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Materials

High temperature oxidation behavior of high speed steel for hot rolls material

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Abstract: The oxidation characteristics of high speed steel (HSS) were studied at 500 to 800°C. The non-isothermal oxidation and isothermal oxidation (500, 575, 650, 725, 800°C) of HSS were investigated by thermo-gravimetric analysis (TGA). The microstructure, morphology and oxide scale thickness of the isothermal oxidation samples were analyzed by optical microscope (OM), electron probe micro analyzer (EPMA), X-ray diffraction spectrum (XRD) and scanning electron microscope (SEM). The results indicate that the oxidation rate of HSS is very slow at 500 to 650°C, increasing gradually at 650 to 750°C, and drastically at 750 to 800°C, because the phase transformation happens at about 750°C.

Key words: high speed steel; high temperature oxidation; isothermal oxidation; non-isothermal oxidation; oxide kinetics

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1 Introduction

High speed steel (HSS) has been successfully used for hot rolls in order to make rolled plates posess homogeneous thickness and uniform surface during hot rolling, thereby leading to enhance the surface quality of rolled plates and extend the roll life because of its excellent hardness, wear resistance, and high temperature properties. The use of HSS rolls has resulted in an improvement of the strip surface quality grade up to 20% [1-2]. The carbon content in HSS rolls is generally 1.5%-2.0%, most of which is combined with strong carbide formers such as V, W, Cr, and Mo to form MC, M_2C, M_7C_3, M_6C, and fine carbides inside the matrix, the rest of carbon, about 0.3%-0.6%, keeps inside the matrix, and forms lath-type martensite when the carbon content is below 0.4%, while the plate-type martensite when it is above 0.4% [3]. The working temperature of hot rolls often exceeds 500°C. The thermal cyclic working of rolls in hot metal forming causes a superficial oxidation scale, which plays a major role because a hard oxidation scale may give abrasive behavior whereas a ductile oxidation scale may decrease the friction coefficient as well as the wear. The oxidation resistance must be high enough to avoid the deterioration of the working surface, the oxidation behavior of HSS material has therefore a great importance for the technological properties of hot rolls [4-8].

The purpose of this paper is to investigate the high temperature oxidation behavior of HSS used as hot rolls material at different temperatures and find the oxidation rule in order to control the oxidation scale in the best conditions, which is significant to improve the strip surface quality and extend the roll life.

2 Experimental

The chemical composition (wt%) of HSS in this study is C, 1.5-2.5; Si, 0.2-1.0; Mn, 0.2-1.0; Mo, 0.5-6; Ni, 0.5-1.5; Cr, 0.5-6; V, 0.5-6; W, 0.1-1.0; and Fe, balanced. The roll was produced by centrifugal casting following the usual production route (casting and heat treatment).

The oxidation characteristics of HSS samples were studied at 500 to 800°C. The non-isothermal oxidation and isothermal oxidation of HSS were researched by thermo-gravimetric analysis (TGA, Thermo-gravi Metric Analyzer 7). The microstructure, morphology and oxidation scale thickness of the isothermal oxidation samples were analyzed by optical microscope (Leica-DMRX), electro-probe micro-analyzer (EPMA, JXA-8800RL), X-ray diffraction spectrum (XRD, RIGAKU2500-SSD) using Cu K_a radiation, and scanning electron microscope (SEM, S4200).

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The specimens were taken from the lateral zone of hot rolls. The oxidation tests were carried out by thermo-gravimetric analysis. The sample size is $\phi 8$ mm × 0.25 mm, polished by the 800 grit SiC paper, washed in acetone and kept sealed in an inert (Ar) atmosphere before the test. The kinetics of the degradation process due to oxidation were followed after putting the samples in a thermo-analytical apparatus working in dry air. The non-isothermal oxidation experiment was carried out from 500 to 800°C, and the temperature raise 2.5°C every minute in 2 h. The isothermal oxidation temperatures were 500, 575, 650, 725, and 800°C for up to 2 h. Every sample was firstly oxidized by TGA, and then analyzed by XRD, EPMA, and SEM respectively, and at last broken to observe the thickness of oxidation scale by SEM.

3 Results and discussion

3.1 Microstructure of HSS sample

Figure 1 shows the microstructure and XRD pattern of the HSS sample, which comprises a martensitic matrix and a noticeable volume fraction of primary carbides. The primary carbides are V-rich M_8C_7 and Cr-rich M_7C_3, M_8C_7 carbides inside the cells and M_7C_3 carbides along the cell boundaries are primarily formed. The hardness of M_8C_7 carbides formed inside the cells is considerably high at Hv 2740, while M_7C_3 carbides in the intercellular region is Hv 2380, the primary carbides is about 20wt%.

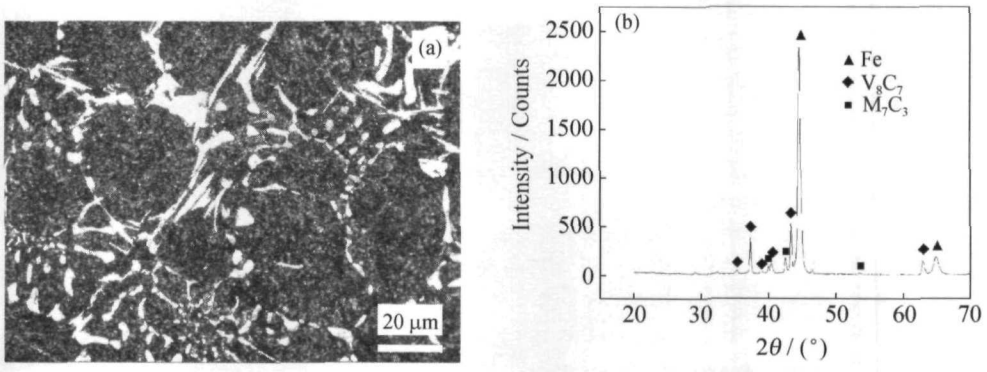

Figure 1 Microstructure (a) and XRD pattern (b) of the HSS sample.

3.2 Oxidation process and kinetics

Figure 2 shows the non-isothermal oxidation curve of the HSS sample from 500 to 800°C in 2 h. It is evident that the oxidation rate of HSS is very slow from 500 to 650°C, increasing gradually from 650 to 750°C and drastically from 750 to 800°C because the phase transformation happens at about 750°C.

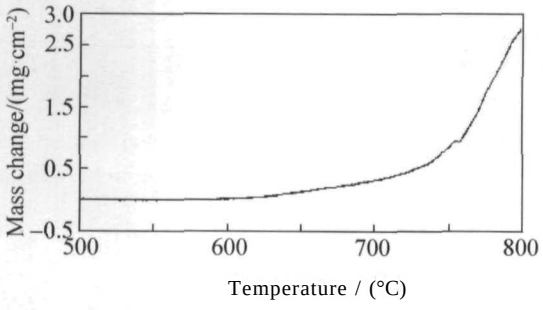

Figure 2 Non-isothermal oxidation curve of the HSS sample.

Figure 3 shows the thermo gravimetric curve of the isothermal oxidation up to 2 h at different temperatures. It is obvious that the oxidation increases with the increasing of temperature as expected. The oxidation rate of HSS is very slow at 500°C, as well as at 575°C, because the oxidation temperature is very low for the HSS containing a lot of oxidation resistance elements such as Cr, W, Mo, and the oxidation scale formed on the surface prevents the oxidation process. At 650°C the sample follows an oxidation kinetics with a parabolic trend, and the high temperature parabolic oxidation indicates that the thermal diffusion of ions is controlling the rate of the oxidation process, such a process may be therefore connected with a uniform diffusion of the reactants through a growing compact scale. At 725 and 800°C, the oxidation curves are close to be linear because it is commonly accepted that the reaction mechanism is the result of the electrical transport of electrons or ions across the oxide scale at very high temperature.

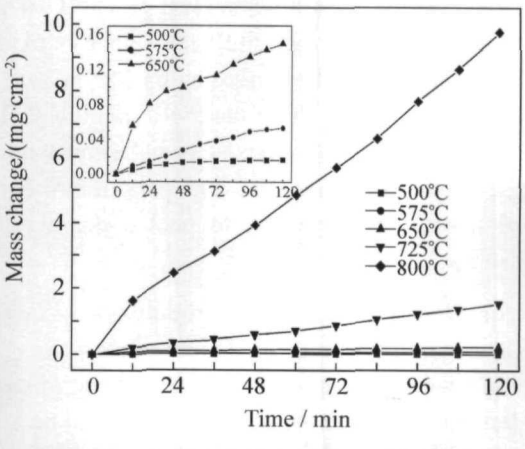

Figure 3 Isothermal oxidation curves of HSS samples at different temperatures.

3.3 Characterization of oxidation scale

Figure 4 shows the XRD patterns of the isothermal oxidation samples. It is obvious that at 500, 575 and 650°C only Fe and hematite (Fe_2O_3) are revealed, hematite and magnetite (Fe_3O_4) are revealed at 725°C, whilst only hematite is detected at 800°C by XRD.

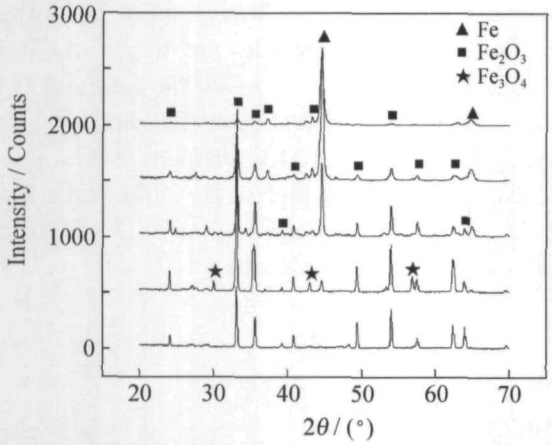

Figure 4 XRD patterns of isothermal oxidation samples, (a) 500; (b) 575; (c) 650; (d) 725; (e) 800°C.

Figure 5(a) shows the SEM morphology of the isothermal oxidation sample at 575°C. Figures 5(b) and (c) are the EPMA patterns. It is V-rich oxide in area A and Cr-rich oxide in area B, which shows that at this condition the matrix is oxidized evenly and the V-rich carbides are oxidized more deeply than the matrix, but the Cr-rich carbides are hardly oxidized. Selective oxidation happens by reason of the difference of oxidation resistance of alloy elements.

Figure 6 shows the SEM micrographs of the isothermal oxidation samples at different temperatures. It can be seen that the selective oxidation happens at 500, 575 and 650°C (figures 6(a)-(c)). Only the matrix and the V-rich carbides are oxidized, but the Cr-rich carbides are hardly oxidized. With the increasing of oxidation temperature, the Cr-rich carbides are also covered by the oxidation scale. The oxidation scale of the sample surface is loose and uneven at 725°C (figure 6(d)), and at 800°C (figure 6(e)) the selective oxidation can not be seen because the oxidation rate increases drastically. At this time the oxidation scale is thicker than others, and cracks can be seen obviously because of the thermal stress and growth stress. The oxidation scale is very easy to peel under a rolling shear stress.

Figure 7 shows the SEM micrographs of oxidation scale sections at different oxidation temperatures. The scale thickness increases with the increasing of oxidation temperature. The oxidation scale thickness are about 0.25, 0.5, 2, 10, and 20 μm at 500, 575, 650, 725, and 800°C, respectively. The oxidation scale is compact and even at 500, 575, and 650°C, so the oxidation scale should be adhesive. The oxidation scale is loose and uneven at 725°C, so the oxidation scale should be slight adhesive. At 800°C the oxidation scale is very thicker, and there are a lot of caves under the oxidation scale, so the oxidation scale is very easy to peel. As the sections of samples were obtained by breaking the oxidation samples, the adhesive capability of oxidation scale can not be completely manifested for the effect of outer force.

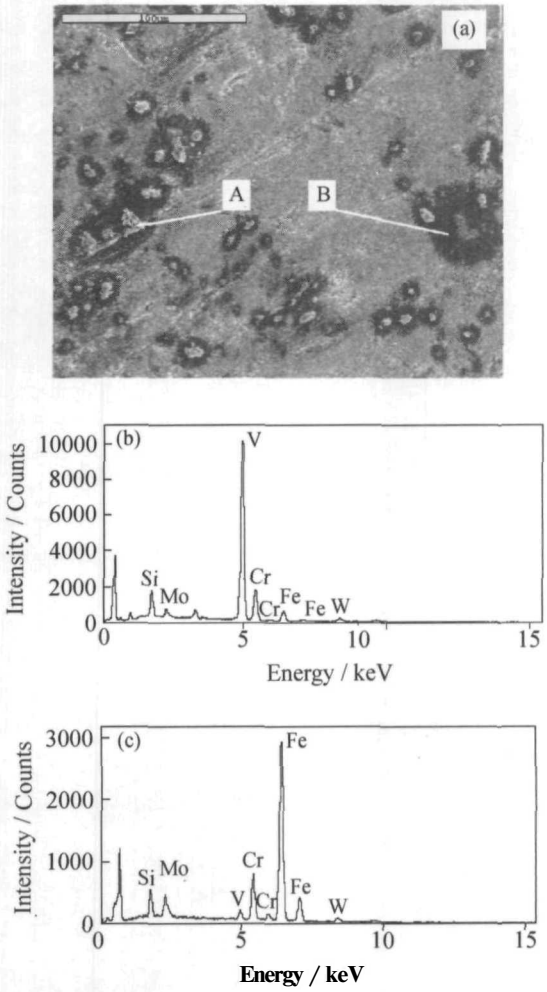

Figure 5 SEM morphology of the isothermal oxidation sample at 575°C (a), the EPM A pattern in area A (b) and the EPMA pattern in area B (c).

The oxidation behavior of pure Fe in the air or oxygen has been systematically analyzed. Above 700°C, the typical microstructure of oxidation scale are made up of the outer Fe_2O_3 (hematite) layer, middle Fe_3O_4 (magnetite) layer and inner FeO (wustite) layer. Between 700 and 1250°C, the proportion of the three layers is about 1:4:95. Between 580 and 650°C, the thickness of the outer and middle layers slightly increase, but FeO is also dominating. Below 570°C, FeO is unstable, the oxidation scale is mainly made up of other two layers, the layer of Fe_3O_4 is about 80%, and the microstructure is slightly different with the

oxidation time and other conditions changing [9]. HSS contains many oxidation resistance elements, so the oxidation rule is slightly different with pure Fe.

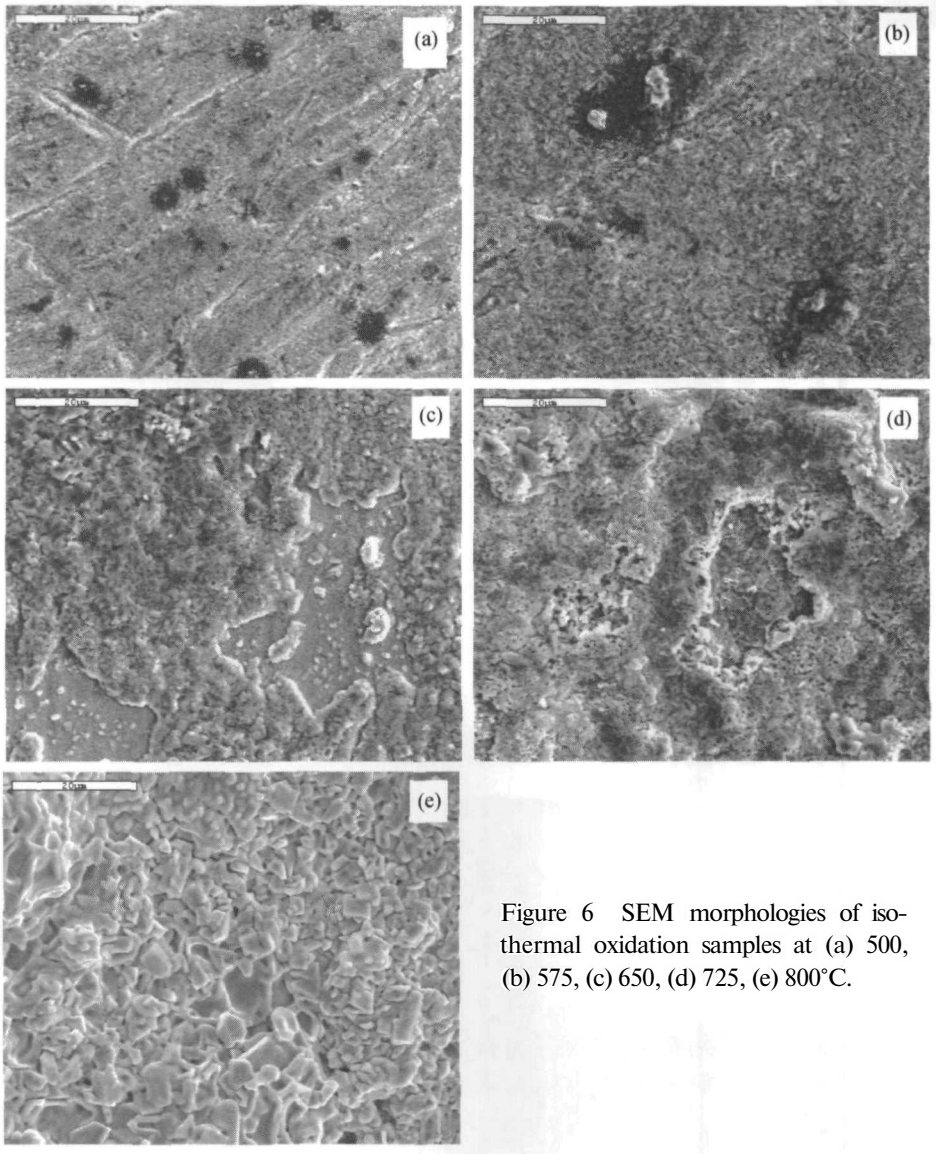

Figure 6 SEM morphologies of isothermal oxidation samples at (a) 500, (b) 575, (c) 650, (d) 725, (e) 800°C.

According to the basis of above results, it is possible to interpret the oxidation mechanism of HSS. Oxidation nucleates first at the carbide-matrix interface due to the high free energy content. Because of the high thermal stability and low oxidation rate of the Cr-rich carbides, at the beginning the oxide grows mainly on the metal matrix and the V-rich carbides, giving rise to an uneven oxidation scale. With the oxidation temperature increasing, the oxidation scale tends to cover the whole surface, but it maintains the irregular morphology at high oxidation temperature. The growth of the oxidation scale occurs in the following steps: in the first step, the outer a-hematite layer is very thin and the in-diffusion of oxygen ions can support the development of the internal Fe_3O_4, at the same time the out-diffusion of iron ions supports the growth of the outer α-hematite layer. When the oxidation scale reaches a given thickness, the γ-hematite starts to form at the interface between the a-hematite and Fe_3O_4. The equilibrium between the fluxes of oxygen and iron ions determines the oxidation kinetics, which must obey the Arrhenius rule [10]: $K_P=Ae^{-Q/RT}$, where K_p is the oxidation rate, A the constant, T the temperature, and Q the reaction activation energy. On the basis of this, the higher the temperature, the faster the oxidation rate, and the thicker the oxidation scale, which is obvious in figure 7. At low temperature, the oxidation scale is compact and adhesive, but at high temperature, the oxidation scale loses the adhesive and has obvious cracks because of the thermal stress and growth stress. This oxidation scale loses shearing resistance, peeling will be the consequence under the mechanical stress and thermal cyclic stress in hot rolling.

According to the analysis, the working temperature of HSS rolls should be controlled under 650°C, here the oxidation scale is compact, even and adhesive, which can obviously improve the strip surface quality

and extend the roll life. The working temperature of HSS rolls should be controlled as low as possible, so it is critical to optimize the roll-cooling water under a satisfied finishing rolling temperature.

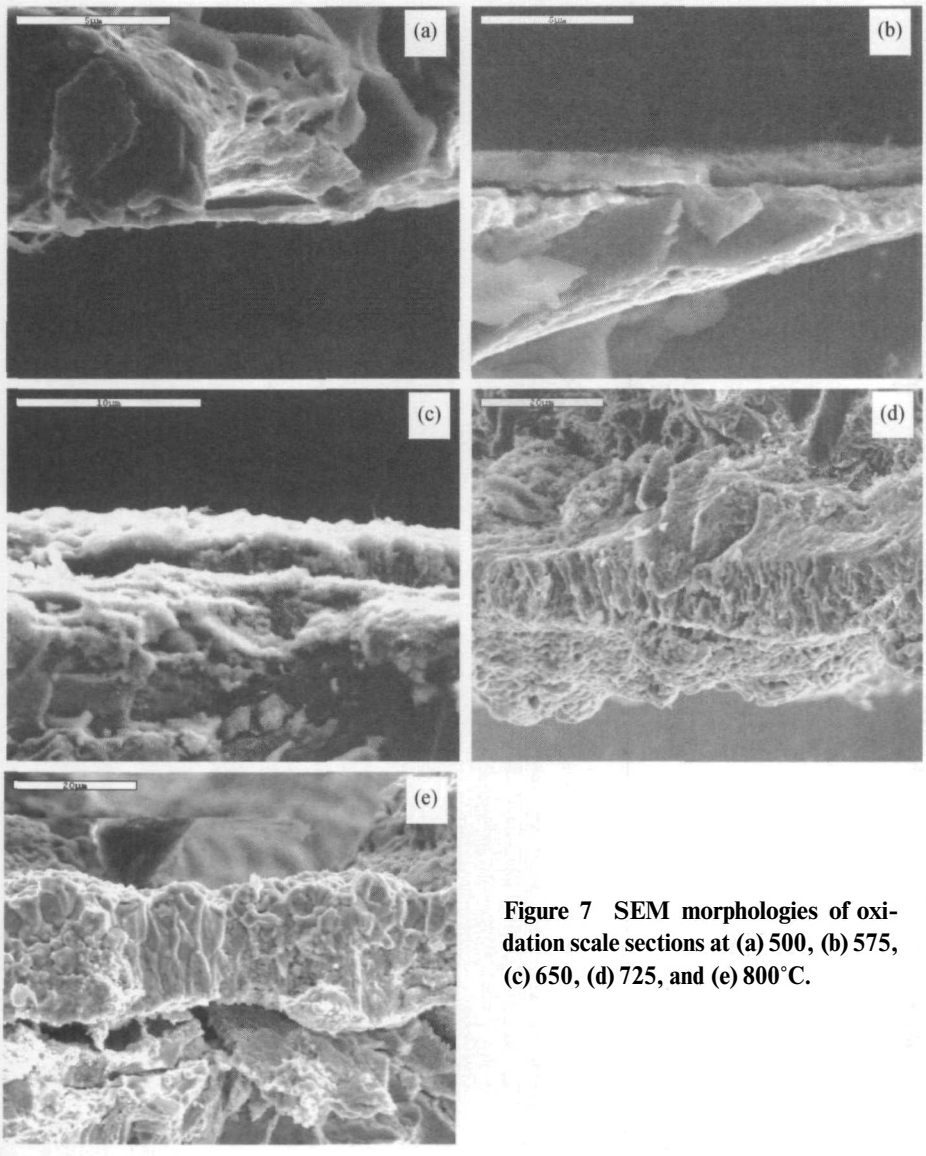

Figure 7 SEM morphologies of oxidation scale sections at (a) 500, (b) 575, (c) 650, (d) 725, and (e) 800°C.

4 Conclusions

(1) The oxidation rate of HSS is very slow from 500 to 650°C, increasing gradually from 650 to 750°C and drastically from 750 to 800°C because the phase transformation happens at about 750°C. The thickness of the oxidation scale increases with the increasing of the oxidation temperature, and the thickness are about 0.25, 0.5, 2, 10, and 20 μm at 500, 575, 650, 725, and 800°C, respectively. The oxidation scale is thinner and has better adhesive at low oxidation temperature than that at high oxidation temperature.

(2) Only Fe and hematite (Fe_2O_3) are revealed at 500, 575 and 650°C by XRD, hematite and magnetite (Fe_3O_4) are revealed at 725°C, whilst only hematite is detected on the oxidized surface at 800°C.

(3) The selective oxidation happens at low oxidation temperatures. The Cr-rich carbides have better oxidation resistance than the V-rich carbides and the matrix. The V-rich carbides are oxidized more deeply than the matrix. The selective oxidation disappears at high oxidation temperature.

(4) The working temperature of HSS rolls should be controlled as low as possible, at least below 650°C.

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