Rhodium electrodeposition on pyrolytic graphite electrode: Analysis of chronoamperometric curves

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Abstract

The electrodeposition of metallic rhodium on pyrolytic graphite from 10 mM Na₃RhCl₆ +0.5 M NaCl aqueous solution was investigated for the first time. From the analysis of chronoamperometric curves, the nucleation kinetics was compared for two-dimensional (2D) and three-dimensional (3D) electrodeposition processes, applying various models. Rh electrodeposition at −172 and −232 mV vs. Ag/AgCl was interpreted in terms of 3D process of progressive type which turns into instantaneous one at more negative potentials. The principal nucleation parameters (nucleation rate constant, nucleation density) are calculated by using two frequently used models for 3D nucleation and growth (Scharifker–Mostany and Mirkin–Nilov–Heerman–Tarallo), using different fitting procedures. It is shown that both models give similar results.

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1. Introduction

Rhodium is a well-known noble metal, belonging to the platinum-group, which plays an important role in many industrial applications [1,2]. The study of rhodium deposits is motivated by the well-known catalytic properties of the metal. In fact, rhodium is a common component of the catalysts used for the removal of nitrogen oxides, carbon monoxide, and hydrocarbons in automobile exhausts and it has been successfully applied for nitrate reduction in acidic [3,4] and neutral medium [5], in groundwater [6,7], showing the highest activity among transition and coinage metals.

However, the cost of Rh restraints its industrial application: hence it is of a significant interest to obtain thin Rh films. The electrodeposition is widely used for this purpose. Rhodium has been electrodeposited on polycrystalline and single crystal gold [8–10], Pt [11], Ti [12], vitreous carbon [13,14], and carbon-fiber materials [15].

Concerning the Rh source, different Rh salts have been used, for example, (NH₄)₂RhCl₆ [16], nitric acid solutions containing various complex forms of Rh(III) [15], RhCl₃ [11,17], Rh₂(SO₄)₃ [14], and Na₃RhCl₆ [8,11,13]. The last one is usually considered as the cheapest among them and its chemistry in aqueous solutions proves to be surprisingly simple [13], hence, it is used in our investigation.

The scope of this paper is to investigate Rh electrodeposition on pyrolytic graphite, which is a cheap substrate and, for that reason, one of the most appropriate for further industrial applications (e.g. nitrate removal from groundwater). Chronoamperometric experiments will be used to investigate in details the nucleation and growth mechanism for rhodium parti-
cles. Only a small number of papers is devoted to the detailed analysis of chronoamperometric curves and initial stages for Rh electrodeposition and to our knowledge none for Rh electrodeposition on pyrolytic graphite. The results of initial stages of Rh deposition on Au(111) were reported [9]. Arbib et al. [8] showed that the bulk rhodium electrodeposition on gold included the nucleation process combined with a diffusion-controlled growth and fitted the chronoamperometric curves in terms of Heerman–Tarallo model [18]. However, Langerock and Heerman [10] warned against the interpretation of potentiostatic transients with models based on simple diffusion controlled growth and show that the electrodeposition of rhodium is characterized by very slow charge transfer kinetics. To our knowledge, there is no literature data for Rh electrodeposition on pyrolytic graphite, which also involve a comparison of existing models for nucleation and growth process. Scanning electron microscopy (SEM) will be also used as complement to the conventional electrochemical methods, to study the mechanism and kinetics of rhodium electrocrystallization.

2. Experimental

Before use, graphite electrodes were carefully washed with nanopure H2O (17.3 MΩ), 1 M HNO3 and CH3OH subsequently (30 min with ultrasound), polished with alumina powder (0.05 µm, Buehler), washed again as described above, and dried in vacuum at 100 °C during 5 h. Typical geometrical surface area of graphite electrodes varied from 2 to 4 cm2. All the aqueous solutions were prepared using nanopure H2O and purged with N2 during 20 min.

In order to investigate the Rh deposition, the electrochemical cell was assembled from pyrolytic graphite (Carbon of America) (working electrode), Pt grid (counter electrode), and Ag/AgCl (3 M KCl) as a reference electrode. The potentials values quoted in the text are referred to the Ag/AgCl electrode. The electrochemical apparatus was composed of a potentiostat/galvanostat Solartron model 1287 interfaced with a PC and the Corrware 2 and CorrView 2 software (Scribner Associates). All charge and current densities are quoted in terms of apparent geometric area of the substrate graphite electrode.

The Rh electrodeposition on pyrolytic graphite was carried out from 10 mM Na3RhCl6 · 12H2O (Alfa Aesar) in 0.5 M NaCl aqueous solution at room temperature. The potentiostatic electrodeposition of rhodium was performed over a wide potential range (from −172 to −772 mV). Seven sets of experiments were carried out with the deposition time varying from 60 to 960 s. Before each potentiostatic experiment the initial potential of 0.6 V was maintained during 20 s.

The fit of chronoamperometric curves was carried out using Origin software. The morphology of Rh crystallites was examined using a Hitachi S-4300 scanning electron microscope equipped with EDX detector. SEM micrographs were taken both in SEM and in backscattered electron (BSE) mode. Then ‘general’ EDX analysis of the sample (2.5 × 3 mm zone) was performed, together with the analysis of its particular zones and spots.

3. Results and discussion

Cyclic voltammograms for Rh electrodeposition from a 10 mM Na3RhCl6, 0.5 M NaCl solution on pyrolytic graphite at different scan rates are represented in Fig. 1. On the scan to negative potentials, there is a well-formed cathodic peak at −318 mV Fig. 1(b), which is shifted to more negative potentials upon increasing the scan rate. This value of the cathodic peak potential is in agreement with that reported for the deposition of Rh on glassy carbon electrode [14]. On the return scan, there is no anodic peak which could be attributed to stripping of rhodium and a ‘nucleation loop’ is observed (i.e. there is a range of potentials where the cathodic current is higher than on the forward one). It is possible that the nucleation of Rh is followed by rapid growth because the overpotential for the Rh(III) → Rh reaction is relatively high, the formal potential for the Rh(III)/Rh in this solution is approximately +305 mV vs. Ag/AgCl [19]. This conclusion will be confirmed by the analysis of ‘current–time’ curves obtained during potentiostatic Rh deposition (see below).

The study of nucleation and growth via electrochemical methods offers certain advantages over other methods, because the driving force of nucleation can be simply varied by changing the applied potential. Hence,
the analysis of ‘current–time’ curves is an important method for studying the kinetics of electrocrystallization. Fig. 2 shows a family of potentiostatic current transients for Rh electrodeposition for various applied potentials. These transients are typical of those for a metal deposition process involving nucleation and growth and resemble those obtained for Rh deposition on glassy carbon electrode [14]. At very short time, a sharp decrease in the current is observed and in the succeeding part of the transient, the current increased with time and passed through a maximum value, \( I_M \), at the time \( t_M \). The decreasing part of the transients obeys the Cottrell equation. For a more negative potential, the current gradually decreased with time without reaching a maximum.

The non-dimensional plots of \( I/I_M \) or \( (I/I_M)^2 \) vs. \( t/t_M \) are widely used for the determination of the nucleation and growth type by comparing theoretical values and experimental results. The ‘current–time’ data were compared with the theoretical model for the limiting cases of 2D instantaneous and progressive nucleation and growth process. Both theoretical curves for 2D nucleation type did not fit our experimental results. However, 3D character of nucleation and growth might be expected for such a substrate as pyrolytic graphite, usually having a large number of 3D defects (e.g. pores and steps). In fact, the transient responses have the shape expected for a 3D nucleation process with diffusion control. According to the theory of Scharifker and Hills (SH model) [20], the rise in current corresponds to an increase in the electroactive area. This increase in area, limited by spherical diffusion around each nucleus, is due to (i) an increase in the nucleus size and/or (ii) an increase in the number of nuclei. The spherical diffusion zones then overlap and the mass transfer becomes linear to a planar surface. This change in diffusion regime leads to a decrease in the current with time.

In multiple nucleation, two limiting cases have to be considered: high or low nucleation rate. At a high nucleation rate, all the nuclei are immediately created and their number remains constant during the growth process, i.e. instantaneous nucleation occurs. It can be described by the following equation:

\[
I = \frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-N\pi kDt)],
\]

where \( z = 3 \), \( F \) is the Faraday constant (96,500 C mol\(^{-1}\)), \( c \) is the RhCl\(_3\) concentration (mol cm\(^{-3}\)) in solution, \( D \) is the diffusion coefficient, \( N \) is the density of nuclei (cm\(^{-2}\)), and \( k \) is a material constant. The material constant \( k \) for Rh is calculated from

\[
k = (8\pi cM/\rho)^{1/2},
\]

where \( M = 102.9 \text{ g mol}^{-1} \) is the atomic weight of Rh, and \( \rho = 12.4 \text{ g cm}^{-3} \) is the density of Rh. It is dimensionless and equal to 0.046. On the other hand, at low nucleation rate, new nuclei are continuously formed during the whole deposition process, i.e. progressive nucleation occurs, described by

\[
I = \frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-AN_0\pi kD t^2/2)],
\]

where \( k^l \) is a new material constant for Rh (\( k^l = 4k/3 \) and equal to 0.061), \( N_0 \) is the density of active sites (cm\(^{-2}\)), and \( A \) is the nucleation rate constant expressed as an appearance rate per active site per second (s\(^{-1}\)).

In order to characterize the nucleation process, the transient responses are plotted in dimensionless variables, \( (I/I_M)^2 \) vs. \( t/t_M \) together with the theoretical curves for instantaneous and progressive nucleation (Eqs. (4) and (5), respectively) (Fig. 3):

\[
\left( \frac{I}{I_M} \right)^2 = \frac{1.9542}{(t/t_M)} \left[ 1 - \exp \left( -1.2564 \frac{I}{I_M} \right) \right]^2,
\]

\[
\left( \frac{I}{I_M} \right)^2 = \frac{1.2254}{(t/t_M)} \left[ 1 - \exp \left( -2.3367 \frac{t^2}{I_M} \right) \right]^2.
\]

The curves fitting in terms of SH model reveals that at lower potential (−232 mV) a good correlation with the theoretical curve for progressive nucleation is obtained (Fig. 3(a)). In all other cases the nucleation seems to become instantaneous (Fig. 3(b)–(d)). When instantaneous nucleation occurs, \( N \) is equal to \( N_0 \) and can be estimated from [20]

\[
I_M = 0.6382zFDc(kN)^{1/2}.
\]

The diffusion coefficient, \( D \) (cm\(^2\) s\(^{-1}\)), is estimated according to

\[
I_M^2 t_M = 0.1629D(zFc)^2.
\]

Taking account of the geometrical surface area of graphite electrode the calculation yields the values of \( D \) and \( N \) reported in Table I. The values of diffusion coefficient are almost the same in this potential range.

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**Fig. 2.** Typical family of potentiostatic current density transients for the nucleation of Rh on pyrolytic graphite at different potentials.
On the other hand, when progressive nucleation occurs, the product $AN_0$ is calculated by
\[ I_M = 0.4615 z F c D^{3/4} (k AN_0)^{1/4}, \]
where $N_0$ is the density of active sites, while the diffusion coefficient, $D$, is now estimated from
\[ I^2 M = 0.2598 D (z F c)^2. \]

Since $c = 10^{-5}$ mol cm$^{-3}$, $I_M = 1.49 \times 10^{-3}$ A cm$^{-2}$, and $t_M = 7.2$ s, the calculations yield $AN_0 = 3.6 \times 10^4$ s$^{-1}$ cm$^{-2}$ with $D = 9.0 \times 10^{-6}$ cm$^2$s$^{-1}$. The density of nuclei at saturation, $N_s$ (cm$^{-2}$), is finally given by
\[ N_s = (AN_0/2kD)^{1/2} = 1.8 \times 10^5 \text{ cm}^{-2}. \]

When the progressive nucleation turns into the instantaneous one, the density of nuclei rapidly increases with the overpotential, as expected. In both cases, instantaneous and progressive nucleation, the calculated values for the diffusion coefficient are similar and in good agreement with values reported in the literature [8,10,13]. Another way of estimating the diffusion coefficient is the direct application of Cottrell equation:
\[ -j = \frac{zF D^{1/2} c}{\pi^{1/2} t^{1/2}}. \]
The descending parts of transients are traced in the coordinates $j - t^{1/2}$, and define straight lines (Fig. 4), which allow the diffusion coefficient to be calculated. Within the whole potential range (from $-172$ to $-712$ mV) its average value is $2.0 \times 10^{-5}$ cm$^2$s$^{-1}$, which is close to the values obtained from transients analysis (Tables 1 and 2). However, residual cathodic currents and slightly increasing slopes for decreasing potentials are observed, which were noticed earlier [21].

It should be emphasized that Eqs. (1) and (3) deal only with two extreme cases of nucleation, and the electrococrystallization in several systems cannot be described in such terms.

![Fig. 3. $(IM)^2$ vs. $t IM$ analysis of transient responses for Rh electrodeposition on pyrolytic graphite together with the data calculated for instantaneous and progressive nucleation from Eqs. (5) and (6). Deposition potential: (a) $-232$ mV, (b) $-252$ mV, (c) $-272$ mV, (d) $-292$ mV.]

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**Table 1**

<table>
<thead>
<tr>
<th>$E_{dep}$ (mV)</th>
<th>$I_M$ (mA/cm$^2$)</th>
<th>$t_M$ (s)</th>
<th>$D$ (10$^{-3}$ cm$^2$s$^{-1}$)</th>
<th>$N$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-252$</td>
<td>$1.67$</td>
<td>$5.51$</td>
<td>$1.1$</td>
<td>$2.5 \times 10^4$</td>
</tr>
<tr>
<td>$-272$</td>
<td>$2.44$</td>
<td>$2.12$</td>
<td>$0.9$</td>
<td>$4.4 \times 10^5$</td>
</tr>
<tr>
<td>$-292$</td>
<td>$4.16$</td>
<td>$0.61$</td>
<td>$0.8$</td>
<td>$1.9 \times 10^6$</td>
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</table>
by them. Moreover, it is difficult to extract useful parameters from this model and it suffers from the requirement that ‘progressive’ and ‘instantaneous’ cases must be treated separately. It should be also noted that these parameters are calculated using the single point ($i_M$, $I_M$) on the experimental transient which restraints the accuracy of parameters determination. The model proposed by Mirkin and Nilov [24] and Heerman and Tarallo [18] gives the following general current density–time expression is finally deduced:

$$I_{SM} = \frac{zFD^{1/2}C}{\pi^{1/2}D^{1/2}} \left[ 1 - \exp \left( -N_0\pi kD \left( t - \frac{1 - \exp(-At)}{A} \right) \right) \right].$$

(12)

All the parameters ($A$, $D$, and $N_0$) can be extracted for both types of nucleation contrary to Eqs. (1) and (3).

At present, there is considerable debate about the mathematical solution and computational simulation than Eq. (12). Fortunately, the function $F(x) = \exp(-x^2) \int_0^\infty \exp(\lambda^2) d\lambda$ can be well approximated with the polynomial expression $[8,26]$ (except very small values of $x$), yielding the following expression for $\Phi/\Theta$:

$$\Phi = \frac{0.5208934t - 1.206814D^{1/2}t^{1/2} + 1.185724D^{1/2}t^{1/2} - 0.0513144D^{1/2}t^{1/2}}{[At - 1 + \exp(-At)][1 - 1.206814D^{1/2}t^{1/2} + 1.185724Dt]}.$$  

(14)

This allows Eq. (13) to be expressed in a relatively simple mathematical form for computational fitting of experimental chronoamperometric curves.

The application of the models, mentioned above, fits the experimental chronoamperometric curves quite well, as shown in Fig. 5. The values of three free parameters ($A$, $N_0$, and $D$) for the two models are listed in Table 2.

Table 2

<table>
<thead>
<tr>
<th>$E_{dep}$ (mV)</th>
<th>SM model</th>
<th>MNHT model</th>
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<tbody>
<tr>
<td></td>
<td>$A$ (s$^{-1}$)</td>
<td>$D$ (10$^{-5}$ cm$^2$/s)</td>
</tr>
<tr>
<td>-172</td>
<td>0.3</td>
<td>2.3</td>
</tr>
<tr>
<td>-232</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>-252</td>
<td>27.7</td>
<td>2.0</td>
</tr>
<tr>
<td>-272</td>
<td>142</td>
<td>1.4</td>
</tr>
<tr>
<td>-292</td>
<td>1162</td>
<td>1.3</td>
</tr>
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</table>
However, the significant variation of $A$ value does not cause a substantial change of the fitting curve. Thus a computational simulation could be used for a better fit of experimental transients [27]. The values of the parameters for both models are quite similar as it was already observed for cobalt deposition on gold electrodes [28]. The values of $A$ obtained from MNHT model (Table 2) for low overpotential are smaller than those reported

Fig. 5. Comparison of experimental current density transients, recorded during Rh electrodeposition on pyrolytic graphite at: (a, b) –172 mV, (c, d) –252 mV, (e, f) –292 mV, and theoretical transients generated by non-linear fit of Eq. (12) (a, c, e) and Eq. (13) (b, d, f). Parameters obtained by best fit are reported in Table 2.
for the electrodeposition of rhodium on polycrystalline gold [8].

SEM micrographs, obtained for the bare substrate (Fig. 6(a)) and for different Rh deposits, revealed the increase in nuclei density for more negative potentials (Fig. 6(b) and (c)), finally forming large Rh clusters (Fig. 6(d)). However, the observed nuclei density ($10^7$–$10^9$ cm$^{-2}$) is higher than the calculated one ($10^5$–$10^7$ cm$^{-2}$), which has been already shown for the deposition of Rh on gold [10] and for the deposition of Pt on graphite [29].

A different way of interpreting the current transients has been recently suggested [30]. The equation corresponding to progressive nucleation can be written in the form:

$$\ln \ln \left( \frac{1}{C_0} a_j t^{1/2} \right) = \ln \left( \frac{1}{2} AN_0 \pi kD \right) + 2 \ln t, \quad (15)$$

where $a = a_{SM} = \pi^{1/2}/zFD^{1/2}c$ according to SM model and $a = a_{MNHT} = (3/4)a_{SM} = (3/4)\pi^{1/2}/zFD^{1/2}c$ according to MNHT model, respectively. The values of $D$ necessary to calculate the constant $a$ are determined from Cottrell equation and the linear plots of $\ln \ln (1 - a j t^{1/2})^{-1}$ vs. $\ln t$ obtained according to the SM model are shown in Fig. 7. The average slope of straight lines is 1.97 which is in a good agreement with theoretical predictions. The density of nuclei at saturation calculated according to Eq. (10) is equal to $2.0 \times 10^5$ cm$^{-2}$ at $-172$ mV and to $3.1 \times 10^5$ cm$^{-2}$ at $-232$ mV respectively, that is in a good agreement with the above-mentioned value ($1.8 \times 10^5$ cm$^{-2}$). The fits obtained by means of MNHT model result in similar results with a smaller intercept from the ordinate.

When instantaneous nucleation occurs, Eqs. (12) and (13) are transformed into Eq. (1) which can be also rewritten in the form:

$$\ln \ln (1 - a j t^{1/2})^{-1} = \ln (N_0 \pi kD) + \ln t \quad (16)$$

that predicts a linear relationship between $\ln \ln (1 - a j t^{1/2})^{-1}$ and $\ln t$ with a slope equal to 1. The fits for the transient recorded at $-272$ mV, corresponding to both models, are represented in Fig. 8, the average

Fig. 6. SEM micrographs of pyrolytic graphite (a) (magnification $\times 25000$, scanning electrons mode) and Rh deposit on pyrolytic graphite (magnification $\times 25000$, backscattered electrons mode). Deposition time 60 s. Deposition potential: (b) $-172$ mV, (c) $-232$ mV, (d) $-592$ mV.
slope is 0.98 which means a good agreement with the theory. The values of $N_0$ are listed in Table 3 and they are 2–3 times higher than the values obtained from Eqs. (12) and (13).

Fig. 9 shows a plot of $\ln A$ vs. $E$. A linear relationship is found using the values obtained from SM and MNHT models represented by Eqs. (12) and (13). From the slope $d(\ln A)/dE$, it is possible to estimate the critical size of the nuclei using the relationship [31]:

$$n_c = \left( \frac{kT}{2e_0} \right) \left( \frac{d\ln A}{dE} \right) - \alpha,$$

(17)

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $e_0$ is the elementary electric charge, and $\alpha$ is an ion transfer coefficient. Taking $\alpha = 0.5$, one can obtain $n_c \equiv 0$ for both models. That means that within the investigated potential range the thermodynamic barrier for nucleus formation is zero and only the kinetics determine the nucleation rate constant $A$ for Rh electrodeposition on the pyrolytic graphite, which is also the case for polycrystalline gold [8].

The analysis of potentiostatic transients for the deposition of metals is usually restricted to the substrates characterized by well-defined and smooth surface, such as single crystal and polycrystalline gold [8,28] and highly oriented pyrolytic graphite [32]. On the other hand, it is well known that surface inhomogeneities, such as defects, grain boundaries, dislocations, monatomic steps, can act as nucleation sites for the deposition of metals [33]. Thus, it is of interest to investigate the nucleation and growth phenomena for disordered materials such as pyrolytic graphite. In a very recent study, it was shown that the current transients could not be explained in terms of 3D nucleation models with diffusion controlled growth [10]. Instead, a model combining mixed kinetics, charge transfer and diffusion was used to interpret the $(\Pi/I_M)^2$ vs. $t/t_M$ plots. The very good agreement with 3D nucleation and growth processes for the Rh electrodeposition on pyrolytic graphite is indicative of the enhancement of the kinetics for the

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<td>SM model</td>
<td>MNHT model</td>
</tr>
<tr>
<td>−252</td>
<td>9.2 x 10$^5$</td>
</tr>
<tr>
<td>−272</td>
<td>2.5 x 10$^6$</td>
</tr>
<tr>
<td>−292</td>
<td>2.2 x 10$^7$</td>
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initial growth compared to the polycrystalline gold electrode [10]. Finally, it would be interesting to further investigate the difference between ‘well-defined’ and ‘inhomogeneous’ substrates by changing the composition of the deposition solution and consequently the chemical nature of the rhodium species present in the deposition solution. This might be an important factor considering the variety of surface groups that can be present at the surface of a carbon electrode [34].

4. Conclusion

The electrodeposition of rhodium on pyrolytic graphite substrates was investigated with electrochemical techniques and SEM. Our results show that the Rh deposition proceeds through a nucleation and growth mechanism. The analysis of chronoamperometric curves confirms the 3D character of Rh deposits. It turns out that the Rh deposition firstly occurs as a progressive nucleation process, which becomes an instantaneous one for more negative deposition potentials. This allows the principal nucleation parameters (nucleation rate constant, nucleation density) to be calculated, involving different existing models for 3D nucleation and growth (Scharifker and Mostany [20], Mirkin and Nilov [24] and Heerman and Tarallo [18]). The fit of our experimental data to both models gives similar values of nucleation parameters. However, there is a mismatch between microscopically observed number of nuclei and the calculated number of active sites, resulting from the best fit of chronoamperometric curves. This can be due to inadequacies of the theoretical models used for the description of the number density of nuclei. However, this difference can be substantially decreased by applying the fitting procedure suggested by Milchev and Heerman [30] which deals especially with initial parts of chronoamperometric curves ($\tau_1 \leq 1$). The mismatch between theory and experiment can also be related to the disordered nature of pyrolytic graphite, contrary to ordered substrates commonly used, and the state of its surface, which would make necessary further development of nucleation and growth models.

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