

Effect of grain size on high temperature oxidation behavior of Cu80Ni alloy^①

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Abstract: The thermogravimetric analysis of binary Cu80Ni alloys prepared respectively by conventional casting (CA) and mechanical alloying (MA) techniques and presenting widely different grain sizes was performed at 800 °C in air in order to study the effect of grain size change on the oxidation behavior of a solid solution alloy. The results show that the kinetic curves for the oxidation of the two alloys are complex and deviate from the parabolic rate law and usually are not composed of a single stage. Mixed scales were produced on the CACu80Ni alloy surface, which consists of a mixture of copper and nickel oxides. However, oxide scale for MACu80Ni alloy is mainly composed of a thick compact and continuous inner layer of nickel oxide. The reduction in the alloy grain size speeds up the diffusion of the more reactive component nickel from the alloy to alloy/oxide scale interface and completes the transition from a mixed scale to continuous scale of nickel oxide.

Key words: copper-nickel alloy; Cu80Ni 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. While the high-temperature oxidation of Cu-Ni alloys, also studied a number of times to date^[1-3], is an example of a relatively simple class of scaling of binary alloys by a single oxidant, because the metals form a continuous series of solid solutions, while their oxides, CuO, Cu₂O and NiO, exhibit small mutual solubilities and show significant differences in the thermodynamic stability and parabolic growth rates. Thus, copper-rich alloys form external scales of copper oxide plus a region of internal oxidation of nickel, while nickel-rich alloys form exclusively external scales of nickel oxide (NiO). Alloys with intermediate nickel contents form external scales containing mixtures of Cu₂O and NiO with a complex spatial distribution. LI et al^[4] investigated the internal oxidation behavior of nickel in Cu-10Ni alloy and the effect of grain size on it, but Ni content is too low to finish the transition between the formation of Cu₂O and NiO mixtures and that of continuous NiO scale. The authors^[5] also studied that the oxidation of the two alloys with nominal composition Cu-50% and 70% Ni (mole fraction), but these alloys were not able to produce the transition between

the formation of Cu₂O and NiO mixtures and that of continuous NiO scale even if the maximum Ni content in the alloy reached 70% (mole fraction). In the present paper, Cu-Ni alloys containing 80% Ni (mole fraction) (denoted as Cu80Ni) prepared by conventional casting (denoted as CA) technique and mechanical alloying (denoted as MA) were selected to study their scale structure, kinetic behavior and the effect of grain size change on the oxidation behavior of Cu-Ni solid solution alloy in order to complete the transition between the formation of Cu₂O and NiO mixtures and that of a continuous NiO scale.

2 EXPERIMENTAL

CACu80Ni alloy obtained by conventional casting appropriate mixtures of two pure components (99.99%) under a Ti-gettered argon atmosphere using non-consumable tungsten electrodes. The alloy ingot was subsequently annealed for 24 h at 800 °C under vacuum to remove the residual mechanical stresses. The actual composition of CACu80Ni alloy is Cu79.8Ni.

MACu80Ni alloy was prepared as below. Elemental copper and nickel powders (purity > 99.9%) with particle size about 100 μm were blended with a

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Cu/Ni atomic ratio of 1:4. Mechanical alloying was carried out in a QM-1SP planetary miller. Two powders were first stir-mixed in a stainless steel vial with hardened GCr15 steel balls. The ball to powder mass ratio was $\sim 10:1$. The vial with powders was evacuated to ~ 10 Pa and then filled with pure argon. During ball milling a relay was used to control intermediate stops of 15 min every hour to avoid excessive heat effect. The whole powders were prepared by mechanical alloying for 60 h in order to obtain alloying on atomic level. Nearly fully dense sample was prepared by hot pressing at 750 °C for 10 min and the pressure of 60 MPa in vacuum of 0.06 Pa using a graphite die with inner diameter of 20 mm. During hot pressing all signals including the temperature, its displacement and deformation can be input into a computer, from which the deformation and densification curve can be obtained, which was described in detail in the literature^[6].

Finally, the resulting ingot was annealed for 12 h at 800 °C to stabilize the grain structure and relieve mechanical stresses induced by hot pressing. Both the MA powder and alloys by hot pressing and annealing were analyzed by X-ray diffraction using Cu K α_1 with pure silicon as internal standard. A measurement of the average grain size for using the Scherrer Formula^[7] gave a value of about 10 nm of ball milling for 60 h, which increased up to 25 nm after hot pressing and to 40 nm after annealing. The actual composition of MACu-80Ni alloy is Cu-80.1Ni

Plate specimens about 1 mm thick with a surface area of about 2 cm² were cut from the alloy ingots by means of a diamond-wheel saw and then ground down to 1 000 grit paper, washed in acetone and dried immediately before use. Isothermal air oxidation tests were carried out at 800 °C for 24 h using a Cahn 2000 microbalance. The oxidized specimens were analyzed by X-Ray Diffraction (XRD) and a Scanning Electron Microscope (SEM) equipped with an Energy-Dispersive X-ray spectrometer attachment (EDX).

3 RESULTS

3.1 Oxidation kinetics

The kinetic curves for the air oxidation of the two Cu-80Ni alloys at 800 °C for 24 h are shown in Fig. 1. The oxidation kinetics for CACu-80Ni alloy is complex and deviates from the parabolic rate law and usually is not composed of a single stage. The kinetic curve at 800 °C can be approximately described as composed of two main quasi-parabolic stages up to 10 h, the first with a rate constant $k_p = 8.0 \times 10^{-10}$ (all k_p values in g²/(cm⁴·s)) for the initial 30 min, the second with an average k_p value of 1.9×10^{-10} up to about 10 h, afterwards, it follows linear law. The oxidation kinetics for MACu-80Ni alloy is relatively

regular and composed of the two parabolic stages, the first with an average k_p value of 7.4×10^{-10} for initial 5 h, the second with an average k_p value of 1.9×10^{-9} , an average k_p value is equal to 1.3×10^{-9} from the initial to 24 h. The oxidation rate for MACu-80Ni is a little slower than that for CACu-80Ni before 2 h, but afterwards, it is evidently faster than that for CACu-80Ni up to 24 h.

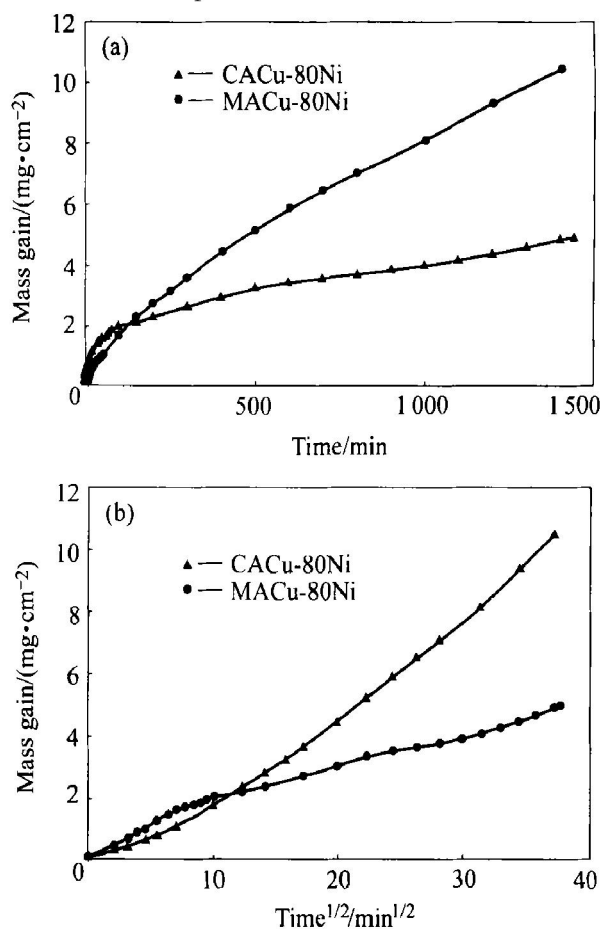


Fig. 1 Kinetic curves for CA and MACu-80Ni alloys oxidized for 24 h in air at 800 °C
(a) —Mass gain vs time; (b) —Mass gain vs time^{1/2}

3.2 Scale microstructure and composition

The scale microstructures of the two alloys are shown in Fig. 2. Typical double-layered scales were formed on the CACu-80Ni alloy surface when it was oxidized for 24 h in air at 800 °C. 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 alloy/scale interface. The most external layer is composed of CuO with some nickel (about 1.8% in mole fraction, possibly in solution) followed by an inner layer composed of a mixture of Cu₂O and NiO. However, oxide scales for MACu-80Ni alloy are composed of a thin CuO external layer and a thick compact inner NiO layer. The reduction in the alloy grain size finishes the transition from a mixed scale of Cu₂O and NiO to a continuous scale of NiO.

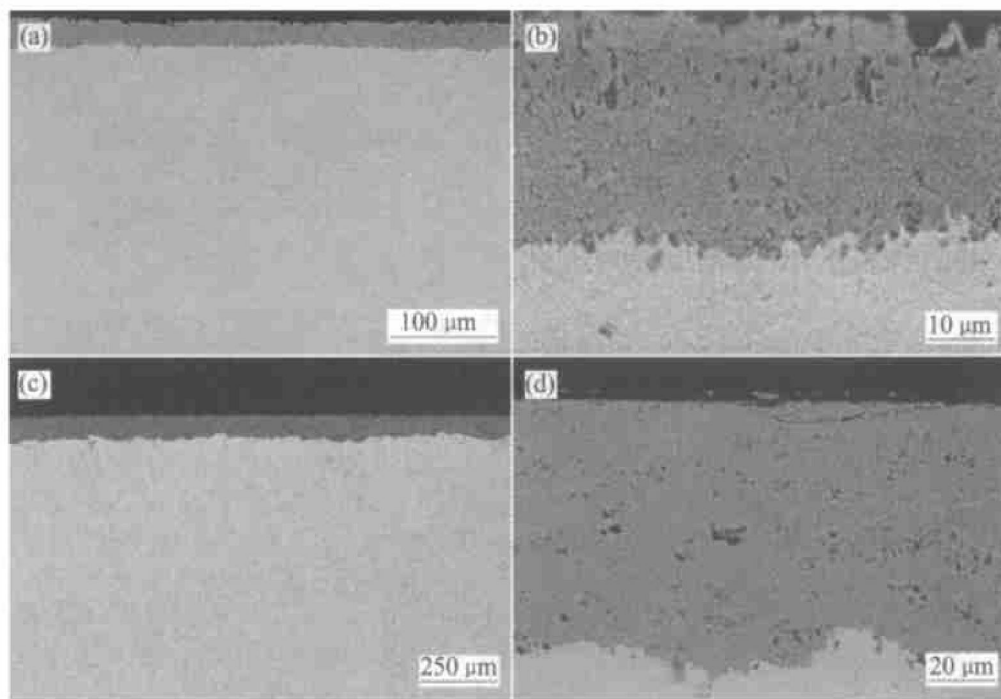


Fig. 2 Cross sections of CA and MACu-80Ni alloys oxidized for 24 h in air at 800 °C (BEI)
(a) —CA, General view; (b) —CA, Expanded view; (c) —MA, General view; (d) —MA, Expanded view

4 DISCUSSION

The gas-phase oxygen pressure used here is much larger than the dissociation pressures of the oxides of both metals. However, the formation of NiO is thermodynamically favored, since it is considerably more stable than the copper oxides^[8]. Kinetically, the growth rates of copper oxides are evidently faster than that of NiO. When oxidation starts, all copper and nickel oxides may be produced on the alloy surface, but copper oxides recover nickel oxide quickly because they have faster growth rates. Hence, a continuous CuO layer forms on the two alloys surface. In fact, the growth of external scales of pure NiO can only occur above a critical nickel content needed to avoid the formation of external scales of a mixture of Cu-Ni oxides or of external scales of copper oxides associated with internal oxidation of nickel^[1, 9, 10].

For binary solid-solution A-B alloys where B is the more reactive component, thermodynamically, there is a unique composition for which the alloy is in simultaneous equilibrium with both oxides, AO and BO_v, which may be expressed by means of the mole fraction of B in the alloy, N_B^e , which may be calculated from the equation

$$[K(AO)(1 - N_B^e)]^v = K(BO_v) N_B^e \quad (1)$$

where $K(AO)$ and $K(BO_v)$ are the equilibrium constants for the formation of 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^[11]. Kinet-

ically, there are two critical bulk alloy compositions, one of which corresponds to the transition from the formation of external scales of pure AO to that of mixtures of AO and BO_v, $N_B^{0*}(1)$, and the other between the formation of mixed scales and the exclusive growth of external BO_v, $N_B^{0*}(2)$; in addition, $N_B^{0*}(2)$ is the minimum N_B^0 value necessary to provide a flux of B from the alloy to oxide/alloy interface sufficient to maintain the growth at the correct rate and at the same time to prevent the formation of the less stable oxide AO^[10, 11]. Thus, alloys with a bulk B content N_B^0 in the range between 0 and $N_B^{0*}(1)$ will form AO scales only, while those with a B content ranging from $N_B^{0*}(2)$ to 1 will form exclusive pure BO_v scales. On the contrary, alloys with $N_B^{0*}(1) < N_B^0 < N_B^{0*}(2)$ will form scales containing mixtures of AO + BO_v.

According to a treatment developed by Wagner^[11], the critical B content required by the second criterion, $N_B^{0*}(2)$, is given by

$$N_B^{0*}(2) = (V_{all}/z_B M_O) [\pi k_p(BO_v)/D_B]^{1/2} \quad (2)$$

where $k_p(BO_v)$ is the parabolic rate constant for the growth of BO scales in terms of mass gain per unit surface area, V_{all} is the molar volume of the alloy, z_B is the valence of B in the oxide, M_O is the atomic mass of oxygen and D_B is the diffusion coefficient of B in the alloy. The same equation can be also written in equivalent form^[12]:

$$N_B^{0*}(2) = (1/2) [\pi k_c(BO_v)/D_B]^{1/2} \quad (3)$$

where $k_c(BO_v)$ is the parabolic rate constant for the

growth of a BO scale in terms of the thickness X of metal consumed, according to the equation

$$X^2 = k_c(\text{BO}_v) t \quad (4)$$

Eqs. (2) and (3) neglect the displacement of the alloy-scale interface due to the growth of the external scales. Upon considering this aspect, Eq. (3) is modified to^[10,12]

$$N_{\text{B}}^{0*}(2) = N_{\text{B}}^{\text{e}} + [1 - N_{\text{B}}^{\text{e}}] F(u_{\text{B}}) \quad (5)$$

where $u_{\text{B}} = (1/2) [k_c(\text{BO}_v)/D_{\text{B}}]^{1/2}$. Finally, $F(r)$ is the auxiliary function defined as^[11]

$$F(r) = \pi^{1/2} r \exp(r^2) \cdot \text{erfc}(r)$$

The parabolic rate constants for the oxidation of pure Cu and the growth of copper oxides on Cu-Ni alloys are $k_c^0(\text{Cu})(1) = 5.2 \times 10^{-9} \text{ cm}^{-2} \text{ s}^{-1}$ and $k_c(\text{Cu})(2) = 1.1 \times 10^{-9} \text{ cm}^{-2} \text{ s}^{-1}$, respectively. The $k_c^0(\text{Ni})$ value for the growth of NiO scales on pure Ni, $k_c^0(\text{Ni})(1)$, ranges from 3.7×10^{-12} to $9.5 \times 10^{-12} \text{ cm}^{-2} \text{ s}^{-1}$, while that for the growth of NiO on Cu-Ni alloys is $k_c^0(\text{Ni})(2) = 5.6 \times 10^{-12} \text{ cm}^{-2} \text{ s}^{-1}$. The tracer-diffusion coefficient of Cu in pure Cu is given by^[13]

$$D_{\text{Cu}}^*/(\text{cm}^{-2} \text{ s}^{-1}) = 0.78 \exp(-211.3/RT) \quad (6)$$

and that of Ni in Cu is given by

$$D_{\text{Ni}}^*/(\text{cm}^{-2} \text{ s}^{-1}) = 1.1 \exp(-225.1/RT) \quad (7)$$

Finally, the solubility of oxygen in the Cu-CuO equilibrium (mole fraction) and the diffusion coefficient of oxygen in Cu are given by^[14]

$$N_{\text{O}}^{\text{S}}(\text{Cu}) = 154 \exp(-149.6/RT) \quad (8)$$

and

$$D_{\text{O}}(\text{Cu})/(\text{cm}^{-2} \text{ s}^{-1}) = 1.16 \exp(-67.3/RT) \quad (9)$$

The calculated values of $N_{\text{Ni}}^{0*}(2)$ range between 0.47 and 0.86. The quite wide range values calculated for $N_{\text{Ni}}^{0*}(2)$ are due to large uncertainties in the parameters used in the calculation. The scale structure actually observed in the oxidation of CACu-80Ni alloys is basically in agreement with the conclusions of the above analysis.

The effects of a reduction in the grain size on the scaling behavior of alloys are related to possible changes in the values of important parameters, such as the solubility of the oxidant in the alloy, the diffusion coefficients of the two components in the alloy and possibly also those of the reactants through the scales. Mechanical alloying can be used to produce materials with extremely fine grain sizes^[15-17]. The most direct effect of the strong reduction of the grain size obtained by this method is the appearance of large concentrations of grain boundaries^[18]. As a consequence of their rather open and disordered structure, the grain boundaries allow a faster transport of the metal components in the alloy in comparison with normal bulk diffusion in the presence of chemical potential gradients^[16,19]. Thus, for fine-grained materials

the bulk diffusion coefficient of any given species, D_{bulk} , must be replaced by an effective diffusion coefficient, D_{eff} , which is a weighted average of the diffusion coefficient in the bulk and that along the grain boundaries, D_{gb} , according to Hart^[19], the effective diffusion coefficient is given by

$$D_{\text{eff}} = (1-f) D_{\text{bulk}} + f D_{\text{gb}} \quad (10)$$

where f is the fraction of the total number of diffusion sites located at the grain boundaries, which for cubic grains if side d is equal to $2\delta/d$, where δ is the grain boundary width, is typically around $10^{-7} \text{ cm}^{[19]}$. The increase in the effective diffusion coefficient will thus depend on the relative magnitude of D_{bulk} and D_{gb} , but, for a given system will also depend on temperature. The grain-boundary diffusion coefficient has a larger activation energy than the lattice diffusion coefficient, so that the ratio $D_{\text{gb}}/D_{\text{bulk}}$ decreases as the temperature increases. Typically, for metals, the activation energy for short-circuit diffusion is 0.5–0.7 times smaller than that for lattice diffusion, while $D_{\text{gb}}/D_{\text{bulk}}$ is usually in the range of 10^4 – 10^6 . In turn, the larger value of D_{eff} as compared to D_{bulk} favors the formation of the most stable oxidation as an external scale by reducing the critical concentration of the same component both for solid-solution alloys. Hence, MACu-80Ni alloy completes transition from a mixture of Cu_2O and NiO to a continuous NiO.

The increase in oxidation rate observed for nano-MACu-80Ni alloy is very likely a result of faster transport of the reactants through the scales due to a significant contribution from grain boundary diffusion. In fact, even though no clear trend or relation has apparently been established between the grain size of an alloy and that of the corresponding scales, the scales growing on finer-grain materials tend to have also smaller grains, i.e. to contain a larger density of grain boundaries, which can affect the rate of growth of external scales by the same mechanism involved in mass transport through metallic materials^[20]. In principle, both the anionic and cationic species can diffuse across compact and adherent scales more rapidly along the grain boundaries or other short-circuit paths than through the bulk, resulting in faster overall rates of scale growth.

5 CONCLUSIONS

The oxidation kinetics for the two alloys containing 80% Ni (mole fraction) is complex and deviates from the parabolic rate law and usually is not composed of a single parabolic stage. Mixed scales are produced on the CACu-80Ni alloy surface, which consist of a CuO outer layer and an inner layer containing a mixture of Cu_2O and NiO. However, the oxide scale for MACu-80Ni alloy is composed of a thin

external layer of CuO and a thick compact inner layer of NiO. The reduction in the alloy grain size finishes the transition from a mixed scale of Cu₂O and NiO to a continuous scale of NiO.

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