Functional Materials 18, No.2 (2011)

Contrast enhancement of X-ray fluorescence spectra using the secondary two-layer radiator

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Received December 12, 2010

The distribution of scattering radiation background and the contrast of the sample analytical lines have been theoretically calculated and experimentally measured under fluorescence excitation using a two-layer secondary radiator. The top layer serves to excite light element lines and to absorb the continuous spectrum scattered by the bottom layer. The expression has been obtained for calculation of the top layer optimum thickness, at which the maximum spectra contrast is achieved. At the coating optimum thickness, it became possible to obtain experimentally thrice or fourfold contrast increase and significantly improved sensibility for revealing minor impurities in the wavelength range 0.7÷10 Å in comparison with a homogeneous radiator.

Теоретически рассчитаны и экспериментально измерены распределение фона рассеянного излучения и контрастность аналитических линий образца при возбуждении флуоресценции с помощью двухслойного вторичного излучателя. Верхний слой служит для возбуждения линий легких элементов и является абсорбером сплошного спектра, рассеянного нижним слоем. Получено выражение для расчета оптимальной толщины верхнего слоя, при которой достигается максимальная контрастность спектров. При оптимальной толщине покрытия экспериментально удается получить 3÷4 кратное повышение контрастности и заметное улучшение чувствительности при выявлении малых примесей в диапазоне длин волн 0.7–10 Å по сравнению с однородным излучателем.

1. Introduction

The sensibility of conventional X-ray fluorescent analysis is generally insufficient for measurements of <10–50 ppm impurity traces. This is caused by low contrast of the fluorescence spectrum having substantial background due to continuous spectrum scattered by the sample. To lower the background, the monochromatization of the primary spectrum is used [1, 2]. It is possible either by reflection from a crystal-monochromator, or by means of re-emission using a secondary radiator. Both the ways provide a large gain in the spectrum contrast in comparison with a conventional scheme of excitation by the X-ray tube total spectrum. However, a substantial disadvantage of the monochromatization way is low efficiency of line excitation for a wide wavelength range. Indeed, the light element lines positioned far from the monochromatic line of the radiator are excited inefficiently and even the loss in sensibility is possible for light elements in comparison with a conventional scheme. The natural problem solution would be use of two intermediate emitters: the first — for excitation of short and medium wavelengths, and the second — for long-wave analytical lines of light elements.

In this work, the two-layer assembling of the secondary radiator is considered. In this radiator, the top layer serves for excitation of light element lines and at the same time, it is an absorber of the continuous spectrum scattered by the bottom layer. The bottom layer provides hard radiation for excitation of short and medium wavelengths.

2. Samples and measurement technique

The objects under study were Government Standard Samples (GSS) of SCh grade cast irons with 0.005–0.67 mass. % of sulfur and phosphor, and 0.2–1.14 mass. % of silicon. Measurements of X-ray fluorescent spectra were carried out using "SPRUT" spectrometer ("Ukrrentgen" Co., Ukraine) under excitation either using the monochromatized radiation of the secondary Ag radiator or with the Ti/Ag two-layer radiator. The spectrum registration in the 0.35–11 Å wavelength range was carried out with Si-PIN X-123 detector (Amptek, USA). The full-profile analysis of the spectra was realized using the base program package of the "SPRUT" spectrometer.

The experimental comparison of sample analytical line intensities and background level for different spectral ranges was carried out using the Ag secondary radiator and the Ti/Ag two-layer radiators with various Ti layer thicknesses. The data were normalized to the spectrum integrated intensity. Comparing the secondary radiators is convenient to realize by the spectrum distribution of their radiation scattered by high-purity amorphous carbon. This material has no absorption bands in the range under consideration and reflects adequately the radiator spectrum. Obviously, the Ag lines total scattering (coherent + incoherent) fraction in the amorphous carbon scattering spectrum determines the fluorescence intensity of the sample elements lines with absorption edges λ_{edi} being in $\lambda_{Ag}<\lambda_{edi}<\lambda_{Ti}$, while the Ti lines scattering portion — the light element fluorescence intensity $\lambda_{edi}>\lambda_{Ti}$.

3. Results

Theoretical Principles. Let us consider the secondary radiator formed of a Z_1 material thin layer deposited onto Z_2 semi-infinite substrate. The Z_1 layer with ρ_1 density and d thickness scatters the λ wavelength radiation according to [1, 2]

$$I_1(\lambda) = \frac{S}{4\pi r^2}\cdot\frac{\sigma_1(\lambda)}{\mu_1^*}\cdot\frac{\partial\Phi_0(\lambda)}{\partial(\lambda)}[1-\exp(-\mu_1^*(\lambda)\cdot\rho_1\cdot d)], \quad (1)$$

where $\sigma_1(\lambda)$ is the mass coefficient of scattering; $\mu_1^*(\lambda)=\mu_1(\lambda)\cdot\left(\frac{1}{\sin\varphi}+\frac{1}{\sin\psi}\right)$, $\mu_1(\lambda)$, the layer mass attenuation coefficient; φ and ψ, radiation incident and exit angles, respectively, and $S/4\pi r^2$, the solid angle of lighting the secondary radiator.

The scattering by the semi-infinite substrate lying under the Z_1 layer is determined by the expression

$$I_2 = \frac{S}{4\pi r^2}\cdot\frac{\sigma_2(\lambda)}{\mu_2^*}\cdot\frac{\partial\Phi_0(\lambda)}{\partial(\lambda)}\cdot\exp(-\mu_1^*(\lambda)\cdot d_1),$$
$$\mu_2^*(\lambda)=\mu_2(\lambda)\cdot\left(\frac{1}{\sin\varphi}+\frac{1}{\sin\psi}\right), \quad (2)$$

where $\mu_2(\lambda)$ is mass attenuation coefficient in the substrate and the exponent corresponds to absorption in the first layer. Then the total scattering by the secondary radiator $I = I_1 + I_2$ can be written in the form

$$I \sim \frac{\sigma_1}{\mu_1^*(\lambda)} - \exp(-\mu_1^*(\lambda)\cdot\rho_1\cdot d)\cdot\left(\frac{\sigma_1}{\mu_1^*(\lambda)}-\frac{\sigma_2}{\mu_2^*(\lambda)}\right). \quad (3)$$

It follows from (3) that, depending on the top layer thickness d, the scattering level at λ wavelength is in the range from $\frac{\sigma_1}{\mu_1^*(\lambda)}$ at $d\to\infty$ (for scattering in the first infinite layer) to $\frac{\sigma_2}{\mu_2^*(\lambda)}$ at $d\to 0$ (for scattering in the substrate).

Let the substrate absorption band edge wavelength λ_{ed2} is lower than λ_{ed1} of the coating material. Then for $\lambda_{ed2}<\lambda<\lambda_{ed1}$ wavelengths, the condition $\frac{\sigma_1(\lambda)}{\mu_1^*(\lambda)}<\frac{\sigma_2(\lambda)}{\mu_2^*(\lambda)}$ holds true, i.e. the scattering level before the absorption jump is lower than that behind the substrate absorption jump. Calculations show (Fig. 1) that the Ti coating in the Ti/Ag secondary radiator provides a substantial lowering of the scattered radiation background and improving the contrast in the specified wavelength range in comparison with the bulk Ag intermediate radiator. However, at the same time, the intensity of the substrate fluorescent radiation coming from under the coating will decrease. For a single-component substrate being under the layer of d thickness, by analogy with [2], the analytical line λ_2 intensity is written as

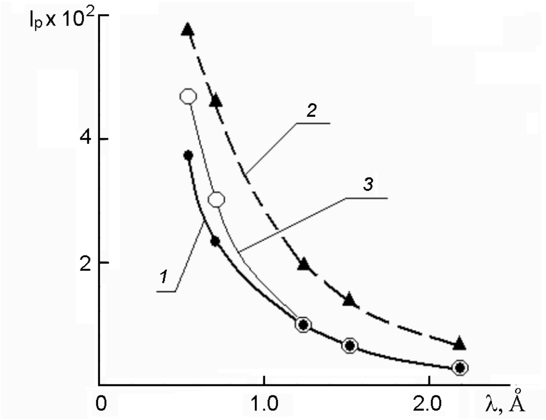

Fig. 1. Calculated wavelength dependences of the secondary radiator scattering intensity: *1*, bulk Ti radiator; *2*, bulk Ag radiator; *3*, two-layer Ti(50 μm)/Ag (bulk) radiator.

$$I(\lambda_2,d) = \frac{S}{4\pi r^2}\cdot\left(1-\frac{1}{S_{q2}}\right)\cdot\omega_2\times \tag{4}$$
$$\times\, p_2\int_{\lambda_0}^{\lambda_{q2}}\frac{\tau_2(\lambda)}{\mu_2^*(\lambda)}\cdot\frac{\partial\Phi_0(\lambda)}{\partial\lambda}\cdot\exp\{-\mu_1^*\rho_1 d\}d\lambda,$$

where $\partial\Phi_0/\partial\lambda$ is the spectral distribution of X-ray tube [2], exciting the fluorescence; $\tau_2(\lambda)$, mass absorption coefficient in the substrate material; the exponent is due to attenuation of incident $\mu_1(\lambda)$ and exit $\mu_1(\lambda_2)$ radiation in the film; $\mu_1^*(\lambda) = \frac{\mu_1(\lambda)}{\sin\varphi}+\frac{\mu_1(\lambda_2)}{\sin\psi}$; $\mu_2^*(\lambda) = \frac{\mu_2(\lambda)}{\sin\varphi}+\frac{\mu_2(\lambda_2)}{\sin\psi}$; where φ and ψ are incident and exit angles, respectively; ω — fluorescence yield; p — the fraction of an analytical line intensity in the spectral series; S_q, the absorption jump; $S/4\pi r^2$, the solid angle of lighting the secondary radiator. For a single-component film, the intensity of a λ_1 analytical line [1, 2]:

$$I(\lambda_1,d) = \frac{S}{4\pi r^2}\cdot\left(1-\frac{1}{S_{q1}}\right)\cdot\omega_1\times \tag{5}$$
$$\times\, p_1\int_{\lambda_0}^{\lambda_{q1}}\frac{\tau_1(\lambda)}{\mu_1^*(\lambda)}\cdot\frac{\partial\Phi_0(\lambda)}{\partial\lambda}\cdot\left(1-\exp\{-\mu_1^{**}\rho_1 d\}\right)d\lambda,$$

with $\mu_1^{**}(\lambda) = \frac{\mu_1(\lambda)}{\sin\varphi}+\frac{\mu_1(\lambda_1)}{\sin\psi}$, where $\mu_1(\lambda)$ and $\mu_1(\lambda_1)$ are the incident and the exit radiation attenuations, respectively, in the film, $\tau_1(\lambda)$, absorption by the film atoms.

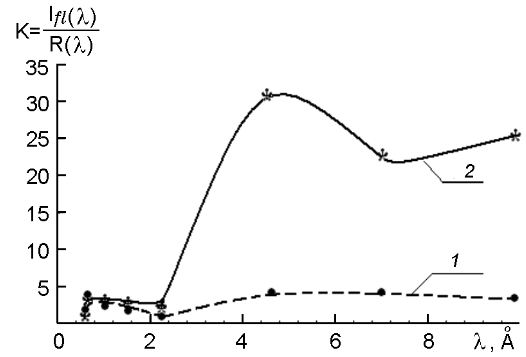

Fig. 2. Calculated contrast K values vs. wavelength λ for analytical lines of $C = 1$ mass. % impurities of Mo (λ = 0.71 Å), Ga (λ = 1.25 Å), Cu (λ = 1.54 Å), Cr (λ = 2.29 Å), Cl (λ = 4.7 Å), Si (λ = 7.11 Å), and Mg (λ = 9.9 Å) in Fe matrix: *1*, Ag re-radiator; *2*, Ti (20 μm)/Ag re-radiator. The points show the calculated contrast K values.

Under irradiation of a sample by the secondary radiator, the intensity of i-th analytical line from the atoms contained therein at C_i concentration

$$I_i = C_i\left\{I(\lambda_2;d)\cdot\Pi(\lambda_2-\lambda_{edi})\cdot\frac{\tau_{2i}}{\mu_{2i}^*}+\right. \tag{6}$$
$$\left.+\,I(\lambda_1,d)\cdot\Pi(\lambda_1-\lambda_{edi})\cdot\frac{\tau_{1i}}{\mu_{1i}^*}\right\},$$

where

$\mu_{1i}^*(\lambda) = \frac{\mu_{sp}(\lambda_1)}{\sin\varphi_{sp}}+\frac{\mu_{sp}(\lambda_i)}{\sin\psi_{sp}}$,

$\mu_{2i}^*(\lambda) = \frac{\mu_{sp}(\lambda_2)}{\sin\varphi_{sp}}+\frac{\mu_{sp}(\lambda_i)}{\sin\psi_{sp}}$, μ_{sp}, the attenuation coefficient in the sample for radiations with λ_1, λ_2 and λ_I, respectively;

$\Pi(x) = \begin{cases}1, \text{at}\, x > 0;\\ 0, \text{at}\, x \le 0\end{cases}$, a step function.

The scattered radiation $R(\lambda)$ from the sample can be obtained by multiplying the (3) by a corresponding expression $\left(\frac{\sigma_{sp}}{\mu_{sp}^*}\right)$. Then the contrast value $K = I_{fl}(\lambda_i)/R(\lambda_i)$ for different analytical λ_i lines depends on the top layer thickness d.

The task solution on the contrast extremum $\partial K/\partial d = 0$ gives the value of the coating optimum thickness:

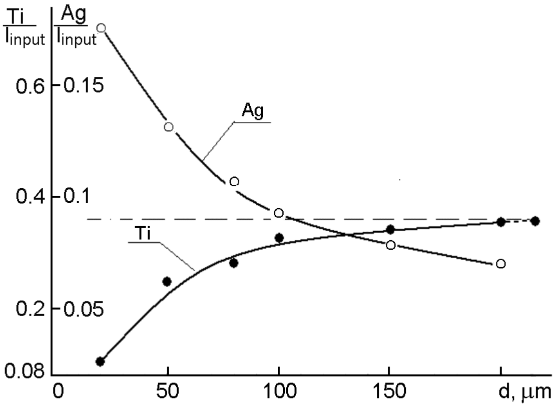

Fig. 3. Experimentally measured fractions of Ti–K_α and Ag–K_α line intensities in the scattering spectrum of amorphous carbon irradiated by Ti/Ag secondary radiators with various Ti-coating thicknesses *d*.

$$d(\lambda) = \frac{1}{\rho_1 \cdot \mu_1^*(\lambda)} \cdot \ln\left\{\frac{\left(\frac{\sigma_1(\lambda)}{\mu_1(\lambda)} - \frac{\sigma_2(\lambda)}{\mu_2(\lambda)}\right) \cdot (\mu_1^*(\lambda_2) - \mu_1^*(\lambda))}{\mu_1^*(\lambda_2) \cdot \frac{\sigma_1(\lambda)}{\mu_1(\lambda)}}\right\}. \quad (7)$$

Direct calculations for Ti/Ag pair show that for the 0.71–2.29 Å wavelength range, the Ti layer optimum thickness decreases from 20 to 10 μm in approaching to Ti coating absorption jump.

It follows from Fig. 2, that using two-layer Ti/Ag radiator, the line contrast of trace impurities in the Fe matrix is twice or triple higher than for the bulk Ag radiator. The most effectively the contrast enhancement should become apparent for lines of light elements, such as sulfur, phosphor, silicon etc.

Experimental. According to our technique, we investigated the secondary radiator spectrum incident using the scattering spectrum of high-purity amorphous carbon as a sample.

As the re-radiator top layer thickness grows, in the amorphous carbon sample scattering spectrum, the fraction of titanium lines increases and attains an asymptotic value ≈0.37 at $d \approx 100$ μm (Fig. 3). This indicates that fluorescence intensity of light elements in the sample irradiated by such radiator will increase and reach the maximum value at $d = 100$ μm. At the same time, the Ag–K_α line attenuated in the top layer of the re-radiator decreases monotonically resulting in lowering the line intensities in the $\lambda_{Ag} < \lambda < \lambda_{Ti}$ range. Thus, using the two-layer Ti/Ag radiator it is possible to achieve substantial increasing the ratio of light element line intensity to that of the rest elements in the sample spectrum. In fact, application of the two-layer radiator provided the intensity gain for analytical lines of silicon, phosphor and sulfur in comparison with the bulk Ag radiator (Fig. 4). This provided increasing the sensibility on these elements by a factor of 3 or 4. According to our calculations for Ti/Ag re-radiator, for the sample with $C_p = 0.6$ mass. % phosphor concentration, its line contrast should be $K = 6.9$, that is rather close to the experimentally achieved value $K = \frac{I_{\text{line}} - I_{fl}}{I_{fl}} = \frac{(380 - 90)}{90} = 3.2$. The detectability threshold of 0.005÷0.01 mass. % for these elements is quite enough for practical measurements in cast irons and steels.

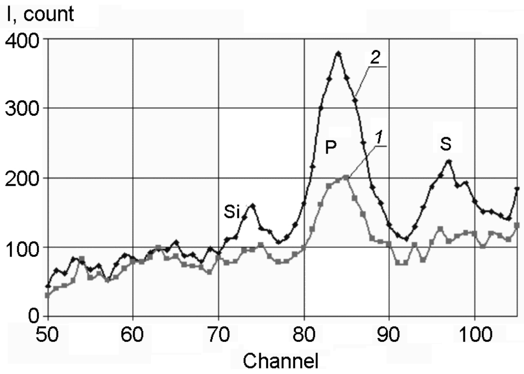

Fig. 4. A fragment of a cast iron standard spectrum with lines of Si, P and S. The mass portions of the elements are 0.3, 0.6 and 0.15 mass. %, respectively. Exposure is 60 s. *1*, Ag re-radiator; *2*, Ti (50 μm)/Ag re-radiator.

Let us consider the results of measurements for the background scattered by amorphous carbon at $\lambda = 0.78$ Å, i.e. near the Ag substrate $\lambda = 0.59$ Å. Compton line (Fig. 5, curve *1*), and at $\lambda = 2.26$ Å near the titanium coating absorption edge $\lambda_{edTi} = 2.50$ Å (Fig. 5, curve *2*). The curve *2* drops to an asymptotical value already at 20 μm coating thickness, and further thickness increase does not result in any background decreasing but lowers the Ag–K fluorescence radiation exit. Therefore, the maximum contrast of lines with $\lambda < \lambda_{edTi}$ is provided at $d \approx 20$ μm. The background at $\lambda = 0.78$ Å after fast falling in the initial part of the curve continues to decrease slowly in the range of $d = 20$–200 μm. Such difference between the curves in Fig. 5 supports the conclusion about absence of a single opti-

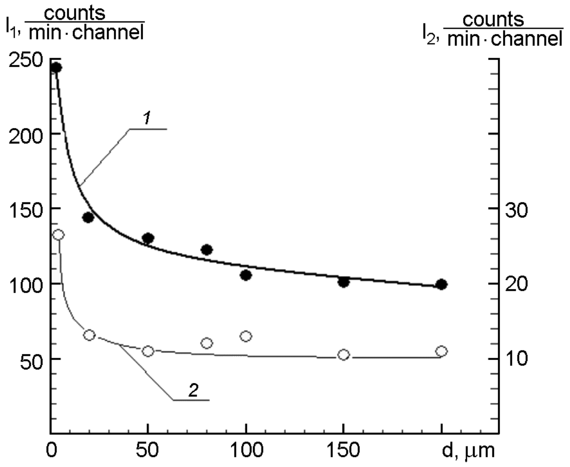

Fig. 5. Amorphous carbon scattering background intensity $I\left(\frac{\text{counts}}{\text{min}\cdot\text{channel}}\right)$ at λ_{b1} = 0.78 Å (curve *1*) and λ_{b2} = 2.26 Å (curve *2*) depending on Ti coating thickness *d* of Ti/Ag re-radiator. Averaging was carried out by 25 channels (spectrum of 1024 channel).

mum value *d* for whole wavelength range.

4. Discussion

Theoretical and experimental investigations of scattering spectra have supported the conclusion that, compared to the convenient bulk secondary radiator, the two-layer re-radiator provides significant lowering the scattering background and increasing the contrast of fluorescent lines in the wavelength range between the substrate material analytical line Ag–K_α and the absorption edge λ_{ed} of the coating material (titanium). These provides an increase of the analysis sensibility in the specified range. We believe that the multi-layer secondary radiator, combining functions of a radiator and a filter for initial radiation, provides a number of advantages for the spectrum contrast enhancement in comparison to filters of initial and secondary radiations [4]. As it was expected, a large gain in the spectrum analytical line intensity is observed for $\lambda>\lambda_{\text{Ti}}$, i.e. for light element lines. Intense *K*-series lines of the coating material are positioned close enough to absorption edges of III period elements of the Periodic Table, so they excite these elements more effectively than *L*-series of Ag substrate. This implies that application of the two-layer radiator significantly extends the effective excitation wavelength range, hence, the high-sensibility analysis as well. The optimization task solution for the coating thickness $d_{opt}(\lambda)$ is wavelength depending. For instance, $d_{opt}(\lambda)$ varies by 2.5 times in the $\lambda_{\text{Ag}}<\lambda<\lambda_{\text{Ti}}$ range for Ti/Ag pair. At the same time, $d_{opt}(\lambda)$ is generally less than the thickness which provides fluorescence asymptotical intensity ($d_{min}\approx 100$ μm for Ti/Ag). Therefore, the practical choice of the coating thickness is subjective, depending on importance of one or another wavelength range contrast enhancement.

5. Conclusions

Application of the two-layer secondary radiator with analytical lines λ_1 and λ_2, when compared to a homogeneous one (λ_2), provides the analysis sensibility enhancement in the whole wavelength range due to the following: (i) three-four times efficiency gain for excitation of light elements with $\lambda_{ed}>\lambda_1$ in the analyzed sample; (ii) two-three times contrast enhancement for the sample lines positioned in $\lambda_1>\lambda_{ed}>\lambda_2$ range, being the larger, the closer to the coating absorption edge.

References

1. N.F.Losev, Quantitative X-Ray Spectral Fluorescent Analysis, Nauka, Moscow (1969) [in Russian].
2. V.P.Afonin, N.I.Komyak, V.P.Nikolaev, R.I.Plotnikov, X-Ray Fluorescent Analysis, ed. by N.F.Losev, Nauka, Novosibirsk (1991) [in Russian].
3. E.M.Lukyanchenko, R.I.Plotnikov, *Zavodskaya Laboratoria*, **73**, 16 (2007).
4. A.Yu.Gryaznov, E.M.Lukyanchenko, in: XVII Ural Int. Sci. Techn. Conf. Spectrosc., Rep. Abstr., Ekaterinburg (2005) [in Russian].

Контрастування спектра рентгенівської флуоресценції за допомогою двошарового вторинного випромінювача

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Теоретично розраховано і експериментально виміряно розподіл фону розсіяного випромінювання та контрастність аналітичних ліній зразка при збудженні флуоресценції за допомогою двошарового вторинного випромінювача. Верхній шар служить для збудження ліній легких елементів і є абсорбером суцільного спектра, розсіяного нижнім шаром. Отримано вираз для розрахунку оптимальної товщини верхнього шару, при якій досягається максимальна контрастність спектрів. При оптимальній товщині покриття експериментально вдається отримати 3–4-кратне підвищення контрастності і помітне поліпшення чутливості при виявленні малих домішок у діапазоні довжин хвиль 0.7–10 Å у порівнянні з однорідним випромінювачем.