# SECONDARY ION EMISSION OF
# HOMOGENEOUS ALLOYS

By

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The secondary ion emission of dilute and concentrated alloys was studied on the basis of the one-dimensional pseudo-atom emission model [5]. The original model was extended to alloys. The computed relative ionization probabilities were compared with experimental results and agreement better than one order of magnitude was found for most alloys.

## Introduction

The quantitative and qualitative description of the secondary ion emission of alloys including highly concentrated alloys and that of their components prove to become very interesting theoretically as well as experimentally. Recently, the secondary ion emission due to metals containing only one component has been studied theoretically, and several models have been elaborated [1—7]. A few attempts were made to apply some of these models for dilute many-component alloys [8—16]. Several authors have recently compared experimental results on concentrated alloys with extended versions of the LTE model (RÜDENAUER [17], RODRIGUEZ [18], RIEDEL [19, 20]), of the ASI model (NARUSAWA [21] and [18—20]) and with some other simple models (PIVIN [22], JIRICEK [23]), but there is no proper model worked out for concentrated alloys. In this paper, we are going to describe the secondary ion emission of concentrated alloys using the pseudo-atom model [5] and to make a comparison between theoretical and experimental results collected from the literature.

It is well-known that the secondary ion yield depends also on the spatial distribution of different atoms in the bulk. This is the reason why we studied as the simplest case, homogeneous alloys only. The elements from the first row of transition metals easily form homogeneous alloys [24], they have great practical significance and experimental data are known only concerning their alloys.

Table I shows the binary systems investigated. These can be divided into two important groups: Fe- and Ni-based alloys.

**Table I**

Investigated alloys

| Atomic number | Component (1) | Component (2) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | V | Cr | Mn | Fe | Co | Ni | Cu |
| 23 | V | | | | × | | | |
| 24 | Cr | | | | × | | × | |
| 25 | Mn | | | | × | | | |
| 26 | Fe | × | × | × | | × | × | |
| 27 | Co | | | | × | | × | |
| 28 | Ni | | | × | × | × | | × |
| 29 | Cu | | | | | | × | |

## Theoretical

For pure metals, the probability of a secondary ion emission $R^+$ can be calculated by the one-dimensional pseudo-atom emission model, which can be written in the following form [5]:

$$R^+ = \left(\frac{1-\beta}{1+\beta}\right)^2, \tag{1}$$

where

$$\beta = \sqrt{\frac{2E_i - \Phi}{E_F + 2E_i \exp(-\lambda r_0)}} \, . \tag{2}$$

$E_i$ is the first ionization energy of the emitted atoms, $\Phi$ is the work function, $E_F$ is the Fermi energy and

$$\lambda^2 = 4\pi e^2 N(E_F), \tag{3}$$

$$r_0 = \left(\frac{3}{4\pi\varrho}\right)^{1/3}. \tag{4}$$

$N(F_F)$ is the density of states of electrons at the Fermi energy and $\varrho$ is the atomic density in the bulk.

In the case of alloys $\Phi$, $E_F$ (and $\lambda$) depend on the composition which can be expressed by the concentration $(c)$ of one of the components. If $E_{ix}$ means the first ionization energy of the atom, we get

$$R^+(c) = \left(\frac{1-\beta_x(c)}{1+\beta_x(c)}\right)^2, \tag{5}$$

**where**

$$\beta_x(c) = \sqrt{\frac{2\,E_{ix} - \Phi(c)}{E_F(c) + 2E_{ix}\exp\left(-\lambda(c)\,r_{0x}\right)}} \qquad (6)$$

**and**

$$r_{0x} = \left(\frac{3}{4\pi\varrho}\right)^{1/3}. \qquad (7)$$

According to RÜDENAUER's assumption [17], $\Phi\,(c)$ can be approximated by a linear form. Recent experimental data and theoretical calculations confirm its validity in case of several alloys [25—27]. So we used the work functions for alloys as follows:

$$\Phi(c) = c\Phi_1 + (1 - c)\,\Phi_2. \qquad (8)$$

The Fermi energy of the bulk was approximated as:

$$E_F(c) - \frac{\hbar^2}{2m}\,(3\pi^2)^{2/3}\left[n(c)\right]^{2/3}, \qquad (9)$$

**where**

$$n(c) = v_1\,\varrho_1 c + v_2\,\varrho_2(1 - c). \qquad (10)$$

$v_1$, $v_2$, $\varrho_1$, $\varrho_2$ are the valencies and atomic densities of the two components, respectively [41].

## Calculations

For calculating the probability of secondary ion emission according to formula (5), the necessary experimental data are: atomic densities, ionization energies, free electron numbers and work functions. The first two of them are well-known, the published data are accurate and correct [28, 29]. The valency of a single atom can be found but this value is not, in all cases, equal to the "free" electron number in metal [30]. There are no reliable data for the latter in the literature. In our calculation we considered the free electron number to be 2 as a most probable value.

There are further doubts concerning the work function of metals. A number of different measured values are available. Therefore, we have calculated the probability of secondary ion emission for every component with the preferred value of the work function [31, 32] and have repeated the calculation with its minimum and maximum value (see Table II). $R^+$ $(c)$ has been calculated in the range of $0-100\%$ concentration in $10\%$ steps for each

## Table II

Data collected from the literature (see [42])

| Element | Ionization energy (eV) | Work function, eV | | | Atomic density $10^{22}/cm^3$ |
|---|---|---|---|---|---|
| | | preferred | maximum | minimum | |
| V | 6.74 | 4.21 | 4.42 | 3.80 | 7.12 |
| Cr | 6.76 | 4.54 | 4.68 | 3.72 | 8.33 |
| Mn | 7.43 | 3.97 | 4.25 | 3.77 | 7.93 |
| Fe | 7.90 | 4.40 | 4.80 | 3.92 | 8.49 |
| Co | 7.86 | 4.70 | 4.09 | 4.98 | 8.97 |
| Ni | 7.63 | 4.90 | 5.34 | 4.02 | 9.14 |
| Cu | 7.72 | 4.53 | 5.26 | 3.85 | 8.46 |

## Table III

Probability of secondary ion emission calculated by Eq. (5) concerning dilute alloys ($\times 10^{-3}$)

| Matrix | Components | | | | | | |
|---|---|---|---|---|---|---|---|
| | V | Cr | Mn | Fe | Co | Ni | Cu |
| V | 3.2 | | | 0.14 | | | |
| Cr | | 7.9 | | 1.5 | | 2.6 | |
| Mn | | | 1.3 | 0.41 | | | |
| Fe | 7.2 | 7.6 | 3.1 | 1.5 | 1.7 | 2.5 | |
| Co | | | | 2.7 | 3.0 | 4.1 | |
| Ni | | 12.3 | | 3.4 | 3.8 | 5.1 | 4.3 |
| Cu | | | | | | 2.8 | 2.2 |

combination of the preferred, maximum and minimum value of $\Phi_1$ and $\Phi_2$. In the following we are using the values calculated by preferred work functions. The dependence of $R_{rel}^+$ on the work function is indicated in Figs. 1—8 by bars for 3 different concentrations.

Considering the infinitesimally dilute alloys (see Table III) first it seems that the calculated absolute value of probability of secondary ion emission varies in the range of $10^{-2}-10^{-4}$ in this case. According to the present model when Fe is the solute, the probability depends on the matrix, while in the case of Ni and Co the dependence is not so significant. The calculated probability of element emitted from its own matrix in a dilute alloy does not depend, of course, on the solute of very low concentration, because the above-mentioned approximations are used.
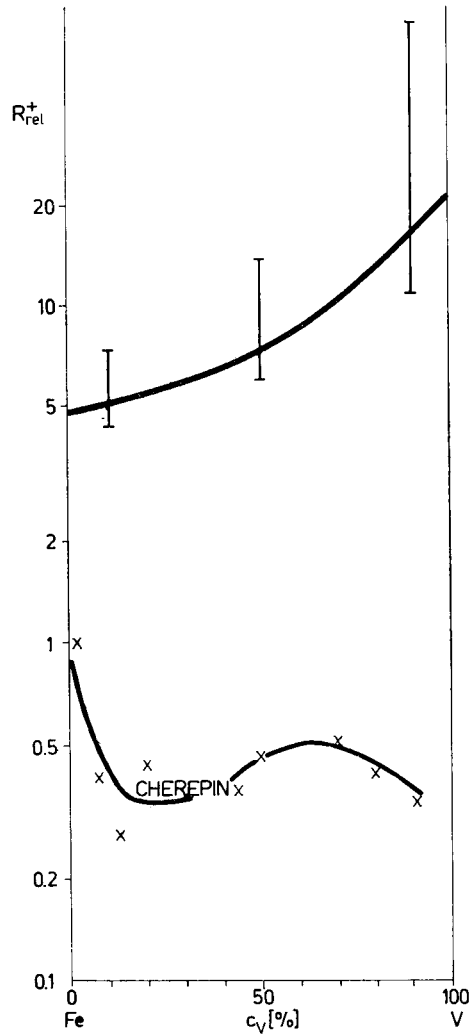
*Fig. 1.* Relative probabilities of secondary ion emission for Fe-V alloys (Fe is $M_1$). (Calculated values are denoted by the upper thick line). Experimental data: CHEREPIN [33]

Since all the experimental data published so far for concentrated alloys present only relative ion yields or yields in arbitrary units, the relative ionization probability of both components $(R_1^+, R_2^+)$ in the concentrated alloys is calculated

$$R_{rel}^+ (c) = \frac{R_{Me2}^+ (c)}{R_{Me1}^+(1-c)} \tag{11}$$

which is used for a comparison with the experimental results.
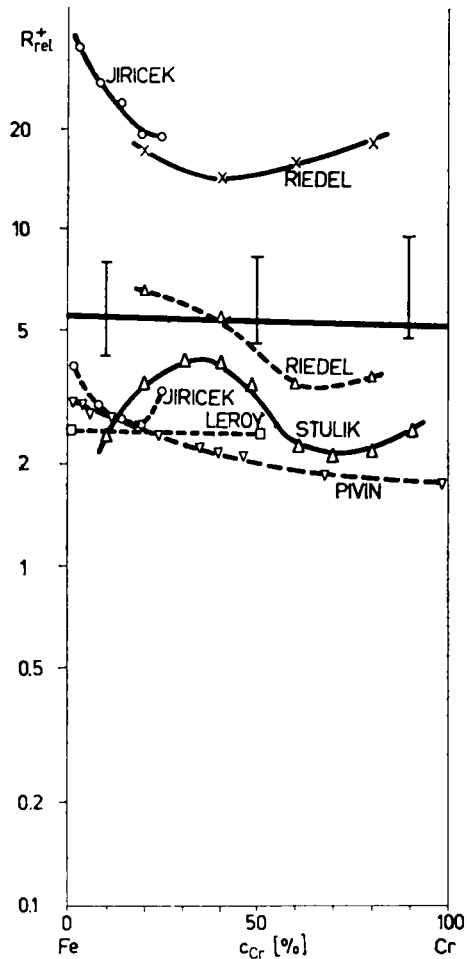
*Fig. 2.* Measured and calculated relative probabilities for Fe-Cr. Experimental data: JIRICEK
[23], RIEDEL [20], LEROY [34], PIVIN [22], STULIK [36]

The computed results and their spread (due to the different values of
the work function) are shown (thick full lines) in Figs. 1—8. As function of
the concentration, the calculated relative probabilities do not change too
much and they generally are of the order of 1.

## Discussion

Experimental data for secondary ion emission of concentrated alloys
have been collected from the literature. The thin full and dotted lines of
Figs. 1—8 are the averages of experimental data for clean and oxidized surfaces,
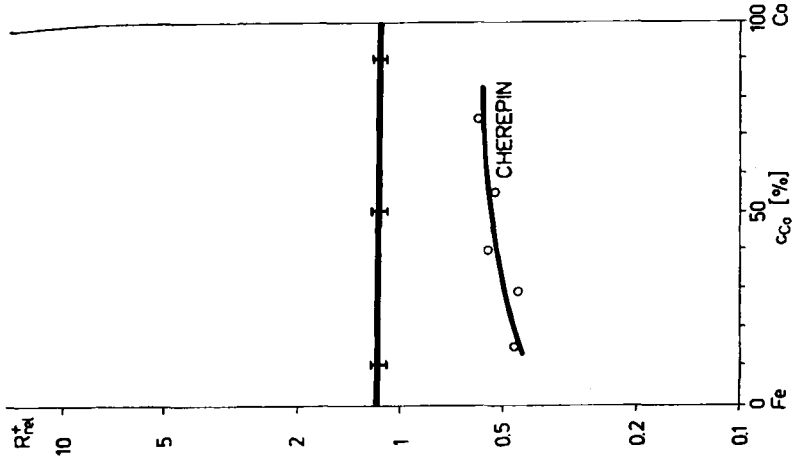
*Fig. 4.* Calculated and measured (CHEREPIN [33]) relative probabilities for Fe-Co
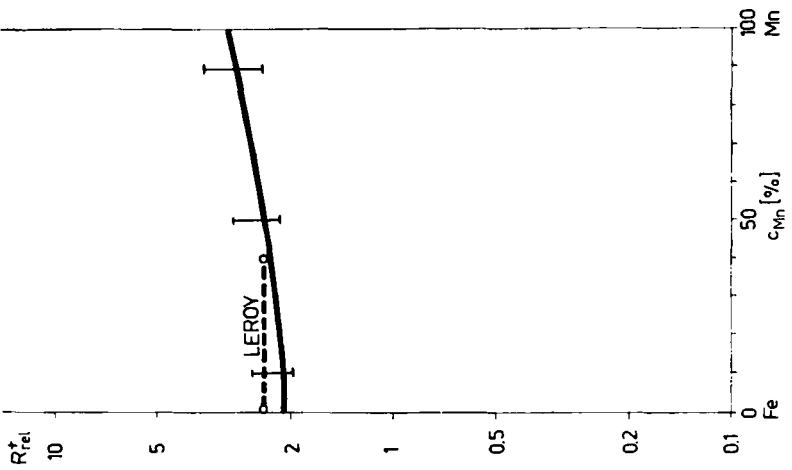


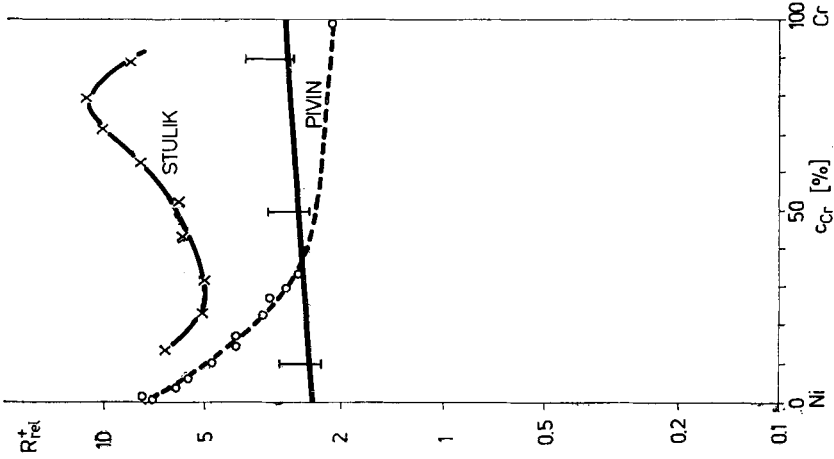*Fig. 3.* Calculated and measured (LEROY [34]) relative probabilities for Fe-Mn

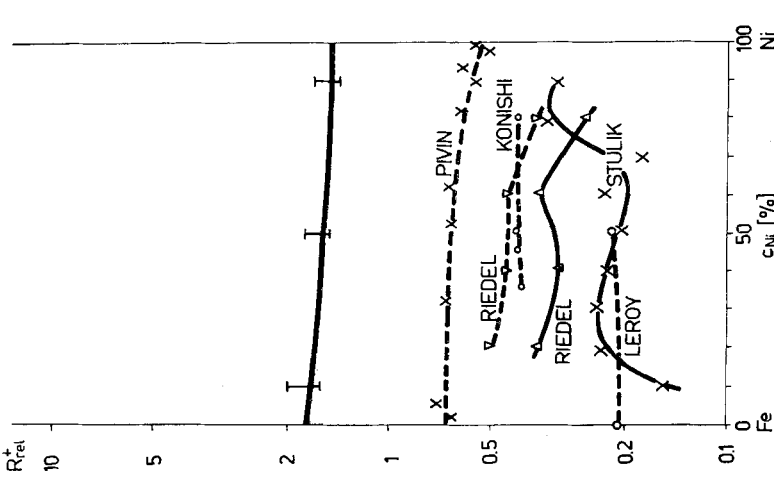Fig. 6. Calculated and measured relative probabilities for Ni-Cr (STULIK [36], PIVIN [22])

Fig. 5. Measured and calculated relative probabilities for Fe-Ni. Experimental data: LEROY [34], PIVIN [22], RIEDEL [20], KONISHI [35], STULIK [36]
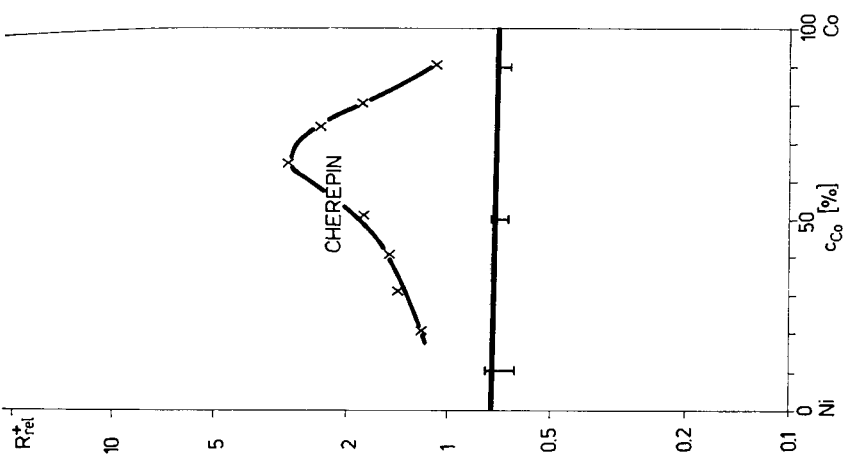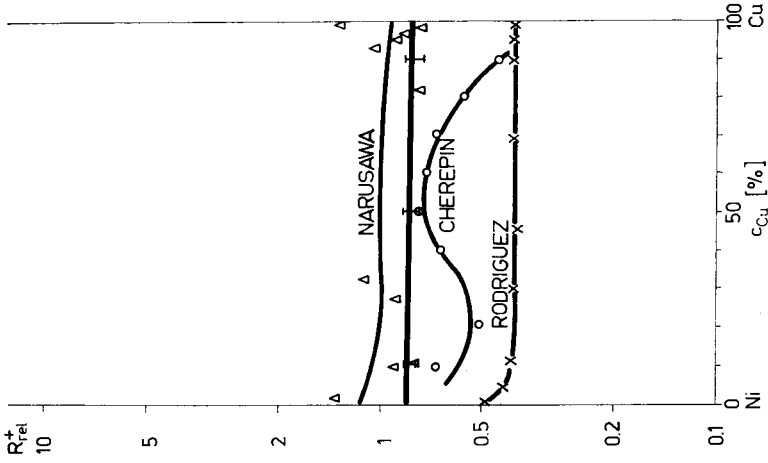
*Fig. 8.* Measured and calculated relative probabilities for Ni-Cu. Experimental data: NARUSAWA[21], CHEREPIN[33], RODRIGUEZ[18]



*Fig. 7.* Calculated and measured (CHEREPIN [33]) relative probabilities for Ni-Co

8

respectively. The most important parameters of the measurements collected
are shown in Table IV. The comparison of the calculated and experimental
curves shows that the pseudo-atom model provides good results for Fe—Mn,
Fe—Co, Ni—Cu, but the deviation between the theoretical and measured
results is larger than one order of magnitude for clean Fe—V. The shapes of
curves are, however, rather different in some cases (Fe—Co, Fe—Mn). But

### Table IV

Most important parameters of measured data

| Author | Pressure (Pa) | Bombarding ion | Current density $\alpha A/cm^2$ |
|---|---|---|---|
| CHEREPIN [33] | $10^{-4}$ | 5 KV Ar$^+$ | 1000 |
| LEROY [34] | $10^{-2}$* | O$^+$ | 100 |
| RODRIGUEZ [18] | $10^{-7}$ | 11 KV Ar$^+$ | 1500 |
| JIRICEK [23] | — | O$^+$, Ar$^+$ | — |
| RIEDEL [19, 20] | $10^{-4}$ | 4 KV Kr$^+$ | 2 and 15 |
| NARUSAWA [21] | $10^{-7}$ | 1,5 KV Xe$^+$ | 25 |
| KONISHI [35] | $10^{-3}$ | 12 KV Ar$^+$ | 500 |
| STULIK [36] | $10^{-4}$ | 3 KV Xe$^+$ | — |
| PIVIN [22] | $10^{-3}$* | O$^+$ | 300 |

* in oxygen

we have to mention here that the data measured by different authors are
rather scattered as shown in the Figures.

Even if the correlation is not always good enough, it is remarkable,
however, that as far as we know this is the only model at present in which
no fitting parameter is needed. The pseudo-atom model in this rough one-
dimensional approximation may be rather sensitive to the density of the
valence electrons and to the work function. In any case, one should develop
a more elaborate model for concentrated alloys and should get more reliable
values of the mentioned input data.

The relative degree of ionization is frequently used for analysis by SIMS.
One usually assumes that they are more reliable than the absolute values
owing to standard errors occurring in the experiments [9, 19]. On the other
hand, it is remarkable that the variation of sputtering yield can cause further
deviation depending on the concentration within one order of magnitude
[37—40].

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