in the reaction mixture [1]. However, he did not isolate the element and, thus, described its properties imprecisely. In 1939, K. Meisel elaborated a roentgenographic study of metallic scandium, but again in a mixture [2]. One of important points was notice on possibility of scandium allotropic modification alpha and beta. In the next 10 years, the research of scandium was practically absent. In 1952, a large amount of a scandium concentrate emerged in the Czech chemical plant Spolek pro chemickou a hutní výrobu (Corporation for Chemical and Metallurgical Production) in Ústí nad Labem, where wolframites from Krušné hory (Ore Mountains, Erzgebirge) were processed. This was the very scandium concentrate whose tale we are going to follow in this memorandum.
2. HISTORICAL PREFACE

The Czech lands - and later Czechoslovakia - were always considered an industrially advanced country, competitive especially in mechanical engineering and metallurgy. Development of mechanical engineering demanded mainly high-quality machining tools. Traditional company Carborundum Electrite Benátky nad Jizerou, established in 1893, produced silicon carbide and silicon carbide tools according to the Acheson’s patent. After the World War II, the company became also an important exporter; due to large amounts of high-quality raw material from war provisions. In Poldina hušův (Poldi hütte), later Poldi n. p. Kladno, tools from sintered carbides of G (Guss) and S (Stahl) types were produced according to the Krupp-Widia patent. After the War, when German production of sintered carbides was in wrecks, the production and usage of machining tools expanded in such an extent that a new enterprise, Pramet (today Seco Tools), was established in Ústí. The production of sintered carbides not only from Poldi Kladno, but also from Přípešek near Děčín (where prominent powder metallurgist C. Agte worked [3]), was moved there.

The range and quality of sintered carbides, in which the main constituents are tungsten carbide and cobalt, was enhanced by additives, mainly titanium, niobium and tantalum carbides. Except an import, tungsten was obtained also from domestic sources, mainly from tin-tungsten ore mined in Ore Mountains in Cínovec (Zinnwald) locality. The mined ore was primarily processed on place; chemical processing was done in Spolek pro chemickou a hutní výrobu in Ústí nad Labem. Wolframite and zinnwaldite from Cínovec locality contained, besides tungsten and tin, also other important elements, mainly thorium, scandium, niobium and lithium, together with trace elements such as Y, Ta, Rb or Cs.

During chemical processing, complicated waste material was produced. Its analysis was in 1952 - done by a mineralogist J. Kařík, the first rector of independent ICT in Prague (Vysoká škola chemicko-

technologická v Praze, Institute of Chemical Technology, Prague). In fluoride wastes, he detected a significant content of thorveitite (Sc,Y)2Si2O7. At that time, new education programmes were designed at the Institute. Because the Department of Inorganic Technology, which was established lately and was directed by A. Regner, was specialised in so-called "heavy inorganic chemistry", the problems of these industrial wastes were assigned to a newly established Department of Inorganic Chemistry directed by F. Petrříček. Employees B. Hájek and V. Procházka focused on isolation of scandium (III) oxide and in cooperation with Výzkumný ústav Monokrystaly Turnov (Monocrystals Research Institute) and J. Barta succeeded in isolating of the very first monocrystal of Sc₂O₃ and determining its crystallochemical properties [4].

In 1955, in connection with the Geneva Protocol and the USA-USSR treaty of the declassification of nuclear research related technologies, the unofficial race for rare earth elements (lanthanoids) started. The rare earth elements are formed in a spent nuclear fuel and must be taken away during the purification of uranium. Today, scandium and yttrium are counted among rare earth metals. In connection with the above mentioned facts and also due to electrotechnical industry demands for model compounds of rare earth metals, their production has grown. Scandium commodities were rare, their availability was low and prices high. Only rich research institutes, such as work groups of F. H. Spedding at the Ames University in Iowa, Spicyn in Moscow, G. V. Samsonov in Kiev or J. Loriers at CNRS in Paris, could afford to finance the scandium compounds research. At the time, Czech wolframite wastes represented the most concentrated resource of scandium and there was plenty of it at the Institute of Chemical Technology, Prague.

On an international scale, the first relevant publications about metallic scandium were published in 1956. The first Czech paper on scandium was published in 1956, in Czech journal Chemické listy (Chemical Letters) [5]. In the very same journal, with the date of submission the 3rd July 1956, Petrříček, Hájek and Procházka informed in a form of a short communication about the preparation of metallic scandium by the reduction of ScF₅ by calcium in a molybdenum crucible heated under argon atmosphere by a high-frequency heating; the metal was then purified by subsequent vacuum sublimation at 10⁻⁴ torr. The research was done in Tesla
Vr̆ovice, with Dr. Schneider’s workgroup [6]. A competitive paper about the metallic scandium preparation by V.I. Spicyn in Moscow [7] was submitted in 1961 and the most cited article by Achard et al. [8] was published as late as on the 22nd July 1956. Our primacy was challenged probably because the work was published in the Czech language and in the journal that was not available worldwide. In 1958, Petří et al. published a sort of apology for their results in the internationally acknowledged journal Collection [9].

The situation corresponded with specific conditions, which were significantly influenced by a monetary reform of 1953. The reform put an end to the convertibility of our currency and also created the need for acquisition of a foreign currency at any cost. At this point, in connection with the development of machining technologies in machine engineering-focused Czechoslovakia, it is important to remind a difficult decision that was to be done by so-called captains of our industry. They were to decide destiny of the North-Bohemian (from Krugňe hory) wolframites processing. The process of separation could be carried either on acid or alkaline path. One of these processes provided concentrates with high content of Nb and Ta, carbides of which (especially TaC) significantly improved properties of sintered carbides based on WC-Co. The other process provided a scandium-yttrium concentrate. The general management of KOVOHUT’s Department in Ministry of Industry CSSR decided that the scandium concentrate from Ústí nad Labem should be sold by Lachema n. p. to foreign countries, concretely to the United Kingdom. Domestic raw materials were intended for processing to tantalum compounds, which were demanded by the electrotechnical industry for capacitors production. The decision was not favourable for the Department of Inorganic Chemistry; however, about 20 kg of the scandium concentrate were saved from exportation. This action provided the Czech scandium chemistry research with enough material for the next 20 years. Just to reconsider the exportation: in the Czech scandium concentrate, thorium can be also found. Its chemical separation was very difficult at the time. If we came at industrial scandium compounds, produced by renowned companies such as Koch Light or Johnson-Matthey & Co., we found traces of thorium, which unequivocally marked the origin of the raw material. Captains of our industry did not think about the possibility of producing scandium compounds and exporting of them in exchange for foreign currency.

In the fifties and sixties of the last century, there were only three information sources and databases of chemistry publications: Chemical Abstracts, Referativný Zhurnal and Chemische Zentralblatt. Although there were Czech employees among paid abstractors of these databases, who selected the most interesting papers, the number of information was limited; therefore the notice about Chemické listy was not passed on. This was probably due to the fact that it was marked only as a řid hot communicationů i so probably the abstractors waited for information with more impact. This was published as late as in 1957, in the journal Collection [9], which was always internationally acknowledged. As a result, in connection with scandium the world of chemistry cited rather publications from 1956 by Achard et al. [8] and Spedding [10] or Spicyn and Savicky [7, 11] than Czech authors i even though V. Procházka attended Symposium on rare earths in November 1956 in Leipzig, organised by the German Chemical Society. Among others, professor Loriers, who published the paper about metallic scandium preparation together with Achard and Caro on the 23rd July 1956 i.e., three weeks later, was there. Spedding’s publication bears the date of the 9th July 1956 [10].

![Fig.1 Prof. T. Horowitz address in ICT Prague](image-url)
Our work was properly cited not before 1975, when one of the first monographs, *Scandium* [12], was published. The editor of the monograph was professor T. Horowitz, who visited our laboratory in 1968 (see Fig. 1).

For the successful preparation of metallic scandium crowned by the ambiguous European primacy, F. Petrů, B. Hájek and V. Procházka were in 1957 prized by the prestigious Cena hlavního města Prahy (Capital City of Prague Award).

After 1957, the research divided into two parts. One group of scientists from ICT, Prague, focused on the systematic preparation of all possible scandium compounds, eventually with other elements of the 3rd group. The others had task to find the industrial use for scandium and its compounds. Papers about scandium and its compounds published by the Department of Inorganic Chemistry were numbered for better clarity. After professor Petrů’s passing in 1974, the number of Beiträge zur Chemie der seltenen Elemente (or Contribution to the Chemistry of Rare Elements) stopped on 88. In preparation of some scandium compounds, such as ScOF, Sc₂OC, Y₂OC, Sc(BrO₃)₃ and others, the Department has primacy, certified by citation in the Gmelin Handbook or in the Powder Diffraction Files (PDF) database [13-16]. We also tried to draw the attention of scientific public to the inconsistent facts about scandium allotropy [17, 18].

The demand for commercial scandium use was stagnant, as it was generally acknowledged that scandium is expensive and hardly available. The use was considered to be worth only in case of some unique property of scandium or its compound themselves or if some economically acceptable minor addition of scandium to other substances would have changed their properties significantly. However, no anomalous or unique applicable property was found. The proverbial first swallow was the remark of professor G.V. Samsonov from Kiev Institut Problemy Materialovedenia (Kiev Institute of Materials Science), that addition of scandium carbide increased titanium carbide hardness to almost 56 GPa [19]. It would mean that it was ranking among the third or fourth hardest substance, after diamond and cubic boron nitride and exceeding hardness of boron and silicon carbides. After receiving this information, professor Hans Nowotny from the University of Vienna, co-worker of the Austrian enterprise Metallwerk Plansee AG in Reutte, focused on the issue [20]. Our Department joined in as well, in cooperation with potential industrial producer Pramet Šumperk [21, 22]. In 1965, professor Hans Nowotny conferred in Prague about scandium with academician Rudolf Brdička and with professor Petrů, see Fig. 2.

In 1972, the member-corporrespondent of the National Academy of Sciences of Ukraine, professor G. V. Samsonov also visited the ICT, Prague (Fig. 3) and showed deep interest in scandium carbide research. Our Department published a series of 27 impacted publications on scandium and lanthanides carbides titled Hydrolysable carbides [23, 24]; however, the result was amazingly negative. All carbides, starting with scandium, through yttrium, lanthanum to lutetium ones, are hydrolysable. During the reaction with water, they decompose forming hydrogen and hydrocarbons, from methane and acetylene to analytically proved saturated hydrocarbons of the C₁₂ type. On the other hand, all other transition elements on the right side of
scandium, starting with titanium and followed by V, Cr, Mn, Fe, Co, Ni, Zr, Hf, Mo, W and so on, form interstitial carbides that are chemically very stable and also very hard, for example, the hafnium carbide HfC with the highest melting point of 3820 °C or tungsten carbide with the highest toughness whose industrial importance is on the increase. However, the hydrolysability of scandium carbide was surprising. The negative effect of the phenomenon was that the samples of titanium carbide doped with scandium carbide progressively disintegrated due to the air humidity.

Fig.3 V. Procházka (third from left) and G.V. Samsonov (on the right), ICT Prague 1972

Interesting point is the fact that the scandium carbide (Sc$_{15}$C$_{19}$) hydrolysis yields mainly (apart from hydrogen) allylen, which was by that time detected only as a product of magnesium carbide hydrolysis [25]. This discovery is in good correspondence with the so-called diagonal law of elements.

In the seventies and eighties of the last century, the interest in scandium and its compounds fell off progressively, measured by the number of publications and citations. As the compound to be much easily prepared was scandium (III) oxide; the oxide ceramics were the most probable consumer and supporter of the research. From the point of view of physical properties, scandium (III) oxide is very similar to the aluminium (III) oxide; however, no evidence of significant change or even improvement of physical properties as a result of scandium (III) oxide addition to aluminium (III) oxide were found.

The very low interest in scandium may be confirmed when looking into the international market almanacs i the world consumption of scandium compounds did not exceed 100 kg. Per year, approximately 20 kg of Sc$_2$O$_3$ was used in the USA and 80 kg was used in the rest of the world for the high-power discharge tubes and halogen lamps. Scandium iodide strongly increases the emission of the white light with high colour rendering index which can replace sunlight in the film studios. Small amounts of radionuclide $^{46}$Sc are used as a trace agent in crude oil plants.

In the Czech Republic, the attempt to change the attitude towards scandium took place in nineties. After the USSR dissolution, the Trade Representation of the Russian Federation started to hold Czech-Russian seminars, where specialists informed each other of production, market and (partly) research possibilities, the last being tabooed until that time, mainly because of military-strategic aspects. In 1997, during one of the seminars, it was announced that the Russian Federation offers large amounts (several tons) of special scandium alloys which were redundant after the space research cutback. The majority of cosmic apparatuses were made from light alloys based on aluminium and magnesium. The reduction of specific weight under 1.5 g/cm$^3$ was achieved by significant amounts of metallic lithium added to the alloy. The
Metallic lithium specific weight is approx. 0.5 g/cm³ but it significantly lowers the corrosion resistance of the constructions. This may not impose serious problems in the space; however, before being taken into the space, the apparatuses were produced and stored on Earth and the maintenance of proper anticorrosive environment was considerably expensive. It was found that the addition of metallic scandium to the Al-Mg-Li-based alloys might significantly improve the corrosion resistance of these alloys. The price of these alloys made them initially uninteresting. Of course, enormous prices of material were not important when it concerned cosmic race and MIG fighters production. Here, we may cite the popular source in Wikipedia:

*The addition of scandium to aluminium limits the excessive grain growth that occurs in the heat-affected zone of welded aluminium components. This has two beneficial effects: the precipitated Al₃Sc forms smaller crystals than are formed in other aluminium alloys and the volume of precipitate-free zones that normally exist at the grain boundaries of age-hardening aluminium alloys is reduced. Both of these effects increase the usefulness of the alloy. However, titanium alloys, which are similar in lightness and strength, are cheaper and much more widely used. The main application of scandium by weight is in aluminium-scandium alloys for minor aerospace industry components. These alloys contain between 0.1% and 0.5% of Sc. They were used in the Russian military aircraft, specifically the MiG-21 and MiG-29. The American gunmaking company Smith&Wesson produces revolvers with frames composed of scandium alloy and cylinders of titanium (end of citation).*

As late as in 2005, the Czech Republic obtained a research grant focused on the influence of scandium on the properties of aluminium alloys. The research was performed at Research Institute of Metals - VUK Panenské Břežany. One part of the results was the discovery of the positive influence of precipitated Al₃Sc phase on the properties of extruded alloys [26, 27]. However, the new alloys did not call the interest of the market so far.

The last attempt to procure scandium in the production schemes of our machining industry was the development of technical coatings of machining tools. In the seventies, the machining tools were coated mainly by titanium nitride TiN having both decorative and anticorrosion functions. The main advantage was increasing of hardness that was twice of that of the substrate. Titanium nitride-based coatings, having the thickness of few micrometers only, were prepared by CVD (Chemical Vapour Deposition) and granted five times longer working life of the product. The next step was the preparation of coatings from the solid solutions of TiC and TiN; based on the Vegard’s law a part of the titanium was replaced by other elements that seemed to improve coatings properties. The CVD method was progressively replaced by newer techniques of surface engineering and functional coatings production, such as functionally-graded (FGM), ion-planted (IP) or magnetron-sputtered (MS) materials. In the nineties, TiAIN or TiAlCₓNᵧ coatings were the hit of the season [28]. It is self-evident that we examined the properties of Ti-Al-C-N system doped with scandium in the production of wear-resistant sintered carbides thin coatings. It was found that the wear resistance of coatings containing 8-13 % of Sc is almost two times (or more precisely 1.8 times) higher than those of the popular TiAIN coatings [29]. The results of our research, presented at the world powder metallurgy congress in Stockholm [30] were well accepted, especially as there was a Czech company that guaranteed semi-industrial production. However, again, these materials did not establish themselves in the machining industry, mainly because of the price and because of the other new coatings development.

Elaboration of this paper was supported by the Development Project C52 of the Ministry of Education, Czech Republic, for the year 2010.
REFERENCES


