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Oxidation of a ternary Cu–Ni–Fe alloy under low oxygen pressures at 800–900°C

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Abstract

The oxidation of a Cu-based ternary alloy containing 30 at% Ni and 25 at% Fe has been studied at 800–900°C under low oxygen pressures. The alloy contains a mixture of a phase α rich in Cu and Ni with little Fe with a phase β rich in Fe and Ni with little Cu. The scaling kinetics show rather large deviations from the parabolic law and are much slower than those of pure Fe and of a binary Cu–25Fe alloy oxidized under the same conditions. The growth of an external layer of iron oxide is coupled to the formation of oxide particles dispersed uniformly within the alloy. The internal oxidation of Fe produces a transformation of the β phase into the Cu–Ni solid solution which becomes the matrix of the internal oxidation zone. The β phase disappears also beneath the internal oxidation front to some depth, producing a single-phase α layer. The spatial distribution of the oxide particles in the alloy is rather uniform and does not correspond to that of the two-phases in the original material, which have a largely different iron content. This is the result of a transformation of the β phase into the α phase and of the lateral diffusion of the various components through the α layer before the arrival of the internal oxidation front.

Keywords: Cu–Ni–Fe; Ternary alloy; High temperature; Oxidation

1. Introduction

Cu and Ni are completely soluble into each other, while Cu and Fe have a small mutual solubility and do not form any intermediate phase [1]. On the contrary, the phase diagram of the Ni–Fe system is rather complex and strongly temperature-dependent [1]. In particular, the fcc FeNi solid solution (ss) can only form between 912 and 1394°C, while both fcc and bcc Fe–Ni ss exist between 912 and 517°C and finally below 517° also the intermediate $FeNi_3$ phase becomes stable. The phase diagram for the Fe–Ni–Cu system has only been reported at 400°C and above [2]: each phase stable in the binary Fe–Ni system can dissolve small amounts of Cu and is in equilibrium with a Cu–Ni ss with a small Fe content, while its Ni content increases with the Ni content of the Fe-rich phase. In principle, the phase diagram at room temperature should involve only two invariant equilibria, one of which is between the bcc–Fe–Ni ss, the Cu–Ni ss and $FeNi_3$ (E_1), while the other is between the fcc–Ni–Fe ss, the Cu–Ni ss and $FeNi_3$ (E_2). Thus, Cu–Ni–Fe alloys can contain two or even three phases in a large range of compositions, while the oxides of the three components have very different thermodynamic stabilities [3]. Therefore, Cu–Ni–Fe alloys can be used to investigate the high temperature oxidation of ternary multiphase systems containing components with widely different reactivities with respect to oxygen. Alloys within the Cu–Ni–Fe system are currently being considered as possible candidates as anodes for the electrolysis of Al [4], even though their oxidation resistance at high temperatures under high oxygen pressures, which has only been examined for two different compositions so far [5,6], may be a limiting factor. The scaling behavior of a Cu–30Ni–25Fe (at%) alloy under low oxygen pressures is examined here in an effort to improve the current understanding of the oxidation mechanism of multicomponent multiphase alloys.

2. Experimental

A ternary alloy containing 29.2 at% Ni and 25.0 at% Fe, balance Cu (Cu–30Ni–25Fe) was prepared by repeated melting appropriate amounts of the three pure (99.8%)

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components under a Ti-gettered inert atmosphere using non-consumable tungsten electrodes. The alloy composition falls inside the triangle for the invariant equilibrium E_1, so that in principle it should contain three phases, one composed of almost pure Fe, one very rich in Cu with some Ni and little Fe and one richest in Ni but containing large amounts of Fe with only little Cu. The alloy microstructure (Fig. 1) shows apparently the presence of only two phases, one of which is Cu-rich (light, denoted as α), while the other is Fe- and Ni-rich (dark, denoted as β), presenting similar volume fractions. Under higher magnifications the islands of each phase appear to contain small particles of the other phase, so that the two phases are actually highly intermixed. X-Ray Diffraction (XRD) of the alloy shows only the presence of three main peaks, which correspond to Cu, Ni, fcc–Fe and $FeNi_3$, all almost overlapping each other, while the two strong peaks typical of bcc–Fe are missing. Thus, the alloy apparently contains only the two phases expected to be stable at high temperatures, i.e. a fcc Fe–Ni ss with some Cu and a fcc Cu–Ni ss with little Fe. Even though the presence of a third phase cannot be completely excluded, also in view of the limited contrast between the different phases in the SEM/BEI micrographs for this system due to similar values of atomic numbers of its components, the alloy is considered as a two-phase $\alpha+\beta$ system.

Samples of size 10×10×1.2 mm were oxidized at 800–900°C in H_2–CO_2 mixtures with continuous mass change recorded by a Cahn 2000 thermobalance for a duration of 24 h. The volume fractions of H_2 in the mixtures were 5.7 and 2.7%, which provide equilibrium oxygen pressures of 10^{-16} and 10^{-13} atm at 800 and 900°C, respectively. These pressures are below the stability of the oxides of both Cu and Ni and only slightly above those for the Fe/FeO and FeO/Fe_3O_4 equilibria, equal to 7.4×10^{-20} and 1.5×10^{-18} atm at 800°C and 1.2×10^{-17} and 4.5×10^{-16} atm at 900°C, respectively. A Pt gauze was placed close to the sample to help to equilibrate the gas mixtures at the reaction temperatures. The oxidized samples were examined by means of XRD and Scanning Electron Microscopy (SEM) to identify the microstructure and spatial distribution of the different phases in the oxidation-affected region of the samples.

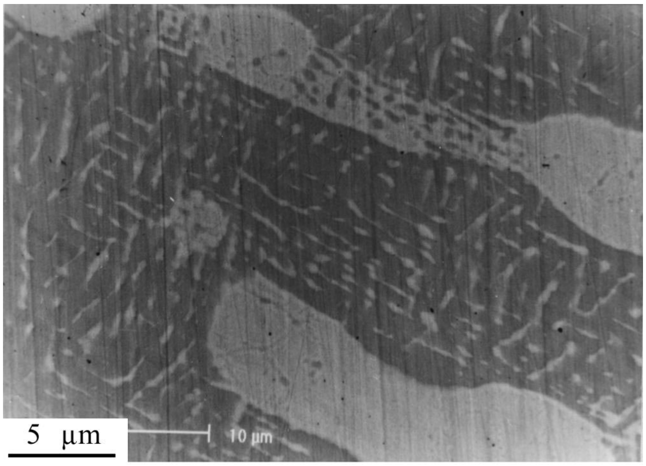

Fig. 1. Microstructure (SEM/BEI) of Cu–30Ni–25Fe: light phase=Cu-rich α; dark phase=FeNi-rich β.

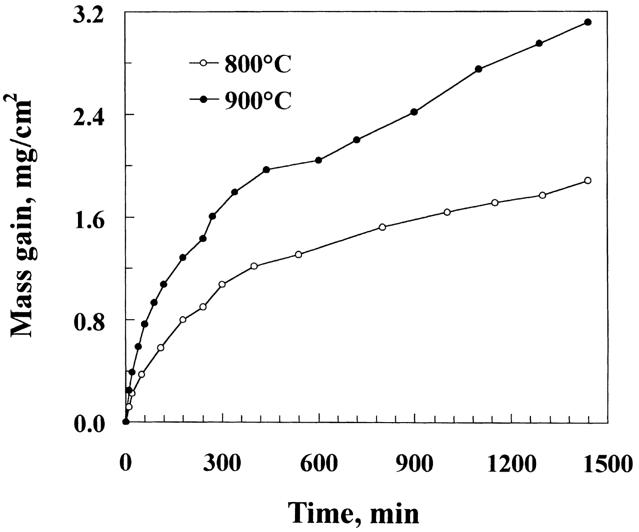

Fig. 2. Oxidation kinetics of Cu–30Ni–25Fe for 24 h under 10^{-16} atm O_2 at 800°C and 10^{-13} atm O_2 at 900°C.

3. Results

The kinetics of oxidation of Cu–30Ni–25Fe under the present low oxygen pressures (Fig. 2) show significant deviations from the parabolic rate law. At both temperatures the scaling rates of the present ternary alloy are much lower than those of pure Fe and of the binary Cu–25Fe alloy oxidized under the same conditions [7]: approximate values of the parabolic rate constants for the three systems are reported in Table 1.

The general features of the samples oxidized at the two temperatures are practically the same, and involve the presence of a thin external layer of Fe_3O_4 of irregular thickness (Fig. 3) plus an internal oxidation zone (ioz) of Fe containing small oxide particles dispersed nearly uniformly within a single-phase Cu–Ni matrix. The spatial distribution of these particles in the ioz has no special relation with that of the two metal phases in the original

Table 1
Approximate parabolic rate constants for the oxidation of pure Fe and of the Cu–25Fe and Cu–30Ni–25Fe alloys under 10^{-16} atm O_2 at 800°C and 10^{-13} atm O_2 at 900°C ($g^2\ cm^{-4}\ s^{-1}$)

T (°C)/Materials	Fe[a]	Cu–25Fe[a]	Cu–30Ni–25Fe
800	4.1×10^{-8}	1.5×10^{-10}	4.2×10^{-11}
900	2.3×10^{-7}	3.6×10^{-9}	1.1×10^{-10}

[a] Average values from Ref. [7].

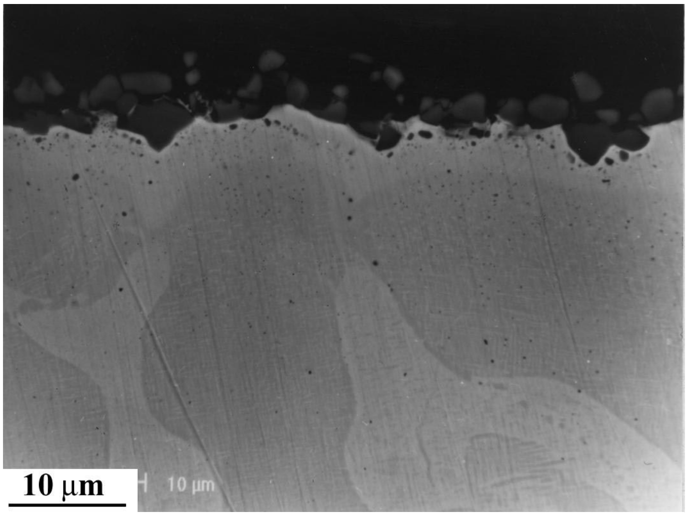

Fig. 3. Micrograph (SEM/BEI) of a cross section of Cu–30Ni–25Fe oxidized for 24 h under 10^{-16} atm O_2 at 800°C.

alloy since the volume fraction of the oxide should be higher in correspondence with the β phase, in view of its high Fe content. A layer of α phase depleted in Fe is also observed at both temperatures beneath the ioz. The interface between the external scale and the ioz is not flat due to the presence of a number of large oxide stringers protruding into the alloy, sometimes even to a considerable depth. Finally, small alloy particles are sometimes incorporated into the inner region of the external scale (Fig. 4).

4. Discussion

The oxygen pressures used in this work are below the stability of the oxides of both Cu and Ni [3]. However, in the oxidation of Fe–Ni alloys Ni can enter in the scales even under oxygen pressures below the stability of NiO by forming a solid solution with FeO or an iron-rich iron–nickel spinel of formula $Ni_xFe_{3-x}O_4$ [8,9]. In agreement with the Fe–Ni–O phase diagram, the (Fe,Ni)O ss is only stable in contact with alloys quite rich in Fe and under very low oxygen pressures, while the double oxide is stable in contact with alloys richer in Ni up to oxygen pressures very close to that for the Ni–NiO equilibrium [9]. The oxidation of Fe–Ni alloys under low oxygen pressures has never been examined so far, but Fe–Cu alloys oxidized under the same low oxygen pressures can only form Fe oxides (FeO and Fe_3O_4) both as an external scale and internally to the alloy [7].

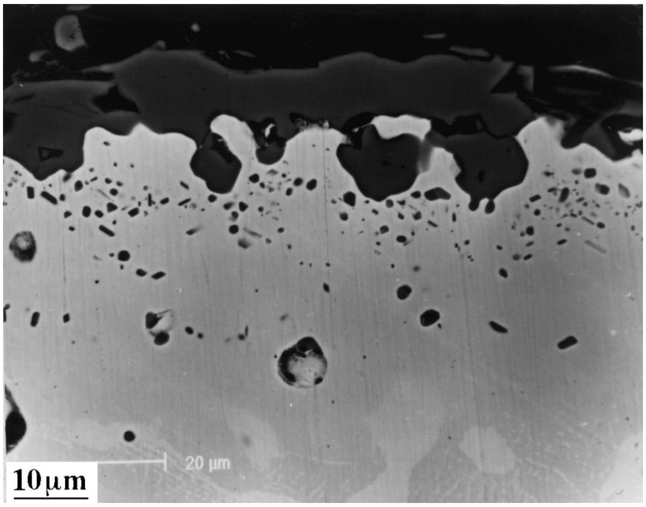

Fig. 4. Micrograph (SEM/BEI) of a cross section of Cu–30Ni–25Fe oxidized for 24 h under 10^{-13} atm O_2 at 900°C.

The scaling behavior of ternary alloys containing two or three phases with different compositions may differ in principle from that of ternary solid solution alloys with similar properties as a consequence of their particular nature, even if from a thermodynamic point of view all the phases are equivalent because they contain the three components under the same activities. The main reason for this difference is the restriction imposed to the diffusion processes in the alloy by the limited solubility of the various components. In particular, the maximum number of phases that can coexist in ternary alloys under constant temperature is three, in which case the system becomes invariant. On the contrary, in the presence of two phases the system has still one degree of freedom, so that they can be in equilibrium in finite ranges of composition. However, no matter transport can take place in ternary systems containing three or even two phases, except if they are not in equilibrium. For two-phase systems this may occur if one phase changes composition or even disappears completely as a consequence of its interaction with the oxidant [10–13]. However, even when possible, diffusion in binary or ternary two-phase alloys is usually much more restricted than in corresponding solid-solution alloys as a consequence of the limited solubilities of the various components, especially if they are very low [10–13]. For binary A–B alloys the presence of two phases tends to produce an internal rather than an external oxidation of the most reactive component B, so that the transition between these two oxidation modes becomes more difficult than in ss alloys [12,13]. Moreover, when the solubility of the two components is very low, the internal oxidation (io) is very often of the in-situ or diffusionless type, which does not involve any important transport of the metal components in the alloy [10–13]. Even though no general treatment is presently available to predict the general behavior of ternary multiphase alloys, this should for many aspects be similar to that of two-phase binary alloys, except for special changes induced by the presence of the third alloy component.

The oxidation of two-phase binary Fe–Cu alloys under the same low oxygen pressures as used in the present study produces a combination of the growth of external Fe oxide scales with an io of Fe, similar to what observed here [7]. However, the io of binary Fe–Cu alloys is of the diffusionless type even for an alloy with an Fe content as large as 75 wt%, since the distribution of the internal FeO particles is the same as that of the Fe-rich phase in the original alloy [7]. The behavior of the present ternary alloy is somewhat different because the distribution of the FeO particles in the ioz is approximately uniform and is therefore not correlated with the spatial distribution of the two metal phases in the original alloy. Moreover, the ioz is followed by a single-phase layer containing a solid solution of Cu in Ni nearly free from Fe, while no Fe depletion develops beneath the io front in the oxidation of binary Fe–Cu alloys [7].

The uniform spatial distribution of the internal oxide observed for the present alloy requires the existence of diffusion processes in directions parallel to the alloy surface, which cancel the effects of the different composition of the two phases. The mechanism for this involves a transformation of the β phase into a Fe-depleted α phase in advance of the io front, due to the exclusive consumption of Fe by internal oxidation. The composition of this α layer tends to become uniform by means of a lateral transport of the various components, so that the original alloy microstructure is lost and any effect of the difference in composition between the two phases disappears. This process is impossible for two-phase Fe–Cu alloys, since the very low solubility of Fe in Cu does not allow any significant diffusion of Fe through the Cu phase. Thus, no dissolution of the β phase or transformation of the β into the α phase can actually occur in binary Fe–Cu alloys beneath the io front. A phase transformation in Fe–Cu alloys takes place only upon the arrival of oxygen at the io front and involves the disappearance of the β phase with formation of a conglomerate of Fe oxide and almost pure Cu.

The growth of the external scale requires a continuous supply of Fe by means of its outward diffusion through the α phase in the alloy. For binary Fe–Ni alloys this is permitted by the fact that the Fe content in the alloy in equilibrium with the internal oxide changes as a function of the local value of the oxygen pressure. In fact, as the oxygen pressure in the alloy increases in moving from the bulk towards the alloy/scale interface, the corresponding Fe content decreases quite significantly, in agreement with the thermodynamic predictions [9]. The situation is similar for the present ternary alloy, for which Ni is replaced by a Cu–Ni ss where Cu behaves as a noble component. The volume fraction of internal iron oxide is rather small, so that most of Fe within the α phase is actually able to reach the alloy/scale interface to form the external scale.

The oxidation rate of the present alloy is significantly lower than that of pure Fe or of a binary Fe–Cu alloy containing 25 wt% Fe [7] under the same conditions, even if the scale structure shown by the binary alloy is very similar to that observed here. The reason for the decrease of the oxidation rate with respect to pure Fe is the larger value of the oxygen pressure prevailing at the alloy/scale interface due to the small value of the Fe activity in the alloy at the same location. This effect is particularly important in the case of oxidation of Fe because it produces a thermodynamic destabilization of FeO [8,9], which is the fastest-growing iron oxide [14]. The difference in scaling kinetics with respect to the binary Fe–Cu alloys has the same origin. In fact, Cu–25Fe forms external scales composed of an outermost Fe_3O_4 layer followed by an inner FeO layer [7]. This is possible, in spite of the io of Fe, because the iron activity at the alloy/scale interface is larger than the value for the alloy/FeO/Fe_3O_4 equilibrium, equal to about 0.42 at 800°C [3], as a consequence of the two-phase nature of the Fe–Cu alloys. In fact, the iron activity in these alloys is very close to unity down to the very low average Fe content corresponding to the solubility of Fe in Cu, equal to about 0.0125 (mole fraction) at 800°C [1,15]. For the present ternary alloy the Fe activity cannot be evaluated precisely. However, the activity coefficient of Fe at 1000°C in a Cu–Ni–Fe alloy with a composition very similar to that examined here is close to 2 [16], so that the activity of Fe in the present alloy can be estimated as 0.5 to a reasonable approximation. This value is only slightly higher than that for the FeO/Fe_3O_4 equilibrium, implying that FeO cannot form on the surface of the present alloy, especially in view of a partial io of Fe which reduces the Fe activity at the alloy/scale interface below the bulk value. The absence of FeO reduces the growth rate of the external scale quite significantly, as noted above. In particular, the rate constant for the direct growth of Fe_3O_4 on an alloy under an oxygen pressure at the alloy/scale interface equal to the value for the FeO/Fe_3O_4 equilibrium and a gas-phase oxygen pressure equal to that for the Fe_3O_4/Fe_2O_3 equilibrium, k_p (Fe_3O_4), can be estimated as 1.1×10^{-10} and 5.6×10^{-10} g^2 cm^{-4} s^{-1} at 800° and 900°C, respectively [14]. As expected, these values are slightly larger than those measured experimentally for the present system, because the oxygen pressure at the alloy/scale interface is presumably larger and that in the gas phase much lower than those involved in the calculation of the previous value of k_p (Fe_3O_4): both these factors produce a decrease of the actual k_p value with respect to those reported above [14].

The presence of two phases in Cu–30Ni–25Fe does not affect its scaling behavior under the low oxygen pressures considered here, except for the transformation of the β phase into the α phase in the ioz and for the limited degree of Fe depletion in the alloy behind the io front. The main effect of the presence of Ni with respect to the oxidation of the binary Fe–Cu alloys is to increase the solubility of Fe in Cu [2,16]. This allows the dissolution of the β phase before the arrival of the io front, producing a transition from an io of the in-situ type into one of normal type [12,13]. Finally, the important kinetic effect with respect to the oxidation of binary Fe–Cu alloys is related to a large difference between the activity coefficients of Fe in the two systems.

5. Conclusions

A simultaneous internal and external oxidation of Fe was observed in the oxidation of a two-phase Cu–Ni–Fe alloy exposed to low oxygen pressures at 800–900°C. The particles of internal oxide were distributed rather uniformly in a single-phase Cu–Ni matrix, while a thin region of the same phase depleted in Fe formed in the alloy beneath the ioz. Lateral diffusion of Fe through this layer was responsible for the lack of correlation between the distribution of the internal oxide and that of the two phases with widely different iron contents in the original alloy. The overall scaling kinetics of this alloy were much lower than measured for pure Fe and for a two-phase Cu–25 at% Fe alloy under the same low $P(O_2)$ as a result of the thermodynamic destabilization of FeO connected with larger positive deviations from the ideal behavior for Fe in binary Cu–Fe alloys than in the present ternary system.

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