

Paintings pigmented with doped magnetite: preliminary evaluation of anticorrosive properties

Pinturas pigmentadas con magnetita dopada: evaluación preliminar de propiedades anticorrosivas

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Abstract

Pure magnetite and magnetite doped with three different concentrations of chromium and copper was lab synthesized. The relative performance of these products as anticorrosive pigments is compared with commercially available hematite (red iron oxide). Special mixtures of the pigments with a solventless epoxy binder were prepared maintaining the pigment volume contents near the practical critical value. The purpose was to distinguish the inhibitive action of pigments with the least possible influence from the barrier properties of the epoxy resin. The performance of mixtures applied on mild steel is characterized in accelerated outdoor exposure, in alternated immersion tests and in total immersion conditions. The latter test was monitored with open circuit potential and impedance measurements. Complementary tests with freestanding films were also performed. The results show that magnetite is not an inert pigment. Therefore presence of doping elements can improve the performance of anticorrosive magnetite paints. Based on this result, a complete formulation with pigment, solvent and additives is suggested and preliminarily tested in the lab aiming at producing an anticorrosive primer.

----- *Key words:* Coatings, paints, impedance, magnetite, copper, chromium, corrosion

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Resumen

La magnetita pura y las magnetitas dopadas con cobre y cromo se sintetizaron a escala de laboratorio. El comportamiento relativo de estos productos como pigmentos anticorrosivos se comparó con la hematita disponible comercialmente (óxido rojo del hierro). Se prepararon mezclas especiales de los pigmentos con resina epoxy libre de solvente manteniendo el contenido del volumen de pigmento cerca del valor práctico crítico. El propósito es distinguir la acción inhibitoria de los pigmentos con poca influencia de las características de la barrera de la resina epóxica. El comportamiento de las mezclas aplicadas sobre el acero se caracterizó mediante exposición acelerada al aire libre, en pruebas alternadas de inmersión y en condiciones de inmersión total. Esta última prueba se supervisó con medidas de potencial y de impedancia de circuito abierto, y fueron complementadas con evaluación de películas libres. Los resultados demuestran que la magnetita no es un pigmento inerte, y que la presencia de elementos dopantes puede mejorar el comportamiento de las pinturas anticorrosivas de magnetita. Basados en esos resultados, se sugirió una formulación completa con pigmento de magnetita, solvente y aditivos y se evaluó en laboratorio, teniendo como objetivo el uso posible como pintura anticorrosiva.

----- *Palabras clave:* recubrimientos, pinturas, impedancia, magnetita, cobre, cromo, corrosión.

Introduction

One of the current challenges for the anticorrosive paint industry is to reduce the environmental impact of manufacturing operations and to produce environmentally compliant products. In this context, organic coatings with less hazardous solvents and pigments are required. Iron oxides are good candidates for use as active pigments in organic coatings due to their low cost, easy production and environmental acceptability. Hematite (Fe_2O_3), also known as red iron oxide, has been the main iron oxide used as pigment in organic coatings for corrosion protection [1, 2].

The idea of coating mild steel with paints pigmented with magnetite (Fe_3O_4) can be attributed to Miranda [3]. He reports good performance for paintings pigmented with this oxide, which is commonly found in the inner layer of rusts, especially those produced in chloride containing media. Although the inhibitive mechanism of such coating is not yet well established, it is suggested that including magnetite in paints would provide better interaction between the paint and the steel, delaying the deterioration process. Thackeray *et al.* showed the possible charge/discharge property of Fe_2O_3 and Fe_3O_4 oxides in propylene carbonate (PC)/ LiClO_4 electrolyte [4]. This property can be used to extend the oxidizing power of the conducting organic polymer when these materials are used as anticorrosive coatings. Deslouis *et al.* found a significant improvement in the protection efficiency of a polypyrrol (PPy) coating on an iron electrode when Fe_2O_3 and Fe_3O_4 oxides were added [5]. The best results were found using PPy/ Fe_3O_4 composite. In this case, oxides allow the polymer to remain in its oxidized state and, consequently, maintain the passive state of the metal.

In previous studies we evaluated different paints prepared with a solventless epoxy binder doped with 1 and 5 atomic percent of Cu and Cr magnetite pigments [6]. In those studies, steel painted samples and free standing films were evaluated by immersion in $\text{NaCl } 10^{-2} \text{ M}$ solution, and by Electrochemical Impedance Spectroscopy

(EIS). The idea of using doped magnetite came from the stabilizing role of the low alloy elements, Cu and Cr, in the rust on weathering steels [7, 8]. It was found that magnetite paints had better anticorrosive behaviour than commercial hematite pigmented paints. Preliminary results suggest that magnetite is an active pigment that stabilizes the electric properties (resistance and capacitance) of the coating. Additionally, it was verified that performance of the paints containing doped magnetite was better than those containing pure magnetite [8].

The purposes of this paper are: i) to compare the behaviour of pure magnetite and magnetite doped with Cu and Cr, in conventional corrosion laboratory tests; and ii) to look for evidence of the inhibitive action of pure and doped magnetite in anticorrosive coatings. As in previous studies [8], paints were formulated with only the magnetite pigment and solventless epoxy binder at the critical pigment volume content (CPVC). Finally, a complete formula is suggested and preliminarily evaluated in the laboratory, with a view to an eventual commercial application of such pigments in anticorrosive primers.

Experimental

Pigment synthesis and coating preparation

Syntheses of pure and doped magnetite with Cu and Cr were made following the method suggested by Cornell and Schwertmann [9, 10]. The method leads to well-crystallized and highly stoichiometric magnetites. A complete description of the synthesis and characterization of the pigments has been published elsewhere [11, 12]. Coatings were specially formulated with a solventless epoxy binder at the practical critical pigment volume content (CPVC) determined by the epoxy binder without the curing agent. Doped magnetite had a theoretical content of 1.5 and 10% of the doping element. Paints were applied in two coats with a paintbrush on 1010 steel specimens polished with sandpaper #100 and degreased with toluene.

Corrosion tests

Samples of the painted steel with an area of 10 x 15 cm² were submitted to outdoor accelerated exposure during 60 days, according to ISO 11474, with additional spraying every 3 days with 3.0% NaCl solution. Other samples with an area of 3 x 15 cm² were exposed for 30 days to an alternated immersion test in a Cebelcor chamber [13]. The solution used for immersion was 10⁻² M NaCl and the dry temperature was 40 °C. The immersion and drying periods were of 13 and 45 minutes, respectively. A total immersion test was also carried out with 3 x 3 cm² samples in a 10⁻² NaCl solution for 30 days. All tests were carried out with triplicate samples. In all cases, blistering, corrosion and under-film corrosion were evaluated according to ASTM D-714 and D-610.

After these tests, the magnetite paint which showed the best anticorrosion behaviour was chosen for preparation of a complete paint formula (CPF). The CPF coating was tested in the same way as described above. EIS was also used to evaluate the coating properties during immersion in 10⁻² M NaCl. A three electrode

cell with a BAS-Zahner IM6 impedance analyzer was employed. Coated samples with areas of 10 x 15 cm² were used as working electrodes. A saturated calomel electrode (SCE) was employed as reference and a graphite plate with a large area was used as a counter electrode. A sinusoidal perturbation of 10 mV of amplitude was superimposed at the open circuit potential (OCP). Resistances and capacitances obtained from the high frequency capacitive loop were used to characterize the deterioration process of the coatings.

Results and discussion

Magnetite pigments

The synthesis method employed leads to well-crystallized and highly stoichiometric magnetites, with the chemical formula calculated as Fe_{2,984}O₄. Table 1 summarizes the synthesized magnetites with their calculated and real doping element content. The same code was used to reference pigments and coatings. The particle size of the pigments was calculated by Mössbauer Spectroscopy.

Table 1 Particle size and doping element content of magnetite pigments

| Pigment | Code | Cu content / (% weight) | | Cr content / (%weight) | | Particle size / nm |
|-------------------------|-------|-------------------------|------|------------------------|------|--------------------|
| | | Calculated | Real | Calculated | Real | |
| Pure magnetite | M | --- | --- | --- | --- | 321 |
| Magnetite doped with Cu | MCu1 | 0.83 | 0.57 | --- | --- | --- |
| | MCu5 | 4.33 | 3.51 | --- | --- | 38.3 |
| | MCu10 | 9.14 | 5.91 | --- | --- | 25.1 |
| Magnetite doped with Cr | MCr1 | --- | --- | 0.67 | 0.57 | --- |
| | MCr5 | --- | --- | 3.51 | 3.21 | 163.5 |
| | MCr10 | --- | --- | 7.41 | 5.71 | 57.1 |

The particle size of magnetite pigments depends on the nature and quantity of the doping element. The synthesis procedure adopted resulted in

pigments with particle sizes similar to micronized industrial particle sizes. On the other hand, it was observed that between the two doping elements

evaluated, Cu induced smaller particle size. This effect is enhanced when the Cu concentration in the magnetite increases. This procedure could be economically attractive for eventual large scale production.

Corrosion tests

The performance of the magnetite pigmented coatings in corrosion tests is shown in table 2.

To compare the values, it is important to consider the thickness of different samples. It can be seen that doping element improves the performance of magnetite coating in outdoor test and, likewise, in the total immersion test; however, in alternated immersion tests the performance was not improved. Cu doped magnetite coatings showed better performance than Cr ones in outdoor tests. Meanwhile, in the total immersion tests, Cr doped magnetite coatings showed the best behaviour.

Table 2 Behaviour of paints in different corrosion tests (average values)

| Test | Analysis | Paint Samples | | | | | | |
|--------------------|--------------------------|---------------|------|------|-------|------|------|-------|
| | | M | MCu1 | MCu5 | MCu10 | MCr1 | MCr5 | MCr10 |
| Outdoor exposition | Thickness (µm) | 59 | 25 | 37 | 33 | 36 | 30 | 40 |
| | Blistering | 3 | 3 | 2 | 1 | 2 | 4 | 2 |
| | Corrosion | 4 | 4 | 2 | 2 | 2 | 5 | 3 |
| | Underfilm corrosion (mm) | 3 | 3 | 2 | 2 | 2 | 3 | 2 |
| Total immersion | Thickness (µm) | 82 | 65 | 36 | 41 | 32 | 16 | 36 |
| | Blistering | 2 | 4 | 5 | 3 | 2 | 2 | 2 |
| | Corrosion | 2 | 3 | 5 | 3 | 2 | 2 | 2 |
| | Underfilm corrosion (mm) | 2 | 3 | 4 | 3 | 2 | 1 | 1 |

0: undetectable, 1: little, 2: low moderate, 3: moderate, 4: elevated, 5: severe.

Evaluation of Complete Paint Formulation

According to results obtained in the corrosion tests, 5% Cu doped magnetite paint (MCu5) showed the best performance and was the pigment chosen to prepare a complete paint formulation (CPF). The CPF was prepared with a PVC/CPVC ratio = 0,8, which is usually adopted for primers with active pigments [14, 15]. The composition of the CPF (% weight) was: epoxy resin (26.83), dispersing agent (0.26), anti-slip agent (0.35), magnetite pigment MCu5 (15.3), plasticizer (1.99), solvent (28.5), extender

(26.77). The main proprieties of the CPF were: dispersion in Hegman scale (6), solids content (62.67%weight), density (1.15 kg.dm⁻³), Stormer viscosity (91 KU), PVC (27.48 %).

The CPF coating was applied by air spray on steel panels degreased and sandblasted to white metal. The coated samples were exposed to the same corrosion tests already described. Additionally, the performance of coated samples and free-standing films submitted to total immersion was monitored by electrochemical impedance spectroscopy (EIS). The dry thickness of the coating was about 54 µm.

Figure 1 shows the impedance diagrams obtained at different immersion times. The impedance diagrams consist of only one depressed capacitive

loop during the whole period. Additional loops which could indicate undercoating corrosion were not observed.

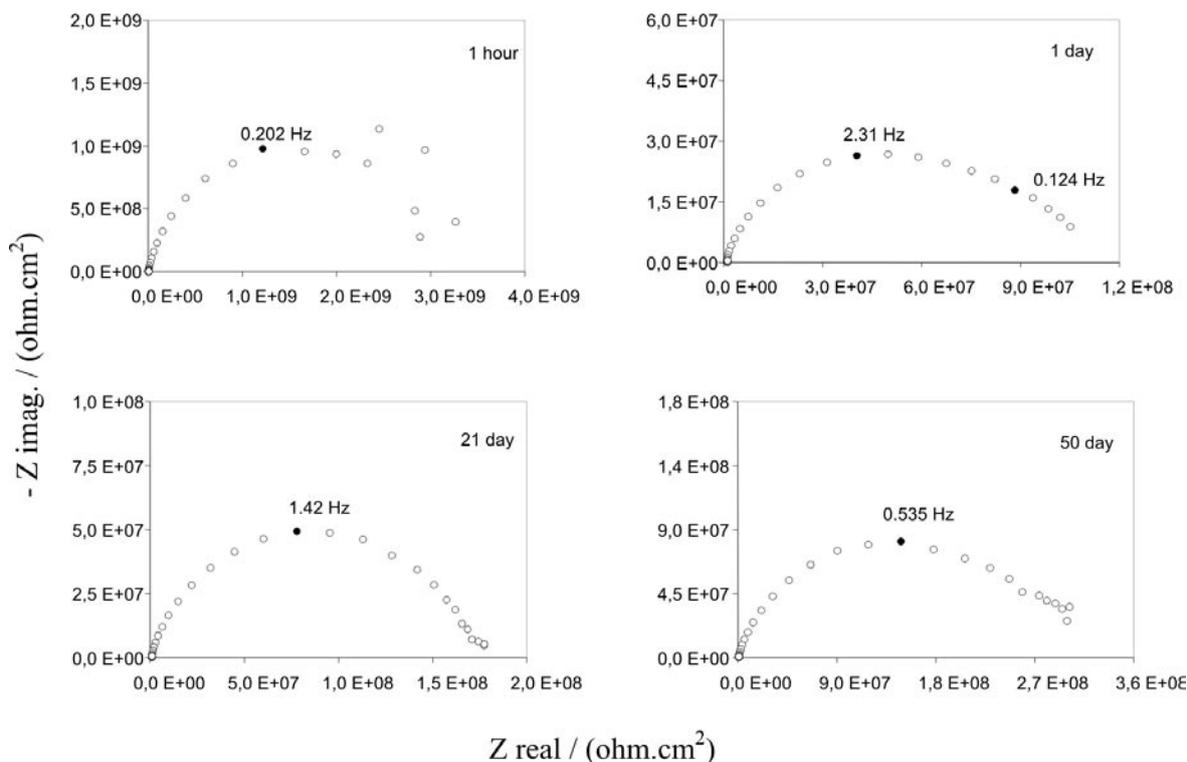


Figure 1 Impedance of CPF coating for different immersion times in 10^{-2} M NaCl solution

Recently, Cao and co-workers evaluated the anticorrosive properties of epoxy-polyamide coatings pigmented with red iron oxide [2] and alkyd coatings pigmented with micaceous iron oxide [16]. Both coatings presented a barrier mechanism of protection, retarding the access of water, oxygen and aggressive species to the metallic substrate. However, the barrier properties of the red iron oxide coating and of the 60% PVC micaceous iron oxide were lost after 5 hours of immersion. This was shown by changes in the impedance diagrams, which presented an additional loop and a straight line of about 45° at low frequencies after only 5 hours of immersion. Changes presented in the impedance diagrams

were associated with diffusion through the coating and corrosion processes happening in the metal-coating interface [2, 16]. Similar behaviour has been reported for epoxy-polyamide amine coatings containing different fillers (talcum powder and barium sulphate) [17]. These coatings presented a second capacitive loop at low frequencies after 8 days of immersion. The appearance of a second capacitive loop preceded blistering and pitting on the painted samples, indicate the beginning of corrosion processes [17]. In the current study the presence of only one capacitive loop in the whole frequency range during immersion time suggests good anticorrosion properties of the CPF coating.

Figure 2 shows the evolution of resistance and capacitance corresponding to impedance measurements of the samples during the immersion time. It can be seen that during the first hours of immersion the resistance decreases and the capacitance increases quickly. This behaviour can be attributed to initial water uptake by the coating, which is also responsible for the depressed form of impedance diagrams after the first day of immersion (figure 1). It is known that water absorption leads to changes in the dielectric properties of the organic coatings. In the current study this process happened quickly during the

first hours of immersion and the water uptake reaches a stationary state at the end of the first day of immersion. After the first day resistance increased gradually by a small amount and the drop in capacitances continued until the end of the immersion period. This unusual behaviour for a protective barrier with organic coatings was already observed in preliminary electrochemical tests made with magnetite coating doped with Cu and Cr [6]. There is no evidence of coating damage, as there are no additional loops in the impedance diagrams during the whole immersion period.

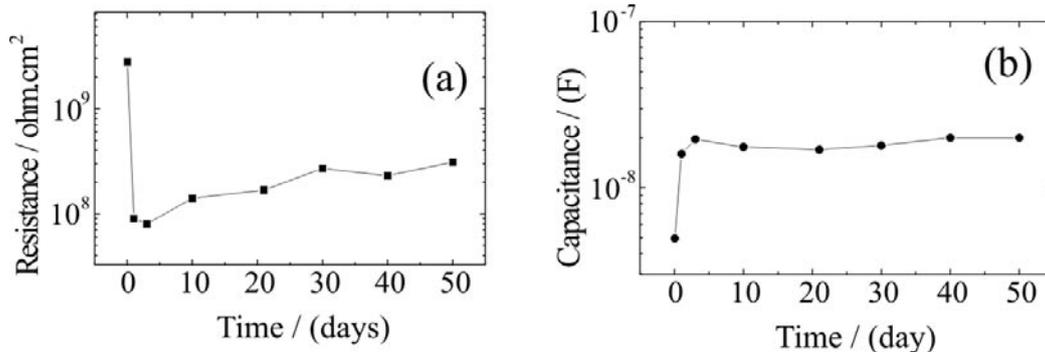


Figure 2 Evolution of the impedance parameters of the CPF coatings during immersion in 10⁻²M NaCl solution

Impedance diagrams of free-standing films are shown in figure 3 for different immersion times. As can be seen at 1 hour immersion time, one open capacitive loop appeared at the Nyquist plot, indicating an initial good barrier property of the film. After the first day of immersion a depressed capacitive loop appears.

The single capacitive loop represents the resistance of the film; it can be seen that the film resistance is almost constant from the first day until the final immersion time. It is important to remark that the impedances of free-standing films are similar to those observed in the coated

steel samples. This fact suggests that the good anticorrosion performance of the coating is related with a high electrolytic resistance of the film improved by the doped magnetite pigment. We propose that the magnetite pigment acts as a dielectric inhibitor, which makes the movement of ions through the film more difficult. The good performance of the CPF coating is confirmed by the results of the corrosion test shown in table 3. Additionally, excellent adhesion of the film on the metallic substrates after one month of total immersion was observed (figure 4). These results confirm the effective corrosion protection properties of the magnetite paint.

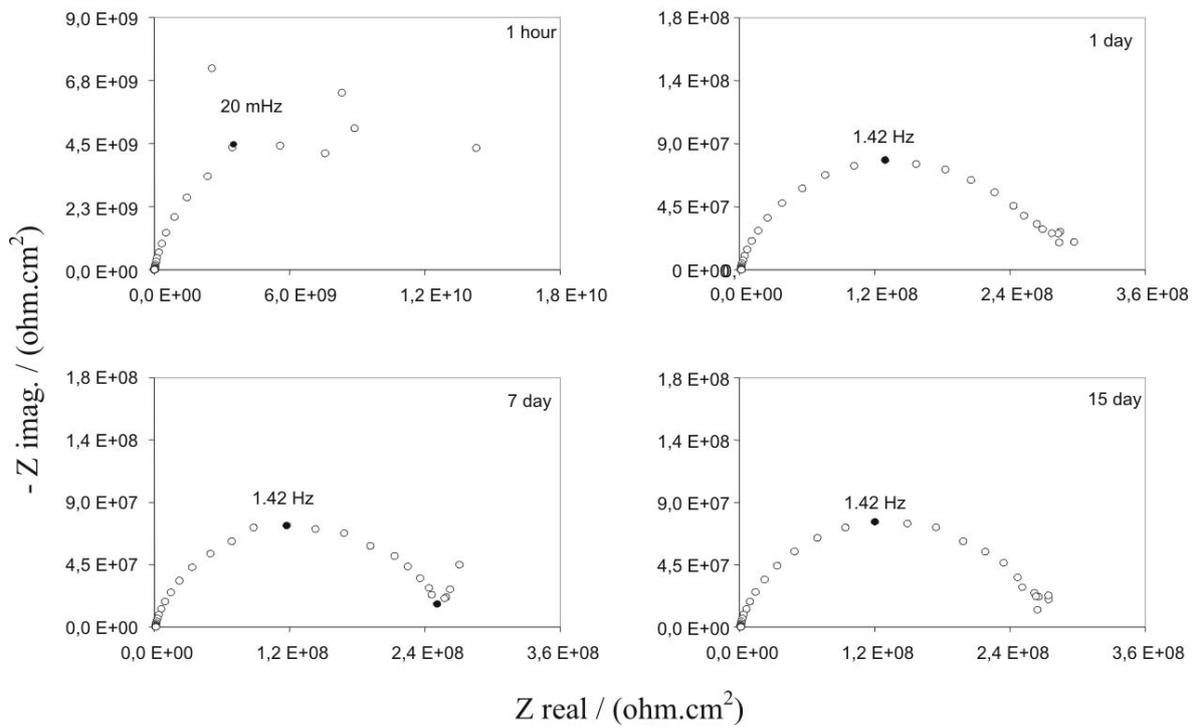


Figure 3 Impedance of the free-standing film of the CPF coatings at different immersion times in 10⁻² M NaCl solution

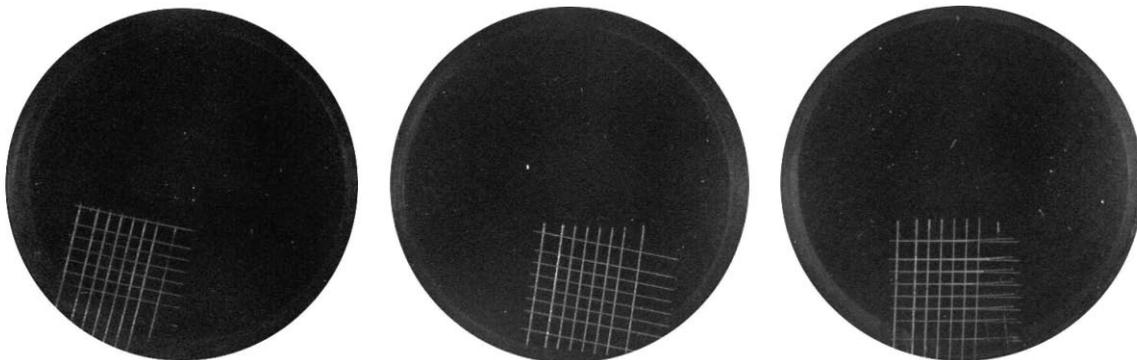


Figure 4 Picture of the CPF coatings after adhesion test. Samples were immersed for 1 month in 10⁻² M NaCl solution

Table 3 Behaviour of CPF coating in different corrosion tests

| Analysis | Test | | |
|-------------------------------------|------------------------------|-----------------------------|-------------------------|
| | Alternated immersion* | Outdoor exposition** | Total immersion* |
| Average thickness (μm) | 61 | 40 | 59 |
| Blistering | 1 | 1 | 1.5 |
| Corrosion | 1 | 1 | 1 |
| Underfilm corrosion (mm) | 2 | 2 | 2 |

0: undetectable, 1: little, 2: low moderate, 3: moderate, 4: elevated, 5: severe.
Time of exposure: *: 1 month, **: 2 months.

Conclusions

The synthesis technique adopted in this study facilitated obtaining a pigment of good crystallinity, stoichiometry and optimal particle size for the developed formulation, which led to better anticorrosive behaviour of evaluated paints.

Elements such as copper and chromium, responsible for the formation of stable oxides in weathering steels, were used successfully as doping up to 5% in the pigments.

The electrochemical impedance technique evidenced the effect of copper and chromium on the anticorrosive behaviour regarding the pure magnetite and the traditionally used commercial hematite. This anticorrosive behaviour is corroborated by the satisfactory evaluation of free-standing magnetite films and the adherence achieved on the metallic substrates.

In the described formulation, magnetite doped with 5% Cu acts as an anticorrosive pigment, presenting a dielectric inhibitor mechanism by establishing conditions of low electric load transfer between the metallic substrate and pigment.

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