Research Article • DOI: 10.2478/amst-2019-0004 AMST • 44(1) • 2020 • 21–27

sciendo

Advances in Manufacturing Science and Technology

Influence of Plasma Parameters on Light Emission in GD-OES Analysis of Ni–Cu System

Wojciech J. Nowak*, Patrycja Wierzba

Department of Materials Science, Faculty of Mechanical Engineering and Aeronautics, Rzeszow University of Technology, al. Powstancow Warszawy 12, 35-959 Rzeszow, Poland

Abstract

In the present work, an effect of plasma-forming parameters on light emission during analysis by glow discharge optical emission spectrometry of Ni–Cu model alloys is studied. To evaluate the effects of plasma-forming parameters on light emission, argon pressure was varied in the range between 600 Pa and 1000 Pa under a constant power of 20 W. Moreover, a variation of power at 20 W and 30 W under a constant Ar pressure of 1000 Pa was investigated. An effect of the element content on light emission was found. Namely, for Cu, a monotonic, non-linear increase in measured light intensity with an increasing Cu content was found. Surprisingly, for pure Ni, a lower light intensity was measured as for Ni90–Cu10 (at.%). Possible reasons causing this was listed as: (i) possible effect of hydrogen, (ii) overlapping of lines for Cu and Ni and (iii) self-absorbing of Ni line at 341.574 nm.

Keywords

glow discharge optical emission spectrometry (GD-OES) • plasma-forming parameters • plasma sputtering • light emission

1. Introduction

Glow discharge optical emission spectroscopy (GD-OES) is a method based on the detection and quantification of photons emitted by sample species within the plasma [1, 2]. The most common analysis performed by GD-OES is depth profiling of metallic as well as non-metallic materials [3, 4, 5]. The GD-OES depth profiling is a relatively fast method allowing to characterize the distribution of elements in the near-surface regions of many groups of materials. The GD-OES depth profiling was successfully used for analysis of overall oxide scale composition of oxidized alloys [6, 7] or specific elements such as boron [8, 9], carbon [10, 11] and sulfur [12, 13, 14]. Also analyses of coatings systems such as chemical vapor deposited (CVD) aluminide layers [15, 16] and MCrAlY coatings [15, 17] were successfully performed using GD-OES.

The GD-OES depth profiling is performed by sputtering of the surface layer by layer. A part of the sputtered atoms from the sample surface becomes excited in the plasma. Shortly after excitation, the atoms become recombined. During recombination, excess of energy is emitted in the form of light with a certain wavelength characteristic for each element. As a result of depth profiling, a plot showing the intensity of the light with a given wavelength as a function of sputtering time is produced. Such a set of data gives only qualitative information about the distribution of elements. Therefore, a number of studies treating with the quantification allowing to recalculate light intensity into concentration using procedure based on emission yields [18, 19, 20] or relative sensitivity factors (RSFs) [15, 21, 22]. All mentioned quantification methods are dependent on intensity of emitted light, and then, the intensity of emitted light is crucial for accuracy of quantification procedure.

As mentioned, the GD-OES measures the emitted light intensity. Light emission is caused by the particular processes of sample species in plasma, namely, excitation and recombination. The plasma-forming parameters that can be adjusted in GD-OES are argon pressure [Pa] and power [W]. Therefore, the aim of the present study was to investigate the influence of plasma-forming parameters on light emission. To exclude additional factors influencing light emission, namely, complex chemistry of studied alloys, high purity model alloys (5N purity) and high purity metals (Ni and Cu 6N purity) were analyzed.

2. Experimental

In the present work, high purity Ni and Cu (both 6N purity) and series of Ni–Cu alloys produced by Goodfellow with chemical compositions given in Table 1 are investigated using a glow discharge optical emission spectrometer (GD-OES) made by

*Corresponding author: Wojciech J. Nowak
E-mail: w.nowak@prz.edu.pl

Horiba Jobin Yvon (Longjumeau, France). Figure 1 shows the Ni–Cu binary phase diagram. As shown, the elements have full mutual solubility over the full concentration range. Since the rods of the alloys were produced by quenching, no formation of secondary phases is expected. To elucidate the effects of plasma-forming parameters on light emission by Ni and Cu in studied alloys, the analyses were performed using variation of argon pressure [Pa] and current power [W] as marked by the red rectangle in Figure 2. Parameters used for GD-OES measurement are shown in Table 2. As visible from Table 1, an effect of argon pressure under a constant power was investigated for parameters 1–3, and also power effect under a constant argon pressure for parameters 3 and 4 was investigated. The sputtering time was set as 10 minutes for each parameter and alloy composition. The measured light intensities were collected from the plots obtained for Ni and Cu close to the end of measurement, as shown in Figure 3. One can immediately see that the value of light intensity measured for Ni is much higher than that for Cu. The wavelengths used for light detection for Ni and Cu were 341.574 nm and 510.696 nm, respectively.

Table 1 Chemical composition of studied model alloys (given in at.%)

Alloy no	1	2	3	4	5	6	7
Ni content	100	90	70	50	30	10	0
Cu content	0	10	30	50	70	90	100

Table 2 Variations of plasma-forming parameters used in the present study

Parameters set	Pressure [Pa]	Power [W]
1	600	20
2	800	20
3	1000	20
4	1000	30

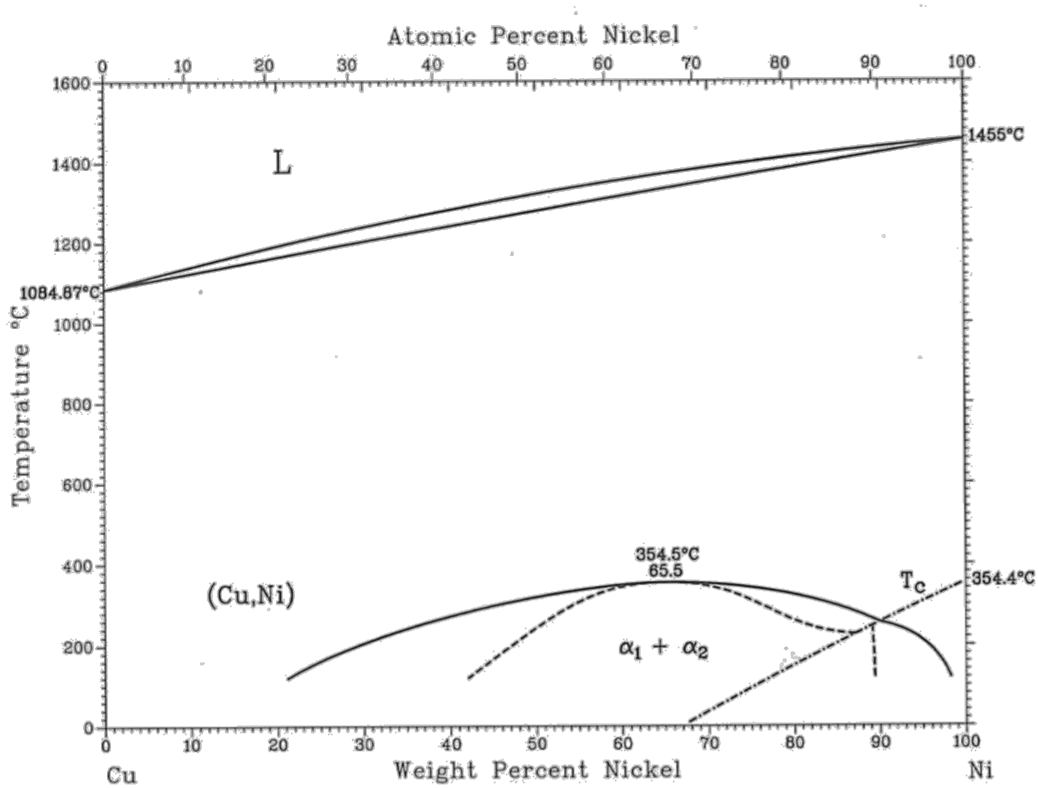

Figure 1 Binary phase diagram for Ni and Cu systems.

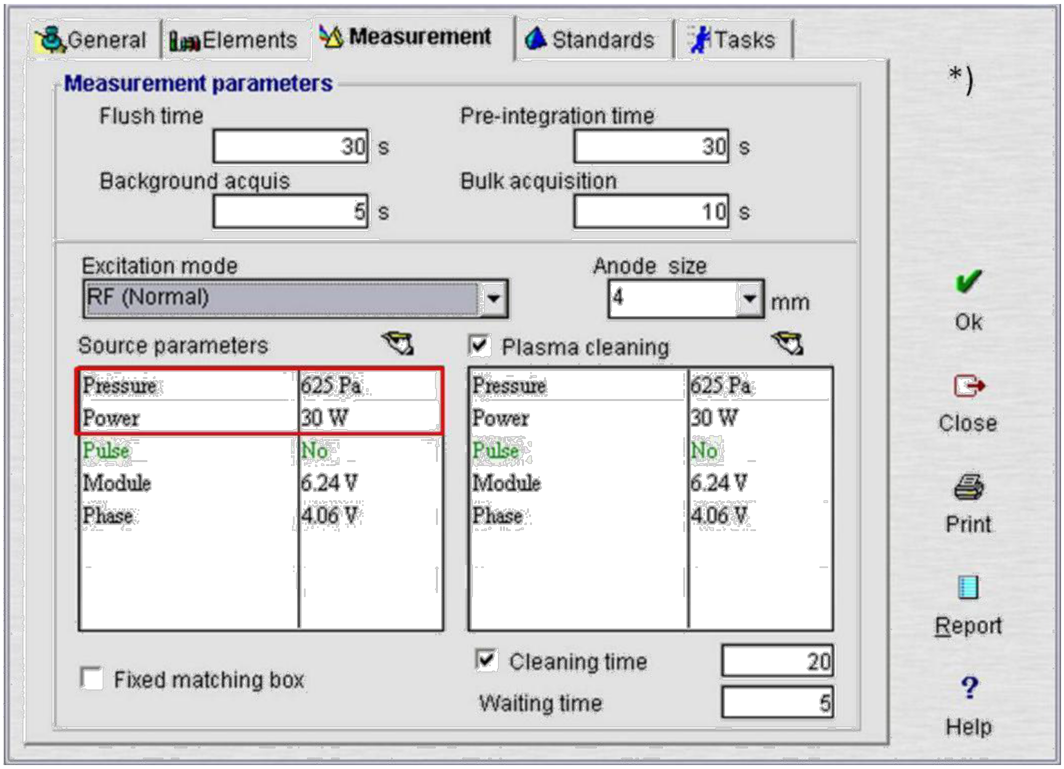

Figure 2 Setting of plasma-forming parameters using Quantum software.

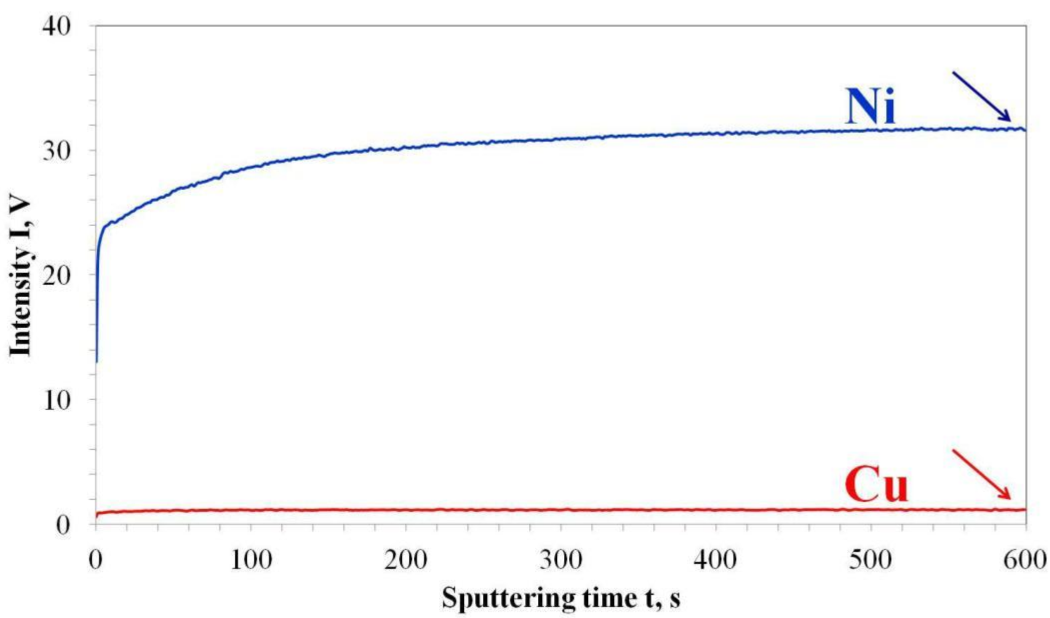

Figure 3 An exemplary GD-OES depth profile obtained for $Ni_{50}Cu_{50}$ alloy showing the procedure of light emission value collection.

3. Results and discussion

Figure 4 shows the values of light intensities measured for Cu (Figure 4A) and Ni (Figure 4B) during GD-OES depth profiling under different plasma forming conditions. Figure 4A shows that increasing of argon pressure under a constant power results in an increase in light emission by Cu. However, it should be mentioned that the increase in pressure from 600 Pa to 800 Pa results in a larger increase in light intensity than the change from 800 Pa to 1000 Pa under the same power current (20 W). An increase in power from 20 W to 30 W with an argon pressure of 1000 Pa caused further increase in light intensity. A similar effect can be observed for light intensity measured for Ni (Figure 4B). A smaller increase in light intensity during increasing of argon pressure from 80 Pa to 1000 Pa under a constant power of 20 W in comparison with an increase from 600 Pa to 800 Pa is connected with ionization efficiency of argon, which is described by equation 1:

$$\delta = \frac{n}{n+N} \tag{1}$$

where δ is the ionization efficiency, n is the number of charged species and N is the number of neutral species.

An increasing argon pressure results in an increase in the number of neutral species. A power of 20 W is apparently enough to provide enough energy to ionize most of the neutral species. Apparently, 20 W is not a high power to ionize most of the neutral species, leading to a decrease in ionization efficiency resulting in a lower benefit of Ar pressure increase with a constant power. This assumption is supported by the fact that the increase in power from 20 W to 30 W for 1000 Pa of argon caused a further increase in light emission. Therefore, an increase in ionization efficiency is observed.

Additionally, it can be observed from Figure 4A that the increase in the Cu content in the analyzed sample results in an increase in light emission. Moreover, in case of Cu, a monotonic, non-linear increase in light intensity with increasing Cu content is observed. A similar trend can be observed for Ni (Figure 4B), however up to 90% of Ni. Surprisingly, the light intensities measured for pure Ni are lower than those measured for $Ni_{90}Cu_{10}$. Moreover, in case of measurement performed with 20 W, light intensity measured for pure Ni is even lower than that measured for $Ni_{70}Cu_{30}$ (see Figure 4B). Apparently, an increase in power from 20 W to 30 W mitigates the latter observation.

The exact reason for lower light intensity measured for pure Ni alloys than for NiCu alloys is not fully understood yet and needs to be studied in detail in the future. However, factors that can possibly cause such a phenomenon will be listened and shortly discussed.

It was previously observed that the presence of hydrogen can significantly alter the light emission of elements such as Cu, Fe, Ni and Mn [23, 24]. It might be that the presence of Cu can positively influence the light emission of Ni.

As described previously, light intensities were measured at 341.574 nm and 510.696 nm for Ni and Cu, respectively. It is known that the elements emit light at several wavelengths. Figure 5 depicts the full optical emission spectra calculated for Cu (Figure 5A) and Ni (Figure 5B). A wavelength of light measurements selected for Cu (510.696 nm) is marked by red arrow in Figure 5A, while the selected line for Ni is marked by blue arrow in Figure 5B. However, as marked by green arrow in Figure 5A, Cu possesses also a line near 341 nm. Then, these emission lines can potentially overlap, and light measured for Ni might be influenced by light emitted by Cu at 340 nm. However, one should keep in mind that

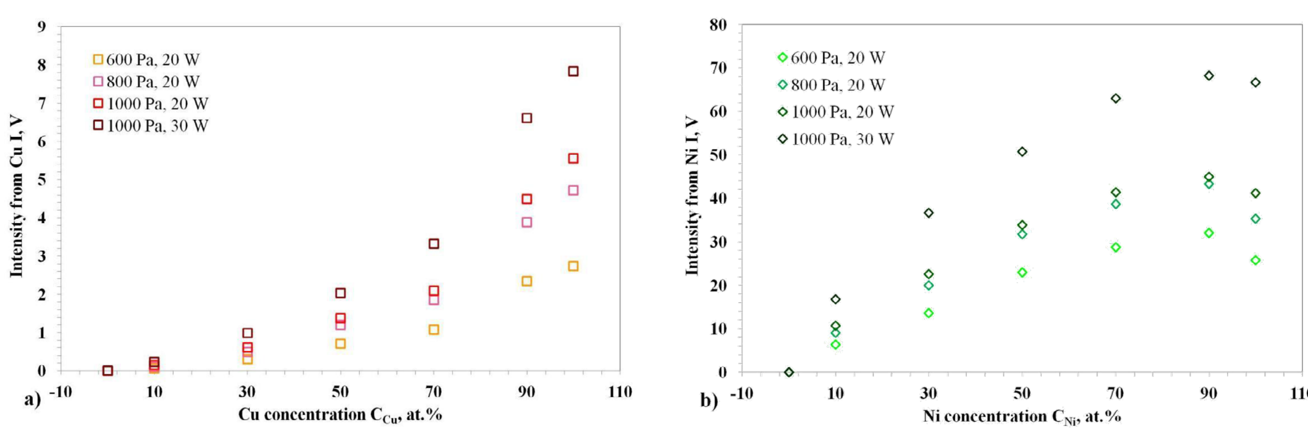

Figure 4 Light intensities measured for: **(A)** Cu and **(B)** Ni during sputtering of Ni–Cu alloys under various plasma-forming parameters.

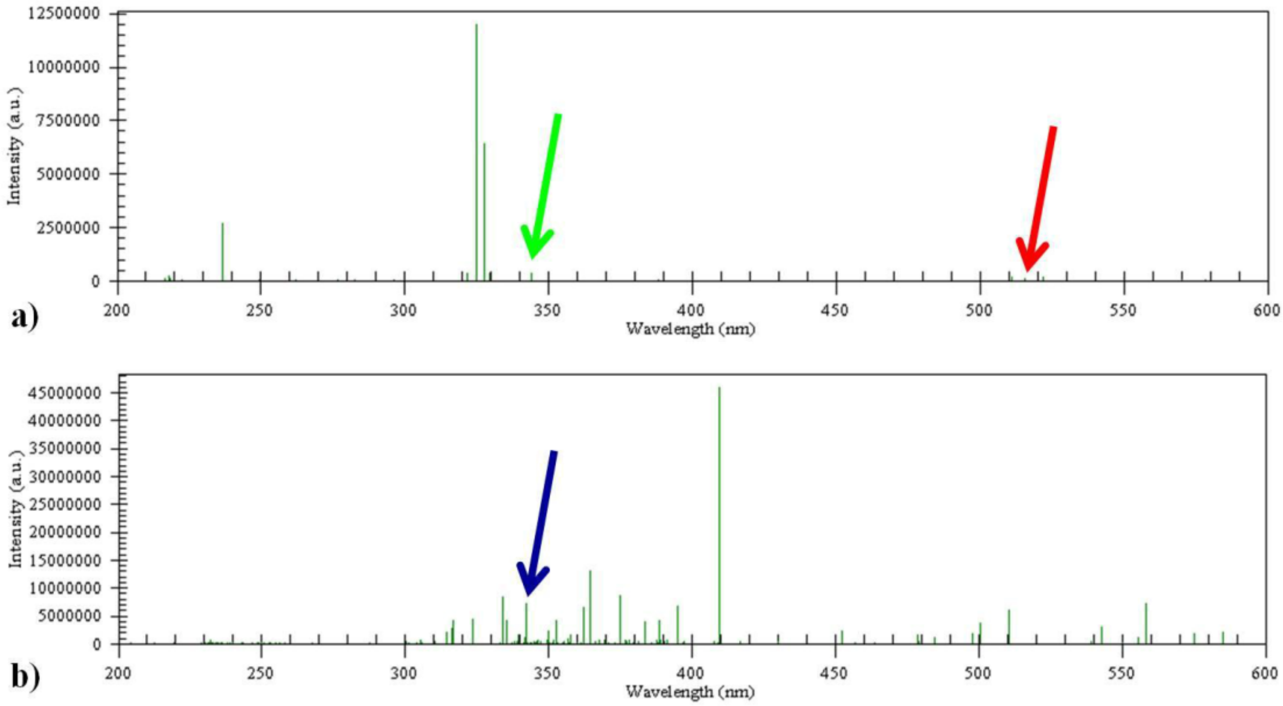

Figure 5 Plots showing optical spectra for **(A)** Cu and **(B)** Ni produced based on literature data obtained from Ref. [25].

the wavelengths depicted in Figure 5 were calculated for vacuum, while in the present work, the detectors are flushed with high purity nitrogen coming from the nitrogen generator. Moreover, the light is emitted in argon plasma. The argon purity can additionally affect the light emission. To investigate the possible overlapping of lines for Ni (341.393 nm in vacuum) and Cu (341.431 nm in vacuum), a measurement of full spectrum by GD-OES was performed for Cu and Ni for spectrum range between 300 nm and 400 nm. The results are shown in Figure 6A and B. Based on Figure 6A and B, the emission line for Cu is 340.942 nm, while for Ni is 341.474 nm. Considering accuracy of detectors' positioning in GD-OES, it is hardly possible that these two lines can overlap.

Based on the database from Quantum software, the selected line for Ni measurement, namely, 341.574 nm reveals self-absorbance. Then, it is assumed that the latter is the most probable reason for lower light intensity measured for pure Ni alloys as compared to NiCu alloys. As claimed before, small amounts of Cu in the alloy most likely mitigate self-absorbance of Ni.

Despite three possible factors potentially influencing the lowering of light emission was discussed, further studies to elucidate the exact reason for this phenomenon are necessary and planned in the near future.

4. Summary and conclusions

In the present work, an influence of plasma-forming parameters on light intensity of Cu–Ni model alloys over whole concentration range is studied. Based on the obtained results, following conclusions can be drawn:

- Increasing of argon pressure under constant power causes an increase in the intensity of emitted light for both studied elements, i.e. Cu and Ni. However, increasing of argon pressure is effective up to a certain threshold.
- Increase in power results in further increase in the light intensity. Combining both observations one can conclude that an effective increase in light emission can be obtained by an optimal increase in both studied plasma-forming parameters.
- Effects of alloy chemical composition on light emission were also observed. For Cu a constant, however a non-linear increase in light intensity was observed. Contrary, for Ni, an increase in light intensity up to a certain Ni content (up to 90 at.%) was observed, while for pure Ni (100 at.%), a lower intensity was noticed. Potential factors causing this phenomenon were discussed as: (i) possible effect of hydrogen, (ii) overlapping of lines for Cu and Ni and (iii) self-absorbing of Ni line at 341.574 nm. Partial mitigation of the presence of Cu was assumed.

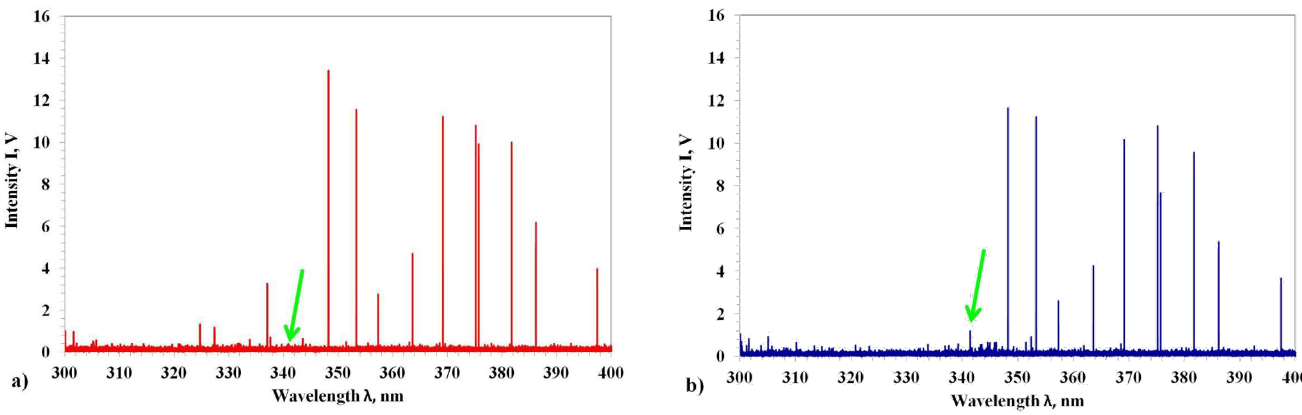

Figure 6 Plots showing optical spectra for **(A)** Cu and **(B)** Ni measured by GD-OES on studied pure metals.

References

[1] M.R. WINCHESTER, R. PAYLING: Radio-frequency glow discharge spectrometry: A critical review, *Spectrochim. Acta Part B.*, **50**(2004), 607-666.

[2] K. SHIMIZU, H. HABAZAKI, P. SKELDON, G.E. THOMPSON: Radiofrequency GDOES: A powerful technique for depth profiling analysis of thin films. *Surf. Interface Anal.*, **35**(2003), 564-574, DOI:10.1002/sia.1572.

[3] J.W. COBURN, E. TAGLAUER, E. KAY: Glow-discharge mass spectrometry – Technique for determining elemental composition profiles in solids. *J. Appl. Phys.*, **45**(1974), 1779-1786.

[4] D.L. DONOHUE, W.W. HARRISON: Radiofrequency cavity ion source in solids mass spectrometry. *Anal. Chem.*, **45**(1975), 1528-1531.

[5] M.R. WINCHESTER, C. LAZIK, R.K. MARCUS: Characterization of a radio frequency glow discharge emission source. *Spectrochim. Acta, B*, **46**(1991), 483-499.

[6] W.J. NOWAK, et al.: Water vapour effect on high temperature oxidation behaviour of superalloy Rene 80. *Adv. Manuf. Sci. Technol.*, **40**(2016)2, 41-52, DOI:10.2478/amst-2016-0009.

[7] W.J. NOWAK, P. WIERZBA, B. WIERZBA, J. SIENIAWSKI: Oxide scale formation on in 792 at early stages of high temperature exposure. *Adv. Manuf. Sci. Technol.*, **41**(2017)1, 65-74, DOI:10.2478/amst-2017-0006.

[8] A. JALOWICKA, et al.: Boron depletion in a nickel base superalloy induced by high temperature oxidation. *Oxid. Met.*, **83**(2015)3-4, 393-413.

[9] W. NOWAK, et al.: Effect of oxide scale composition on boron depletion of Ni-base superalloys. *Mater. Corros.*, **68**(2017)2, 171-185.

[10] R. PILLAI, et al.: Carbides in an aluminised single crystal superalloy: Tracing the source of carbon. *Surf. Coat. Technol.*, **288**(2016), 15-24.

[11] A. CHYRKIN, et al.: Modeling carbide dissolution in alloy 602 CA during high temperature oxidation. *Corros. Sci.*, **96**(2015), 32-41.

[12] A. JALOWICKA, W.J. NOWAK, D. NAUMENKO, W.J. QUADAKKERS: Effect of SO_2 addition on air oxidation behavior of CM247 and CMSX-4 at 1050°C. *J. Met.*, **68**(2016), 2776–2785.

[13] P. HUCZKOWSKI, et al.: Effect of SO_2 on oxidation of metallic materials in CO_2/H_2O-rich gases relevant to oxyfuel environments. *Mater. Corros.*, **65**(2014)2, 121-131.

[14] A. JALOWICKA, et al.: Effect of nickel base superalloys composition on oxidation resistance in SO_2 containing, high pO_2 environments, *Mater. Corros.*, **65**(2014)2, 178-187.

[15] W.J. NOWAK: Characterization of oxidized Ni-base superalloys by GD-OES. *JAAS*, **32**(2017), 1730-1738.

[16] W.J. NOWAK, et al.: Effect of substrate roughness on oxidation resistance of an aluminized ni-base superalloy. *Metals*, **9**(2019), 782-795.

[17] E. HEJRANI, et al.: Isothermal and cyclic oxidation behavior of free standing MCrAlY coatings manufactured by high-velocity atmospheric plasma spraying. *Surf. Coat. Technol.*, **313**(2017), 191-201.

[18] T. NELIS, R. PAYLING: Practical guide to glow discharge optical emission spectrometry. Royal Society of Chemistry, Cambridge, UK, 2003.

[19] C. GONZALEZ-GAGO, et al.: The use of matrix-specific calibrations for oxygen in analytical glow discharge spectrometry. *Anal. Bioanal. Chem.*, **406**(2014), 7473-7482.

[20] Z. WEISS: Calibration methods in glow discharge optical emission spectrometry: A tutorial review. *J. Anal. At. Spectrom.*, **30**(2015), 1038-1049.

[21] J.P. PFEIFER, H. HOLZBRECHER, W.J. QUADAKKERS, J. SPEIER: Quantitative analysis of oxide films on ODS*-alloys using MCs+-SIMS and e-Beam SNMS**. *J. Anal. Chem.*, **346**(1993), 86-191.

[22] W.J. QUADAKKERS, A. ELSCHNER, W. SPEIER, H. NICKEL: Composition and growth mechanisms of alumina scales on

FeCrAl-based alloys determined by SNMS. *App. Surf. Sci.*, **52**(1991), 271-287.
[23] R. PAYLING, M. AEBERHARD, D. DELFOSSE: Improved quantitative analysis of hard coatings by radiofrequency glow discharge optical emission spectrometry (rf-GD-OES). *J. Anal. At. Spectrom.*, **16**(2001), 50-55, DOI:10.1039/b007543o.
[24] V.-D. HODOROABA, V. HOFFMANN, E.B.M. STEERS, K. WETZIG: Investigations of the effect of hydrogen in an argon glow discharge. *J. Anal. At. Spectrom.*, **15**(2000), 1075-1080, DOI:10.1039/B002367L.
[25] R. PAYLING, P.L. LARKINS: Optical emission lines of the elements. John Wiley and Sons, 2000, ISBN-13: 978-0471623786.