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Preliminary communication

PRELIMINARY COMMUNICATION

Corrosion potential of 304 stainless steel in sulfuric acid

BORE JEGDIĆ[1], DRAGUTIN M. DRAŽIĆ[2*#] and JOVAN P. POPIĆ[2#]

[1]*Institute for Chemical Power Sources, Batajnički drum bb, 11070 Belgrade – Zemun and* [2]*Institute of Chemistry, Technology and Metallurgy – Center for Electrochemistry, P. O. Box 473, 11001 Belgrade, Serbia and Montenegro (e-mail: dmdrazic@eunet.yu)*

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Abstract: The potentiodynamic study of the electrochemical behavior of austenitic 304 stainless steel in deaerated aqueous sulfuric acid of pH 1 revealed that the steel achieved a stable corrosion potential of *ca.* – 0.350 V (SCE) independent of whether the electrode had previously been cathodically "activated" or anodically passivated. It was also shown that the experimentally observed anodic peak was not the usually obtained anodic passivation peak, as is the case with a number of metal, but an artifact due to the anodic oxidation of hydrogen absorbed during the previously employed cathodic polarization and hydrogen evolution, intended to activate the initially passive surface, or even hydrogen absorbed on the open circuit potential. It was shown that this potential establishes and electrochemical corrosion potential of the Wagner–Traud type due to the evolution of cathodic hydrogen on a passivated steel surface and anodic metal dissolution through the passive layer. It was impossible to activate 304 stainless steel in sulfuric acid of pH 1 by cathodic polarization, and the usually observed anodic peak obtained under these conditions should not be considered as an active metal dissolution process and a passivation anodic peak, but rather as an artifact due to the electrochemical oxidation of the in the steel absorbed hydrogen.

Keywords: stainless steel, corrosion, corrosion potential, sulfuric acid.

INTRODUCTION

The corrosion properties of 304 stainless steel have been studied by a great number of authors and relevant data can be found in a number of publications.[1–3] Dissolution and passivation of 304 stainless steel in sulfuric acid is also treated in many publications.[4–6] Heumann and Dieköter,[7] Wilde and Hodge,[8] Sukhotin and Khoreva,[9] Safonov *et al.*[10] and Popić and Dražić[11] pointed out that chromium exhibits two stable corrosion potentials in deaerated sulfuric acid, one related to the active, bare chromium surface, and the second one self-establishing on the passive

* Author for correspondence.

Serbian Chemical Society active member.

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surface of Cr. In many studies of the structure of the passive film on chromium stainless steels it was demonstrated that the properties of chromium stainless steels are due to the selective dissolution of Cr alloy and accumulation of Cr_2O_3 on the surface of passive layer, *i.e.*, practically to the formation of a Cr passive layer.[12] The purpose of this communication is to compare the corrosion properties of chromium and austenitic 304 stainless steel in aqueous sulfuric acid solution and to present the preliminary results on the interpretation of the so-called passivation peak of stainless steel. By comparing the behavior of the corrosion potentials and the potentiodynamic curves, we concluded that the stable corrosion potential of stainless steel in dilute sulfuric acid is the corrosion potential established at the passive steel surface, similar to that on passive chromium, while the so-called passivation peak on the anodic potentiodynamic sweep is an artifact due to the anodic dissolution of hydrogen absorbed inside the steel, rather than the anodic dissolution of steel, as is usually considered to be the case.

EXPERIMENTAL

The experiments were performed with metallic Cr (Goodfellow, Berwin, Pa, USA) and austenitic 304 stainless steel (18.12 % Cr, (9.08 % Ni, 0.07 % C, by analysis)). The electrodes were made in the form of a piece of metal sealed in epoxy resin (exposed surface area 1 cm^2). A two channel Phillips X–Y plotter was used. All the experiments were performed in aqueous mixtures of 0.1 M $Na_2SO_4 + H_2SO_4$, (pH 1.0). Merck p.a. chemicals and doubly distilled water were used for the preparation of the solutions. An all-glass electrochemical cell with a thermostating jacket was used. The counter electrode was a Pt wire and the reference electrode a saturated calomel electrode (SCE). All the potentials are referred to SCE. The solutions were continuously deaerated with purified nitrogen. The potential scan rate of the Cr electrode was 2 mV s^{-1}, which appeared to be sufficiently slow to consider the polarization curves to have been obtained under a quasi-steady state condition. Prior to the measurements, the electrodes were activated by cathodic polarization at – 0.9 V for 120 s, since the spontaneously formed open circuit potential of a chromium electrode which had previously been in contact with air was about – 0.350 V, which corresponds to the passive state of the chromium surface. However, similar activation of the steel electrode did not show any significant effect on the corrosion potential, but affected the shape of the anodic polarization sweep, as shown in the Results and Discussion section.

RESULTS AND DISCUSSION

As depicted in Fig. 1 the Cr electrode on introduction into the cell (curve 1) achieved after some time a rather stable corrosion potential of *ca*. – 0.350 V (SCE). However, after cathodic activation of the Cr electrode, the corrosion, or open circuit potential (curve 2) achieved a stable value of *ca*. – 0.760 V (SCE) in a rather short period of time. The initial, primary value, corresponding to the electrochemically passivated surface in our previous papers related to the electrochemistry of Cr,[11,13–15] was *ca*. – 0.450 V (SCE) indicating that the spontaneous oxide film formed in contact with air and water, and the electrochemically formed during the forced passivation are very similar, if not identical, in structure. This initial corrosion potential formed spontaneously on the passive surface was designated as $E_{cor.1,Cr}$, while the corrosion potential formed after the cathodic activation, corre-

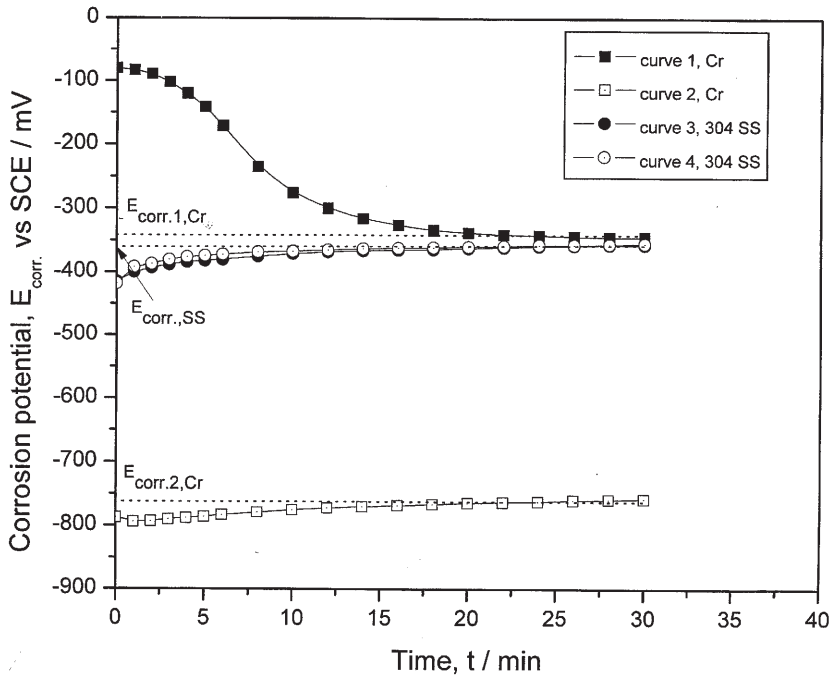

Fig. 1. Change of the open circuit potential over time after introduction of the electrode into the deaerated sulfuric acid (pH 1) (curve 1 for Cr and curve 3 for steel) and after the cathodic "activation" (curve 2 for Cr and 4 for steel). Potentials $E_{cor.1,Cr}$, and $E_{cor.SS}$ correspond to passive state corrosion potentials for Cr and stainless steel, respectively. $E_{cor.1,Cr}$ is the corrosion potential of the active chromium.

sponding to the bare, or active, surface $E_{cor.2,Cr}$. The initial corrosion potentials for the stainless steel electrode (curve 3) after introduction into the cell, and after cathodic activation in a manner similar to that used previously for the electrode (curve 4) converged to the same potential value of – 0.350 V (SCE), $E_{cor.SS}$, indicating that the observed corrosion potential for stainless steel is similar to that for a passivated Cr electrode, $E_{cor.1,Cr}$. All the attempts to activate a stainless steel electrode by cathodic polarization even to – 1.4 V (SCE) for up to several tens of minutes did not change the value of the final corrosion potential, except that the time required to achieve it was prolonged.

The cyclic voltammogram of a Cr electrode after cathodic activation is depicted in Fig. 2. It shows a stable anodic passivation peak starting from the $E_{cor.2,Cr}$ potential, with stable anodic currents[11] in the active Cr dissolution potential range (more negative than the passivation peak potential, E_p). However, in the reverse scan, the anodic current of the passivated Cr at a potential corresponding to $E_{cor.1,Cr}$ changed its sign, became cathodic, and showed a small cathodic peak, presented also in the inset in an enlarged view. At the potential of – 0.580 V (SCE), the cathodic hydrogen evolution started loosing its exponential character, and transformed into a negative peak, which at *ca.* – 0.600 V (SCE) suddenly jumped into

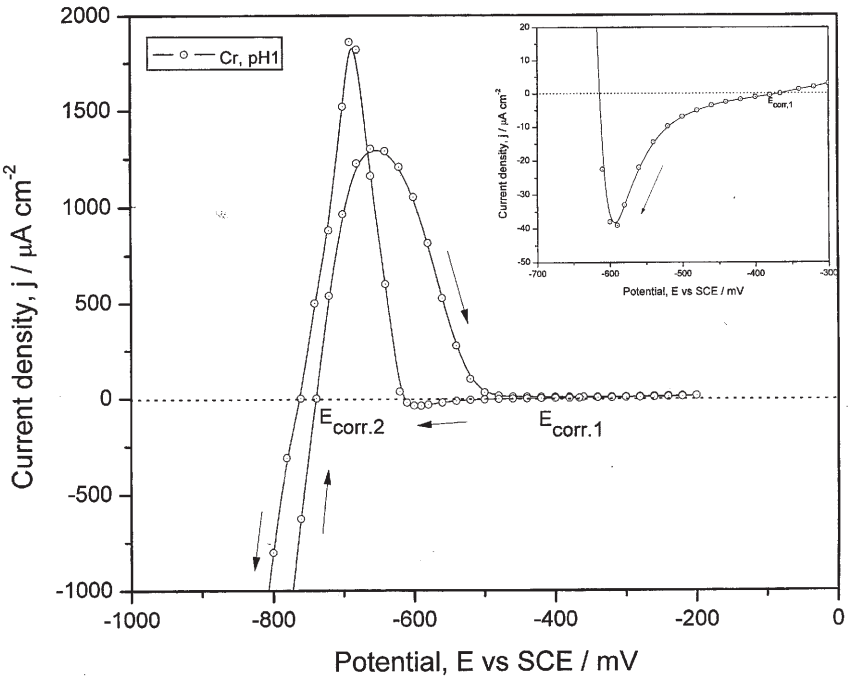

Fig. 2. Cyclic voltammogram for the Cr electrode after cathodic activation. Inset presents the enlarged cathodic peak in the reverse scan, representing cathodic hydrogen evolution on the passive surface.

the positive, anodic current range, in a manner typical of a depassivation peak. In a laborious manner in Ref. 11 working in the pH range 0.5 – 3, it was shown that cathodic peak in the reversed sweep is due to hydrogen evolution by H^+ ions discharge on the passive Cr surface with the cathodic Tafel slope of *ca*. – 0.120 mV/dec, while the $E_{\text{cor.1,Cr}}$ is established as a stable electrochemical corrosion potential in a Wagner–Traud[16] manner.

The cyclic volatmmogram shown in Fig. 3 depicts the electrochemical behavior of a stainless steel electrode, polarized cathodically in an attempt to activate it, and starting the potential scan from the most negative potential value. In the anodic potential region regarding the $E_{\text{cor.SS}}$ value, a typical anodic passivation peak was observed, as often reported in the literature.[4–6] However, the reverse scan was different to the one obtained for the Cr electrode. It was cathodic from rather positive potential values up to the initial starting cathodic potential with the cathodic currents showing certain hysteresis effect, with lower currents in the reverse scan. There was neither a cathodic peak nor a depassivation peak, as observed for Cr (Fig. 2), and for many other passive metals, *e.g.*, Fe, Ni, *etc*.[5] More important are the results obtained in a more detailed study of the stability of the anodic peak currents. When the potential was held in the potential range before the anodic peak, assuming that this potential range corresponds to the anodic dissolution current

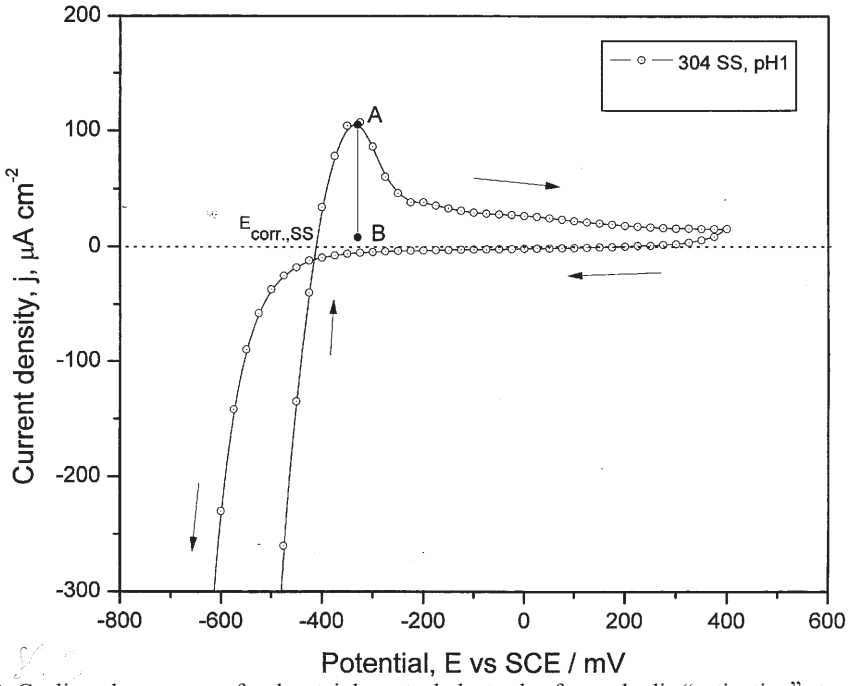

Fig. 3. Cyclic volammogram for the stainless steel electrode after cathodic "activation" at – 0.900 V (SCE) for 10 min. Points A and B connect the current decay during hold of the potential.

and the dissolution current would be fairly stable, as was the case with the anodic dissolution before the passivation potential for chromium (see Fig. 2), a constant current decay was observed as indicated in Fig. 3 by the vertical line between points A and B, point B corresponding practically to the average current in the passive region. The time dependence of this decay is shown in Fig. 4, indicating that about 3 mC/cm^2 of anodic charge was consumed during this decay (black circles). Open circles and open squares represent the similar decays but after waiting for 60 or 600 s, respectively, at the corrosion potential, $E_{cor.SS}$, after cathodic activation. As seen, the decays were somewhat faster than the ones immediately after activation. On the other hand, as shown in Fig. 5, holding at the corrosion potential after activation at the cathodic potential of – 0.900 V (SCE) for 2 h affected the value of the passivation current tremendously, so that in that the passivation peak almost disappeared and the current attained the value of the passive current. Anodic polarization curve after 2 h holding was made first, and the cathodic curve (open circles) afterwards in order to avoid hydrogen absorption. Hence, anodic peak is appearing as a consequence of the presence of absorbed hydrogen. The effect of hydrogen charging on the height of the anodic peak is reported in the literature for stainless steel,[17] but without the corresponding evaluation.

The observed sensitivity of the "passivation" peak on the cathodic pretreatment, and the time dependence of the anodic current in the potential range more

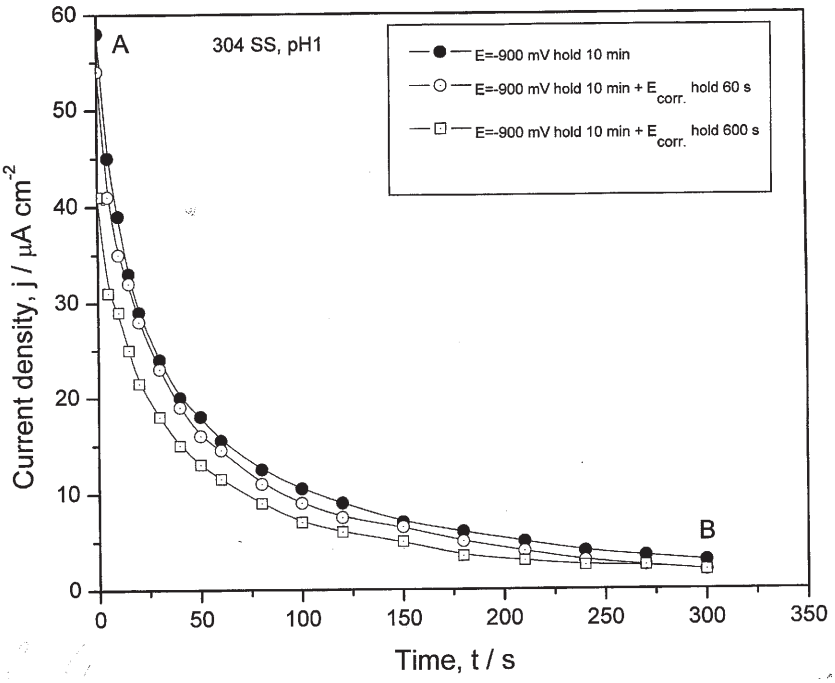

Fig. 4. Depandence of the current over time during hold of potential at the potential corresponding to point A depicted in Fig. 3, but after different holds at the corrosion potential after "activation"; ● – immediately after "activation"; ○ – after 60 s; □ – after 600 s.

negative than the "passivation" potential of the "passivation" peak strongly suggests that the observed "passivation" peak for the stainless steel electrode is, in fact, an artifact, related not to the active–passive transition as usually observed for many metals, but to a pseudo-passivation phenomenon arising from the anodic oxidation of hydrogen absorbed in the steel during cathodic activation, or often used practice to start the potentiodynamic or voltammetric experiments from the potentials more negative than $E_{cor.SS}$, when hydrogen evolution (and hydrogen absorption) occurs.

On the other hand, this means that the surface is passive over almost the whole potential range studied, and that the corrosion potential of "activated" steel, is in fact, the corrosion potential of passive steel, corresponding in some manner to $E_{cor.1,Cr}$. The observed hydrogen evolution during cathodic polarization of a steel electrode is, in fact, hydrogen evolution on a passive surface, and the failed attempts to activate a steel electrode by prolonged cathodic polarization, as observed for a Cr electrode, simply means that the passive layer cannot be reduced in a similar manner as for a Cr electrode. The stable corrosion potentials, $E_{cor.SS}$, for steel electrodes presented in Fig. 1 are, therefore, electrochemical corrosion potentials formed according to the Wagner–Traud model[16] by two opposing electrochemical reactions, *cathodic hydrogen evolution on the passive film* and *anodic dissolution of steel* through the *passive*

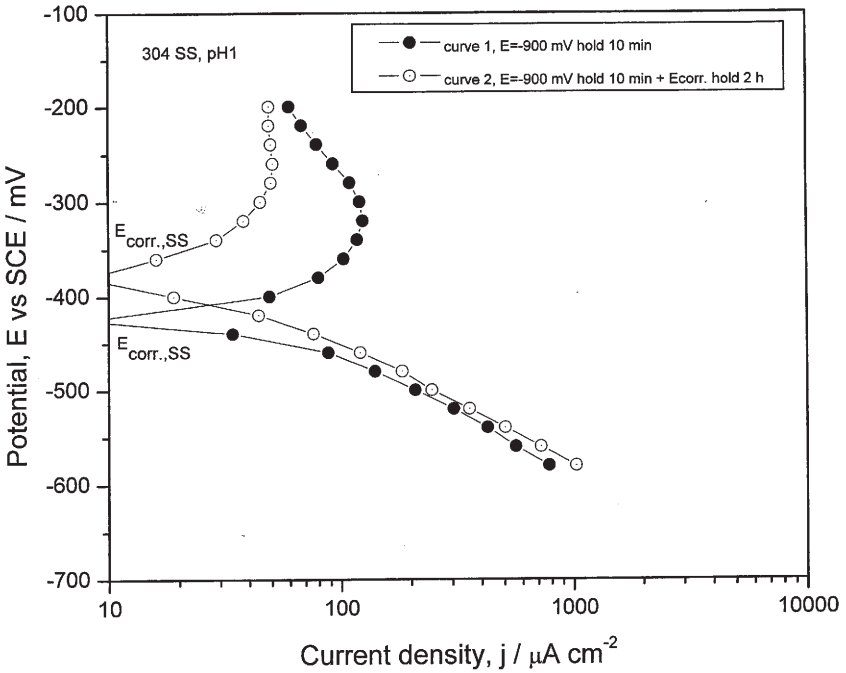

Fig. 5. Two potentiodynamic curves for the same stainless steel electrode after "activation" at – 0.900 V (SCE) for 10 min. Curve 1 – starting from the cathodic potential; curve 2 – starting after 2 h hold from $E_{cor.SS}$ first in the anodic direction.

film, *i.e.*, a passive anodic current. In the present work it was not possible to reduce electrochemically the passive film on stainless steel and obtain stable anodic metal dissolution in an active potential dissolution range, and also the second corrosion potential in the active dissolution range, corresponding to the "bare" metal surface, as observed in the case of metallic chromium.

CONCLUSION

The often observed anodic peak on 304 stainless steel electrodes in deaerated sulfuric acid solutions appears to be not the real anodic passivation peak, as observed for many metals under similar circumstances, but an artifact arising from the anodic oxidation of the hydrogen absorbed during cathodic polarization, or even longer holding at the open circuit, *i.e.*, corrosion, potential. Cathodic hydrogen evolution occurs on the passive film, while the open circuit potential is formed by a Wagner–Traud electrochemical model, with two more-or-less stable opposing electrochemical reactions, *i.e.*, cathodic hydrogen evolution and anodic metal dissolution through the passive layer. Ageing of the passive layer probably affects in some way the rates of both reactions, which might affect the stability of the observed corrosion potential.

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ИЗВОД

КОРОЗИОНИ ПОТЕНЦИЈАЛ НЕРЂАЈУЋЕГ ЧЕЛИКА 304 У СУМПОРНОЈ КИСЕЛИНИ

БОРЕ ЈЕГДИЋ[1], ДРАГУТИН М. ДРАЖИЋ[2] и ЈОВАН П. ПОПИЋ[2]

[1]Институт за хемијске изворе струје, Батајнички друм бб, 11070 Београд-Земун и [2]Институт за хемију, технологију и металургију – Центар за електрохемију, п. пр. 473, Његошева 12, 11001 Београд

Потенциодинамичка испитивања електрохемијског понашања нерђајућег челика 304 у деаерираној сумпорној киселини са pH 1 показала су да се на челику успоставља стабилан корозиони потенцијал од – 0,350 V (ЗКЕ) независно од тога да ли је електрода претходно катодно третирана ради „активације", или је површина била пасивирана. Показано је, такође, да експериментално добијени анодни максимум на потенциодинамичкој криви позитивније од корозионог потенцијала није анодни пасивациони максимум који се обично добија при анодној поларизацији већег броја метала у сличним условима, већ експериментални артефакт који настаје због анодне оксидације водоника апсорбованог унутар челика током катодног „активирања" или чак и при дужем држању на корозионом потенцијалу. Показано је да је спонтано формирани потенцијал отвореног кола заправо корозиони потенцијал који настаје као мешовити потенцијал Вагнер–Траудовог типа супротним деловањем катодне реакције издвајања водоника на пасивном слоју и анодног растварања челика кроз пасивни слој. Није било могућно катодном „активацијом" и дуготрајнијом катодном поларизацијом до значајно негативних потенцијала и врло великих катодних струја да се пасивни слој уклони и постигне активно електрохемијско растварање метала без присуства пасивног слоја, тј. слободна метална површина. Стога, често експериментално констатован анодни максимум на оваквим челицима не треба да се интерпретира као анодно растварање са пасивационим максимумом, већ као последица анодне оксидације апсорбованог водоника у пасивном челику, а који се под овим условима не може електрохемијски активирати, одн. депасивирати.

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