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Composition analysis of some metal alloys using Auger electron spectroscopy

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Composition analysis of some metal alloys, based on quantitative Auger electron spectroscopy, is presented and the effects of preferential sputtering are discussed. It is shown that a simplified model can yield quite satisfactory composition results if certain experimental conditions are fulfilled.

1. Introduction

Auger electron spectroscopy (AES) is currently used in many fields of materials research. Being inherently a surface technique it provides an excellent depth resolution for the study of composition depth profiles and near-surface processes [1].

Controlled removal of upper material layers is necessary for this type of work and an *in situ* ion beam sputtering technique would be the obvious choice for this purpose.

An attempt to evaluate the true composition at an in-depth point, which is the aim of this work, involves a quantitative Auger analysis corrected for the sputtering effects. As sputtering is a very complicated process, its influence on the measured Auger spectrum is quite hard to evaluate. Several theoretical approaches to this problem have been discussed in the literature [2]. The more rigorous approaches are generally incompatible with the routine modes of a surface-science service laboratory. Application of these complicated analytic models would require, for each sample, considerable expensive system time, calibrations and appropriate reference samples. Such a time consuming process should be applied when high precision is essential, but, if reasonable approximations are sufficient simplified models can be used for a higher sampling rate.

In the following analysis we shall adopt an analytical method composed of two separately well-known models, one is used for Auger calculations and the other is used for describing the sputtering process. These models are generally considered as simplifying approaches as both suffer from several inherent drawbacks. However, they are easily applicable to the widest range of elements and compounds at the obvious cost of precision. It has been discovered that the results obtained for a set of metal alloys using this simplified approach are quite satisfactory and are comparable to results obtained using more sophisticated and rigorous approaches.

2. The simplified model

Several types of quantitative Auger formalisms have been so far proposed, but it is agreed, in general, that any suitable method should rely upon reference standards.

In this sense we use the method elaborated in [3] where a common standard (the Auger Ag-line) is used and relative sensitivity factors are given for a wide range of elements. According to this approach the surface concentration, f_i, of an element, i, (in atomic per cent) derived out of the Auger spectrum is

$$f_i = (I_i/S_i)\Bigg/\left(\sum_{j=1}^{n} I_j/S_j\right), \qquad (1)$$

where I_i is the amplitude (PTP) of the representative Auger line of the element in the derivative spectrum and S_i is the relative Auger sensitivity factor, as given in [3]. If the analysed in-depth surface is reached after some sputtering, this set of concentrations f_i should be corrected for different sputtering yields of the alloys constituents.

According to the simple approach presented, for example, in [4], the change in the virtual surface concentration f_i during sputtering will be given by

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$$df_i/dt = \left[-f_iY_i + C_i \sum_{j=1}^{n} f_jY_j\right] J, \quad (2)$$

where C_i is the bulk concentration of element i, Y_i is the sputtering yield of the pure element i (atoms ion^{-1}) and J is the current of impinging ions.

If there are no strong concentration gradients and sputtering takes place at a modest rate (a few nanometres per minute), one can achieve a local steady state after a few minutes of bombardment. In this case $df_i/dt = 0$ and Equation 2 are reduced to a simple set of algebraic equations. If concentration gradients are high or steady-state is otherwise inachieveable one has to solve a set of coupled differential equations. In the following, however, the former case will be assumed for the samples. The local bulk concentration at the analysed point will be given by:

$$C_i = (f_iY_i) \Big/ \left(\sum_{j=1}^{n} f_jY_j \right). \quad (3)$$

It is logical to assume that the increase in local surface roughness imposed by the sputtering destructive action modifies the original ordered local structure. This can, by a mode of averaging, eliminate the selective role of a few fundamental Auger factors (partially neglected by these models), which have a well-defined contribution in an ideal undisturbed "layer" structure. These are, for example, electron-escaping depth and backscattering factor. The resulting C_i values are expected to be accurate to an approximation consistent with the inherent accuracy of this simplified model.

3. Experimental procedure

In this work a set of metal alloys was studied, the constituents of which span a wide range of physical properties (densities, atomic weights, electronic structure and sputtering yields): Ag, Au, Pd, Cu, Ni, Fe, Cr and Co.

Auger spectra have been measured using a Physical Electronics Model 545 system. The electron gun was operated at low currents (~ 0.5 μA) and with energies matching the sensitivity factors recommended in [3]: 5 kV for alloys containing Au and 3 kV for the others. Sputtering was performed with a Physical Electronics differentially-pumped gun using Ar^+ ions. The sputtering power density was about 400 (V mA cm^{-2}). This is very close to the sputtering power used in the fundamental work of Laegreid and Wehner [5] in which a wide set of Ar-sputtering yields was determined. This set is used in our calculations. Although lower bombarding energies (up to 600 V) were used in that work, compared with 3 kV in the present work, a justified use of their yield values is assumed as we partially compensate for the higher energy by using lower current density and especially as, in fact, only relative yields were used (see Equation 3) [6]. Yield values are generally considered to be dependent only on sputtering voltage, as they are normalized to the applied current (atoms ion^{-1}). However, high current densities, in the milliamp per square centimetre range, must contribute to the destructive effects of the sputtering mechanism through multi-particle complicated interactions in the target.

Regarding power-dependent yields rather than voltage-dependent ones (and still adopting Laegreid and Wehner yield values [5]) is an assumption to be justified through the analysis of experimental results.

Typical yield values appearing in this set [5] are the following: W and Ta have low Y, of the order of 0.5 atoms ion^{-1}. Fe and Cr have medium yields, of the order of 1.0 to 1.1 atoms ion^{-1}. Au and Ag have very high yields, 2.0 and 2.7, respectively.

Auger spectra were recorded after removing the upper layer consisting of oxides and other contaminants, deep in the region where, supposedly, a homogeneous composition exists.

In Tables I and II the calculated compositions, as compared to the known bulk compositions, are summarized for binary and $n \geqslant 3$ component alloys, respectively.

4. Discussion

We begin by shortly reviewing some previously published results. In many works which test quantitative Auger formalisms attempts have been made to evaluate the sputtering yield ratio of the constituents out of the known bulk concentrations. A comparison is then made with existing sputtering data.

A binary metal alloy thoroughly treated in the literature is Cu–Ni [4, 6]. In the work of Shimizu *et al.* [4] the calculated yield ratio deviates by about 15% from the ratio directly measured by Tarng and Wehner [7]. In a more rigorous approach to this alloy Ho *et al.* [6] performed an exact solution of the differential equation,

TABLE I Binary alloys: calculated against known bulk concentrations

Alloy	Component	Surface concentration at the analysed point	Surface concentration corrected for sputtering yields	Known bulk concentration	Auger representative line energy (eV)
Au–Cu	Au	17.7	19.9	14.8	2024
Au–Cu	Cu	82.3	80.1	85.2	920
Pd–Au	Pd	10.1	9.6	13.8	330
Pd–Au	Au	89.9	90.4	86.2	2024
Au–Ni	Au	48.5	58.5	57.5	2024
Au–Ni	Ni	51.5	41.5	42.5	848
Ni–Cr	Ni	73.3	78.1	75.5	848
Ni–Cr	Cr	26.7	21.9	24.5	529
Pd–Co	Pd	38.9	50.7	50.7	330
Pd–Co	Co	61.1	49.3	49.3	770
Ag–Cu	Ag	52.4	64.6	60.2	351
Ag–Cu	Cu	47.6	35.4	39.8	920

Equation 2. The $Y(\mathrm{Cu})/Y(\mathrm{Ni})$ ratio thus calculated deviates by no more than 6% from the directly measured one.

It should be understood that any AES formalism should be relatively easy to apply to Cu–Ni alloys, as both elements are of very similar physical properties (density, atomic weight, electronic structure and even Auger line energies). They only differ in sputtering yields and if this is properly accounted for, good results are expected.

This is also the case for 304 stainless-steel, for which Auger analysis yields good results as Fe, Cr and Ni are of very close physical, AES and sputtering properties.

An excellent attempt to treat alloys whose constituents differ greatly in basic physical properties was made by West [8], who studied alloys consisting of Pd, Cr, Ag, Cu and Nb. In his work yield ratio results are compared to the work of Laegreid and Wehner [5]. Good agreement is found in Pd–Ag and Pd–Nb systems which are of similar physical properties. Wide deviations are

TABLE II $n \geqslant 3$ component alloys

Alloy	Component	Surface concentration at the analysed point	Surface concentration corrected for sputtering yields	Known bulk concentration	Auger representative line energy (eV)
Au–Ag–Cu	Au	50.7	51.0	38.8	2024
Au–Ag–Cu	Cu	40.9	36.6	39.2	920
Au–Ag–Cu	Ag	8.4	12.4	23.0	351
Pd–Ag–Cu	Ag	26.8	37.5	47.4	351
Pd–Ag–Cu	Cu	59.3	50.1	44.4	920
Pd–Ag–Cu	Pd	13.9	12.4	8.2	330
304 stainless-steel	Fe	73.0	71.0	69.5	703
304 stainless-steel	Cr	20.0	20.8	21.8	529
304 stainless-steel	Ni	7.0	8.2	8.7	848
In–Cu–Ag	In	4.2	5.6*	11.7	404
In–Cu–Ag	Cu	60.9	48.4*	35.2	920
In–Cu–Ag	Ag	34.9	46.0*	53.1	351
Hastelloy C	Ni	52.8	59.1	61.5	848
Hastelloy C	Mo	11.8	7.5	11.8	186
Hastelloy C	Cr	21.3	21.3	19.2	529
Hastelloy C	Fe	11.6	10.9	6.7	703
Hastelloy C	W	2.5	1.2	0.8	1736

*Y (In) interpolated from [4].

found, however, in the cases of the Pd–Cu and Pd–Cr systems (of the order of tens of per cent).

In our work, as outlined in Section 3, the existing yield values of Laegreid and Wehner [5] are used and the resulting concentrations are compared to the real known ones. In this sense it is actually an attempt to affirm a sufficient justification for a convenient use of sputtering-yield data obtained originally under different configurations and conditions.

From Table I it is evident that, in the cases of Pd–Co, Au–Ni and Ag–Cu a significant improvement was achieved by correcting pure Auger calculations for the sputtering effects. In the cases of Ni–Cr and Pd–Au no actual quantitative change resulted from the sputtering correction. In the case of Au–Cu, the role of this correction is negative. This may be connected to the relatively low gold concentration which makes its Auger amplitude (inherently small for Au) very difficult to measure and probably accompanied by a large error. Table I clearly shows that concentrations measured and calculated for binary alloys deviate by less than 4 atomic per cent from the real bulk ones. These measured values are accurate to about ± 5% for alloys not containing Au and to ± 10% only, for those containing Au.

From Table II it can be seen that whenever an $n \geqslant 3$ component system is under consideration and at least one of its components has a very high sputtering yield, $Y > 1.7$, the model should be modified and improved.

Results for 304 stainless-steel and Hastelloy C are relatively good and are comparable with those obtained for binary alloys. The components of these alloys have medium-to-low Y-values [5]. However, when Ag, Au or In, all having high Y-values [5], are present, the measured compositions differ significantly from the known bulk compositions. For such cases ($n \geqslant 3$ and $Y > 1.7$) an empirical approach was tried in which the calculated C_i value was used as a starting point for a second-step interaction following Equation 3.

The new concentrations C_i' will be:

$$C_i' = (C_i Y_i) \bigg/ \left(\sum_{j=1}^{n} C_j Y_j \right). \tag{4}$$

We have no analytic explanation for this second step. The only justification for this second-order approximation is given by the evident improvement in calculated results, as shown in Table III.

TABLE III Alloys with $n \geqslant 3$ components of high Y-values. C_i are the single-step calculations, C_i' are the two-step iteration values and C_b are the known bulk concentrations

Alloy	Components	C_i	C_i'	C_b (at %)
Au–Ag–Cu	Au	51.0	43.7	37.8
Au–Ag–Cu	Cu	36.6	36.8	39.2
Au–Ag–Cu	Ag	12.4	19.5	23.0
Pd–Ag–Cu	Ag	37.5	49.0	47.4
Pd–Ag–Cu	Cu	50.1	40.3	44.4
Pd–Ag–Cu	Pd	12.4	10.7	8.2
In–Cu–Ag	In	5.6	7.0	11.7
In–Cu–Ag	Cu	48.4	36.1	35.2
In–Cu–Ag	Ag	46.0	56.9	53.1

It is assumed, however, that the surface perturbation imposed by the combination of higher components number *and* higher sputtering yields is too complicated to be treated by a first-approximation model.

It should be mentioned here that a third step did not give any further improvement. The precision of these calculations should be estimated by considering the maximum single deviation (~ 4 at %) in relation to a hypothetical 50–50 alloy. This yields an average relative concentration deviation not larger than 8%. This is comparable to a similar evaluation performed under the more rigorous and extensive works mentioned above [6, 8].

It should be noted that this simple model sets no *a priori* limitation as to the relative component concentrations to which it can be applied. A limitation of this sort is imposed in the interesting quantitative Auger approach for dilute alloys of Hall and Morabito [8].

5. Conclusions

It is our belief that with the modification of the virtual surface during sputtering (manifested in enhanced degree of roughness) the use of the simple model for quantitative Auger calculations is quite satisfactory.

The sputtering-yield data of Laegreid and Wehner [5], although accompanied by certain inherent uncertainties, prove to be most useful provided the proper sputtering power density is used and not necessarily just similar accelerating voltage.

We have suggested here that a second-step for sputtering correction in complex systems containing more than two components, of which at least one is of high sputtering yield, produces predictions of greater accuracy. In order to achieve better precision limits the great improvements achieved so far in pure Auger analysis [9] should be accompanied by a similar progress in understanding sputtering mechanisms and, especially, by the accumulation of experimental sputtering-yield data.

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