Investigation of Molecular Interferences at GDMS Analysis of Main Elements and Microalloing of High-Entropy Alloy AlCrFeCoNiCu

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The peculiarities of the glow discharge mass-spectrometry (GDMS) analysis of the main components and elements of microalloying of high-entropy AlCrFeCoNiCu alloy are considered in the paper. Molecular interferences of $Ar_xA_y^{+i}$, Ar_xG^{+i}, $A_xB_y^{+i}$ types (where A, B are the components of the sample, G are single and 2-3 atomic gases; x, y = 1, 2, i - charge of ion, i = 1, 2), which are formed during cathode sputtering of this alloy in glow discharge plasma were calculated and experimentally tested. It is shown for spectrometers at resolution $R_{0.5} \geq 7000$, the greatest influence of molecular ions of Me_2^+ and $ArMe^+$ types exist in the range of isotope masses from ^{85}Rb to about ^{107}Ag. A careful selection of isotopes is required in this mass range to meet detection limit conditions. In other areas of the mass spectrum, the sensitivity of the analysis is limited by the background current and the sensitivity of the detectors and is at the usual ppb-level for this method.

Keywords: glow discharge mass-spectrometry, high entropy alloy AlCrFeCoNiCu, microalloying, mathematical simulation and experimental investigation of mass-spectra

Дослідження молекулярних інтерференцій при мас-спектрометричному аналізі основних компонентів та елементів мікролегування в високоентропійному сплаві AlCrFeCoNiCu

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В роботі розглянуті особливості аналізу основних компонентів та елементів мікролегування високоентропійного сплаву AlCrFeCoNiCu методом мас-спектрометрії із жевріючим розрядом як джерелом іонів. Методом математичного моделювання та експериментально проаналізовані молекулярні інтерференції типів $Ar_xA_y^{+i}$, Ar_xG^{+i}, $A_xB_y^{+i}$ (де A, B – компоненти зразка, G – одно- та 2-3-атомні гази; x, y = 1, 2, i – заряд іона i = 1, 2), які утворюються при катодному розпиленні цього сплаву. Показано, що на спектрометрах з роздільною здатністю на половині висоти піку $R_{0.5} \geq 7000$ в даному сплаві найбільший вплив молекулярних іонів типів Me_2^+ та $ArMeH^+$ існує в області мас ізотопів від ^{85}Rb до приблизно ^{107}Ag. В цьому діапазоні мас потрібен ретельний вибір ізотопів, які забезпечують необхідну чутливість. В інших областях мас-спектру чутливість аналізу обмежена фоновим струмом і чутливістю детекторів і знаходиться на звичайному для даного методу ppb-рівні.

Ключові слова: мас-спектрометрія жевріючого розряду,високоентропійний сплав AlCrFeCoNiCu, математичне моделювання та експериментальне дослідження мас-спектрів

Atom-spectrometric methods at element assay of high entropy alloys

High-entropy alloys (HEAs), or complex high-concentration alloys, have been actively researched around the world over the last decade. Such alloys contain as a rule more than five major elements in close to equiatomic concentrations. This approach opened up the fundamental possibilities of producing new materials with unique properties that cannot be realized by the traditional microalloying methods of alloys based on a single element. HE alloys have high hardness, wear resistance ($Co_{1.5}CrFeNi_{1.5}Ti$,

$Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti$), strength at room temperature (AlCoCrFeNi), high temperature strength (NbMoTaV). The $Cu_{0.5}$NiAlCoCrFeSi type alloy has a higher corrosion resistance than some stainless steel grades [1, 2]. From the point of view of analytical chemistry, the problems of analysis are complicated by the use of additional doping of HEAs. In [3] it was shown that microalloying with boron, carbon and silicone leads to the formation of secondary phases and increases the hardness of AlCrTiV alloy. Hardness of alloy $Al_{0.5}CoCrCuFeNiB_x$ (x = 0 - 1) also increases linearly with boron content x ≥ 0.6 [4].

In [5], the alloying of $CoCrFeNiTa_x$ alloy with tantalum (x = 0.0 - 1.0) is investigated. It has been shown to localize electrons near tantalum atoms adjacent to nickel atoms and form mixed structures. Also known are studies of the biomedical properties of coatings made of (TiZrNbHfTa)N and (TiZrNbHfTa)C alloys, which demonstrate high biocompatibility with cells *in vitro* experiments [6]. It is shown that the corrosion resistance of $Al_{0.5}CoCrCuFeNi$ alloy is higher than that of stainless steel at lower corrosion current density [1]. In [7], the prospects of using TiZrNbTaFe alloy in orthopedics and as dental implants were considered.

Considering the multicomponent composition of HEAs, their analysis by analytical chemistry methods, including wet chemistry methods, as well as modern instrumental methods - mass spectrometry, X-ray fluorescence, emission spectral analyzes is a difficult task.

There are a number of problems with selectivity, sensitivity, inter-element influence, which in different methods have specific characteristics. Instrumental methods require standard samples to determine the dependence of intensity of the analytical signal from the concentration. For the analysis of traditional alloys based on one major component, standard samples have been developed and produced for various steels grades, copper-based alloys (bronze, brass), aluminum alloys, nickel-based alloys and others. This variety of standard samples is caused by the effects of the difference in composition of a sample and standard and the structure of the alloys on the analytical signal.

The nature of these effects is different for these methods. In the emission spectral analysis (ESA) of metals and alloys, as a rule, a spark discharge is used to transfer sample atoms to plasma and excite spectra. The intensity of the spectral lines depends on the erosion processes on the electrodes, discharge parameters (temperature, electron concentration), which in turn depend on the parameters of the generator, the composition of the electrodes, their thermal and mechanical processing (rolling, forging, casting) [8]. The calibration dependencies are built in coordinates – concentration *vs.* the ratio of the intensity of the spectral line of the element, which is analyzed, to the line of the matrix element. For this purpose, the concentration of the latter must be constant, whereas the concentrations of the alloying components are varying. High-entropy alloys have no major component and changes in the concentration of any component lead to significant changes in the reference intensity of the element conditionally referred to as matrix.

There is also a problem of instrument resolution, which is complicated by the multi-line spectra of most HEAs components, whose concentrations are significant (the so-called spectral interference problem). Such interferences exist in the analysis of conventional alloys, but for HEAs the probability of their occurrence is increased, which requires the use of high resolution spectrometers and provide carefully line selection. These problems require the development of a new concept for the analysis of HEAs using the ESA method [9].

In X-ray fluorescence analysis is known the effect of differences in the composition of standard samples and the material under study on the analytical signal. The cause of the effect is the differences in the absorption of the primary radiation of X-ray tube, the absorption of the fluorescence radiation of the measured component, and the secondary excitation of some elements by others in the standards and a sample. The mutual influence of the elements is taken into account in industry using standard samples with the same composition and regression coefficients.

In the development of new alloys, the problem is solved using the fundamental parameter method, which makes it possible to perform calibration with the help different in composition standard samples and even pure elements. Despite the relatively small number of K- and L-shell lines at high number and concentration of components, the possible spectral interferences should be taken into account, especially on energy-dispersive spectrometers.

Methods of concentrations determination of components and molecular ions in the GDMS of high entropy alloys

Glow discharge mass spectrometry as a source of ions has proven to be a sensitive and versatile method. This method has advantages in the analysis of new materials for which there are no standard samples, in particular high-entropy alloys. When calculating the concentration, a special method of normalizing the intensity of the analytical signal is used according to the formula:

$$[X] = RSF_x \times ((I_x / ab_x) / I_m), \quad (1)$$

where RSF_x is the relative sensitivity factor of element x; I_x is the ionic current of the measured isotope of the element x; ab_x is isotope abundance; $I_m = \Sigma(I / ab_n)\, RSF_n$ is the current referred to as the matrix current. In contrast to the ESA, the normalization of the analytical signal is carried out by dividing analytical signal by the sum of ion currents of all components according to the formula (1). Thus, significant variations in the composition of the HEAs do not affect the total current.

Second, an important factor that makes it possible to analyze new materials using standard RSFs values is their weak dependence on the sample composition. In the glow discharge, there is cathode atomization of the material due to the bombardment of the surface by argon ions with energy of about 1 KeV, that is two to three orders of magnitude higher than the chemical bond energy of the metal atoms. Therefore, the differences in bonding energy in the different alloys have little effect on the sputter yield and relative sensitivity factors. Further, an ion beam from sample components is formed, enters the mass spectrometer, which records the ionic current of the element proportional to its concentration in the alloy. The advantage of this method of ionization is the direct transfer of atoms from the solid phase to the plasma without dissolving the sample, used in inductive-coupled plasma mass-spectrometry or in atomic absorption analysis. This greatly simplifies the procedure of sample preparing for analysis and shortens its time. In the analysis of small impurities, ionization with the help of argon ions guarantees the absence of additional contamination and, moreover, the pre-sputtering of surface by argon ions allows a deep cleaning of the surface from possible technological contamination.

One of the problems with the GDMS method is the formation in the plasma of a glow discharge of molecular ions (MI) and isotopes of other elements that have the same nominal masses with the studied isotope and may not be sufficiently resolved by the available instruments. These obstacles are known as molecular and isobaric interferences [10, 11]. Their mass, or more precisely the ratio of mass to charge m / q, may differ by several units in the second digit after the decimal point. They form ionic clusters of different types, whose ionic currents, in terms of the current of the matrix, can reach percentages and, if the resolution is insufficient, significantly affect the results of the analysis. These are molecules of $Ar_nX_m^{+i}$ type, $Ar_nR_m^{+i}$, where n, m = 1, 2, X are the isotopes of components of the sample (metals or nonmetals), R are gases or radicals, i = 1, 2 is the charge of the molecular ion. Significant concentrations also generate MI from the components of the sample, mainly from the isotopes of the matrix, *i.e.* ions of types $X_nY_m^{+i}$, $X_nR_m^{+i}$. The influence of molecular interferences has previously been considered in the analysis of high-alloy steels, cobalt-chromium-molybdenum alloy, high-grade sapphire as well.

The MI problem is complicated at the increased number of high-concentration components that is the case at analysis of HEAs. Unlike other spectral methods, in mass spectrometry, the number of spectral interferences is also influenced by the isotopic composition of the sample. As one knows, elements with odd number nucleus are usually monoisotopic or have two isotopes. Nuclei with even charge have many isotopes (Sn - 10, Mo - 7) with different abundance. Thus, the sample alloy with 6 elements (AlCrFeCoNiCu) contains 17 isotopes. The number of possible types of MI is determined by the number of combinations with repeats from the number of isotopes and taking into account their general formulas given above. In the immediate vicinity of the studied isotope can be more than a dozen interferences. Even on double-focusing mass spectrometers - the magnetic sector and the electrostatic analyzer at a resolution of 7000 - 9000 at half peak height ($R_{0.5}=m/\Delta m$) in multicomponent high concentrations alloys, molecular ions create significant interference. On low-resolution quadrupole mass spectrometers, these problems significantly reduce sensitivity of the analysis and may lead to misinterpretation of the mass spectra. Standard software supplied with instrument contains a module for molecular interference calculation. But this program allows to show the position of molecular ion only, if the analyst could compile this ion in a mind. Taking into account the number of isotopes in a sample and gas-forming elements (isotopes) this is time consuming procedure, besides the intensity of the molecular ion remains unknown.

The solution of this problem has been proposed by introducing the concept of effective equilibrium constants (EECs) of molecular ion formation reactions [12]. Since the concentrations of atoms and ions in plasma are proportional to their content in the samples the EECs are, by definition, the proportionality coefficients in the equation $[XY^+] = EECs\ (XY)\ [X]_s\ [Y]_s$, where $[X]_s$ and $[Y]_s$ are isotopic concentrations of the reacting components in the solid phase, and $[XY^+]$ is the concentration of molecular cluster. To compare the concentrations of the components of the sample with the concentrations of MI, they are calculated by the same algorithm is used for the components of the sample, that is, by normalizing the ionic current of molecular ions per current of the matrix (eq.1). On the base of proposed concept computer program CLUSTER have been developed and it obtained further development. The program contains also modules for concentration measurements of nonconducting samples and isotope enriched samples, which was impossible with the standard program of the instrument.

The concentration of MI in the glow discharge plasma depends on the concentration of the components in the samples, the discharge parameters (current, voltage, argon pressure). In the plasma, the processes of MI formation and their dissociation occur as a result of collisions with argon ions and atoms, collisions of atoms and ions of a sample, MI with argon, recombination, and wall escape. In [13], it has been shown that the formation of ionic dimers occurs by a mechanism close to the Lindemann reactions, that is, the reaction proceeds through the stage of an intermediate metastable complex, which passes into the final product due to a monomolecular reaction with radiation. In contrast to the Lindemann reaction, destroying of molecular ions occurs not only at collisions of intermediate complex with reagents (argon in our case), but also ionic dimers (the final product) at collisions with argon atoms.

Effective equilibrium constants have been measured using standard samples of various matrices (steels,

aluminum alloys, copper alloys, Ni-based refractory alloys and others). High resolution of the VG9000 instrument allows solving this problem. Quadrupole instruments with glow discharge as ions source can't be utilized because of low resolution power where it is impossible to select certain molecule from the bunch of molecular ions.

Experimental method and instrumentation

Spectra measurements were performed using mass spectrometer VG9000 (VG-Elemental, UK). The spectrometer has a dual focus – magnetic sector and electrostatic analyzer, which provides a resolution of the order of 5000 at 5% above the background or $R_{0.5}$ = 7.000 – 9.000 at half peak height. Calculations were made for the $R_{0.5}$ since they are more convenient for mathematical simulation of mass-spectra as the line shape was approximated by a Gaussian curve. The VG9000 is equipped by two detectors. The first one is Faraday detector. It is designed for large ion currents (10^{-13} – 10^{-8} A) from the main components of alloys. Impurity elements are recorded by the Daily Detector, which converts the ion current to the flow of electrons. The later are registered by a photoelectron multiplier. Operating current range from 10^{-17} to $n \cdot 10^{-12}$ A. The ranges of both detectors overlap. The signal is considered registered if the device registers 5 ions. In terms of concentration, this means that it is possible to analyze from tens of percent to the ppb level (10^{-7} %) in one isotope scan without prior sample preparation.

The relative sensitivity factors (RSFs) were obtained using standard samples. The procedure was also tested on the intermetallic system $MeNi_{5-x}Al_x$. Since concentration of molecular ions are functions of state, EECs and RSFs measurements we conducted at commonly used discharge conditions: current – 2 mA, voltage – 900 V, flat cell without cooling by liquid nitrogen.

Results and discussion

The method of molecular interferences calculation and computer program have been proved using various materials mentioned above. Unfortunately there are no standard samples of the high entropy alloy of this type yet. Efficiency of the method and computer program can be verified using Al-alloy with high concentration of alloying components. In the table are presented results of depth profiling study of standard alloy B-96 type and certified concentration. Aluminum alloy of this type is a suitable model object because of high concentration of Al, Mg, Cu, Zn and other elements. Effective equilibrium constants for molecular ions of Me1Me2, MeAr and three-atomic molecules types have been measured earlier [10] and rectified in further study.

During the analysis, the surface is sputtered by argon ions, and when analyzed for 20-30 elements (there may be several isotopes of one element), a layer of several microns is eluted. The paper presents the results of sequential scanning of the surface, so that the reproducibility of the analysis is also affected by the homogeneity of the distribution of the alloy components. At the same time it is possible to draw conclusions about the linearity of the registration system.

The table 1 shows that relative deviation of average from certified value does not exceed 1-2 % and standard deviation also meet requirement of practice given that homogeneity of standard also affected results.

Result for Zr-concentration draw attention because of discrepancy in results obtained with use of ^{91}Zr and ^{94}Zr isotopes. The computer program calculates element concentration tacking into account the abundance of each isotope so in the absence of MIs results for each isotope of element must coincide within relative error of analysis. This result indicates presence interferences for ^{91}Zr isotope and discrepancy sufficiently exceed possible error. As shows mathematical simulation (fig. 1a) the main contribution into sum intensity gives molecular ion $^{64}Zn^{27}Al^+$ (980 ppm) and also $^{67}Zn^{24}Mg^+$, $^{66}Zn^{25}Mg^+$, $^{63}Cu^{28}Si^+$, $^{65}Cu^{26}Si^+$, $^{55}Mn^{36}Ar^+$ ions (1 – 3 ppm). This result coincides with difference between measured concentration and certified value within calculation error.

Comparison calculated and measured spectra are presented in the fig.1b – 1g.

Table 1. Depth profiling study of reference Al-alloy B96-type and certified concentration (element concentration, mass units).

Isotope	units	B96-7.001	B96-7.002	B96-7.003	B96-7.004	Average	Std Dev	Certified
Mg 25	%	3.1	3.2	3.2	2.9	3.1	4.32	3.0
Al 27	%	87.2	87.2	87.1	87.2	87.2	0.06	up to 100%
Si 29	ppm	2280	2319	2356	2234	2297	2.28	2300
Ti 48	ppm	796	806	827	810	810	1.58	820
Cr 52	ppm	1741	1672	1694	1721	1707	1.77	1700
Mn 55	ppm	1664	1673	1672	1711	1680	1.26	1700
Fe 56	ppm	3593	3478	3707	3669	3612	2.80	3600
Cu 63	%	2.2	2.2	2.3	2.3	2.25	2.72	2.3
Zn 66	%	6.3	6.0	6.6	6.3	6.30	4.22	6.36
Zr 91	ppm	2119	2344	2341	2368	2293	5.10	(1300)
Zr 94	ppm	1261	1263	1276	1347	1286	3.15	(1300)

Fig. 1. Calculated and experimental spectra for some isotopes of standard sample of aluminum alloy.

Simulated spectra reproduce not only the shape of spectra. "Concentrations" of molecular ions agree well with experiment. The program developed is of high importance for correct interpretation of measurements. The problem is that because of thermal drift of spectra along mass scale the instrument erroneously may tag interference as a normal peak, especially if it is higher than the signal from the true isotope. Fig. 1d represents such a case. Intense molecular ion $^{66}Zn^{40}Ar^{+}$ and the group of minor interferences the instrument erroneously considered as ^{106}Pd with concentration 1650 ppm. Calculated "concentration" of molecular interferences peak is 1740 ppm (upper right window in the simulated spectra). The similar case is with ^{128}Te isotope (fig. 1g) that is actually $^{64}Zn_2^{+}$ and group of smaller two- and three-atomic molecular ions. Calculated intensity is in a good agreement with measured one.

The previous investigations show that effective equilibrium constants for ion-molecular reactions of certain type are mainly functions of discharge parameters and only slightly depend on sample composition. This fact makes it possible in first approximation use EECs measured in standard samples for mathematical simulation of mass-spectra of new materials.

Taking into account above reasons in this section we will discuss results of mathematical simulation of mass-spectra of high entropy alloys. The composition of a sample is shown in the table 2. In using of high purity Ar concentration of interferences with isotopes of gas and gas-forming elements may be considerably reduced. In such a case we show in table 3 along with high gaseous impurities.

The ionic currents of the major components of the alloys are typically orders of magnitude greater than the MI currents (excluding the isotopes of the discharge gas and their diatomic MIs), so the MIs do not cause problems in determining the major components. The mass-spectra in the region of ^{56}Fe and ^{59}Co isotope are shown as example of this rule (Fig. 2). Similar ratios also exist for other major components of this alloy.

The properties of high-entropy alloys are highly dependent on impurity elements. The known alloying of AlCoCuFeMnNi alloy with CeO_2 impurities improves grain growth and alloy structure [14]. The trace amounts of Sc, Zr, also used as alloying elements, which influence the microstructure and mechanical properties of the alloy [15]. HEAs can be used for implant producing. At this stage of the study of a new type of the HEAs influence of many impurity elements on the properties of the alloy has not been sufficiently studied. Therefore, it is necessary to consider an expanded list of elements that include toxic and biologically active elements, as well as other elements having molecular interference issues.

Table 2. Composition of a sample (wt. ppm) used for interference calculation of $AlCrFe_{0.5}CoNiCu$ alloy.

Element	C, (wt.) ppm	Element	C, (wt.) ppm
H*	1.00E+04	Al	9.36E+04
C*	1.00E+04	Cr	1.80E+05
N*	7.00E+03	Fe	9.70E+04
O*	1.00E+03	Co	2.05E+05
Si	1.00E+02	Ni	2.04E+05
S	1.00E+02	Cu	2.20E+05

* – Gases and gas-forming elements content correspond to their equilibrium concentration in plasma (including residual impurities in argon), but not the true content in the sample.

One of the most common impurity elements is silicon. Figure 3 shows the calculated spectrum in the mass range of ^{28}Si at a resolution of $R_{0.5} = m/\Delta m$ = 7000, 5000 and 1000. High concentrations of iron and nickel reduce the sensitivity of silicon determination. Next to the most common isotope ^{28}Si (92 % abundance) is the $^{56}Fe^{+2}$ double charged ion (mass separation occurs in accordance with the value

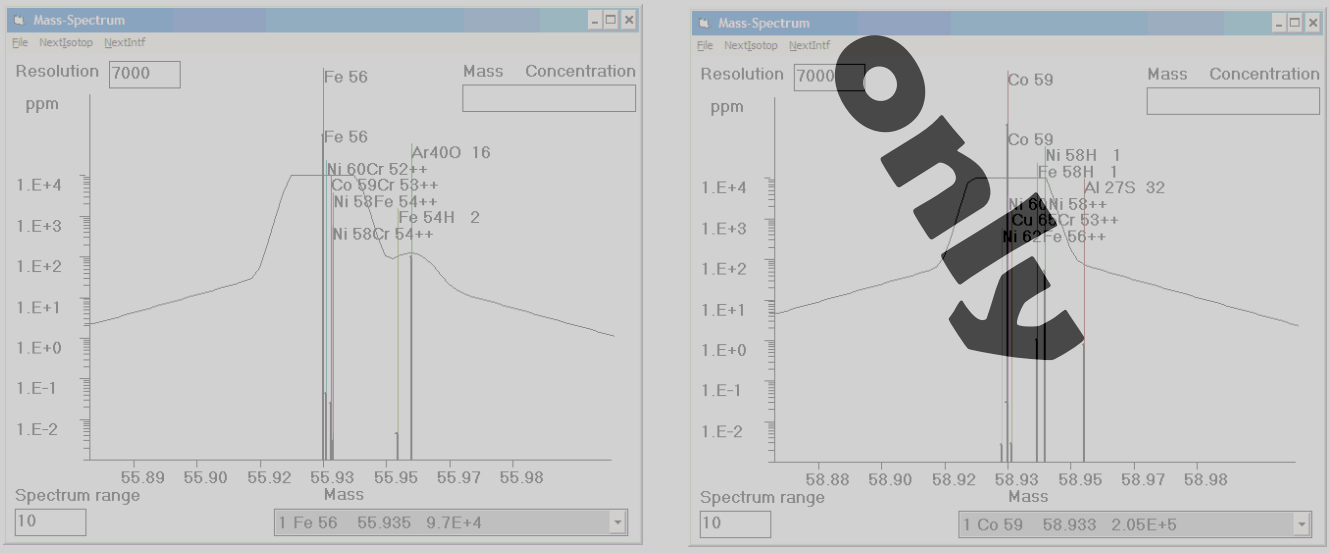
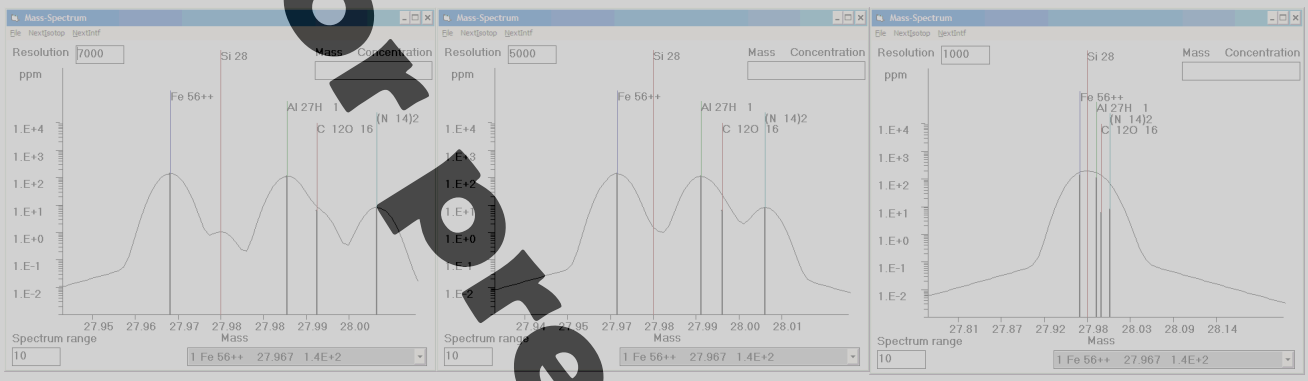


Fig. 2. Calculated mass-spectra for ^{56}Fe and ^{59}Co isotopes.

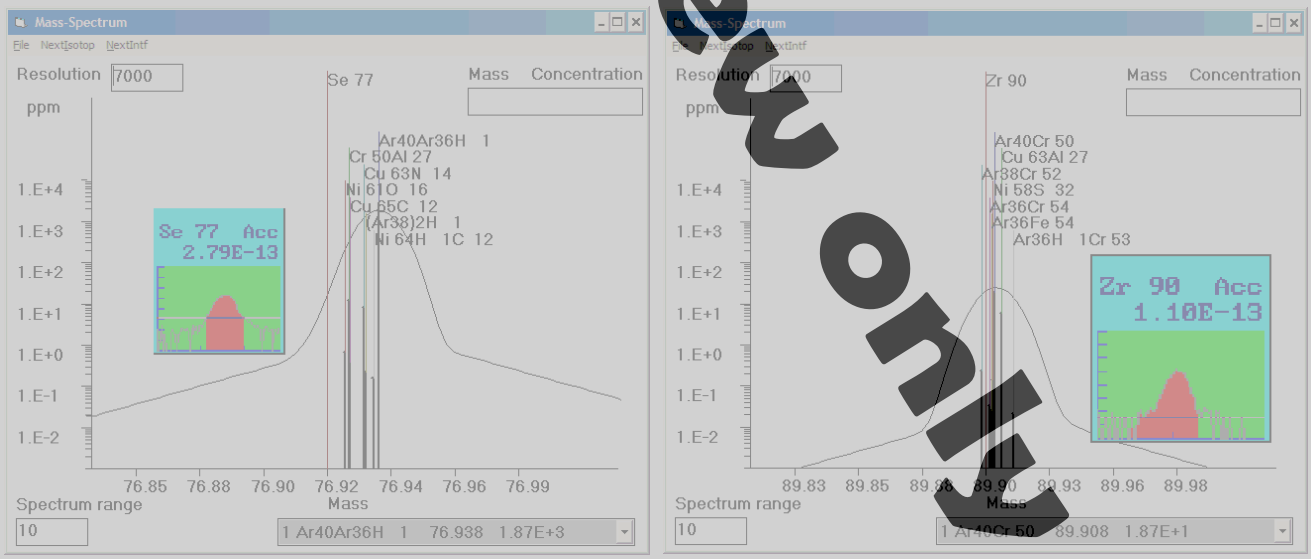
of m / q, where q is a charge of an ion). Other isotopes (^{29}Si, ^{30}Si) are less abundant, the sensitivity of analysis using them is much smaller and, in addition, there are also intense lines of two-charged ions ^{58}Ni^{+2} and ^{60}Ni^{+2} ions. On double-focusing VG9000 device at half-height resolution ($R_{0.5}$ = 7000 - 9000) can be achieved sensitivity about of 1 ppm. Sensitivity significantly worsens and becomes >200 ppm with the use of quadrupole devices at resolution of $R_{0.5}$ ≈ 1000. The same degree of influence of the double charged ^{62}Ni^{+2} ion is observed in determination of phosphorus (^{31}P). Since phosphorus is monoisotopic element no other isotope can be selected for analysis, so a resolution of ≥ 7000 is also required to obtain detection limit ≤ 1 ppm.

In high-entropy alloys, so as in other alloys with high concentration of components (steels, Co-alloys for implants, Ni-based refractory alloys, alloys for hydrogen storage *etc*) molecular ions of the type Me_2^+ and $ArMe^+$ are the main obstacles, that reduce detection limit. Their location, as well as the location of other polyatomic MI, with respect to the studied isotopes changes with mass variation. In the mass range up to ^{75}As, they are concentrated at the side of larger masses. Gradually, they form groups near the exact mass of isotopes (^{85}Rb - ^{95}Mo) and then the center of mass of the MI group shifts towards smaller masses (^{95}Mo - ^{123}Sb) and further this shift increases until the end of the periodic table (Fig. 4).



a b c

Fig. 3. Mass-spectra for ^{28}Si calculated at resolving power $R_{0.5}$ = 7000, 5000 and 1000 (a, b, c – respectively), ($R_{0.5}$ is shown in the upper left corner of the figure).



a b

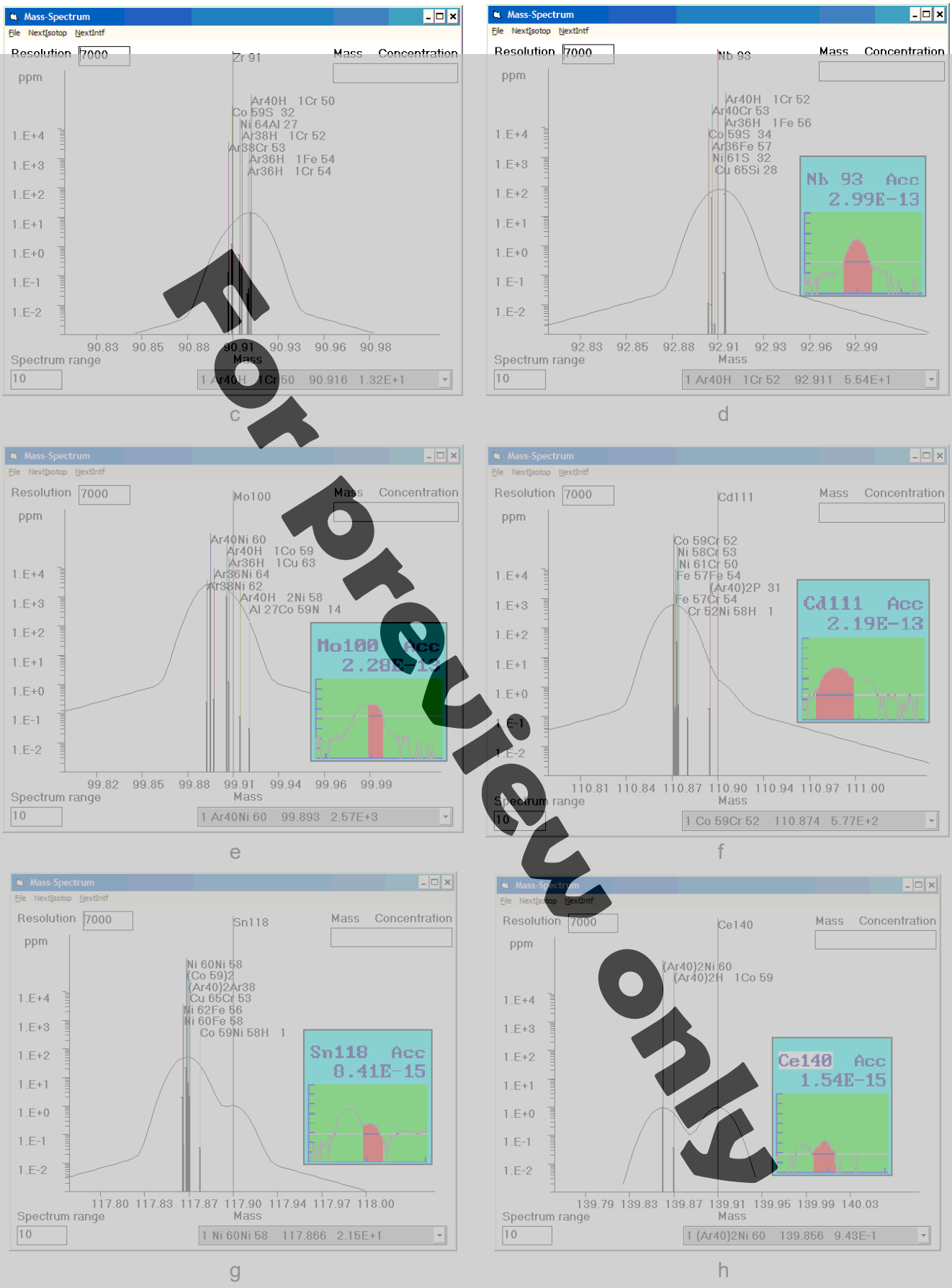


Fig. 4. Position of the group of molecular ions Me_2^+ and $ArMe^+$ with respect to the peaks of isotopes of elements in the range m / q = 77 - 140 at the resolution $R_{0.5}$ = 7000. ^{77}Se, ^{90}Zr, ^{91}Zr, ^{93}Nb, ^{100}Mo, ^{111}Cd, ^{118}Sn, ^{140}Ce (a, b, c, d, e, f, g, h - respectively).

Calculations and experiment show that the most unfavorable analytical conditions, which require high resolution of the device, in this alloy exist for the group of isotopes in the mass range ^{85}Rb - ^{95}Mo. The highest sensitivity of zirconium determination is provided by isotopes ^{90}Zr and ^{91}Zr. Other isotopes give less sensitivity due to the molecular ions $^{40}Ar^{52}Cr^{+}$, $^{40}Ar^{54}Cr^{+}$ (> 1000 and > 100 ppm, respectively). Table 3 represents the main molecular interferences for some selected elements (isotopes) that represent above discussed mass ranges and are of importance being alloying components or biologically active in this HEA. Relative standard deviation of molecular concentration measurements is a little bit higher then this value for ordinary isotope measurements and does not exceed 5 % (table 2). Using 3σ criteria we assume that maximal error of interference measurements is about 15% in the centre of molecular interference line. That is why detection limit is determined by sum "concentration" of interferences enlarged at least in 15 % and added more 5% for reliable registration signal above molecular ion. This method applicable in the case of nonseparable interferences, like for ^{45}Sc and ^{48}Ti. When interferences are partly resolvable and only wing of interference line underlying isotope measured we have used profile of simulated mass-spectra obtained by the computer program taking into account 3σ rule (^{55}Mn for instance). In this case very important is resolving power of the instrument. Fig 2. illustrates the case for ^{28}Si. Detection limit depends on intensity and shape of the interferences sum profile and resolving power of the instrument.

The two-charged molecular ions of $^{63}Cu^{27}Al^{+2}$ and $^{50}Cr^{40}Ar^{+2}$ at $R_{0.5}$ = 7000 are nonseparable from the ^{45}Sc isotope, but their total contribution does not exceed 0.1 ppm, which provides high sensitivity of ^{45}Sc detection in this alloy. Fig. 3 shows that molecular interferences do not interfere with the determination of cerium by the ^{142}Ce isotope. The sensitivity is determined by the background current and is at ppb level.

Thus, the major alloying components of this alloy (Sc, Zr, Ce) are determined with sensitive sufficiently high for practice. Content of the toxic elements at production of surgical implants should be kept as low as possible. To obtain detection limit of ~ 1 ppm using the ^{75}As isotope, it is necessary that the total oxygen content in the form of O_2, CO_2 in argon in terms of the conditional content in the sample (see footnote to Table 1) does not exceed 20 - 50 ppm (Table 2). The detection limit for such elements as Nb and Mo is limited mainly by molecular ions of the type $ArMe^{+}$, where Me are the main components of the HEA. The effective "concentration" in the maximum of such ions depends on the abundance of argon and corresponding metal isotopes and ranges from ~ 2000 ($^{40}Ar^{52}Cr^{+}$ - ^{92}Mo) to several tens of ppm ($^{36}Ar^{59}Co^{+}$ - ^{95}Mo). Molecular ions of the type Me_2^{+} create the major interferences for cadmium isotopes. At a resolution of $R_{0.5} \geq 7000$, they slightly reduce the sensitivity of the assay, nevertheless with the isotopes ^{112}Cd and ^{113}Cd, sensitivity of about 1 ppm can be achieved. All rare earth elements are free from interferences formed by $ArMe_2^{+}$ and Ar_2Me^{+} clusters. They are arranged by smaller masses relative to the measured isotope similarly to the location for ^{140}Ce (Fig. 3h). The detection limit is determined by the sensitivity of the detectors and is at ppb level for the VG9000 instrument. Isotopes of elements such as Hg and Pb are characterized by more complex ionic clusters of the $Ar_2Me_2^{+}$ type, whose apparent concentration is tens of ppb, and their maxima are shifted even further toward smaller masses relative to the isotopes considered than for REEs so isotopes of these elements in this alloy are free of molecular interferences.

Table 3. Molecular interferences and detection limit for some elements (biologically active, toxic) in AlCrFeCoNiCu matrix with impurities.

Isotope, molecular ion	Mass (m / q)	Maximal «concentration», ppm	Detection limit, (ppm) at $R_{0.5}$ = 7000	Resolution $R_{0.5}$ required for 1 ppm detection limit
^{45}Sc	44.95591		0.1	-
$^{63}Cu^{27}Al^{+2}$	44.95557	4.64E-02		
$^{50}Cr^{40}Ar^{+2}$	44.95422	3.95E-02		
^{48}Ti	47.94795		0.3	-
$^{36}Ar^{12}C^{+}$	47.96754	8.12E-01		
$^{56}Fe^{40}Ar^{+2}$	47.94866	2.63E-01		
$^{60}Ni^{36}Ar^{+2}$	47.94917	2.03E-03		
$^{58}Ni^{38}Ar^{+2}$	47.94904	1.06E-03		
^{55}Mn	54.93805		20	12000
$^{54}Fe^{1}H^{+}$	54.94744	3.31E+01	0.2	
$^{40}Ar^{15}N^{+}$	54.96249	2.71E+00	at H < 10ppm	
$^{54}Cr^{1}H^{+}$	54.94670	1.76E+00		
$^{58}Ni^{52}Cr^{+2}$	54.93793	1.23 E-01		

Table 3. (continuation).

Isotope, molecular ion	Mass (m / q)	Maximal «concentration», ppm	Detection limit, (ppm) at $R_{0.5}$ = 7000	Resolution $R_{0.5}$ required for 1 ppm detection limit
^{66}Zn	65.92603		20	12000
$^{65}Cu^{1}H^{+}$	65.93562	9.50E+00		
$^{52}Cr^{14}N^{+}$	65.94358	3.62E+00		
$^{50}Cr^{16}O^{+}$	65.94096	2.75E+00		
$^{54}Fe^{12}C^{+}$	65.93961	1.09E+00		
^{75}As	74.92159		20	19000
$^{59}Co^{16}O^{+}$	74.92812	8.68E+00	1 (at oxygen	
$^{61}Ni^{14}N^{+}$	74.93413	1.49E-01	concentration	
$^{36}Ar^{38}Ar^{1}H^{+}$	74.93810	1.33E-01	< 10 ppm)	
^{77}Se	76.91991		200	18000
Ar40Ar36H 1	76.93776	1.87E+03	20	
Cr 50Al 27	76.92758	1.18E+01	(at H < 10 ppm)	
Cu 63N 14	76.93267	8.23E+00		
^{90}Zr	89.90471		25	45000
Ar40Cr 50	89.90843	1.87E+01		
Cu 63Al 27	89.91114	5.79E+00		
^{91}Zr	90.90565		20	17000
$^{40}ArH^{50}Cr^{+}$	90.91625	1.32E+01	10 (H, S < 10	
$^{59}Co^{32}S^{+}$	90.90527	1.17E+00	ppm)	
$^{64}Ni^{27}Al^{+}$	90.90951	5.00E-01		
^{93}Nb	92.90638		100	55000
Ar40H 1Cr 52	92.91072	5.54E+0	50 (H < 10ppm)	
Ar40Cr 53	92.90303	4.08E+01		
^{95}Mo	94.90584		40	45000
$^{36}Ar^{59}Co$	94.90074	1.32E+01	20 (H < 10 ppm)	35000 (H < 10 ppm)
$^{40}ArH^{54}Fe$	94.90982	1.27E+01		
^{140}Ce	139.9054		0.1	-
$^{40}Ar_2\ ^{60}Ni$	139.8556	9.43E-01		
$^{40}Ar_2H\ ^{59}Co$	139.8658	3.46E-02		

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