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Isothermal Oxidation Of Fe-Mn-Al-C-Cr-Si-Mo And Fe-9Cr-Mo Alloys

J. D. Betancur-Ríos[1], C. J. Wang[2], G. A. Pérez Alcazar[1], J. A. Tabares[1]

[1]*Departamento de Física, Universidad del Valle, A. A. 25360, Cali-Colombia*
[2] *Department of Mechanical Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 106, Taiwan, ROC*

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Resumen

En este trabajo se estudia la oxidación isotérmica de las aleaciones Fe-Mn-Al-C-Cr-Mo-Si (Mo(1)) y Fe-Mn-Al-C-Cr-Si (Mo(0)) en comparación con la aleación comercial Fe-9Cr-1Mo (FCR). Las oxidaciones se ejecutaron a 600, 700, 750 y 850 ^{o}C, durante 72 horas, en aire estático. Se utilizó un analizador termogravimétrico (TGA) para medir la cinética de oxidación. Para caracterizar la capa de óxido se utilizaron difracción de rayos X (DRX) y espectrometría de energía dispersa (EDS). Los resultados TGA muestran que para todas las temperaturas de oxidación la muestra FCR exhibe la menor cinética de oxidación al igual que la menor ganancia en peso, mientras que la muestra Mo(1) exhibe las más elevadas, mostrando que la adición de Mo tiene un efecto importante. Los productos de oxidación encontrados por DRX y EDS en la parte externa de la capa de óxido fueron $(Mn, Fe)_2O_3$ para las muestras Mo(0,1) y Fe_2O_3 para la muestra FCR. En la parte interna de la capa de corrosión se encontró $Mn(Fe, Al)_2O_4$ y $(Fe, Cr)_2O_3$, para las aleaciones Mo(0,1) y FCR, respectivamente. Se discute la contribución de la adición de Mo en el mecanismo de oxidación.

Palabras claves: alta temperatura, Corrosión; Aleación Fe-Mn-Al-C; Aleación Fe-9Cr-1

Abstract

The aim of this paper is to investigate the oxidation behavior of Fe-Mn-Al-C-Cr-Mo-Si (Mo(1)) and Fe-Mn-Al-C-Cr-Mo-Si (Mo(0)) alloys and compare it against Fe-9Cr-Mo (FCR)commercial alloy. The experiments were carried out at 600, 700, 750 and 850 ^{o}C, during 72 hours in static air. The oxidation kinetics was measured using a Thermogravimetry Analyzer. In order to characterize the oxide scale, X-ray diffraction (XRD) and Energy Disperse Spectrometry it were used. TGA results show that at all temperatures the sample FCR exhibits the lowest kinetic corrosion and the lowest weight gain, whereas Mo(0) the highest, showing an important effect of Mo addition in Mo(1) alloy. The oxidation products found by XRD and EDS were $(Mn, Fe)_2O_3$ in Mo(0) and Mo(1) and Fe_2O_3 in FCR samples corresponding to the external layer. In the internal part $Mn(Fe, Al)_2O_4$ and Fe_2O_3 species were found for Mo(0,1) and FCR alloys, respectively. The roll of the Mo addition on the oxidation mechanism is discussed.

Key Words: High Temperature Corrosion; Fe-Mn-Al-C alloy; Fe-9Cr-1Mo alloy

1. Introduction

The alloys based on the Fe-Mn-Al system are good candidates to replace the conventional stainless steel, which are based on the ternary alloy Fe-Ni-Cr. The Fe-Mn-Al system offers the possibility to replace strategic elements as Ni and Cr by others lighter and cheaper as Mn and Al. In addition, it has attractive mechanical and corrosion resistance properties. Al stabilizes the ferritic phase and gives the stainless character, due mainly it produces a passivating layer of Al_2O_3 on the surface of the metal; and Mn stabilizes the austenitic phase, essential to get good mechanical properties at several temperature [1-5]. It had been reported that the optimal weight composition for which the Fe-Mn-Al-C system will present good properties is 25-30 % Mn, 8-10% Al and near 1 % C. Moreover, the addition of chromium has the tendency to form carbides to hindered carbon diffusion and causes a slowing down the oxidation kinetics. The Cr addition also improves the oxidation resistance, producing a protective Cr_2O_3 layer near to the metal substrate [3, 4]. Wang and Lins [4-6] pointed out that the addition of silicon into the Fe-Mn-Al-C alloy improves their oxidation resistance, because of it forms a protective passive film. By other hand, an important material for use on high temperature applications, for example on super heater tubes in a power plant, is the Fe-9Cr-Mo (FCR) alloy. The pipes that are used in pressurized water reactors to transport the steam from boiler to turbines are fabricated in according to international standards with Fe-9Cr-Mo stainless steel due to its good corrosion properties at high temperatures [7]. We used this alloy as a commercial product to compare the TGA results. We are expecting that the oxidation behaviour must be parabolic, in according to $x = kpt^n$, where x is the weight gain obtained by TGA measurement and t is the time in hours. When $n = 0.5$, we have a completely parabolic oxidation growth law. From the slope of TGA curves is possible to obtain the n coefficient. The aim of this work is to study the oxidation kinetics of Fe-Mn-Al-C-Cr-Si-Mo and Fe-Mn-Al-C-Cr-Si alloys in the temperature range of 600-850 ^{o}C, in static air, for 72 hours, and compare the results to study the effect of Mo addition.

2. Experimental procedure

The chemical compositions of the studied alloys in this work are Fe-27.3Mn-7.6Al-1.0C-6.5Cr-0.25Si-0.88Mo and Fe-27.3Mn-7.6Al-1.0C-6.5Cr-0.25Si, named as Mo(1) and Mo(0), respectively. They were prepared from high purity materials and then melted in an argon-shielded induction furnace. The ingots were forged at 1100 ^{o}C, homogenized at 1100 ^{o}C for 11 hours and laminated until 2.5 mm thickness. The alloys were then cut at the size of 15 mm × 12 mm × 2 mm with a water-cooled cutting machine and then annealing at 1100 ^{o}C for one hour in a tubular furnace with an argon flux, and fast tempering was done in air at room temperature. Later, the alloys were ground through 100 to 600 grit SiC paper to remove any tarnish film and depleted zones. Finally, they were ultrasonically cleaned in an acetone bath and dried in air before their use. Then, the alloys were oxidized at 600, 700, 750 and 850 ^{o}C in static air during 72 hours. Continuous mass change measurements were carried out by a Pyris 6 Thermogravimetric Analyzer (TGA) from PerkinElmer. The corrosion products were analyzed by X-ray diffraction, using monochromatic Cu-Kα radiation in a Rigaku Dmax B difractometer. To fit the diffraction pattern it was used the MAUD program (http://www.ing.unitn.it/). To characterize the cross section scales a JEOL JSM 6500-F scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) attachment to the SEM were used.

3. Results and Discussion

Fig. 1 shows the weight change-time curves of all alloys oxidized at 600, 700, 750 and 850 ^{o}C, respectively. For all temperatures, the highest weight gain was exhibited by Mo(0) specimen. The Mo(0) and Mo(1) alloys not fluctuates with the temperature increase, in which the lowest value appears at 600 ^{o}C.

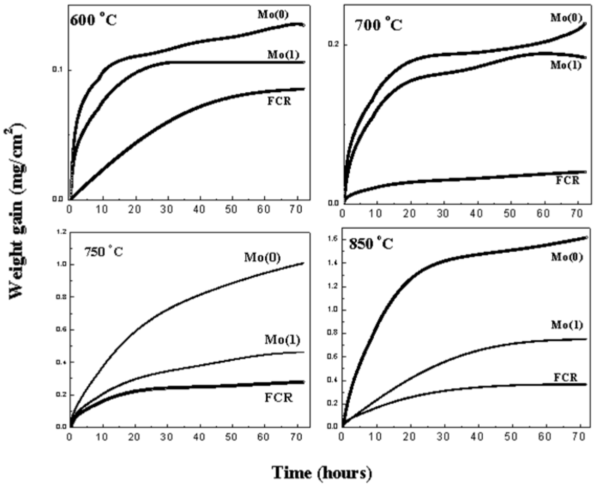

Fig. 1 Thermogravimetric curves of oxidized alloys in static air during 72 hours

A large increase of the oxidation kinetics at temperatures above 700 ^{o}C is clearly observed, but the highest increase occurs at 850 ^{o}C. At 750 ^{o}C, Mo(0) sample exhibit two sub-parabolic behaviors, the first around 20 hours ($n = 0.35$) and the second around 60 hours ($n = 0.15$). For Mo(1), the observed curves are very similar, but in the first part the oxidation kinetics is close to parabolic (n= 0.60) and the final looks sub-parabolic ($n = 0.20$). At 750 ^{o}C, all alloys also exhibit two different parabolic behaviors and the oxidation rate increases continuously. Again, Mo(1) alloy show the lowest weight gain compared with Mo(0) alloy. However, the difference between both parabolic behaviors is small ($n = 0.65$ for Mo(0) and n = 0.54 for Mo(1)). At 850 ^{o}C, all samples exhibit two different close-parabolic behaviors ($n = 0.71$ for Mo(0) and n = 0.86 for Mo(1)). At around 25 hours of exposure a change in the oxidation kinetics is observed in all alloys. It can be observed in Mo(1) alloy that until 10 hours the oxidation kinetics at 750 and 850 ^{o}C are similar. However after this time the oxidation at highest temperature increases continuously for Mo(0) alloy and for times longer than 58 hours it reaches a constant level, after which the weight gain becomes negligible. In contrast, the weight gain of the Mo(0) alloy continuously increases at highest temperatures. At all temperatures, FRC specimen exhibits the lowest weight gain and kinetics oxidation rate. It was also observed two parabolic regions: first region indicates a fast initial oxidation process and the second is related with steady state and diffusion control, in according to obtained values closest to $n = 0.5$. Thus, if a comparison between the results of Mo(0) and Mo(1) samples is made, it is clearly noticed that Mo addition has an important effect to reduce the oxidation process.

The XRD patterns of sample Mo(0) oxidized at high temperatures are showed in Fig. 2. At 600 °C were found the solid solution (Fe, Mn)$_2$O$_3$, the spinels MnAl$_2$O$_4$ and MnFe$_2$O$_4$ and the γ-Fe and α-Fe phases. At 700 °C, the Mn$_3$O$_4$ phase appears, the spinel MnAl$_2$O$_4$ is not detected and the remaining phases are the same that at 600 °C.

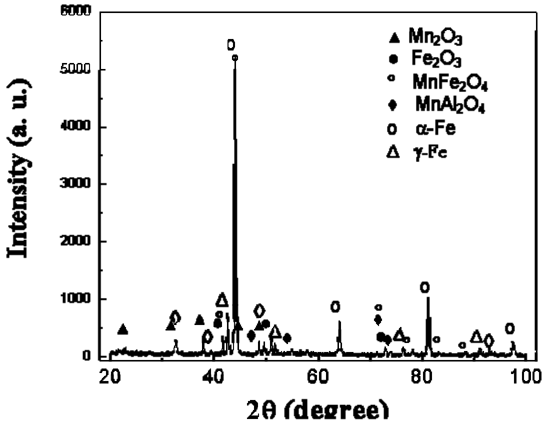

Fig.2(a) X-ray patterns of Mo(0) alloy at 600 °C

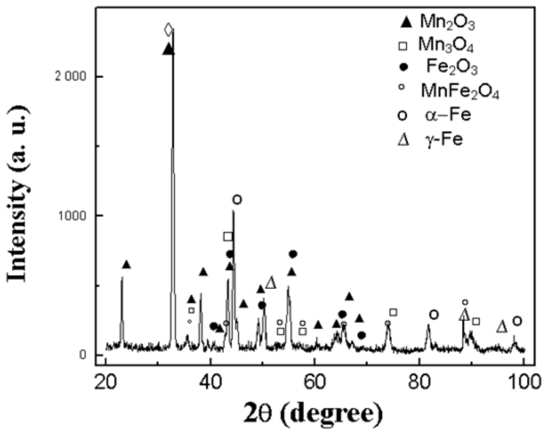

Fig.2(b) X-ray patterns of Mo(0) alloy at 700 °C

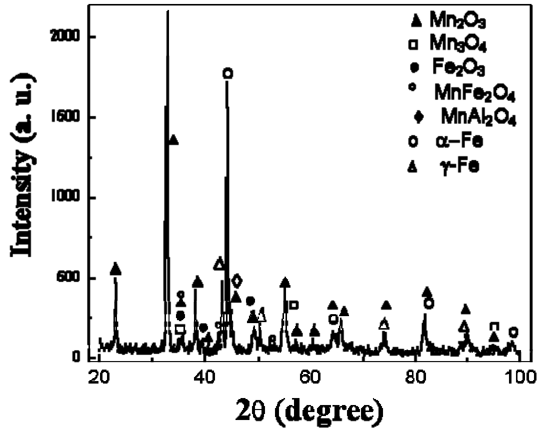

Fig.2(c) X-ray patterns of Mo(0) alloy at 750 °C

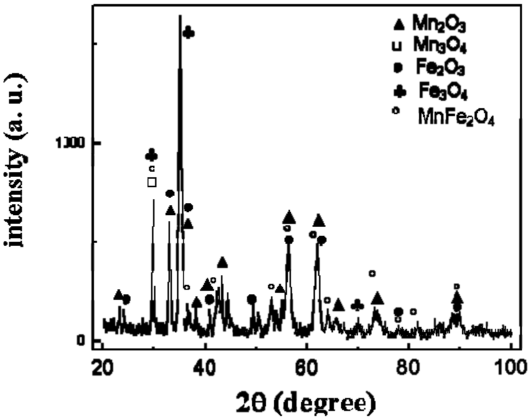

Fig.2(d) X-ray patterns of Mo(0) alloy at 850 °C

At 750 °C Fe$_2$O$_3$ is not detected and those detected are Mn$_2$O$_3$, Mn$_3$O$_4$, the spinel MnFe$_2$O$_4$, γ-Fe and α-Fe. At 850 °C, XRD shows (Fe, Mn)$_2$O$_3$ and (Fe, Mn)$_3$O$_4$ solid solution and Fe$_2$O$_3$ as a principal Bragg reflections. At this temperature, it is also possible to distinguish small peaks of Mn$_3$O$_4$. The XRD pattern of the Mo(1) (not showed here) oxidized at 600 ˚C exhibit the same phases of the Mo(0) sample at this temperature. At 750 and 750 ˚C were observed MnAl$_2$O$_4$ and MnFe$_2$O$_4$ spinels, Mn$_3$O$_4$, γ-Fe and α-Fe phases, very similar to those obtained for Mo(0) specimen. At 850 °C, XRD shows Mn$_2$O$_3$, Fe$_2$O$_3$, probably (Fe, Mn)$_2$O$_3$ solid solution and MnFe$_2$O$_4$ as the principal Bragg reflections. It is also possible to distinguish small peaks of Mn$_3$O$_4$ oxide. In addition, the peaks are finer than in the Mo(0) oxidized alloy at the same temperature. By EDS analysis Mn$_2$O$_3$ and Fe$_2$O$_3$ in cubic solid solution as an external layer were found; in the inner layer they were found FeMn$_2$O$_4$ and MnAl$_2$O$_4$ species, respectively.

For FCR alloy they were found Fe$_2$O$_3$ as external layer and (Fe, Cr)$_2$O$_3$ as inner layer, respectively. For the Mo(0) and Mo(1) samples the α-Fe corresponds to the formation of a ferrite layer, maybe due to consumption of Mn and Al from the matrix alloy during oxidation procedure [3-6]. Although FCR alloy exhibit the lowest weight gain, it was observed by visual inspection that FCR alloy looks so damaged at 850 °C.

4 Conclusions

The results obtained in this work show that the mechanism that control the oxidation of the Mo(0) and the Mo(1) alloys was similar, although the addition of Mo to Fe-Mn-Al-C-Cr-Si decreased the oxidation rate but mantaining similar scale structure. Exposure to high temperatures brings the formation of molybdenum oxides such as MoO$_2$ and MoO$_3$. These oxides eventually diffused outward thought into the grain boundaries and formed a protective barrier to the oxidation process, such that it retards the outward diffusion of metallic cations on Fe-Mn-Al-C system. Other point is that the Mo hindered the formation of CO and/or CO_2, which at high-temperature degrade the adherence and the dense of oxide scale. As results, if the carbon in alloy is "free" or "solute" carbon, the formed oxidation scale will be breakaway and increase the oxidation rate.

Acknowledgements

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