Differential Thermal Analysis in Metallurgy, used at the Department in Ljubljana

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Abstract: The paper deals with the history and the development of differential thermal analysis (DTA) as research method with applications in metallurgical examinations at the school of metallurgy in Ljubljana till now. Fields of metallurgical examinations in which DTA as research method was applied are presented chronologically. Starting with simple examinations of raw materials for metallurgical production processes, DTA became later a method of calorimetric measurements of metallic systems, and a method of metallographic and structural examinations of metals and alloys. New equipment, purchased in recent times, enabled even research of thermomechanical working of alloys.

Key Words: Differential thermal analysis (DTA), metallurgical examinations

Last year, 50 years passed since the first research was made at the Department of Metallurgy of the former Faculty of Mining and Metallurgical Engineering, Technical University in Ljubljana, in which differential thermal analysis (DTA) was used. The first written document on the use of DTA was the Diploma Thesis of Stanko Čop "Thermal Decomposition of Barite" [1], made in 1952, in which one of used research methods was also DTA. The scheme of the apparatus, being assembled by the then Assistant Professor, later Full Professor, Bogomir Dobovišek, is shown in Figure 1.

Professor Dobovišek was the person who was intensively engaged in the study of DTA and its applicability in metallurgical research immediately after his graduation in 1950. DTA was namely the method that in those times demanded a relatively simple research equipment and the analysis itself did not last long. The set-up was then composed of two imported sensitive galvanometers, Radiometer Copenhagen GVM 22, and of the at home made resistant heating furnace with corresponding system for temperature regulation. The imported instruments were purchased by the Department with the help of American Slovenes J.N. Rogelj and V. Cajnkar and the assistance of Slovenska narodna podporna enota (S.N.P.J.) – Slovene National Support Unit - from Chicago.

The principle of DTA was given by Le Chatelier [2] already in 1897 who introduced in the standard thermal analysis another thermocouple inserted into furnace, thus measuring temperature difference between the furnace and the sample in which took place endo- or exother-

Scientific paper

Figure 1. DTA apparatus (1).

mic reactions. His method was later modified by ROBERTS-AUSTEN [3], while BURGES [4] developed it approximately into the form in which it was used in the first half of the last century. Essential improvements in measuring techniques of DTA occurred in the early 1950s. MCCONNELL [5] and BECK [6] reported on improved conditions for application of DTA in studying chemical processes.

DTA was first used for examination of ores, clays and foundry sands. The first research published in our professional magazines was the study of C. PELHAN [7] on synthetic sands for foundry moulds. It was published in Rudarstvo i metalurgija (Mining and Metallurgy), Belgrade, and immediately afterwards in Nova proizvodnja (New Production) (Ljubljana) [8]. The second examination was the study of Istrian bauxites by S. ZALAR [9] in 1954, followed by the research of clays by C. PELHAN [10]. As example of one of the first DTA curves are the thermograms of Istrian bauxites from Žminj and Karojba [9], presented in Figure 2.

Further examinations made were measurements of reactivity of zinc ferites [11], reduction of iron oxides with solid carbon [12], determination of dehydration temperatures [13], analysis of solid fuels [14], study of roasting metallic sulphides [15], and again analysis of clays [16]. Reference by M. WITTELS [17] with its results enabled to apply DTA for measuring thermal effects [18] and to use DTA for calorimetric measurements [19, 21, 26, 28] which was the basis to apply DTA in thermodynamic analysis of binary (later also ternary) systems of metals [22, 24, 32-33]. Further examinations were made to determine influence of various parameters on fundamental theoretical parameters of DTA [20] and determination

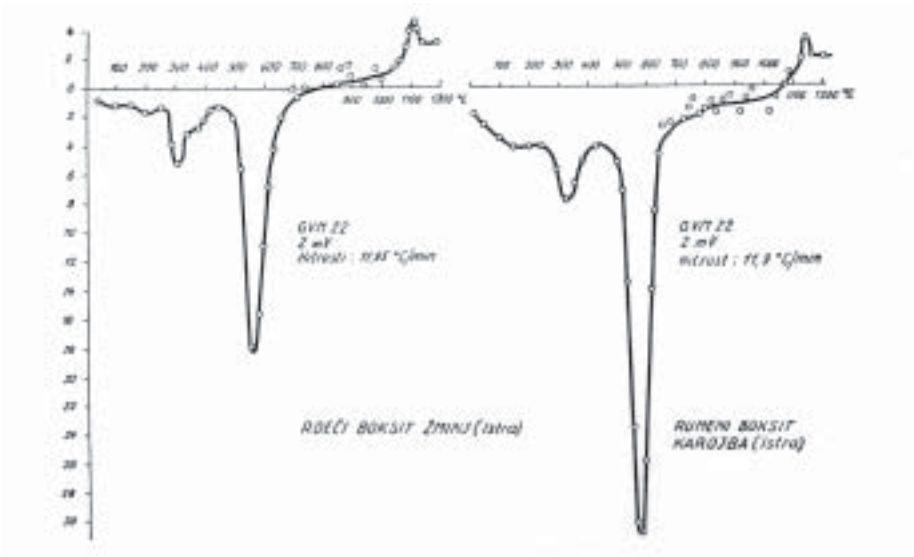

Figure 2. Thermogram of Istrian bauxites from Žminj and Karojba [9].

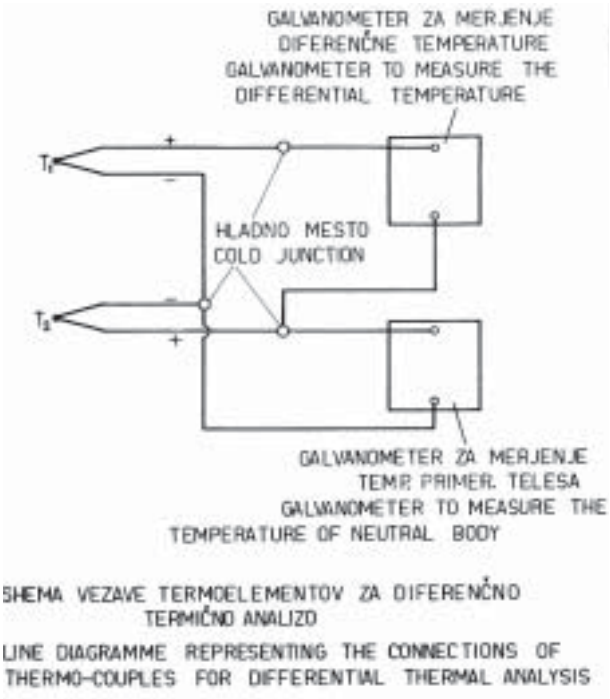

Figure 3. Scheme of connecting thermocouples in thermodynamic analysis of binary systems of metals.

of liquid-vapour diagrams by DTA [23].

The first international publication of results on application of DTA as a research method in metallurgy, made in Ljubljana, were the abstracts of the First International Conference on DTA in Aberdeen, Great Britain, in 1965 [25], and a little later the published papers in Microchimica Acta [26, 27]. Extensive studies on applicability of DTA for various metallurgical examinations and their publications in scientific literature were the reason for increased interest of professional public for those examinations. This was exhibited in wishes of a series of foreign researchers, who arrived to Ljubljana with the intension to study the applicability of DTA in metallurgy, and to become acquainted with this research method. The results of those studies are numerous publications in our professional magazines [28-33, 36].

A wide range of use of DTA in metallurgy in Ljubljana is represented by examinations of oxidation of exothermic powders in foundries [37-50]. Later, DTA was used in all the cases where thermal effects of chemical or physical reactions were measurable. Improved quality of research equipment, and especially the possibility to measure very small electrical potentials, using electronic equipment and later computer control of heating (and also of cooling) processes made possible to extend the application of DTA to various research fields.

Already the previous review of applicability of DTA indicated that DTA became an examination method for studying a series of various chemical and physical processes in which heat is evolved or consumed that lead to fundamental research of laws being the basis of this method. These laws were treated in already mentioned papers [18, 20], but they were also objects of further examinations which results were published [34, 35, 64-65]. DTA proved to be successful method also in studying kinetics of metallurgical reactions [31, 36, 52].

Researchers presented results of their examinations at numerous scientific meetings and conferences at home (Ljubljana, Portorož, Sisak, Belgrade, Zagreb, Novi Sad, Hercegnovi) and abroad (Aberdeen – Great Britain, Chicago, Paris, Graz – Austria, Budapest, Baltonszéplak, Székesfehérvar – Hungary, Salford – Great Britain, Bayreuth, Clausthal – Germany and Bucurest – Romania) too.

DTA is the method that was applied at the Department of Metallurgy in Ljubljana also for other types of examinations [51, 63], with a special attention to analyses of reduction of iron ores [52-54, 56-57, 62] and examinations of reactivity of solid fuels [55, 58-61].

Further improvement of the measuring techniques lead to development of the equipment that completed methods of standard DTA, and examinations with those methods could be made by such newly developed equipment simultaneously to DTA. Such methods are the thermogravimetric analysis (TG) and the differential thermogravimetric analysis (DTG). Examinations of that type were made for the needs of the Department of Metallurgy by the Netsch STA 409C apparatus for DTA, TG and DTA at the Nuclear Institute Josef Stefan in Ljubljana. The first publication of such an examination was in RMZ in 1974/75 [60], while the results of a further such examination were obtained with the Derivatograph 1500 apparatus of Hungarian

company MOM, and published later in the Ph.D. Thesis of D. Blečić [118].

In the reports on examinations in which DTA was used and which are referred in references of this paper, there it is possible to remark that the high frequency of publications in 1980s dropped later a great deal. The accuracy of analyses on apparatuses, which were made in the laboratories of the Department of Metallurgy became insufficient for examinations of metallurgical processes. Therefore it was necessary to purchase a new apparatus for DTA. This was the apparatus of the Bähr Company of series DTA 701 which was purchased by the Department in 1998. The examinations of which the results are cited in the references of this paper were made after 1998 with the mentioned apparatus. The new equipment enabled substantially more accurate measurements and thus the continuation of research by using DTA in the Department of Metallurgy. Emphasis in that period was given to some new research fields:

- metallographic examinations with DTA of some binary and ternary metallic systems with Cu, Ni, Si, Al, Zr, and later also with B, metallic borides and rare-earth elements (e.g., Sm),
- examinations of nodulizing agents and inoculants for grey cast iron,
- examinations of exothermic insulating materials in foundries,
- examinations in thermomechanical working of Al alloys.

The first examinations of Cu alloys alloyed with metals such as Ni, Be, Si, Mn, Sn, Cr, Zr etc started already 20 years ago [67-72]. Their results showed that DTA is a very suitable method also in the field of development of new alloys and determination of their properties. This awareness enabled that DTA in combination with other research methods, such as X-ray structural analysis, optical and electron microscopy, hardness measurements etc, was indispensable in research of constitution of binary and ternary metallic systems. Extension of research possibilities with those methods highly increased also the number of publications not only in Slovenian professional magazines but also in acknowledged foreign magazines and that, anyhow, made an increased contribution to scientific reputation of metallurgical school in Ljubljana in international scientific circles. This trend can be especially recognized in the recent years and it is characterized mainly by examination of binary and ternary systems with Al, Ti, and B [91-97].

The newest examinations deal with the Al-Cu-Mg alloy to which elements of rare earths are added, e.g., Sm [101-103, 105]. Use of DTA as one of research methods is important also in thermomechanical examinations of Al alloys, including superplastic alloys [109-112].

Confirmation of DTA as a very useful research method in numerous fields of metallurgical examinations is given also by other research achievements, cited in references. Thus, DTA was successfully applied in research of inoculation of grey cast iron with various nodulizing agents [76-81], as well as in research of exothermic insulation materials [86-90].

An extensive research activity in the field of applicability of DTA is exhibited also in considerable number of Ph.D. Theses, made at the Department of Metallurgy in Ljubljana. Anyhow, the first thesis was that of B.

DOBOVIŠEK who was pioneer in examining this interesting and for many purposes – especially in metallurgy – very applicable research method [113]. R. D. BHARGAVA, as scholar of Yugoslav Government, who made his Ph.D. Thesis at the Department of Metallurgy in Ljubljana, applied DTA as one of methods in thermodynamic analysis of the binary Sn-Bi metallic system [114]. The same is valid for A. ROSINA who made a comparison of research methods in the thermodynamic analysis of the metallic Cd-In system in his Ph.D. Thesis [116]. Analysis of the influence of various parameters on the value of the gK_s constant and the accuracy of quantitative DTA, respectively, was the object of the Ph.D. Thesis of N. SMAJIĆ [115]. Further, Ph. D. Thesis of Ž. D. ŽIVKOVIĆ represented examination of the influence of some physical parameters on the characteristics of DTA curves for powdery samples[117], while D. BLEČIĆ studied kinetics of heterogeneous processes with isothermal and non-isothermal method of thermal analysis [118].

As seen from the upper review of activities in studying and applying DTA in metallurgical examinations at the school of metallurgy in Ljubljana, the research activities were continuous from the middle of the last century on, i.e. for fifty years, and they were again intensified in the last decade when the new Bähr DTA 701 apparatus was purchased, enabling enough accurate measurements. Thus the research of metals and their alloys, as well as in other fields of metallurgical examinations, again joined to international research trends.

It is my pleasure to state that the Department of Materials and Metallurgy, Faculty of Natural Sciences and Engineering, University of Ljubljana, succeeded with financial help of Slovenian metallurgical industry and the Ministry of Science to purchase a new Netzsch STA 449 C apparatus for simultaneous thermal analysis that enables simultaneous differential thermal and thermo-gravimetric analysis and/or differential scanning calorimetry with the accompanying computer support. This apparatus enables to analyse various samples of numerous materials, to determine variations of mass in heating, temperatures of decomposition of various substances, and the temperatures of oxidation, reduction and solidification. It, further, enables measurements needed in the constitution of phase diagrams, in determining melting points, boiling points, and phase transformation temperatures, and in measuring various enthalpies and thermal capacities. Measurements up to 1650 °C are enabled. The accuracy of thermogravimetric

Figure 4. STA 449 C apparatus of the Netzsch Company.

measurements is 1 μg and the measurements of enthalpies ± 3 %.

The new apparatus for simultaneous thermal analysis will enable much more accurate examinations in the field of metals, alloys and other materials, and thus also a corresponding increase of publications of research workers at the Department of Materials and Metallurgy is expected.

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