A SHORT EXPLANATION OF NOTIONS OF SPECIATION AND SPECIATION ANALYSIS IN METALLURGY AND MATERIALS ENGINEERING

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Abstract

Speciation and speciation analysis is currently the subject of research in various domains of science and technology, such as chemistry, metallurgy, materials engineering, medicine and environmental protection, being an important factor in the material and environmental analytics development. Speciation is the occurrence of various physical and chemical forms of a given chemical element, the existence of species in tested material. Speciation analysis helps in identification of those forms and their quantitative marking in a given object. Therefore, assuming with a certain degree of simplification that speciation is the presence of various chemical forms of an element in a sample and the speciation analysis allows for quantitative determination of these forms, similarly in reference to metallurgical samples the notion of phase identification and phase analysis is used including chemical analysis as well. The rule, possibilities and limitations of chemical and electro-chemical phase isolation were also described. Chemical analysis of isolated phases in reference to metallurgy almost always meets the quantitative requirements of speciation analysis. Taking into account the numerous advantages of atomic absorption spectrometry (AAS), the role of the method was underlined as significant in research pointing out particularly the applications in determination of chemical composition of intermetallic phases type γ' in multi-component nickel alloys and carbide phases in tool alloys. The determination of aluminium in steel is also presented with division into aluminium soluble in acids and total aluminium as a classic example of speciation analysis in metallurgy.

Keywords: Speciation, speciation analysis, metallurgy, material science

1. INTRODUCTION

Speciation is the occurrence of various physical and chemical forms of a given chemical element, the existence of species in tested material. Speciation analysis helps in identification of those forms and their quantitative marking in a given object. Therefore, assuming with a certain degree of simplification that speciation is the presence of various chemical forms of an element in a sample and the speciation analysis allows for quantitative determination of these forms, similarly in reference to metallurgical samples the notion of phase identification and phase analysis is used including chemical analysis as well. The identification of phases and inclusions, and their analysis are important for the quality of metallurgical products [1,2] and for the proper functioning of chemical and metallurgical laboratories. Direct phase identification is possible owing to the use of the following methods: X-ray diffraction, electron diffraction, scanning electron microscopy, X-ray microanalysis, Auger electron spectroscopy and electron backscattered pattern (EBSP) technique. Electron probe microanalysis (EPMA), electron spectroscopy for chemical analysis (ESCA) and chemical microanalysis (CMA) are used for the analysis of chemical compositions. Atomic Absorption Spectrometry (AAS) and iductively coupled Plasma (ICP) techniques are mainly applicable in the chemical analysis of electrolytically isolated phases [1-5]. This field of studies is part of the currently expanding research area, which includes speciation and speciation analysis. Phase identification basically fulfils the criteria for speciation. Much more difficult and complex in confrontation with phase analysis is the speciation analysis. The problems here concern quantitative requirements, i.e. the determination of the mass fraction of the individual phases (precipitates) and, above all, the precise determination of their chemical composition.

2. CHEMICAL AND ELECTROCHEMICAL PHASE EXTRACTION

Chemical and electrochemical anodic extraction of phases and inclusions is used as a tool in the determination of their content, structure and chemical composition [1-6].Chemical methods of phase extraction are rarely used nowadays, and this is due to a number of constraints and drawbacks, mainly associated with a very long duration of the dissolution process, difficulties in selecting suitable digestion mixtures and conditions for selective conversion of the sample matrix into the state of solution, ensuring at the same time the required degree of purity in the isolate obtained. These methods only apply to the separation of the most chemically resistant phases, like NbC, TaC, TiC, and VC carbides as well as some M (C, N) carbonitrides [1,3,5].

Electrochemical methods of extraction are used to separate the complex carbides, nitrides and, above all, intermetallic phases, which play a fundamental role in complex materials research, especially in evaluating the quality of various grades of steel and multicomponent metal alloys [1-4].Electrochemical phase extraction can be performed in two ways: galvanostatic, i.e. at constant current density and, more frequently, potentiostatic, i.e. with constant potential [1,3]. In the latter case, electronic potentiostats, automatically supporting the potential of the electrode, are used. In the anodic phase extraction process, the following condition must be met: the dissolution potential of the primary metallic phase (solid solution) should be more negative than the solubility potential of the extracted phase. Typically, the extracted phase is precipitating on the anode in the form of fine dispersion powder. The test sample operates as an anode with appropriately selected electrolyte and voltage. These parameters are essential in the phase isolation process, which can also be regarded as a targeted and selective corrosion [3]. Schematically, with some simplifications, using the data contained in [3], the principle of electrochemical phase extraction is shown in **Figure 1**.

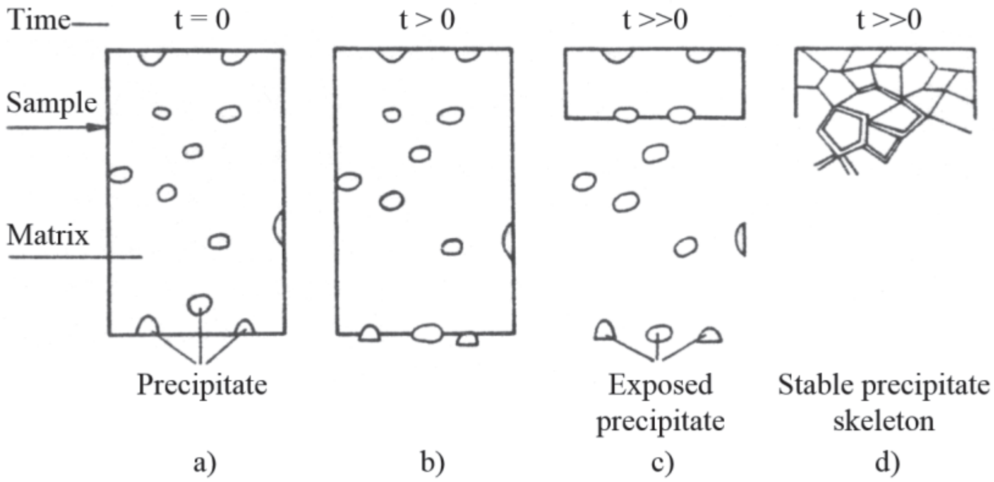

Figure 1 The principle of electrochemical phases extraction [3]

3. TECHNIQUES OF TESTING ISOLATES

Electrochemical isolation of precipitates, as one of the basic steps in phase analysis, enables - through the use of modern research methods - obtaining very valuable information on the morphology of metal alloys and the kinetics of chemical reactions. The use of analytical scanning electron microscopy (SEM) allows testing the isolate morphology. X-ray analysis of the isolate can determine the structure and parameters of the lattice, the phase composition and, possibly, the ordering processes taking place in the precipitates. It is worth stressing that the results obtained by these methods are free from the disturbing effects of the solid solution. The chemical analysis of the isolate made by a "wet method", or using other microanalytical instrumental techniques without the need for dissolution of this isolate, allows determining the exact chemical composition as well as the quantitative ratio of individual components present in the isolate, e.g. $M_{23}C_6$ carbide - $(Cr_{16,3}Ni_{3,6}Mo_{3,1})C_6$ or $(Cr_{21}Mo_2)C_6$ [1,3-8]. Determination of chemical composition of isolated phases in studies of metallurgical materials is equivalent to speciation analysis in analytical chemistry. The Author of this chapter has developed a calibration method for the flame AAS, using one base reference standard and other modified version of AAS, that is flow injection technique [1,5].

4. TOOL ALLOYS - SPECIATION AND SPECIATION ANALYSIS

In the Department of Materials Science of the Silesian University of Technology, a research has recently been carried out on the concept of tool alloys with trace distribution of carbide segregations and on the development and implementation of a technology for the manufacture of semi-finished products and tools from these materials. In the investigated group of non-ledeburite tool steels, by major changes inroduce the chemical composition with respect to conventional high speed steels, the reduced level of segregations and changes in the phase composition of carbides were obtained. The essence of the solution, addressed mainly to the discussed grade of high speed steels, consisted in the replacement of conventional primary carbides of the M_6C, M_2C and MC type with MC type carbides formed by elements characterised by higher affinity for carbon than tungsten, molybdenum and vanadium, i.e. titanium and niobium [8-10]. The chemical composition of the investigated steel, designated as SM5Ti3Nb2, is shown in **Table 1**. In this high-speed steel of non-ledeburite class, in which tungsten and part of molybdenum and vanadium were replaced by titanium and niobium, the obtained phase composition and microstructure differed from other common steel grades included in this group. The prevailing carbides were large (over 10 µm) MC-type carbides in the shape of polyhedrons, often octahedrons, evenly distributed in the matrix, additionally accompanied by M_6C and $M_{23}C_6$ carbides [5,8-10]. This was confirmed by the results of X-ray phase analysis demonstrating the presence of MC, M_6C and $M_{23}C_6$ carbides [1,7,8].

Table 1 Chemical composition of tested SM5Ti3Nb2 tool steel in mass % [8]

C	Mn	Si	P	S	Cr	W	V	Mo	Nb	Ti	Al	Zr	Fe
1.98	0.46	0.54	0.016	0.017	4.26	0.10	1.16	5.25	2.10	3.19	0.30	0.18	Matrix

Knowing the average chemical composition of the carbide phase, when several types of carbides are present in the steel microstructure and form solid secondary solutions, the determination of their stoichiometric formulas is practically impossible. It is possible, however, to predict the precipitation and dissolution of carbides or their transformations during heat treatment and to indirectly determine the chemical composition of the matrix. These studies, carried out by the method of AAS method using a Perkin-Elmer Model 503 absorptions meter, were based on the use of carbide isolates obtained by electrochemical isolation (5 % HCl, 20 °C, 20 mA / cm^2) from sections of 25 mm diameter rods of the test steel previously subjected to different cycles of heat treatment. Carbon content was determined by the coulometric method using Strohlein's Coulomate. The results are shown in **Table 2**. Due to the presence of metallic constituents in the examined carbide isolates, detected by the X-ray phase analysis and using small magnets, attempts were made to remove the non-carbide part of the isolates. For this purpose, two methods were used, i.e. application of small magnets and selective dissolution of the metallic residue.At the beginning, from a practical point of view, the use of small magnets seemed to be a very convenient and easy way to remove metallic particles present in carbide isolates. Unfortunately, further tests have proved that this procedure was not effective enough in separating the metallic residue from the matrix because, due to the high degree of the isolate refinement, the magnet - while attracting the metallic components - was also "catching" the fine particles of the carbide phase. Selective dissolution in acids leaving carbides undissolved has proved to be a much more effective way to remove the metallic residue. Based on the results of own experiments on the dissolution of metallurgical samples and using guidelines given by the technical literature [1,8-10], a 2 : 1 diluted orthophosphoric (V) acid, often included in the steel sample digestion mixtures, was selected for further investigations. The use of this acid has finally yielded the reproducible results.

Table 2 The results of AAS chemical analysis of carbide phase isolates [7]

Isolate1)	**Content of elements in % by mass**									
	C 2)	Mn	Ti	Cr	Fe	Mo	V	W	Zr	Nb
1	10.52	0.41	12.60	13.30	19.90	18.40	3.96	0.85	0.65	9.35
1’ 3)	9.54	0.41	13.70	14.00	21.50	19.70	4.30	0.86	0.62	9.40
2	8.29	0.19	16.60	4.92	25.00	12.90	3.24	0.84	0.75	12.21
2’	15.62	0.09	26.20	1.85	8.76	13.30	3.97	0.90	0.72	14.70
3	8.94	0.09	15.20	8.31	10.50	14.40	3.60	0.86	0.61	9.10
3’	9.19	0.08	18.80	7.21	8.10	16.80	3.72	0.90	0.55	11.30

1)1 - steel annealed (850°C/4 hours)
2 - steel hardened (1150°C/7 minutes)
3 - steel hardened (same as above) and tempered (2 x 540°C/1 hour)
2) carbon content was determined by coulometric method
3) `chemical composition of isolate treated with orthophosphoric (V) acid

Considering the fact that some isolated carbide phases can contain different types of carbides that are qualifiable but not quantifiable, slight modifications to the acid mixtures given in papers [1,8-10] may be necessary to ensure that all types of the identified carbides are equally well dissolved. Then the average chemical composition of the isolated carbide phases is given. This is a typical example of speciation, but not speciation analysis.

5. SPECIATION IN CREEP-RESISTANT FE-NI ALLOYS

In studies of iron-nickel alloys carried out by K. Ducki at the Silesian University of Technology [6], a modified austenitic X5NiCrTi25-15 grade, belonging to the group of creep-resistant Fe-Ni alloys precipitation hardened with γ' phase - Ni_3 (Al, Ti), was developed and implemented in the production of tools used by non-ferrous metal processing plants. The chemical composition of the test alloy is given in **Table 3**.

Table 3 Chemical composition of X5NiCrTi25-15 alloy used for testing [6]

Content of elements in mass %															
C	Si	Mn	P	S	Cr	Ni	Mo	V	W	Ti	Al	Co	B	N	Fe
0.05	0.56	1.25	0.026	0.016	14.3	24.5	1.35	0.42	0.10	1.88	0.16	0.08	0.007	0.0062	55.3

This part presents only fragmentary results of phase analysis studies performed by K. Ducki [6]. Studies of phase transformations and changes in morphology of the microstructural phase constituents, with attention focused on their effect on the strength and plastic properties of the tested Fe-Ni alloy, were conducted under conditions simulating the heat treatment process. The alloy was subjected to solution heat treatment (980 °C/2h/water) and prolonged ageing at 715, 750 and 780 °C for 0.5 to 500 h with air cooling in **Table 4**.

The results of studies conducted by K. Ducki [7], presented in this chapter, fulfil all the requirements of speciation. The presence of so many phases in the test material makes their quantification required by the speciation analysis impossible. Only in some cases, and this to a limited extent, it becomes possible to roughly conclude what their quantitative fraction.

Table 4 Phase composition of Fe-Ni alloys after solution heat treatment and ageing at 715 °C [7]

Alloy condition	**Phase constituents**
Solution heat treatment: 980 °C / 2 h / water	TiC; $TiC_{0,3}N_{0,7}$; $TiN_{0,3}$; $Ti_4C_2S_2$; Ni_2Si; MoB
Ageing: 715 °C / 0.5 h	TiC; $TiC_{0,3}N_{0,7}$; $TiN_{0,3}$; $Ti_4C_2S_2$; Ni_2Si; MoB; *G* - $Ni_{16}Ti_6Si_7$
Ageing: 715 °C / 2 ÷ 500 h	TiC; $TiC_{0,3}N_{0,7}$; $TiN_{0,3}$; $Ti_4C_2S_2$; Ni_2Si; MoB; G - $Ni_{16}Ti_6Si_7$; γ' - $Ni_3(Al,Ti)$

6. SPECIATION ANALYSIS IN MULTICOMPONENT NICKEL-BASED ALLOYS - γ' PHASE

Multicomponent nickel alloys (superalloys or hyperalloys) can contain up to 18 alloying constituents, including nickel, cobalt, chromium, molybdenum, aluminium, titanium, niobium, tantalum, tungsten, vanadium, zirconium, boron, hafnium, silicon and carbon. All these alloys have a multiphase microstructure, which consists of four basic phases, i.e. γ solid solution, γ' intermetallic phase, carbides, and topologically closed packed intermetallic phases of σ and μ type. Taking into account the complexity of the chemical composition of these alloys, the suggested breakdown into individual categories is of an illustrative nature only. Nickel is the main alloying constituent and it determines the alloy structure, phase stability, and technical and technological properties. Cobalt reduces aluminium and titanium solubility in γ solution, and also affects the amount of γ` phase and the extent of its stability. The presence of aluminium, titanium and niobium increases hardness of the nickel alloys, mainly through precipitation of the dispersed γ'- Ni_3 (Al, Ti) phase. Carbon, the content of which is up to 0.2 % by mass, reacts with carbide-forming elements and forms various carbide phases of the MC, $M_{23}C_6$, M_6C and M_7C_3 type, characterised by different morphologies. Interactions of carbide-forming elements make their atoms highly interchangeable, e.g. (Ti, Nb) C. In many cases, the volume fraction of the γ' phase precipitates in the structure of nickel superalloys is up to 68 %. Depending on the amount of alloying constituents added to nickel alloys and their final content in these alloys, and on the applied variant of alloy heat treatment, the chemical composition of the γ'- Ni_3(Al, X) phase, where X = Ti, Ta, Nb, can vary in a very wide range of values. This is due to the fact that cobalt can replace nickel, while titanium, niobium and tantalum can occupy the position of aluminium in the ordered γ' phase lattice. Molybdenum, chromium and iron can replace both aluminium and nickel in the Ni_3Al compound [1-7]. Typically, in the precipitates of γ' phase, the content of from five to ten metal elements is determined. The process of isolation of γ' phase and the method of determining the content of metallic elements in γ' phase isolates using AAS was described in detail in [1,5]. Exemplary results are shown in **Table 5**.

Table 5 Chemical composition of alloy tested and the results of chemical analysis of γ' phase isolates

Alloy	**Content of elements mass %**												
	C	Cr	Co	Ti	Al	Ta	W	Mo	B	Zr	Fe	Nb	Ni
A	0.13	10.50	6.52	3.00	4.60	-	3.99	4.99	0.03	-	2.00	-	64.24
Chemical composition of γ' phase isolates in mass %													
Ageing, K	C	Cr	Co	Ti	Al	Ta	W	Mo	B	Zr	Fe	Nb	Ni
1123	-	3.02	3.08	3.71	6.10	-	4.56	1.98	-	-	-	-	R
1223	-	4.73	3.09	3.84	6.56	-	4.97	2.32	-	-	-	-	R
1323	-	3.88	3.28	5.41	6.49	-	5.22	2.62	-	-	-	-	R

7. DETERMINATION OF ALUMINIUM IN STEEL AS A TYPICAL EXAMPLE OF SPECIATION AND SPECIATION ANALYSIS IN METALLURGY

The problem of aluminium determination in steel using AAS method has already been described in detail in many papers, therefore in this chapter only the leading aspects of this methodology are briefly outlined citing the most commonly used analytical procedure [1, 9-12]. Aluminium in steel is determined in a fairly wide range of concentrations, but most commonly in the range of 0.002-0.060 %. Taking into account the range of concentrations so wide, aluminium is determined by both flame and flameless atomic absorption techniques [9-12]. H. Bosch et al. [11] have developed a rapid procedure for the determination of acid-soluble aluminium in steels in the concentration range of 0.002-0.060%. The standard deviation is then 0.001 %. F. Shaw and J.M. Ottaway [12] described the determination of aluminium in steel using flameless technique. For the determination of total aluminium, the residue was fused with a mixture of sodium carbonate and sodium tetra borate and dissolved in nitric (V) acid. I. Persson et al [13] utilised flameless technique for the determination of aluminium in various grades of steel.

8. SUMMARY

Apart from the basic data on the chemical composition of metallurgical materials, modern research instruments also provide additional information on the types of phases, chemical compounds, etc. This information, in turn, when transferred to technologists and materials engineers allows them to upgrade the properties of the already manufactured products and design new metallurgical materials for specific applications. So, it can serve as a typical example of feedback between “(metallurgical) material analytics development” and “(metallurgical) technology development". This area also includes problems of phase analysis, speciation and speciation analysis in metallurgy [1]. Chemical analysis of isolated phases in reference to metallurgy and material science almost always meets the quantitative requirements of speciation analysis.

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