High-Temperature Oxidation of Fe-12Cr-0.3C-4Mn-(13-15)Cu Composite Alloys

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Abstract: Alloys of Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu (wt%) were cast using an induction furnace. They were structurally heterogeneous composites that consisted of a relatively stiff α -Fe matrix and a soft (Cu, Mn)-rich secondary phase. They were developed as self-lubricating, wear-resistant metals. Since the formation of oxides plays an important role in wear, understanding the oxidation behavior of two-phase, multi-component composites is of practical interest. This study was undertaken to understand the effect of varying Cu concentration on the formation of oxide scales. When the concentration of Cu in the alloys was increased to 13, 14, and 15 wt%, the volume fraction of the secondary phase also increased from 10.3, 11.2, and 13.3 vol%. When oxidized at 700 °C for 30 h, the secondary phase preferentially oxidized to oxide nodules due to Cu and Mn, which could not form a protective scale. The matrix was uniformly oxidized, forming a thin surface scale, due mainly to oxidation-resistant Cr in the matrix. When oxidized at 800-900 °C for 30 h, not only the secondary phase but also the α -Fe matrix oxidized rapidly, because of the increased reaction and diffusion rates, resulting in the formation of thick, bi-layered oxide scales. An Fe-rich outer scale was formed by the outward diffusion of Fe, Cr, Mn, and Cu, while a Cr-rich inner scale was formed by the inward diffusion of oxygen. Mn and Cu were rather uniformly distributed in the outer and inner oxide scales. The oxidation rates increased with increasing amounts of Cu, and significantly more with increasing temperature.

(Received April 18, 2019; Accepted June 28, 2019)

Keywords: composite, alloy steel, copper, oxidation, oxidation scale

1. INTRODUCTION

Self-lubricating metals are used in bearings, automotive components, pumps, motors, drilling and grinding machines because they provide economical, ecological benefits and allow simplified designs [1,2]. They do not require oil or grease because the lubricants are already incorporated in the metals, which means they are lubricated for their lifetime. They are maintenance-free, and ideally suited for use in difficult working environments, high temperature applications, etc. In one type, strong cast bronze is embedded with a solid lubricant in the form of powdered graphite [3]. However, bronze consists primarily of costly Cu combined with 12-12.5% Sn. In order to replace bronze with more cost-effective

metals, and produce self-lubricating metals that can be employed in heavy load, low speed, and high-temperature applications, Fe-based cast self-lubricating composites, consisting of a relatively stiff matrix and soft secondary phase, have been introduced [4,5]. One example is cast composite alloys of Fe-12%Cr-0.3%C-4%Mn-(13-15)%Cu, which are comprised of an iron matrix with Cu-rich secondary particles [6,7]. By increasing the Cu concentration, the volume fraction of the Cu-rich secondary particles, and overall wear resistance are increased. Protective tribofilms consisting of CuO, Cu₂O, Fe₂O₃ and Fe₃O₄ are formed during dry sliding wear.

Wear inevitably occurs with oxidation, so controlling oxides is important in efforts to obtain low wear rates and friction coefficients [8,9]. Because most engineering alloys are multi-phase, it is of practical interest to determine how two-phase, multi-component composites oxidize at high temperatures.

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Table 1. Chemical compositions of Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys (wt%)

Nominal composition	Fe	Cr	C	Mn	Cu
Fe-12Cr-0.3C-4Mn-13Cu	Bal.	12.21	0.281	4.212	12.89
Fe-12Cr-0.3C-4Mn-14Cu	Bal.	11.89	0.288	4.132	13.78
Fe-12Cr-0.3C-4Mn-15Cu	Bal.	12.41	0.279	4.038	14.84

Accordingly, this study examined the oxidation behavior of Fe-12%Cr-0.3%C-4%Mn-(13-15)%Cu cast composite alloys at high temperatures. The volume fraction of Cu-rich phases, the oxidation kinetics, and the morphology of the oxide scales are discussed as a function of the Cu concentration.

2. EXPERIMENTAL

Lumps of electrolytic Fe, Cr, Mn, and oxygen-free high thermal conductivity (OFHC) Cu, and graphite powder were melted in an alumina crucible using an induction furnace at a frequency of 24 kHz in an argon atmosphere, and were then poured into a water cooled copper mold to prepare Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu composite alloys. Table 1 lists the compositions that were analyzed using an optical emission spectrometer. The prepared alloys were cut into coupons $5 \times 10 \times 10 \text{ mm}^3$ in size, ground to a 1000 grit SiC finish, degreased with acetone and alcohol, and oxidized at 700, 800, and 900 °C in atmospheric air for 5-50 h using a thermogravimetric analyzer. They were inspected by an optical microscope, a field-emission scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), an electron probe microanalyzer (EPMA), a high-power X-ray diffractometer (XRD) with Cu-K α radiation at 40 kV and 100 mA, and an X-ray photoelectron spectrometer (XPS).

3. RESULTS AND DISCUSSION

The optical microstructures of the Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys are shown in Fig. 1. Round secondary particles of various sizes are randomly distributed in the α -Fe matrix. Their average volume fractions, which were evaluated using an image analyzer, were 10.3, 11.2, and 13.3 vol% for 13Cu, 14Cu and 15Cu alloys, respectively. In the 13Cu alloy, the average concentration of the matrix was 70.1Fe-14.9Cr-3.7Mn-11.3Cu (at%), while that of the

Fig. 1. Optical microstructures of (a) Fe-12Cr-0.3C-4Mn-13Cu, (b) Fe-12Cr-0.3C-4Mn-14Cu, and (c) Fe-12Cr-0.3C-4Mn-15Cu alloys.

secondary phase was 84.5Cu-9.9Mn-4.7Fe-0.9Cr (at%), according to the SEM/EDS analysis. The results indicated that the matrix and secondary phase were (Fe, Cr)- and (Cu, Mn)-rich, respectively.

The oxidation kinetics of Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys are depicted in Fig. 2. At 700 °C, the (13, 14)Cu alloys oxidized quite slowly, while the 15Cu alloy suffered

Fig. 2. Weight gain versus oxidation time curves of Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys at (a) 700 °C, (b) 800 °C, and (c) 900 °C

breakaway oxidation after 7 h. At 800 °C, after the initial incubation period all the alloys oxidized rapidly with large weight gains. At 900 °C, they oxidized excessively fast, displaying negligible oxidation resistance. Clearly, the alloys oxidized progressively faster with increasing oxidation temperature and Cu concentration. Of these, the effect of temperature was larger than that of Cu content.

The Ellingham diagram of oxides that can form on Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys is shown in Fig. 3 [10]. Oxide stability increases in the order of Cu_2O , FeO , Cr_2O_3 , and MnO . The secondary phase was rich in both the most noble Cu and the most active Mn, while the matrix was rich in Fe and Cr, both of which have intermediate oxygen affinities in their standard state.

From the oxidation curves displayed in Fig. 2, the

Fig. 3. Ellingham diagram of the oxides of Fe, Cr, Mn, and Cu [10]

Fig. 4. Arrhenius plot of the parabolic rate constants for the growth of oxides of Fe [11], Cr [11], Mn [12,13], and Cu [14,15]. Superimposed are k_p values of Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys at 700, 800, and 900 °C

parabolic rate constants, k_p , of Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys were obtained using the equation, $\Delta W^2 = k_p \cdot t$, where ΔW is the weight gain per unit area and t is the oxidation time. The Arrhenius plot shown in Fig. 4 indicates that the Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys oxidized at almost similar rates at each temperature, and their oxidation rates increased sharply when the temperature increased from 700 to 800 °C. The k_p value of the 15Cu alloy at 700 °C was evaluated for a period of 0-7 h, while all other values were evaluated for the entire oxidation period. The k_p values of the pure metals decreased in the order of Fe [11], Mn [12,13] or

Cu [14,15], and Cr [11]. The k_p values of the Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys were located between those of Fe and Cr (Fig. 4).

On the other hand, the deviation from stoichiometry, defined by δ , ranges between 0.04-0.17 for $\text{Fe}_{1-\delta}\text{O}$ [11,16], 0-0.06 for $\text{Cu}_{2-\delta}\text{O}$ [16], and 0-0.15 for $\text{Mn}_{1-\delta}\text{O}$ [16,17]. With such cation-vacancy concentrations, the mobilities of cations are high, resulting in the fast oxidation of Fe, Mn, and Cu compared to Cr, which forms highly stoichiometric Cr_2O_3 . The oxidation of Fe is mainly controlled by the outward diffusion of Fe^{2+} and Fe^{3+} ions, resulting in the formation of a triple-layered scale consisting of $\text{FeO}/\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$, with a thick FeO layer next to the metal [11].

Manganese is oxidized by the outward diffusion of Mn^{2+} ions through MnO [12,18]. The oxidation of Cu results in the formation of an outer, thin CuO layer, and an inner, thick Cu_2O layer [14,15]. Since CuO is an intrinsic semiconductor and Cu_2O is the cation-deficient, nonstoichiometric oxide, the oxidation of Cu is mainly controlled by the outward diffusion of Cu ions through Cu_2O [14,15]. The outward diffusion of Fe, Mn, and Cu was observed during the oxidation of the Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys, as will be shown below.

Figure 5 shows the XRD/SEM/EPMA results of the Fe-12Cr-0.3C-4Mn-13Cu alloy after oxidation at 700 °C for 30 h. In Fig. 5(a), the Cu peaks are weaker than α -Fe peaks, because there was a 10.3 vol% secondary phase in the (Fe, Cr)-rich matrix. The peaks of α -Fe and Cu were stronger than those of FeMnO_3 , Cu_2O , and CuO, indicating the small extent of oxidation. The secondary phase oxidized preferentially, while the α -Fe matrix oxidized slightly, revealing the grinding grooves that formed during sample preparation (Fig. 5(b)). Manganese oxidizes rather easily (Fig. 3) and fast (Fig. 4), which helps the oxidation of the more noble but still rather fast oxidizing Cu in the secondary phase. This results in the nodular oxidation of the secondary phase (Figs. 5(c-d)). Iron oxidizes fast, but Cr oxidizes quite slowly (Fig. 4). This leads to the uniform oxidation of the (Fe, Cr)-rich matrix (Figs. 5(c-d)). Oxide nodules protruded from the initially flat sample surface because of the outward diffusion of Fe, Cu, and Mn (Figs. 5(b-d)), which accompanied the formation of voids in the oxide nodules (Fig. 5(c)). Manganese oxidized to stable FeMnO_3 spinel

Fig. 5. Fe-12Cr-0.3C-4Mn-13Cu alloy after oxidation at 700 °C for 30 h. (a) XRD pattern, (b) SEM top view, (c) EPMA secondary electron (SE) cross-sectional image, (d) EPMA maps of (c)

(Fig. 5(a)). Copper oxidized to Cu_2O and CuO. Chromium, which forms highly stoichiometric, quite slowly growing Cr_2O_3 , was primarily oxidized by the inwardly diffusing oxygen (Fig. 5(d)).

When the oxidation temperature was increased to 800 °C, oxide nodules were no longer noticeable because not only the (Cu, Mn)-rich secondary phase but also the (Fe, Cr)-rich matrix oxidized considerably, as shown in Figs. 6(a-b). Voids and cracks developed in the thick oxide scale owing to the outward diffusion of Fe, Cr, Cu, and Mn, anisotropic volume expansion, and stress generated during scaling. The Pilling-Bedworth ratios are 1.78 for $\text{Fe}/\text{Fe}_2\text{O}_3$, 2.1 for $\text{Fe}/\text{Fe}_3\text{O}_4$, 2.02 for $\text{Cr}/\text{Cr}_2\text{O}_3$, 1.72 for Cu/CuO , 1.67 for $\text{Cu}/\text{Cu}_2\text{O}$, and 1.77 for Mn/MnO [19]. The outer and inner oxide scale was about 95 and 85 μm -thick, respectively. The base element, Fe, diffused outward appreciably to form a Fe-rich outer oxide layer, which depleted Fe and thereby enriched Cr in the inner

Fig. 6. Fe-12Cr-0.3C-4Mn-13Cu alloy after oxidation at 800 °C for 30 h. (c) EPMA SE cross-sectional image, (b) EPMA backscattered electron (BSE) cross-sectional image, (c) EPMA maps of (a), (d) XRD pattern

oxide layer (Fig. 6(c)). The outer oxide scale consisted mainly of Fe₂O₃ and some Fe₃O₄, and was dissolved with Cr, Cu, and Mn (Figs. 6(c-d)). A small amount of the unoxidized secondary phase containing the most noble element, Cu, was retained in the inner oxide scale, while that phase was unobservable in the outer oxide scale. Hence, it is suggested that the inner and outer oxide scale is formed by the inward diffusion of oxygen, and the outward diffusion of Fe, Cr, Cu, and Mn, respectively.

When the oxidation temperature was increased further to 900 °C, a bi-layered, porous, fragile oxide scale formed, as shown in Figs. 7(a-b). The outer oxide scale with coarse voids was 220 μm-thick and Fe-rich, while the inner, dense

oxide layer was 240 μm-thick and Cr-rich (Figs. 7(a-b)). Manganese diffused out faster than Cu from the secondary phase in the inner oxide scale (Fig. 7(b)). Again, it is seen that the outer oxide scale grew by the outward diffusion of Fe, Cr, Cu, and Mn, while the inner oxide scale grew by the inward diffusion of oxygen. Arrayed fine voids at the boundary of the outer and inner oxide scale resulted from the Kirkendall effect and the compositional difference between the outer and inner oxide scales (Fig. 7(a)). The outer oxide scale consisted mainly of Fe₂O₃ and some MnFe₂O₄ spinel that formed through the reaction of Fe₂O₃ with MnO (Fig. 7(c)). This result also confirmed that both Mn and Fe diffused up to the oxide surface considerably, while Cr

Fig. 7. Fe-12Cr-0.3C-4Mn-13Cu alloy after oxidation at 900 °C for 30 h. (a) EPMA SE cross-sectional image, (b) EPMA maps of (a), (c) XRD pattern

tended to reside in the inner oxide scale (Fig. 7(b)). The elemental distribution in the oxide scale depends on the concentration or activity, diffusivity, and oxygen affinity of the participating elements.

In order to study the oxides that formed in the initial stage, an XPS analysis was performed on Fe-12Cr-0.3C-4Mn-13Cu alloy after oxidation at 700 °C for 5 h, as shown in Fig. 8. The XPS-analyzed scale composition was 20.5Fe-15.9Cu-2.7Mn-60.9O in at%, indicating that the oxidation of Fe was suppressed to a certain extent by Cr in the matrix, while the (Cu, Mn)-rich secondary phase oxidized appreciably. The spectra of Fe_{2p_{3/2}}, Cu_{2p_{3/2}}, and Mn_{2p_{3/2}} were centered at the binding energies of 710.6, 933.1, and 641 eV, respectively, which closely matches the binding energies of Fe₂O₃ (710.9 eV) [20], CuO (933.6 eV) [20], and MnO (640.3eV) [21].

Fig. 8. XPS spectra of Fe-12Cr-0.3C-4Mn-13Cu alloy after oxidation at 700 °C for 5 h

The small deviation in binding energies may be attributed to the dissolution of dissimilar cations in the formed oxides.

Results similar to Figs. 5-8 were also observed for the Fe-12Cr-0.3C-4Mn-(14, 15)Cu alloys, which indicates that all the alloys oxidized at similar rates, forming similar oxide scales.

4. CONCLUSIONS

Fe-12Cr-0.3C-4Mn-(13, 14, 15)Cu alloys consisting of an (Fe, Cr)-rich matrix and a (Cu, Mn)-rich secondary phase were prepared. They were oxidized at almost similar rates between 700-900 °C. Their oxidation rates increased with increasing amounts of Cu, and increased considerably more with increasing temperature. At 700 °C, the α -Fe matrix oxidized slower than the secondary phase because of highly oxidation-resistant chromium, leading to the formation of oxide nodules. At 800-900 °C, the α -Fe matrix also oxidized quickly, facilitating the formation of bi-layered oxide scales. The outer oxide scale grew by the outward diffusion of Fe, Cu, and Mn, which facilitated the formation of voids in the inner oxide scale. The outward diffusion of Cr was weak. The inner oxide scale grew by the inward diffusion of oxygen. The alloys oxidized to Fe₂O₃, Fe₃O₄, FeMnO₃,

MnFe₂O₄, MnO, Cu₂O, and CuO. Since Cr was dissolved in those oxides, Cr₂O₃ was not detected.

ACKNOWLEDGEMENT

This work was supported by the project “Development of the High-Efficiency Low-Emission Future Energy Production Technology (EO15580)” of National Research Council of Science & Technology (NST) grant by the Korea government (MSIP) (No. CRC-15-07-KIER).

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