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Air oxidation of Cu-50Ni and Cu-70Ni alloys at 800 ℃①

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[Abstract] The air oxidation of Cu-Ni alloys with 50% and 70% nickel (mole fraction) at 800 ℃ was studied. The kinetic curves for the oxidation of the two alloys are complex and deviate from the parabolic rate law. Typical double-layered scales are produced, which consist of a CuO outer layer and an inner layer containing a mixture of Cu_2O and NiO with many pores. Cu-50Ni presents a small degree of internal oxidation of nickel, which is observed in many binary double-phase systems, but is quite rare in single phase systems.

[Key words] copper-nickel alloy; single-phase; high-temperature oxidation
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1 INTRODUCTION

The oxidation of unalloyed copper and nickel has already been studied in detail, but there are rather few studies on the high-temperature oxidation of binary Cu-Ni alloys. In fact, Cu and Ni form a substitutive solid solution without miscibility gap, but their oxides, CuO and Cu_2O and NiO, exhibit small mutual solubility and show significant differences in the thermodynamic stability and parabolic growth rates. Therefore Cu-Ni alloys are often used as model alloys to examine the high-temperature oxidation mechanism of binary alloys. Whittle et al[1] investigated the oxidation of Cu-Ni alloys containing 10%, 55% and 80% Ni in pure oxygen at 800 ℃. Haugsrud et al[2, 3] studied the oxidation of Cu-rich Cu-Ni alloys containing 2%, 5%, 10% and 15% Ni at 800~ 1050 ℃ under 50~ 10^5 Pa oxygen pressures. Recently LI et al[4] investigated the internal oxidation behavior of nickel in Cu-10Ni alloy and the effect of grain size on it. In the present paper, the two alloys with nominal compositions of Cu-50Ni and Cu-70Ni (mole fraction, %) are selected to study the scale structure and kinetic behavior.

2 EXPERIMENTAL

Cu-50Ni and Cu-70Ni alloys were obtained by arc-melting appropriate mixtures of two components (with purity of 99.99%) under a Ti-gettered argon atmosphere using non-consumable tungsten electrodes. The alloy ingots were subsequently annealed for 24 h at 800 ℃ under vacuum to remove the residual mechanical stresses. The actual compositions of two alloys are Cu-50.2Ni and Cu-70.9Ni. Plate specimens about 1mm thick with a surface area of about 2 cm^2 were cut from the alloy ingots with a diamond-wheel saw and then ground on 1000# grit paper, washed in acetone and dried immediately before use. Isothermal air oxidation tests were carried out for 24 h at 800 ℃ using a Cahn 2000 microbalance. The oxidized specimens were analysed by X-ray diffraction (XRD) and a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer attachment (EDX).

3 RESULTS

The kinetic curves for the air oxidation of the two alloys at 800 ℃ are shown in Fig. 1. It can be seen that the oxidation kinetics for the two alloys are complex and deviate from the parabolic rate law. The kinetic curve for the oxidation of Cu-70Ni alloy is composed of three parabolic stages and that of Cu-50Ni alloy consists of two parabolic stages. The oxidation rate of Cu-50Ni is higher than that of Cu-70Ni. Approximate parabolic rate constants calculated from the kinetic curves for the two alloys are listed in Table 1. It can be seen that the oxidation of the two alloys is slower than that for pure Cu, but faster than that for pure Ni.

The scale microstructures of the two alloys are shown in Fig. 2. Typical double-layered scales are formed on the alloy surface when they are oxidized for 24 h in air at 800 ℃. The general structure of the scales is uniform in direction parallel to the alloy surface, while their composition changes significantly with the distance from the substrate/scale interface.

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Table 1 Approximate parabolic rate constants for two pure metals and two alloys($g^2 \cdot cm^{-4} \cdot s^{-1}$)

Material	Initial	Average	Final
Cu[5]		5.4×10^{-9}	
Ni[6]		3.8×10^{-11}	
Cu-50Ni	2.1×10^{-9}	4.2×10^{-10}	1.8×10^{-10}
Cu-70Ni	2.2×10^{-10}	2.4×10^{-10}	2.7×10^{-10}

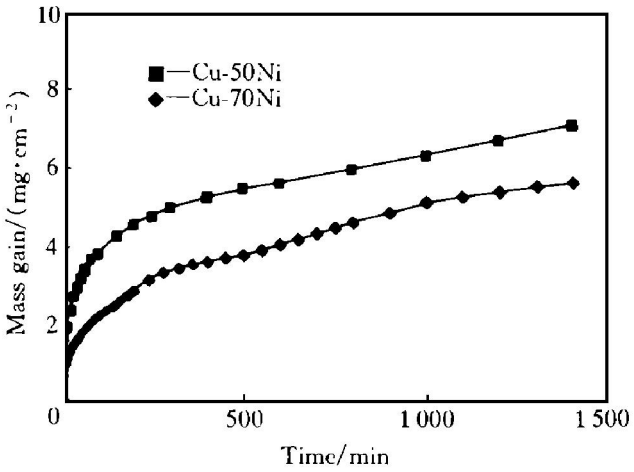

Fig. 1 Air oxidation kinetic curves at 800 ℃ for Cu-Ni alloys

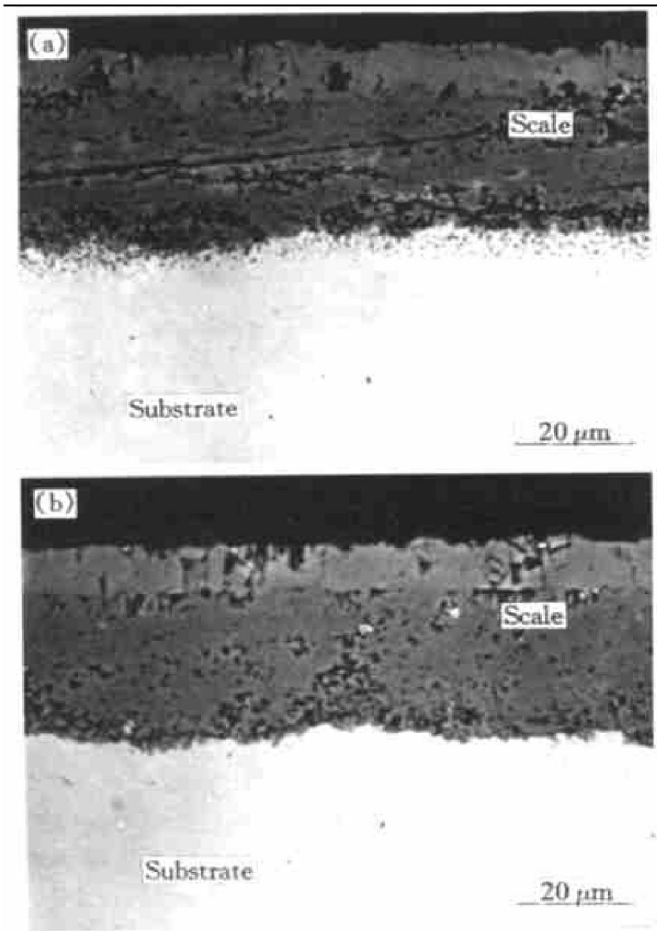

Fig. 2 Back electron images of cross section for Cu-Ni alloys oxidized for 24 h in air at 800 ℃
(a) —Cu-50Ni alloy; (b) —Cu-70Ni alloy

In all cases the external layers are composed of copper oxide with some nickel (about 2%, mole fraction, possibly in solution) and the inner layer composed of a mixture of Cu_2O and NiO with many pores. Cu-50Ni alloy shows a small degree of internal oxidation of nickel (XRD results are shown in Fig. 3). However, the mixed layer in Cu-70Ni alloys is thicker than that in Cu-50Ni. The interface between the two layers reflects the location of the original alloy surface because the self-diffusion coefficient of Cu in Cu_2O is several orders of magnitude larger than that of Ni in NiO[7].

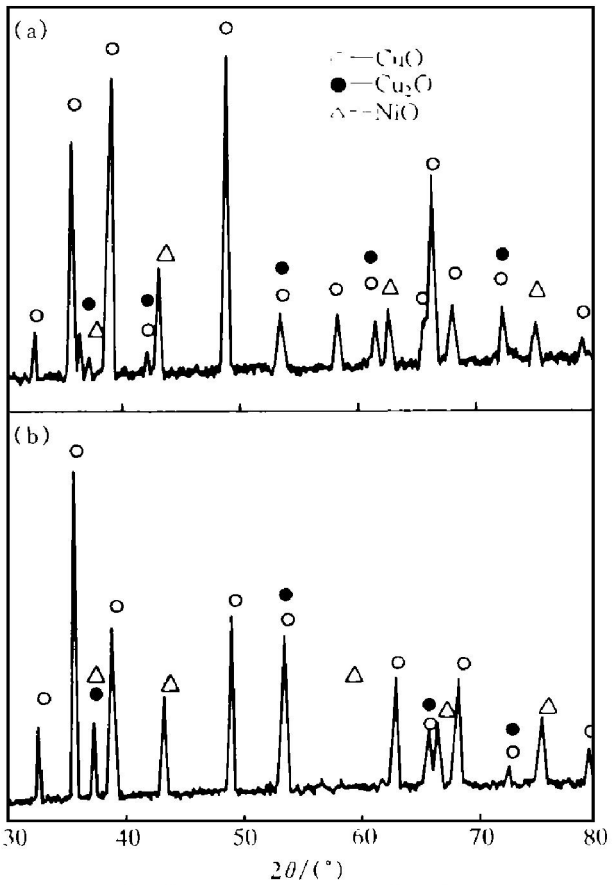

Fig. 3 XRD patterns for Cu-Ni alloys oxidized for 24 h in air at 800 ℃
(a) —Cu-50Ni alloy; (b) —Cu-70Ni alloy

4 DISCUSSION

If NiO forms only on the alloy surface, Ni content must exceed a critical value[8], otherwise scales will form containing a mixture of Cu_2O and NiO. For binary solid-solution A-B alloys (A is more noble component), the oxide scale structure formed on the surface can be predicted on the basis of thermodynamic and kinetic considerations. Thermodynamically, there is a unique composition for which the alloy is in simultaneous equilibrium with both oxides, AO and BO_v. Alloys richer in A than this composition will form AO only, while alloys richer in B will form BO_v only[8]. Kinematically, there are two critical bulk alloy compositions. One corresponds to the transition

from the formation of external scales of pure AO to that of mixtures of AO and BO_v, $n_B(1)$, and the other is between the formation of mixed scales and the exclusive growth of external BO_v, $n_B(2)$. In addition, $n_B(2)$ is the minimum n_B value necessary to provide a flux of B from the alloy to the oxide/alloy interface. It is sufficient to maintain the growth at the correct rate and at the same time to prevent the formation of the less stable oxide AO[8,9]. Thus, alloys with a bulk B content (n_B) in the range between 0 and $n_B(1)$ will form AO scales only, while those with B content ranging from $n_B(2)$ to 1 will form exclusively pure BO_v scales. On the contrary, alloys with $n_B(1) < n_B < n_B(2)$ will form scales containing mixtures of AO+ BO_v.

For Cu-Ni system, the parabolic rate constants for the oxidation of pure Cu and for the growth of copper oxides on Cu-Ni alloys are 5.2×10^{-9} and 1.1×10^{-9} $cm^{-2} \cdot s^{-1}$, respectively. The parabolic rate constant for the growth of NiO scales on pure Ni ranges from 3.7×10^{-12} to 9.5×10^{-12} $cm^{-2} \cdot s^{-1}$, while that for the growth of NiO on Cu-Ni alloys is 5.6×10^{-12} $cm^{-2} \cdot s^{-1}$. The tracer-diffusion coefficient of Cu in pure Cu is given by[10]

$$D^*_{Cu}/(cm^{-2} \cdot s^{-1}) = 0.78 \exp(-211.3/RT) \quad (1)$$

and that of Ni in Cu is given by

$$D^*_{Ni}/(cm^{-2} \cdot s^{-1}) = 1.1 \exp(-225.1/RT) \quad (2)$$

Finally, the solubility of oxygen at the Cu-CuO equilibrium (mole fraction) and the diffusion coefficient of oxygen in Cu are given by[11]

$$n^S_O(Cu) = 154 \exp(-149.6/RT) \quad (3)$$

$$D_O(Cu)/(cm^{-2} \cdot s^{-1}) = 1.2 \exp(-67.3/RT) \quad (4)$$

The calculated value of $n_{Ni}(1)$ ranges from 9×10^{-5} to 3.6×10^{-4} and that of $n_{Ni}(2)$ ranges from 0.47 to 0.86. The scale structure actually observed in the oxidation of Cu-Ni alloys is in agreement with the conclusions of the above analysis.

Cu-50Ni presents also a limited degree of internal oxidation of nickel. The simultaneous external and internal oxidation is observed in many binary double-phase alloys[12~16], but is very rare in solid-solution alloys.

The condition for the stability of this special kind of scale structure was firstly analyzed by Wagner[17] in the oxidation of Cu-Pt and Cu-Pd alloy, later this analysis was extended by Smelyzer[18] during diffusion of the different components in internal oxidation zone. In fact, for binary single phase A-B alloys, there is a hypothesis when the external oxidation is formed in all criteria used to predict the formation of external and internal oxidation simultaneously.

For a given alloy system, S is a function of time[17]. Therefore it is convenient to introduce a parameter P which is independent of time and given by

$$P = S(\pi D_{AB} t)^{1/2} \quad (5)$$

When $P < 0$, the component B can only oxidize externally; while the condition of $P > 0$ may lead to the external and internal oxidation of B. In fact, P is only used to predict the trend to simultaneously produce the external and internal oxidation of component B. The larger the P value, the more likely the system accept this oxide scale structure.

P values of Cu-50Ni and Cu-70Ni alloys calculated from the above equations are 2.8×10^6 and 7.4×10^3. The P value for Cu-50Ni is much larger so that it may undergo external and internal oxidation of nickel more easily. This prediction is in agreement with actual oxide scale structure.

Cu_2O and NiO are both metal-deficient oxides and, accordingly, the predominant point defects are metal vacancies[19]. The self-diffusion coefficient of Cu in Cu_2O is several orders of magnitude larger than that of Ni in NiO[7]. The NiO layer can be considered to be relatively stationary. It partially blocks the outward diffusion of copper and reduces the cross-sectional area for diffusion, therefore approximate parabolic rate constants for two alloys are all lower than that for pure copper. Since NiO layer presented in the scale acts as barrier to the copper flux, the copper flowing at scale/alloy interface and across the outer CuO scale under constant temperature decreases with increasing nickel concentration. Therefore the oxidation rates of the two alloys decrease when the nickel concentration increases.

5 CONCLUSIONS

1) The kinetics of the oxidation for the two alloys containing 50% and 70% Ni are complex and deviate from the parabolic rate law.

2) The oxidation rate of Cu-50Ni is much higher than that of Cu-70Ni. For both alloys, the oxidation rates are slower than that of pure Cu, but faster than of pure Ni.

3) Typical double-layered scales are produced, which consist of a CuO outer layer and an inner layer containing a mixture of Cu_2O and NiO with many pores.

4) Cu-50Ni alloy presents a small degree of internal oxidation of nickel. The interface between the inner and the outer layer approximately corresponds to the original alloy surface.

[REFERENCES]

[1] Whittle D P, Wood G C. Two-phase scale formation on CuNi [J]. Corros Sci, 1968, 8: 295- 308.

[2] Haugsrud R, Kofstad P. On the high-temperature oxidation of Cu-rich Cu-Ni alloys [J]. Oxid Met, 1998, 50: 189- 213.

[3] Haugsrud R. On the influence of non-protective CuO on

high-temperature oxidation of Cu-rich Cu-Ni based alloy [J]. Oxid Met, 1999, 52: 427- 445.
[4] LI Y S, NIU Y, WU W T. Effect of grain size on the high temperature oxidation of two Cu-10Ni alloys [J]. Actallurgical Sinica, 1999, 35: 1171- 1174.
[5] NIU Y, Gesmundo F, Viani F, et al. The air oxidation of two-phase Cu-Cr alloys at 700~ 900 ℃ [J]. Oxid Met, 1997, 48: 21, 357- 380.
[6] Rapp R A. High Temperature Corrosion [M]. NACE, Houston, USA, 1983. 110.
[7] Atkinson A, Taylor R I. The diffusion of Ni in bulk and along dislocations in NiO single crystal [J]. Philos Mag, 1979, A39: 585.
[8] Wagner C. Theoretical analysis of the diffusion process determining the oxidation rate of alloys [J]. J Electrochem Soc, 1952, 99: 369.
[9] Gesmundo F, NIU Y. The criteria for the transitions between the various oxidation modes of binary solid-solution alloys forming immiscible oxides at high oxidant pressures [J]. Oxid Met, 1998, 50: 1.
[10] Rothman S J, Peterson N L. Isotope effect and divacancies for self-diffusion in copper [J]. Phys Stat Solidi, 1969, 35: 305.
[11] Narula M L, Tare V B, Worrell W L. Diffusivity and solubility of oxygen in copper using potentiometric techniques [J]. Met Trans, 1983, 14B: 673.
[12] NIU Y, Gesmundo F, Viani F, et al. The air oxidation of two-phase Cu-Ag alloy at 650~ 750 ℃ [J]. Oxid Met, 1997, 47: 21.
[13] Gesmundo F, NiIU Y, Viani F. Possible scaling in high-temperature oxidation of two-phase binary alloy [J]. Oxid Met, 1995, 43: 379.
[14] Monteiro M J, Niu Y, Rizzo F C, et al. the oxidation of Co-Nb alloys under low oxidant pressures at 600~ 800 ℃ [J]. Oxid Met, 1995, 43: 527.
[15] NIU Y, Gesmundo F, Rizzo F C, et al. The oxidation of Co-Nb alloys under 1 atm O_2 at 600~ 800 ℃ [J]. Corros Sci, 1996, 38: 193.
[16] NIU Y, Gesmundo F, Viani F, et al. The oxidation of Ni-Nb alloys under 1 atm O_2 at 600~ 800 ℃ [J]. Corros Sci, 1995, 37: 2043.
[17] Wagner C. Internal oxidation of Cu-Pd and Cu-Pt alloys [J]. Corros Sci, 1968, 8: 889.
[18] Smeltzer W W, Whittle D P. The criterion for the onset of internal oxidation beneath the external scales [J]. J Electrochem Soc, 1978, 125: 1116.
[19] Kofstad P. High-Temperature Corrosion [M]. New York: Elsevier Applied Science Press, 1988.

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