Study on Electrochemical Property of As-Cast and Annealed A_2B_7 Type La-Mg-Ni System Alloy

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Abstract: In order to improve electrochemical property of as-cast La_3MgNi_{14} alloy, the alloy was annealed at 1 123, 1 223 and 1 323 K under 0.3 MPa Argon atmospheres for 10 h. Microstructures and electrochemical properties of different annealed alloys have been investigated by XRD, SEM and electrochemical experiment. The obtained results show that as-cast alloy and alloy annealed at 1 123 K are compose of $LaNi_5$, $(La, Mg)_2Ni_7$ and a small amount of $LaNi_2$ phases. There are some $LaNi_5$, $(La, Mg)_2Ni_7$ and $(La, Mg)Ni_3$ phases in alloy annealed at 1 223 K. However, $LaNi_5$ and $(La, Mg)Ni_3$ phases became main phase at 1 323 K. Compared by as-cast alloy, composition of annealed alloys is more homogeneous, and grains of annealed alloys are coarsened. With increasing annealing temperature, some electrochemical properties and kinetic parameters of the alloys, involving maximum discharge capacity, discharge efficiency, cyclic stability, high-rate discharge ability (HRD) of the alloys all increase, however, potential difference and charge-transfer reaction resistance of the alloys decrease. In order to balance between discharge capacity and cyclic stability, the most suitable annealing temperature for preparation of La_3MgNi_{14} alloy is recommended to be 1 323 K in present work.

Key words: annealing temperature; La-Mg-Ni system alloy; electrochemical property
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铸态和退火态 A_2B_7 型 La-Mg-Ni 系合金的电化学研究

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摘 要: 为了改善铸态 La_3MgNi_{14} 合金的电化学性能, 在 0.3 MPa 氩气气氛下对 La_3MgNi_{14} 合金进行了 10 h 退火处理, 退火温度分别为 1 123, 1 223 和 1 323 K。采用 X 射线衍射(XRD)、扫描电镜(SEM)和电化学实验研究了合金的微观结构和电化学性能。结果表明, 铸态及 1 123 K 温度退火后的合金由 $LaNi_5$ 相、$(La, Mg)_2Ni_7$ 相以及少量的 $LaNi_2$ 相组成。1 223 K 温度退火后合金含有 $LaNi_5$, $(La, Mg)_2Ni_7$ 和 $(La, Mg)Ni_3$ 相。1 323 K 温度退火后合金的主相为 $LaNi_5$ 和 $(La, Mg)Ni_3$ 相。与铸态合金相比, 退火后合金组织更加均匀, 晶粒长大。随着退火温度的增加, 合金的一些电化学性能(如最大放电容量、放电效率、循环稳定性)以及动力学参数(如高倍率放电性能)增强, 而电位差和电荷迁移电阻降低。在本研究范围内, 为了放电容量和循环稳定性之间的平衡, 铸态 La_3MgNi_{14} 合金的适宜退火温度为 1 323 K。

关键词: 退火温度; La-Mg-Ni 系合金; 电化学性能

1 Introduction

As we known, clean hydrogen energy has sprung up due to low or zero carbon energy. Hydrogen storage is more important to all hydrogen energy system. Storage of metal hydride is one of chemical methods of hydrogen storage. A series of metal hydride materials have been discovered, such as rare-earth based AB_5-type alloy[1], rare-earth Magnesium based A_2B_7-type alloy[2], AB_2-type Laves phase alloy[3], Mg-based alloy[4], and V-based solid solution alloy[5]. Of these alloys, rare-earth based AB_5-type alloy has realized large-scale industrialization[6]. However, commercial AB_5-type hydrogen storage alloy could not meet demand of Ni/MH power battery applied to high-

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er power HEV owing to its low discharge capacity (310 ~ 330 mA · h/g)[1]. Therefore, higher capacity of hydrogen storage alloy negative electrode is one of main approaches to improvement of energy density of Ni/MH battery. In a decade, La-Mg-Ni system A_2B_7-type alloys with higher discharge capacity were paid much attention as the candidates for negative electrode materials of Ni/MH power batteries owing to their higher discharge capacity(>350 mA · h/g)[7] co MPared to AB_5-type alloys. However, La-Mg-Ni system hydrogen storage alloy can not industrially product in their present state owing to fast discharge capacity degradation in the process of charge/discharge cycles. For slowing up capacity degradation of La-Mg-Ni system alloy electrodes, researchers have carried out lots of investigations and obtained significant results. It is well known that manufacture technology is extremely important for improving performances of the alloys. Kohno et al.[8] found that La_3MgNi_{14}-type electrode alloy $La_{0.75}Mg_{0.25}Ni_{3.0}Co_{0.5}$ has capacity of 390 mA · h/g and capacity decay is slow during 30 charge/discharge cycles. Zhang et al.[9] investigated that annealing treatment is favorable for improvement of electrochemical property of $La_{1.5}Mg_{0.5}Ni_7$ alloy. Discharge capacities of as-cast and annealed at 1 173 K alloys are 358.2 and 402.5 mA · h/g, respectively. Cycling stability was improved obviously from 47% (as-cast) to 82% (at 1 173 K) after about 150 cycles. Pan et al.[10] prepared $La_{0.67}Mg_{0.33}Ni_{2.5}Co_{0.5}$ alloy annealed at 1 123 K and 1 223 K. Electrochemical results show that, in three alloys(as-cast, 1 123, 1 223 K), discharge capacity of the alloy annealed at 1 123 K is higher, and cycling stability of the alloy annealed at 1 223 K is better, respectively. The above-mentioned results show that appropriate annealing temperature is effective way to improve discharge capacity and cyclic stability of hydrogen storage alloys. In this paper, in order to improve further cyclic stability of the La_3MgNi_{14} alloy, effects of annealing treatment on electrochemical behaviors were investigated systemically.

2 Experimental

La_3MgNi_{14} as-cast alloy was prepared using induction melting in high purity helium with 0.04 MPa. Some of as-cast alloys by sealed under vacuum atmosphere, and in quartz tube were annealed at 1 123, 1 223 and 1 323 K under 0.3 MPa Argon atmospheres for 10 h, respectively. Phase structure of alloys was determined by X-ray diffractometer of D_{MAX}-RB in RigaKu Ltd. Diffraction was performed with $CuK_{\alpha 1}$ radiation filtered by graphite. Experimental parameters for determining phase structure are 150 mA, 40 kV and 8°/min, respectively. Samples thus prepared were etched with a 15 g $FeCl_3$ + 50 ml HCl + 100 ml deionized aqueous solution. Morphologies of the alloys were observed by SEM of Cambridge S-360.

Electrode pellets with 15 mm diameter were prepared by mixing 0.200 g alloy powder(≤74 μm) with Ni carbonyl powder in a mass ratio of 1:4 together, and then pressing under 35 MPa. Electrode pellets were immersed in 6 mol/L KOH solution containing 15 g/L LiOH for 24 h in order to fully wet the electrodes before measurement. Electrode pellet was fixed on terminal line of negative electrode of open tri-electrode cell. Ni $(OH)_2$/NiOOH is positive electrode of experimental cell, Hg/HgO is reference electrode and 6 mol/L KOH solution containing 15 g/L LiOH is electrolyte. Electrochemical performance of the alloy was measured by battery test system of Land-CT2001A. Voltage between negative electrode and reference electrode is defined as discharge voltage. Each electrode was discharged to cut-off potential −0.500 V vs. Hg/HgO reference electrode. Properties of the electrodes were measured with current density of 100 mA/g. High-rate discharge abilities (HRDs) of the alloys were determined at a series of current densities. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves were conducted at 50% depth of discharge (DOD) using PARSTAT 2273 advanced electrochemical system. Before measured, the electrodes were completely activated by charging/discharging cycles. EIS spectra of the electrodes were obtained in frequency range of 10 KHz to 5 MHz with amplitude of 5 mV under open-circuit condition. Environment temperature of measurement was kept at 303 K.

3 Results and discussion

3.1 Property of the electrode

Cycle behaviors of the as-cast and annealed La_3MgNi_{14} alloys are shown in Fig. 1. As can be seen, maximum discharge capacities are 329.1mA · h/g, 347.6 mA · h/g, 360.0 mA · h/g and 383.0 mA · h/g for as-cast alloy, the alloys annealed at 1 123 K, 1 223 K and 1 323 K, respectively. It is also ascertained from Fig. 1 that absolute value of slope of cyclic stability curves of the as-cast and annealed at 1 123, 1 223 and 1 323K alloys is about 1.074, 0.859, 0.619 and 0.534, respectively, suggesting that annealing treatment can enhance cyclic stabilities of the alloys, that is to say, after 250 charging/discharging cycles, capacity retention rate of the alloys is 17.93%, 39.99%, 59.11%, 62.89% for as-cast alloy and annealed alloys at 1 123, 1 223, 1 323 K, respectively.

Charge and discharge potential curves of as-cast and annealed La_3MgNi_{14} alloys at maximum discharge capacity are presented in Fig. 2. From Fig. 2, it can be obtained that discharge potentials of the alloys at 50% depth of discharge (DOD) increase with rising annealing temperature. Potentials of charge/discharge are 0.951 8/0.883 0, 0.944 6/0.897 8, 0.932 8/0.909 3, 0.926 8/0.909 9 V for as-cast alloy, the alloys annealed at 1 123, 1 223 and 1 323 K, respectively. Potential difference of 50% depth of charge (DOC) and 50% depth of discharge (DOD) decrease from 68.6 mV (as-cast) to 16.7 mV (annealing temperature at 1 323 K) with increasing annealing temperature. Discharge efficiency of the alloy electrode, which is denoted by ratio of discharge capacity to charge capacity, is related to potential difference and widths of discharge potential plateaus. The smaller the potential difference is, the wider the discharge potential plateau is, and the more the discharge efficiency is. From Fig. 2, it is also found that widths of discharge potential plateaus of the alloys are ranked in sequence 1 323 K > 1 223 K > 1 123 K > as-cast. Moreover, discharge efficiency of the alloys increase from 73.13% (as-cast) to 85.11% (annealing temperature at 1 323 K) with increasing annealing temperature. Therefore, the results further show that annealing temperature can enhance discharge capacities of the alloys in our experiment.

High rate discharge ability (HRD), which is determined mainly by electrochemical kinetic property of the alloy electrode, is examined and shown in Fig. 3. High rate discharge ability (HRD) is defined as following equation:

$$\mathrm{HRD} = \frac{C_d}{C_{100}} \times 100\% \qquad (1)$$

where C_d is discharge capacity at discharge current density I_d at cut-off potential of −0.500 V vs. Hg/HgO reference electrode, C_{100} is discharge capacity at discharge current density I = 100 mA/g also at cut-off potential of −0.500 V vs. Hg/HgO reference electrode. High-rate discharge ability (HRD) decrease with increasing discharge current density I_d. For example, for the annealed alloy at 1 323 K, high-

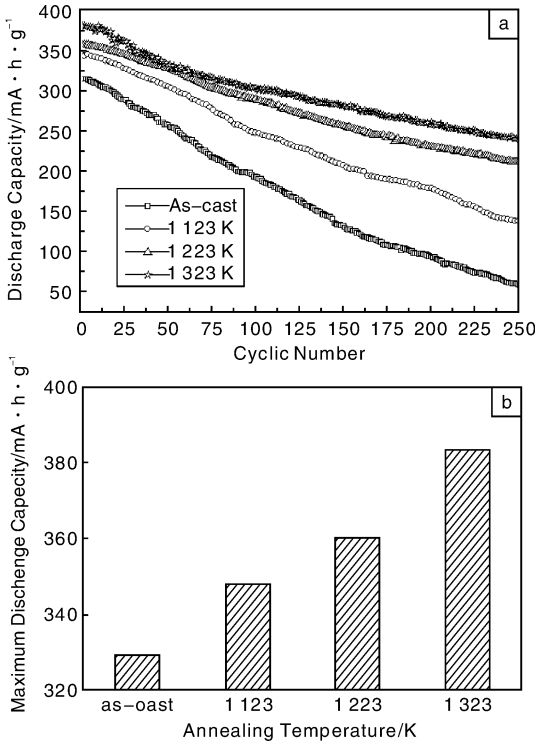

Fig. 1 Cycle behaviors of the as-cast and annealed La_3MgNi_{14} alloys: discharge capacity (a) and maximum discharge capacity (b)

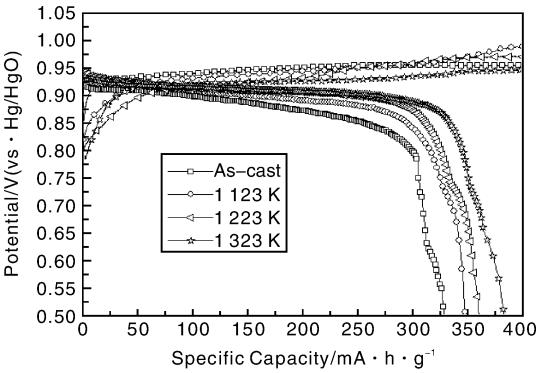

Fig. 2 Charge and discharge potential curves of as-cast and annealed La_3MgNi_{14} alloys at maximum discharge capacity

rate discharge ability (HRD) of the alloy decrease from 94.50% (I_d = 200 mA/g) to 62.50% (I_d = 800 mA/g) with rising current density (Fig. 3). Owing to rising discharge current density, increasing hydrogen atoms diffused to surface of the alloy particles is too late to arise reaction of electron transfer (i.e. Volmer process), as shown in formula (2). Hydrogen gas directly desorbs, i.e. scale of the process of Tafel reaction increase (as shown in formula (3)). Consequently, mechanism of Volmer-Tafel leads to the decrease of discharge capacity of the alloy electrode, and decrease high-rate discharge ability of the alloy.

$$MH_{ads} + OH^- \rightleftharpoons M + H_2O + e \text{ (Volmer reaction)} \quad (2)$$

$$2MH_{ads} \rightleftharpoons H_2 + 2M \text{ (Tafel reaction)} \quad (3)$$

Gradient of curve of high-rate discharge ability reflects sensitivity of high-rate discharge ability and variation of discharge current density. From Fig. 3, it is also found that in 200 ~ 800 mA/g range, high-rate discharge ability of the alloys increase with increasing annealing temperature. Such as 500 mA/g, HRDs of the as-cast and annealed alloys enhance from 56.10% (as-cast) to 62.50% (at 1 323 K) with increasing annealing temperature.

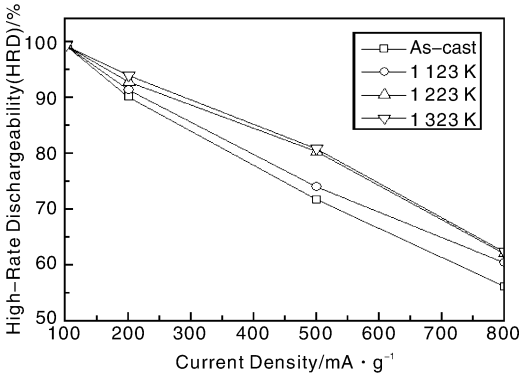

Fig. 3 High-rate discharge abilities (HRDs) of as-cast and annealed alloys

3.2 Discussion of property of the alloy electrode

XRD patterns of the as-cast and annealed La_3MgNi_{14} alloys were exhibited in Fig. 4. As shown in Fig. 4, the as-cast and annealed (at 1 123 K) alloys are compose of $LaNi_5$, $(La, Mg)_2Ni_7$ and a small amount of $LaNi_2$ phases. Phase compositions of the alloys obviously change with rising annealing temperature. There are $LaNi_5$, $(La, Mg)_2Ni_7$ and $(La, Mg)Ni_3$ phases in the annealed alloy at 1 223 K. However, $LaNi_5$ and $(La, Mg)Ni_3$ phases became main phase at 1 323 K. With increasing annealing temperature, relative intensity of $LaNi_5$ phase peak increases because rising annealing temperature benefits formation of $LaNi_5$ phase according to La-Ni phase diagram [11], suggesting that relative amount of $LaNi_5$ phase increase.

Microstructures of as-cast and annealed La_3MgNi_{14} alloys were illustrated in Fig. 5. It should be noted from Fig. 5 that when annealing temperature increase, columnar texture decrease and massive texture increase in the annealed alloy at 1 223 K, massive texture is major in the annealed alloy at 1 323 K. In addition, for La_3MgNi_{14} alloy, isothermal annealing is carried out at the same temperature, there is equal degree of supercooling during cooling. By contrast, composition of the annealed alloys is more homogeneous, grain boundaries are more definite, and grains of the alloys are coarsened.

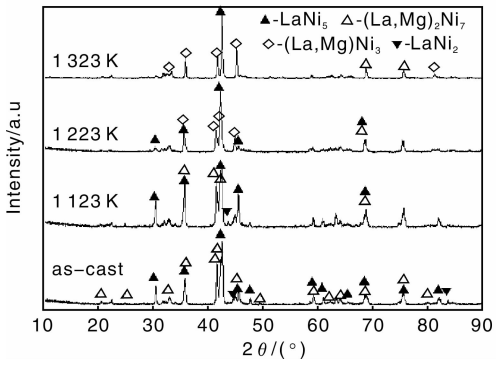

Fig. 4 XRD patterns of the as-cast and annealed La_3MgNi_{14} alloys

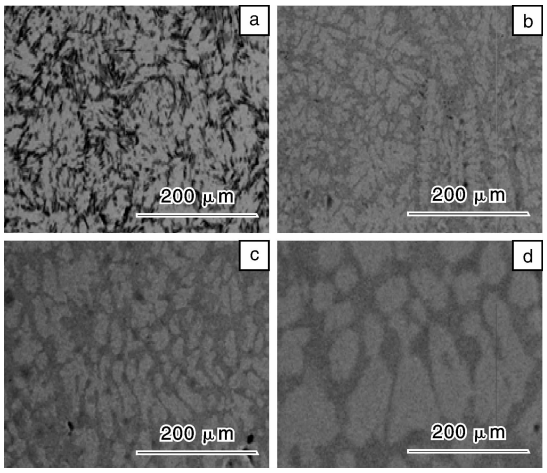

Fig. 5 Microstructure of as-cast and annealed La_3MgNi_{14} alloys (a) as-cast, (b) 1 123 K, (c)1 223 K, and (d)1 323 K

In our experiment, annealing treatment is helpful to enhancing maximum discharge capacity of the alloy, which monotonously increases with increasing annealing temperature. Result is related to phase component. At 1 223 K and 1 323 K, appearance of $(La, Mg)Ni_3$ phase and disappearance of $LaNi_2$ phase are favorable for improving discharge capacity. It can be derived from calculate model of Dunlap et al. [12] that ideal capacity of hydrogen storage (H/M) for La_2Ni_7 phase is 1.17, but that of $LaNi_3$ phase is 1.25[13]. Therefore, the annealed alloys at 1 223 K and 1 323 K have higher discharge capacity. In addition, $LaNi_5$ phase is not only used as hydrogen absorption phase, but also as catalytic phase, and enhances utilization efficiency of hydrogen absorption for $(La, Mg)Ni_3$ or $(La, Mg)_2Ni_7$ phase. Therefore, with increasing annealing temperature, the increase of relative amount of $LaNi_5$ phase is favorable for improving kinetics of hydriding-dehydriding reaction of the alloys, and high-rate discharge ability (HRD) is improved. In addition, annealing treatment can decrease lattice strain and defects and improve the alloy's structure homogenization. These features weaken pulverization and strengthen anti-oxidation/corrosion capabilities during charge/discharge process in KOH/LiOH electrolyte. Owing to occurrence of electrochemical corrosion among grains in alkaline solution, resistance capability of corrosion of coarsened grains better than that of fined grains[14]. Therefore, annealing treatment can enhance cyclic life of the alloy in present work.

It has been reported that electrochemical impedance spectroscopy (EIS) is very useful to analyze kinetics of hydriding-dehydriding reaction of electrodes. Electrochemical impedance spectra of La_3MgNi_{14} alloy electrodes at 50% DOD at 303 K were shown in Fig. 6. Proposed equivalent circuit for the alloy electrode was shown in Fig. 7. Contact resistance (R_f) and charge-transfer reaction resistance (R_{ct}) were obtained by fitting equivalent circuit in Table 1. For all the as-cast and annealed La_3MgNi_{14} alloys, as shown in Fig. 6, at high and medium frequency, plot starts as capacitive loop, respectively, and, as the frequency further decreases, it changes to a straight line. According to result reported by Evgenij et al. [15-16], measured capacitive loop A in high-frequency region is ascribed to resistance and capacitance of current collector and pellet made of alloy powder. While medium-frequency capacitive loop B is considered to be charge-transfer process at electrode/electrolyte interface, as shown in equation:

$$(La_3MgNi_{14})H_{ad} + OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} (La_3MgNi_{14}) + H_2O + e^- \quad (4)$$

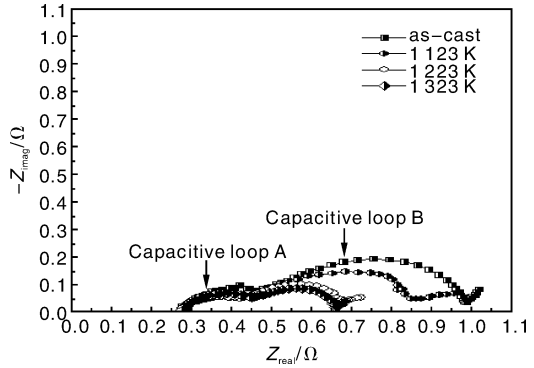

Fig. 6 Electrochemical impedance spectra of the as-cast and annealed alloy electrodes

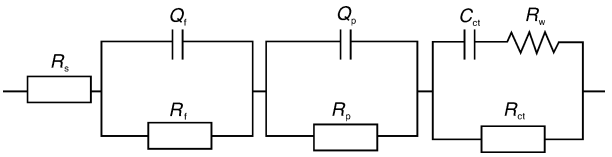

Fig. 7 Proposed equivalent circuit for the alloy electrode

here, in the process of hydrogen releasing reaction, stray capacity and charge-transfer reaction resistance of the electrode are caused by difference of dielectric constant, which is produced by charge-transfer released by $LaNi_5$ and $(La, Mg)_2Ni_7$ or $(La, Mg)Ni_3$ phases of the alloy during hydrogen desorption reaction. It is clearly seen from Table 1 that charge-transfer reaction resistance (R_{ct}) of the alloy electrodes decreases with increasing annealing temperature. Therefore, with increasing annealing temperature, capabilities of hydrogen releasing and number of electrons produced by dehydriding reaction increase in the alloy, and so do electrochemical kinetic characteristics of the alloys, agreeing with HRDs of the alloy electrodes. When frequency is very low, diffusion of hydrogen atom from bulk to surface of the alloy electrode leads to Warburg impedance. Therefore, process of hydrogen desorption of hydride is controlled by electrochemical reaction and hydrogen diffusion.

Table 1 Contact resistance (R_f) and charge-transfer reaction resistance (R_{ct}) of the alloy electrodes

Temperature/K	Contact resistance/mΩ	Charge-transfer reaction resistance/mΩ
as cast	189.9	519.4
1 123	165.5	413.9
1 223	156.9	252.3
1 323	172.6	211.3

4 Conclusions

Effects of annealing treatment on electrochemical properties and structures of La_3MgNi_{14} alloy electrode are studied in this paper. Annealing treatment has important influence on microstructure of the alloys. As-cast and annealed at 1 123 K alloys

are composed of $LaNi_5$, $(La, Mg)_2Ni_7$ and a small amount of $LaNi_2$ phases. Annealing treatment at 1 223K benefit formation of $(La, Mg)Ni_3$ phase. $LaNi_5$ and $(La, Mg)Ni_3$ phases became main phase at 1 323 K. Co MPared by the as-cast alloy, composition of the annealed alloys is more homogeneous, and grains of the annealed alloys are coarsened after annealing treatment.

With rising annealing temperature, maximum discharge capacity of alloy electrodes increase from 329.1 mA·h/g (as-cast) to 383.0 mA·h/g (1 323 K). Cyclic life of the alloy electrodes are all improved after being annealed alloys with more homogeneous composition and coarsened grains. Kinetic properties are improved. In three annealed alloys, discharge capacity and cyclic stability of the annealed alloy at 1 323 K has better than that of others in present work.

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