

COMPARATIVE XPS ANALYSES OF PASSIVE LAYERS COMPOSITION FORMED ON DUPLEX 2205 SS AFTER STANDARD AND HIGH-CURRENT-DENSITY ELECTROPOLISHING

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Original scientific paper

In the paper, there are described XPS results of passive layers formed on duplex 2205 (EN 1.4462) stainless steel after a standard (EP50) and high-current density electropolishing (EP1000). The electrolyte based on orthophosphoric and sulfuric acids in proportion 1:4 was used. The survey and high resolution spectra of Cr 2p, Fe 2p, S 2p, P 2p are presented in the paper. Based on the survey of XPS spectrum it was possible to find the contamination of outer sub-layer consists mainly of nitrogen, sodium, chloride, potassium and partly oxygen and the inner passive sub-layer consists of iron, chromium, nickel, molybdenum, manganese, phosphorus, sulfur, silicon and partly oxygen. The obtained results show that in the passive layers formed on duplex 2205 stainless steel after a standard (EP50) and high-current density electropolishing (EP1000), the following oxides (FeO, Fe₂O₃, Fe₃O₄, Cr₂O₃), hydroxides (FeOOH, Cr(OH)₃, CrOOH) and salts (FeSO₄, Fe₂(SO₄)₃, FePO₄, CrPO₄, Cr₂(SO₄)₃) were detected. In the paper, besides iron and chromium compounds identification the authors propose two coefficients for passive surface characterization, *i.e.* chromium-to-iron coefficient (Cr/Fe) and phosphorus-to-sulfur (P/S). These two ratios obtained after the standard electropolishing (EP50) of 2205 SS are higher than those obtained after EP1000 treatment.

Keywords: Duplex 2205 SS; electropolishing; XPS Analysis

Usporedne XPS analize sastojaka pasivnih slojeva nastalih na Duplex 2205 SS poslije standardnog elektropoliranja i elektropoliranja strujom velike gustoće

Izvorni znanstveni članak

U radu su opisani XPS rezultati pasivnih slojeva nastalih na duplex 2205 (EN 1.4462) nehrđajućem čeliku nakon standardnog elektropoliranja (EP50) i elektropoliranja strujom velike gustoće (EP1000). Primijenjen je elektrolit na bazi fosforne i sumporne kiseline u omjeru 1:4. U radu se daju analiza i spektri visoke rezolucije Cr 2p, Fe 2p, S 2p, P 2p. Na temelju analize XPS spektra bilo je moguće ustanoviti da kontaminaciju vanjskog podsloja tvore uglavnom dušik, natrij, klorid, kalij i djelomično kisik, dok se unutarnji pasivni podsloj sastoji od željeza, kroma, nikla, molibdena, mangana, fosfora, sumpora, silicija i dijelom kisika. Dobiveni rezultati pokazuju da su u pasivnim slojevima nastalim na duplex 2205 nehrđajućem čeliku nakon standardnog (EP50) i elektropoliranja strujom visoke gustoće (EP1000) otkriveni sljedeći oksidi (FeO, Fe₂O₃, Fe₃O₄, Cr₂O₃), hidroksidi (FeOOH, Cr(OH)₃, CrOOH) i soli (FeSO₄, Fe₂(SO₄)₃, FePO₄, CrPO₄, Cr₂(SO₄)₃). Uz identifikaciju spojeva željeza i kroma, autori predlažu dva koeficijenta za obilježavanje pasivne površine, *t.j.* koeficijent odnosa kroma i željeza (Cr/Fe) te fosfora i sumpora (P/S). Ta dva omjera dobivena poslije standardnog elektropoliranja (EP50) nehrđajućeg čelika 2205 viša su od onih dobivenih poslije obrade EP1000.

Cljučne riječi: Duplex 2205 SS; elektropoliranje; XPS analiza

1 Introduction

Duplex 2205 stainless steel represents a steel of good corrosion resistance combined with high strength. It can be used in chemical process, ship, oil, gas, pulp, paper as well as food industries [1]. This type of steel has a higher general corrosion resistance in sulfuric, phosphoric and nitric acids than that in austenitic stainless steels (304, 304L, and 316, 316L). It has a better pitting resistance and crevice corrosion resistance in sea water as well as high stress corrosion resistance. After electrochemical polishing the passive layers, formed on austenitic stainless steels, differ from those grown in air atmosphere [2÷5]. The differences in chemical composition between the surfaces after standard electropolishing (EP) and magnetoelectropolishing (MEP) were also observed for carbon steel [2], austenitic [6÷15] and duplex [16] stainless steels.

In this paper, a new electrochemical method, *i.e.* high-current density electropolishing (EP1000) in a non-commercial electrolyte based on sulfuric and phosphoric acids is presented. The paper is a continuation of the studies performed on AISI 304L stainless steel, presented earlier [17].

2 Method

2.1 Material

The 2205 duplex stainless steel samples were used for the study, with the material composition presented in Tab.

1. The samples were cut off from a cold-rolled metal sheet of stainless steel. They were prepared in the form of rectangular specimens of dimensions 30 × 5 mm cut off the metal sheet 1 mm thick.

Table 1 Chemical composition of 2205 duplex stainless steel (wt%) [1]

Grade: 2205UNS No: S32205				
Cr	C	Ni	Mn	P
22÷23	0,03	4,5÷6,5	2,00	0,030
Si	Mo	N	S	Fe
1,00	3,0÷3,5	0,14÷0,20	0,020	bal.

2.2 Set-up

The electrochemical polishing operations were performed at the current density of 1000±10 A/dm². The main elements of the high-current density electropolishing (EP1000) set-up were: a processing cell, a DC power supply RNG-3010, the cylindrical electrode (cathode), sample (anode) and connecting wiring. The studies were carried out in the electrolyte of initial temperature of 40 °C, with the temperature control of ±5 °C. Generally the final electrolyte temperature was increased up to 55 °C. For the studies, a mixture of sulfuric/orthophosphoric acids electrolyte in the following proportion H₃PO₄:H₂SO₄ = 1:4 was used. No water was added to this mixture of the concentrated acids. The electrolytic cell made of glass was used, containing up to 500 cm³ of electrolyte solution. Additional set of duplex 2205 steel

samples treated in the same solution by a standard electropolishing at the current density of $50 \pm 1 \text{ A/dm}^2$ was used as a reference. Those samples were treated in the same solution in temperature of $65 \pm 5 \text{ }^\circ\text{C}$. Before the samples were measured they were rinsed with ethanol.

2.3 Apparatus and procedures

All XPS studies were carried out by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, UK). The spectrometer was equipped with a monochromatic Al $K\alpha$ ($h\nu = 1486,6 \text{ eV}$) X-ray source of 300 W at 15 kV. The kinetic energy of photoelectrons was determined with a hemispheric analyser set to pass energy of 160 eV for wide-scan spectra and 20 eV for high-resolution spectra. During all measurements, electrostatic charging of the sample was avoided by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same value that was necessary to set the C 1s peak to 285,00 eV. For measurements the take-off angle, here defined as angle between the sample surface normal and the electron-optical axis of the spectrometer, was 0° . Hence, the maximum information depth of the XPS method was not more than 10 nm. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. Shirley background for XPS data analysis was used [18, 19]. The deconvolution of XPS spectra was done in agreement with the data given in the references [20, 21].

3 XPS survey results analysis

In Figs. 1 and 2, there are shown XPS survey results of 2205 passive surface layers after standard electropolishing (EP50) and high-current density treatment (EP1000), respectively. In the survey XPS spectra of the passive layer the following elements were detected:

- iron (Fe $2p_{3/2}$, Fe $2p_{1/2}$, Fe 2s, Fe $3p_{3/2}$, Fe $3p_{1/2}$, Fe 3s, Fe LM1, Fe LM2, Fe LM3),
- chromium (Cr 2s, Cr $2p_{3/2}$, Cr $2p_{1/2}$, Cr 3s, Cr $3p_{3/2}$, Cr $3p_{1/2}$, Cr LM1, Cr LM2, Cr LM3),
- nickel (Ni $2p_{3/2}$, Ni $2p_{1/2}$, Ni 2s, Ni 3s, Ni $3p_{3/2}$, Ni $3p_{1/2}$, Ni LM1, Ni LM2, Ni LM3, Ni LM4, Ni LM5),
- molybdenum (Mo 3s, Mo $3p_{3/2}$, Mo $3p_{1/2}$, Mo $3d_{3/2}$, Mo $3d_{5/2}$, Mo 4s, Mo $4p_{3/2}$ and Mo $4p_{1/2}$),
- manganese (Mn $2p_{3/2}$, Mn $2p_{1/2}$, Mn 2s, Mn 3s, Mn $3p_{3/2}$, Mn $3p_{1/2}$, Mn LM1, Mn LM2, Mn LM3),
- phosphorus (P $2p_{3/2}$, P $2p_{1/2}$ and P 2s),
- sulfur (S $2p_{3/2}$, S $2p_{1/2}$, S 2s),
- silicon (Si $2p_{3/2}$, Si $2p_{1/2}$, Si 2s),
- oxygen (O 1s, O 2s, O KL1, O KL2, O KL3)

as well as contaminants such as:

- carbon (C 1s),
- nitrogen (N 1s),
- sodium (Na 1s, Na KL1),
- chlorine (Cl $2p_{3/2}$, Cl $2p_{1/2}$, Cl 2s),

- potassium (K $2p_{3/2}$, K $2p_{1/2}$, K 2s, K $3p_{3/2}$, K $3p_{1/2}$, K 3s),
- calcium (Ca $2p_{3/2}$, Ca $2p_{1/2}$, Ca 2s, Ca $3p_{3/2}$, Ca $3p_{1/2}$, Ca 3s).

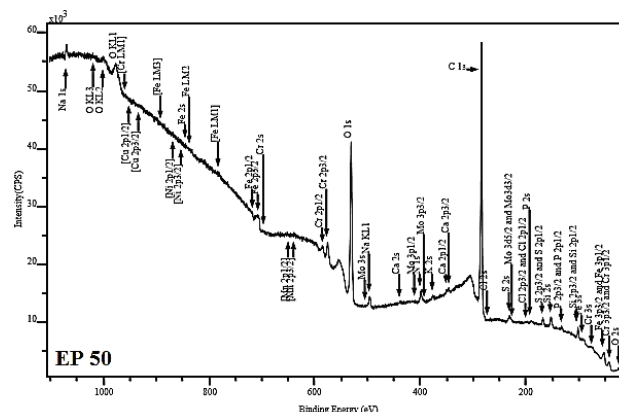


Figure 1 XPS survey results of passive surface layer of 2205 duplex stainless steel after standard electropolishing (EP50) within the binding energy of 0–1100 eV

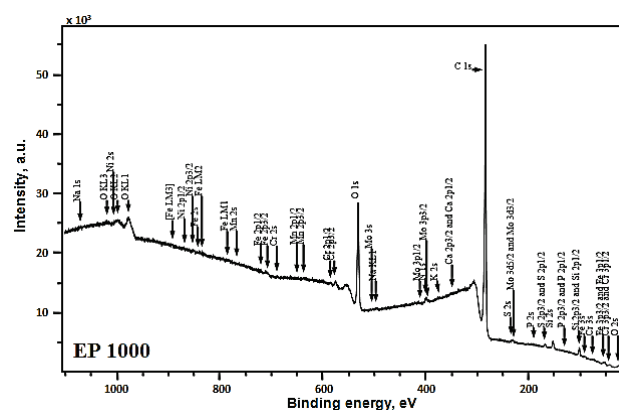


Figure 2 XPS survey results of passive surface layer of 2205 duplex stainless steel after high current density electropolishing (EP1000) within the binding energy of 0–1100 eV

4 High-resolution XPS results analysis

4.1 Iron (Fe 2p) and chromium (Cr 2p) high-resolution spectra

In Fig. 3, the deconvolution of Fe 2p spectra of passive layers formed on 2205 after standard (EP50) and high-current density electropolishing (EP1000) is shown. The difference of the binding energy values between Fe $2p_{3/2}$ and Fe $2p_{1/2}$ is in the range from 13,1 to 13,6 eV. The Fe $2p_{3/2}$ spectra were deconvoluted into the three component peaks. In some cases it was useful to introduce a further peak, which summarized the high-spin states of iron. Component peaks appearing at binding energies in the range from 706,5 eV to 707 eV showed metallic iron (Fe^0). Component peaks at binding energy in range from 708,2 to 710,9 eV could be interpreted as the mixed oxide Fe_3O_4 and the oxides FeO and Fe_2O_3 . Component peaks at binding energies 711,5 eV, 712,1 eV, 713,3 eV, 714,65 eV correspond to FeOOH , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, FePO_4 , respectively.

In Fig. 4, the deconvolution of Cr 2p spectra of passive layers formed on 2205 after standard (EP50) and high-current density electropolishing (EP1000) is presented. The differences of the binding energy values of

the two peaks Cr 2p_{3/2} and Cr 2p_{1/2} are in the range from 9,2 to 9,8 eV. The Cr 2p spectra recorded show differences of binding energy equal to about 9,4 eV for the metallic chromium (Cr⁰), and 9,8 eV for chromium compounds.

All Cr 2p spectra were deconvoluted into four component peaks assigned. According to the binding energy values found, component peaks at binding energy equal to about 574 eV represent metallic chromium (Cr⁰). The other component peaks have binding energy values typical for chromium oxides, hydroxides and salts. Component peaks at binding energies 576,9 eV, 577 eV, 577,3 eV, 578,1 eV, 578,6 eV, correspond to Cr₂O₃, CrOOH, Cr(OH)₃, CrPO₄, Cr₂(SO₄)₃, respectively. Chromium in the oxidation state Cr⁶⁺, such as CrO₃ and chromates (CrO₄²⁻) /dichromates (Cr₂O₇²⁻), is presented as a component peak, with the binding energy (BE) ranging 578,7÷579,1 eV.

The amount of chromium in the passive layer after standard electropolishing EP50 was about twice higher than iron amount. Chromium-to-iron coefficient (Cr/Fe)

after that electrochemical treatment equals 1,9 (atomic concentration). After high-current electropolishing EP1000, the chromium-to-iron coefficient (Cr/Fe) equals 1,7 (atomic concentration).

4.2 Phosphorus(P 2p) and sulfur (S 2p) high-resolution spectra

In Fig. 5, the deconvolution of P 2p spectra of passive layers formed on 2205 after standard (EP50) and high-current density electropolishing (EP1000) is shown. All spectra of the 2p level are composed of the element peaks of the 2p_{3/2} and 2p_{1/2} level. In case of the P 2p spectra, the difference of the binding energy between P 2p_{3/2} and P 2p_{1/2} equals 0.84 eV. The intensity ratio (P 2p_{3/2} : P 2p_{1/2}) is about 2:1. All detected phosphorus spectra showed only one component peak at BE[P 2p_{3/2}] ≈ 133,5 eV, which is a typical value for phosphate ions (PO₄³⁻), i.e. iron and/or chromium phosphates, such as FePO₄, Fe₃(PO₄)₂, CrPO₄.

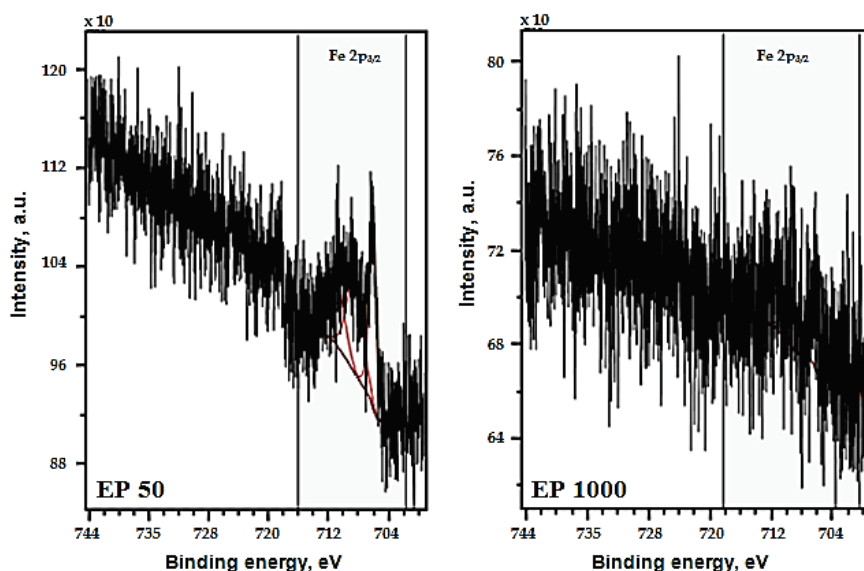


Figure 3 Deconvoluted Fe 2p spectra of passive layers formed on 2205 after standard (EP50) and high-current density electropolishing (EP1000)

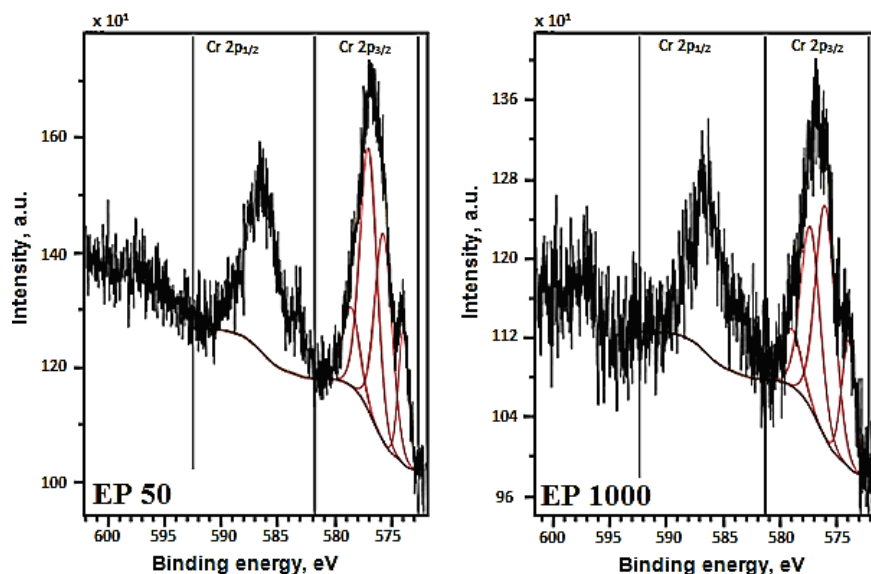


Figure 4 Deconvoluted Cr 2p spectra of passive layers formed on 2205 after standard (EP50) and high-current density electropolishing (EP1000)

In Fig. 6, the deconvolution of S 2p spectra of passive layers formed on 2205 after standard (EP50) and high-current density electropolishing (EP1000) is shown. The difference of the binding energy values between S 2p_{3/2} and S 2p_{1/2} equals 1,18 eV. The intensity ratio of the two peaks S 2p_{3/2} : S 2p_{1/2} equals 2:1. All spectra showed only one component peak at BE[S 2p_{3/2}] ≈ 168,8 eV, which is a typical value for sulfate ions (SO_4^{2-}), i.e. FeSO_4 , $\text{Fe}_3(\text{SO}_4)_3$.

The amount of sulfates in the passive layer after standard electropolishing EP50 was about two times higher than phosphates amount. Phosphorus-to-sulfur coefficient (P/S) after that electrochemical treatment equals 0,5 (atomic concentration). After high-current electropolishing EP1000, the amount of sulfates in the passive layer was over three times higher than phosphates amount. Phosphorus-to-sulfur coefficient (P/S) after high-current electropolishing EP1000 equals 0,3 (atomic concentration).

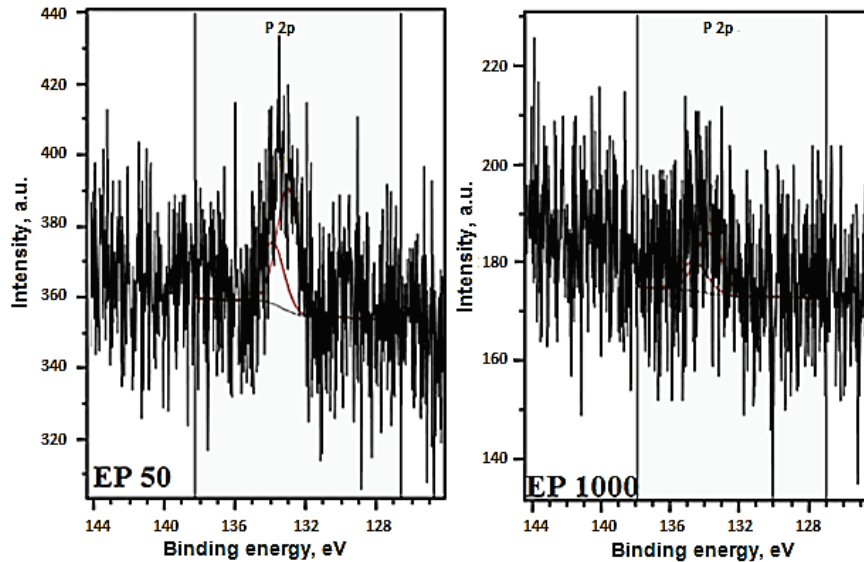


Figure 5 Deconvoluted P 2p spectra of passive layers formed on 2205 after standard (EP50) and high-current density electropolishing (EP1000)

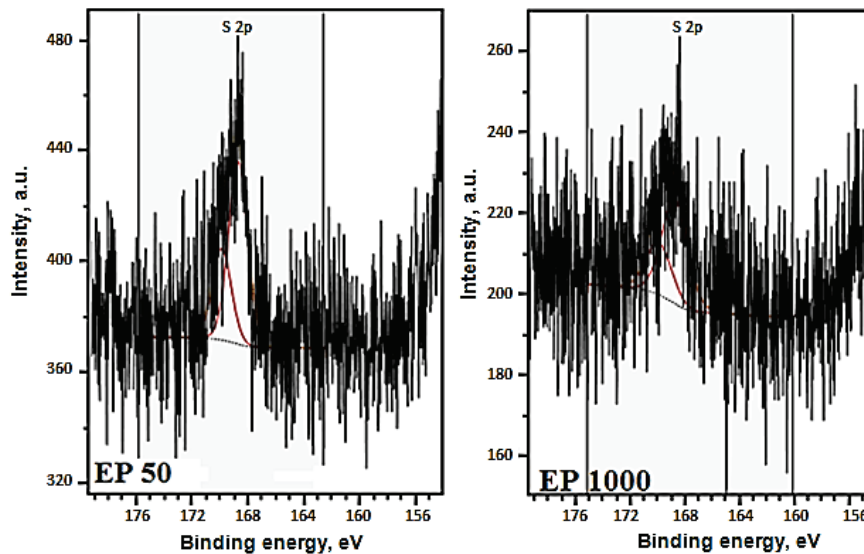


Figure 6 Deconvoluted S 2p spectra of passive layers formed on 2205 after standard (EP50) and high-current density electropolishing (EP1000)

5 Conclusions

In the paper, the XPS analysis of passive surface layer after new electropolishing method using high-current density is presented. In the passive layer there were detected elements, which can be treated as contaminations, such as carbon, nitrogen, sodium, chloride, potassium and partly oxygen as well as components of the passive layer, such as iron, chromium, nickel, molybdenum, manganese, phosphorous, sulfur, silicon and partly oxygen. The iron Fe 2p signal from the surface after EP1000 is lower than that one after EP50

treatment, what can give a better corrosion resistance for the surface after the new proposed polishing. After both polishing (EP50 and EP1000) the clear chromium Cr 2p signals were recorded, which contain metallic chromium and chromium compounds on the third and sixth stages of oxidation. The sulfur (S 2p) and phosphorus (P 2p) signals indicate that the compounds, which they formed on the surface, are mainly sulfates and phosphates. It should be also noted that chromium-to-iron coefficient (Cr/Fe) after that electrochemical treatment (EP) equals 1,9 (atomic concentration), while after the high-current electropolishing (EP1000) it equals 1,7 (atomic

concentration). The second coefficient, i.e. phosphorus-to-sulfur (P/S) for EP50 electropolishing equals 0,5 and for EP1000 treatment it is also smaller than for Cr/Fe ratio and equals 0,3. The new method of electropolishing, i.e. High-Current Density Electropolishing is a novel promising way to modify the passive layer formed on duplex steel. The presented results should be treated as the first approach and preliminary study after which also the XPS depth profiles with bigger amount of sweeps will be performed.

7 References

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