Journal of Alloys and Compounds 480 (2009) 449–453

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Oxidation of a quaternary two-phase Cu–40Ni–17.5Cr–2.5Al alloy at 973–1073 K in 101 kPa O_2

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ARTICLE INFO

Article history:
Received 1 July 2008
Received in revised form 9 December 2008
Accepted 15 December 2008
Available online 24 December 2008

Keywords:
Cu–Ni–Cr–Al alloy
Two-phase
High-temperature oxidation

ABSTRACT

Oxidation of a quaternary two-phase Cu–40Ni–17.5Cr–2.5Al (at.%) alloy was investigated at 973–1073 K in 101 kPa O_2. The alloy is composed of two phases. One light phase with lower Cr content forms the matrix of the alloy, and the other medium gray phase richer in Cr is presented in the form of continuous islands. At 973 and 1073 K, the kinetic curves for the present alloy deviate evidently from the parabolic rate law. They show a large mass gain in initial stage, and then their oxidation rates decrease evidently with time until they become very small up to 24 h. Cross sectional morphologies show the present alloy is able to form continuous external scales of chromia over the alloy surface with a gradual decrease in the oxidation rate. However, the previous studies showed that a ternary two-phase Cu–40Ni–20Cr alloy is unable to form protective external scales of chromia over the alloy surface, but is able to form a thin and very irregularly continuous layer of chromia at the top of the mixed internal oxidation region. Therefore, substituting Cr in Cu–40Ni–20Cr alloy with 2.5 at.% Al is able to decrease the critical content required to form Cr oxide and help to form continuous external scales of chromia under lower Cr content in two-phase alloys.

1. Introduction

High-temperature alloys or coatings need to form stable and slowly growing Cr_2O_3, Al_2O_3 or SiO_2 scales in order to protect them against oxidation [1–4]. The oxidation behavior of ternary or more alloys is more complex than that of binary alloys because the number of possible oxidation of mode is much larger for ternary or more alloys [5]. Cu–Ni–Cr alloys are good materials to study the high-temperature oxidation mechanism of ternary systems containing more than one phase [6,7]. The previous studies of Cu–Ni–Cr alloys showed that a single-phase alloy with about 20 at.% Cr is able to form an external scale of chromia over the alloy surface, while a two-phase alloy with about 20 at.% Cr is unable to form an external scale of chromia, but is able to form a thin and very irregularly continuous layer of chromia at the top of the mixed internal oxidation region with a gradual decrease in the oxidation rate up to very low values [8]. A three-phase alloy with about 20 at.% Cr is unable to form a chromia scale over the alloy surface and at the base of the scale even after an extended period of oxidation [9], while a three-phase alloy with about 30 at.% Cr is able to form a very irregular layer of chromia at the top of the mixed internal oxidation region or an external scale of chromia with an internal oxidation of Cr [10,11]. Finally, a three-phase alloy with about 40 at.% Cr is only able to form an external scale of chromia [11]. Compared with the corresponding binary two-phase Cu–Cr alloys [12], it is found that adding the third component Ni to Cu–Cr alloys is able to decrease the critical content of the reactive component Cr required to form an exclusive external scale of chromia over alloy surface evidently, but it is still higher than that for binary single-phase alloys such as Ni–Cr alloys, etc. [13,14]. In fact, higher content of the reactive component in the alloy may increase the brittleness [15]. This paper examines the oxidation behavior of a quaternary two-phase Cu–40Ni–17.5Cr–2.5Al alloy formed by substituting Cr in Cu–40Ni–20Cr alloy with 2.5 at.% Al. A special attention is focused on establishing the possibility of formation of a continuous external scale of chromia under lower Cr content in two-phase alloys.

2. Experimental

A Cu–Ni–Cr–Al alloy with nominal contents of 40 at.% Cu, 40 at.% Ni, 17.5 at.% Cr and 2.5 at.% Al, denoted as Cu–40Ni–17.5Cr–2.5Al, was prepared by arc-melting appropriate mixtures of the pure components (99.99%) under a Ti-gettered argon atmosphere using non-consumable tungsten electrodes. The alloy ingot was subsequently annealed in vacuum at 800 °C for 24 h to remove residual mechanical stresses and to achieve a better equilibration of the alloy phases.

The microstructure of Cu–40Ni–17.5Cr–2.5Al alloy is shown in Fig. 1. In fact, the present alloy is composed of two different phases with a similar volume fraction by combining scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM/EDX) with X-ray diffraction (XRD) results. According to EDX analyses, the actual average composition of Cu–40Ni–17.5Cr–2.5Al alloy is 39. 9 at.% Cu, 39.6 at.% Ni, 17.6 at.% Cr and 2.9 at.% Al. The light α phase contains about 69.3 at.% Cu, 22.6 at.%

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doi:10.1016/j.jallcom.2008.12.043

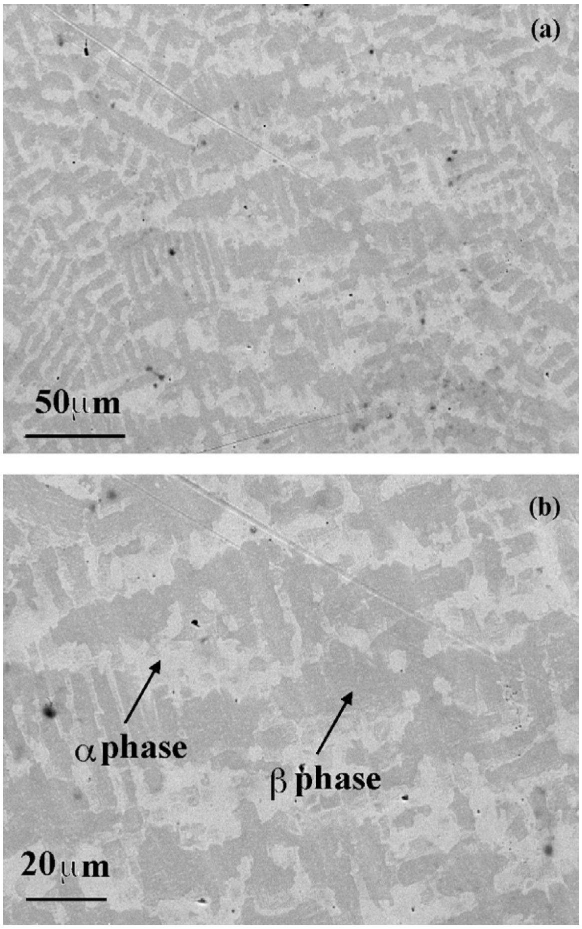

Fig. 1. Microstructures (BEI) of Cu–40Ni–17.5Cr–2.5Al alloy: (a) general view and (b) expanded view.

Ni, 4.8 at.% Cr and 3.3 at.% Al. The medium gray β phase with larger Cr content contains approximately 16.8 at.% Cu, 53.8 at.% Ni, 26.7 at.% Cr and 2.7 at.% Al. The α phase forms the matrix of the alloy, while the β phase is presented in the form of continuous islands. Moreover, the β phase appears to contain a precipitation of the very fine α phase particles.

Flat specimens of about 0.001 m thick with a surface area of about 0.0002 m^2 were cut from the alloy ingot by means of a diamond-wheel saw, ground down to 1000 emery paper, washed in water and acetone and dried immediately before they were oxidized. The oxidation tests were carried out at 973–1073 K in 101 kPa O_2 for 24 h with a continuous mass gain measurements by a Cahn Versa HM microbalance. After specimens were oxidized, they were examined by SEM/EDX and XRD to determine the structure, composition and spatial distribution of the oxidation products.

3. Results

3.1. Oxidation kinetics

The kinetic curves for Cu–40Ni–17.5Cr–2.5Al alloy oxidized at 973–1073 K in 101 kPa O_2 for 24 h are shown in Fig. 2. At both temperatures, the kinetic curves for the present alloy are irregular and deviate evidently from the parabolic rate law. They show a large mass gain in initial stage, and then their oxidation rates decrease evidently with time until they become very small up to 24 h. The kinetic curve can be described approximately as two quasi-parabolic stages. There are the first stage with a rate constant $k_p = 4.4 \times 10^{-4}$ (all k_p values in g^2 m^{-4} s^{-1}) for the initial 2 h and the second stage with an average k_p value of $k_p = 4.3 \times 10^{-5}$ about 6 h at 973 K, while there are the first with a rate constant $k_p = 1.3 \times 10^{-3}$ for the initial 2 h and the second with an average k_p value of 7.5×10^{-5} about 3 h at 1073 K. After two quasi-parabolic stages, the oxidation rates decrease evidently with time until they become very small up to 24 h. The alloy oxidizes more rapidly at 1073 K than that at 973 K. Comparison of mass gain between the present two-phase Cu–40Ni–17.5Cr–2.5Al and the previous two-phase Cu–40Ni–20Cr alloys oxidized at 973–1073 K in 101 kPa O_2 for 24 h is shown in Fig. 3. Obviously, the oxidation rates of the present Cu–40Ni–17.5Cr–2.5Al alloy are significantly smaller than those of the previous Cu–40Ni–20Cr alloy at both temperatures.

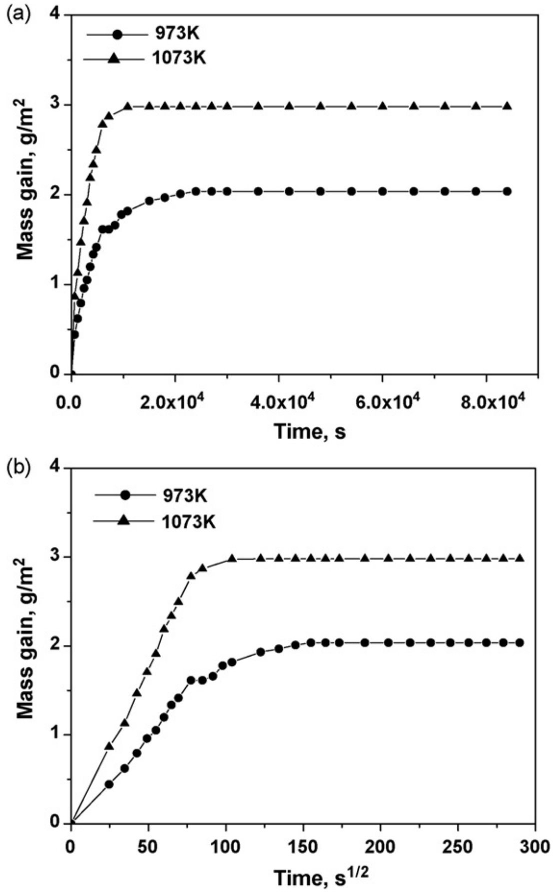

Fig. 2. Kinetic curves for Cu–40Ni–17.5Cr–2.5Al alloy oxidized at 973–1073 K in 101 kPa O_2 for 24 h: (a) normal plots and (b) parabolic plots.

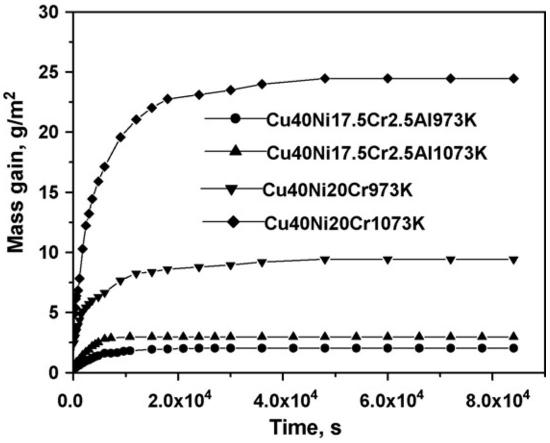

Fig. 3. Comparison of mass gain between the present two-phase Cu–40Ni–17.5Cr–2.5Al and the previous two-phase Cu–40Ni–20Cr alloys oxidized at 973–1073 K in 101 kPa O_2 for 24 h.

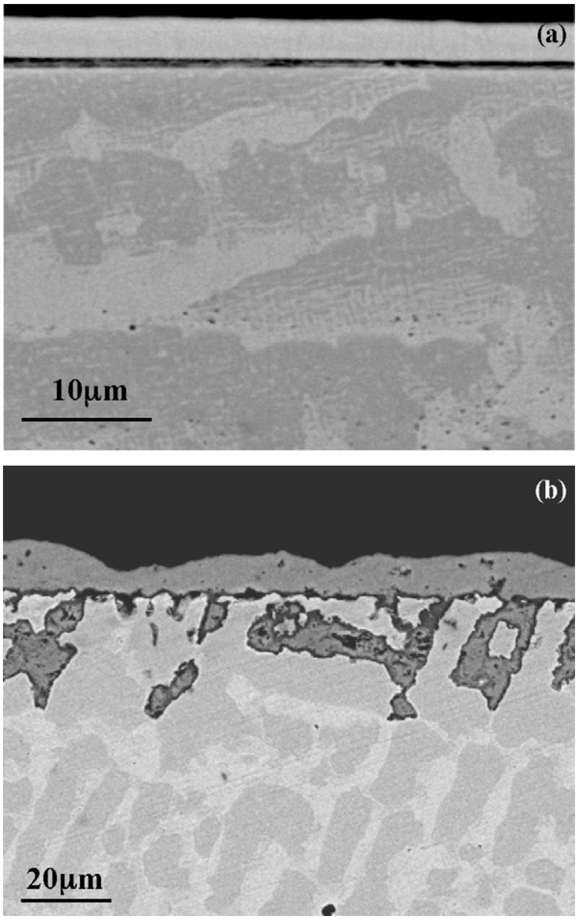

Fig. 4. Cross sectional morphologies of the present Cu–40Ni–17.5Cr–2.5Al and the previous Cu–40Ni–20Cr alloys oxidized for 24 h at 973 K in 101 kPa O_2 (BEI): (a) the present Cu–40Ni–17.5Cr–2.5Al and (b) the previous Cu–40Ni–20Cr [8].

3.2. *Scale microstructure and composition*

The comparison of microstructures of the scales between the present two-phase Cu–40Ni–17.5Cr–2.5Al and the previous two-phase Cu–40Ni–20Cr alloy [8] oxidized at 973–1073 K in 101 kPa O_2 for 24 h are shown in Figs. 4 and 5, respectively. The previous ternary two-phase Cu–40Ni–20Cr alloy (Figs. 4b and 5b) is unable to form protective external scales of chromia over the alloy surface, but is able to form a very irregular, thin but essentially continuous scale of chromia at the base of the mixed internal region with a gradual decrease in the oxidation rate up to very low values. However, the present two-phase Cu–40Ni–17.5Cr–2.5Al alloy (Figs. 4a and 5a) is able to form continuous external scales of chromia over the alloy surface with fewer particles of Cu oxides at selected places only at 1073 K where the light outermost layer is of metal Ni, electroplated on the oxidized sample to avoid scale spallation. At 973 K, the alloy contains a very thin and continuous layer depleted in Cr in contact with the scale, while at 1073 K there is a region containing a mixture of alloy, Cr_2O_3 and fewer Al oxide phases with a region depleted in Cr and Al beneath scales of chromia. In fact, the islands which have been oxidized internally are not those of the β phase but those of the α phase. Obviously, substituting Cr in Cu–40Ni–20Cr alloy with 2.5 at.% Al is able to decrease the critical content required to form Cr oxide and help to form continuous scales of chromia under lower Cr content in two-phase alloys.

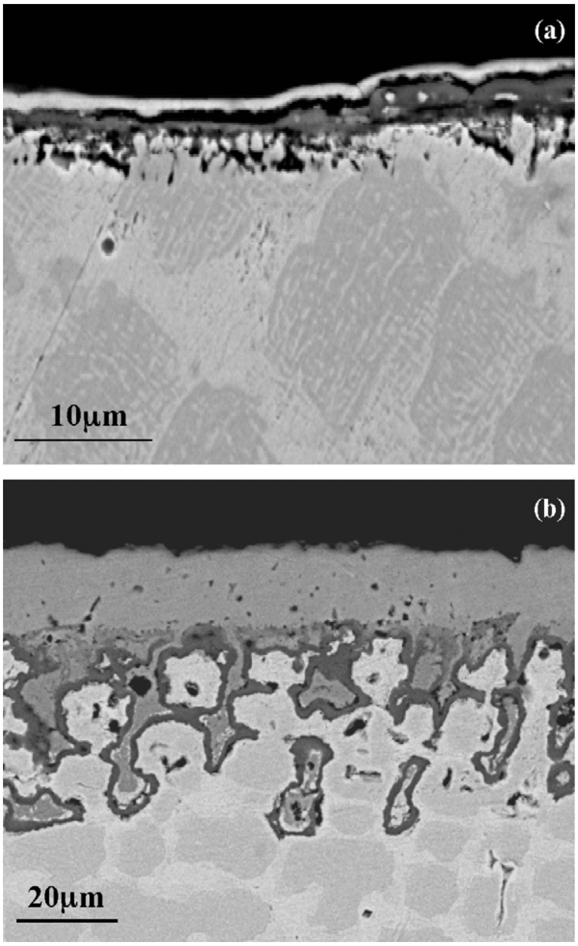

Fig. 5. Cross sectional morphologies of the present Cu–40Ni–17.5Cr–2.5Al and the previous Cu–40Ni–20Cr alloys oxidized for 24 h at 1073 K in 101 kPa O_2 (BEI): (a) the present Cu–40Ni–17.5Cr–2.5Al and (b) the previous Cu–40Ni–20Cr [8].

4. Discussion

The previous two-phase Cu–40Ni–20Cr alloy is unable to form protective external scales of chromia over the alloy surface because the simultaneous presence of two metal phases restricts the metal diffusion from the alloy to the alloy/scale interface. In fact, it forms complex external scales containing Cu oxide and a Ni–Cr spinel with a region where islands of the metallic phase richer in Cr surrounded by a thin scale of chromia are mixed with the island oxides richer in Cu and Cr, producing a situation out of equilibrium. With time, a very irregular, thin but essentially continuous scale of chromia forms at the base of the mixed internal region with a gradual decrease in the oxidation rate up to very low values [8].

On the contrary, the present two-phase Cu–40Ni–17.5Cr–2.5Al alloy is able to form continuous external scales of chromia directly over the alloy surface in spite of its relatively lower Cr content. Thus, a Cr content of 17.5 at.% is likely to produce a selective oxidation of the reactive component Cr over the quaternary two-phase Cu–40Ni–17.5Cr–2.5Al alloy surface. The critical Cr content required to form the selective external oxidation over quaternary two-phase Cu–Ni–Cr–Al alloy surface is rather lower than those over ternary two-phase and three-phase Cu–Ni–Cr alloy, or many binary two-phase alloy surface [8–12,16–19].

The important factors affecting the critical Cr content required to form the selective external oxidation over alloy surface are the solubility of reactive component Cr in noble components and phase microstructure. In fact, the critical content of reactive component B required to form external BO scales for binary A–B alloys increases as the solubility of B in A decreases. For example, a Cr content of 15–25 wt% Cr for binary single-phase solid solution Ni–Cr alloys is able to form external scales of chromia [13,14], while a Cr content of about 75 wt% for binary two-phase Cu–Cr alloys is unable to produce external scales of chromia due to the very low solubility of Cr in Cu [12]. A similar condition also applies to the ternary or more alloys formed by adding the third or fourth component to binary alloys. By substituting Cr with 2.5 at.% Al, the solubility of Cr in the quaternary Cu–40Ni–17.5Cr–2.5Al alloy by EDX analysis is larger than that in binary Cu–Cr and ternary Cu–40Ni–20Cr alloys for the phase with a lower Cr content [8,12]. Thus, the outward flux of the reactive component Cr from the alloy to the alloy/scale interface becomes high enough to sustain the continuous growth of the external scales of chromia.

The previous theoretical and experimental studies have proved that the formation of external scales of the most stable oxide at relatively high temperatures for binary two-phase alloys is more difficult than that for binary single-phase alloys under the same values of all the parameters involved [20–23]. This is a direct consequence of the substantial absence of diffusion in the alloy substrate because two phases keep in equilibrium. In fact, according to Gibbs phase rule, a binary A–B alloy exposed to oxygen can only contain a maximum of three condensed phases at constant temperature, in which the system becomes invariant. Thus, a binary two-phase alloy can be in equilibrium with only one oxide under a single value of the oxygen pressure, while two phases must have a fixed composition. No chemical potential gradients can cause long-range diffusion. As a result, these alloys will oxidize in a diffusionless manner, unless the preferential consumption of one component can make one phase disappear in an alloy substrate layer beneath the scale.

A similar condition also applies to the ternary or more alloys formed by adding the third or fourth component to binary alloys. The maximum number of phases that can coexist in a ternary A–B–C alloy exposed to oxygen at constant temperature is four, in which the system becomes invariant. Thus, if a ternary two-phase alloy can be in equilibrium with only one oxide, the system becomes monovariant, and the two metal phases can coexist with one oxide in a finite range of compositions. The depletion in the reactive component C will produce gradients of concentration of the reactive component C in a direction perpendicular to the alloy surface due to the formation of the external oxide. Thus, it will increase an outward flux of the component forming the external oxide, which may be sufficient to make it stable over the alloy substrate surface under convenient conditions. For example, the ternary two-phase Cu–40Ni–20Cr alloy is able to form a thin and very irregularly continuous scale of chromia at the top of the mixed internal oxidation region with a gradual decrease in the oxidation rate up to very low values [8]. However, if a ternary three-phase alloy remains three phases up to the alloy/scale interface in any case, it can be in equilibrium with only one oxide under a single value of the oxygen pressure, while the composition of the three metal phases must remain constant. Thus, diffusion among the alloy substrate in ternary three-phase alloys is prevented again, exactly as in the case of binary two-phase alloys. Actually, the preferential or even exclusive consumption of one or more components to form the external scale may decrease their content in a subsurface alloy layer, and produce the disappearance of one or more phases. After this, metal diffusion in the alloy make it possible in principle to help to form the most stable oxide under appropriate condition. For example, a ternary three-phase Cu–20Ni–20Cr alloy is unable to form protective external scales of chromia over the alloy surface and at the base of the scale even after an extended period of oxidation, while a ternary three-phase Cu–45Ni–30Cr alloy is eventually able to form protective external scales of chromia because the oxidation proceeds with the disappearance of one phase [9,10]. Finally, the maximum number of phases that can coexist in a quaternary A–B–C–D alloy exposed to oxygen at constant temperature is five. Thus, for a quaternary three-phase alloy, exactly as in the case of ternary two-phase alloys, the compositions of the three phases may change in finite ranges, so that transport by diffusion is possible without requiring the disappearance of one phase. For example, a quaternary three-phase Cu–20Ni–20Cr–5Fe alloy is able to form a very irregular, thin but essentially continuous scale of chromia at the base of the mixed internal region with a gradual decrease of the oxidation rate [24]. However, the two metal phases can only coexist with one oxide in a finite range of compositions for the present quaternary two-phase Cu–40Ni–17.5Cr–2.5Al alloys, in which the system becomes di-variant, and diffusion of the reactive component Cr from alloy to the alloy/scale interface becomes much faster. Thus, the present alloy is able to form flat, and regularly continuous external scales of chromia over the alloy surface.

A peculiar aspect of the oxidation of the present alloy at 1073 K is the existence of an internal oxidation of Cr beneath external scales of chromia, which is somewhat similar to the previous three-phase Cu–45Ni–30Cr alloy [10]. In fact, the internal oxidation proceeds mainly along the α phase. The mechanism for this process is that a quaternary two-phase Cu–40Ni–17.5Cr–2.5Al alloy can be in equilibrium with oxide Cr_2O_3 of the reactive component Cr under a single value of the oxygen pressure at a fixed temperature [23]. Above this critical pressure, the α phase transforms into a mixture of oxide Cr_2O_3 with the β phase. However, in order to maintain the equilibrium with Cr_2O_3, the Cr content within the α phase must decrease continuously along a direction perpendicular to the alloy/scale interface moving away from the front of internal oxidation to the alloy/scale interface. Thus, it provides a driving force for the outward diffusion of the reactive component Cr. Finally, the alloy forms flat, and regularly continuous external scales of chromia over the alloy surface with a Cr internal oxidation.

5. Conclusion

The Cu–40Ni–17.5Cr–2.5Al alloy is composed of two phases with a similar volume fraction, one is the light α phase with lower Cr content, and the other is the medium gray β phase richer in Cr. The light α phase forms the matrix of the alloys, while the medium gray β phase is presented in the form of continuous islands. At 973 and 1073 K, the kinetic curves for the present alloy deviate evidently from the parabolic rate law. They show a large mass gain in initial stage and then their oxidation rates decrease evidently with time until they become very small up to 24 h. The present alloy is able to form continuous external scales of chromia over the alloy surface with a gradual decrease in the oxidation rate. In fact, the two metal phases can only coexist with one oxide in a finite range of compositions, in which the system becomes di-variant, and diffusion of the reactive component Cr from alloy to the alloy/scale interface becomes much faster. Obviously, substituting Cr in Cu–40Ni–20Cr alloy with 2.5 at.% Al is able to decrease the critical content of forming external scales of chromia and help to form a continuous scale of chromia under lower Cr content in two-phase alloys. Thus, the formation of external scales of chromia for quaternary two-phase Cu–Ni–Cr–Al alloys is much easier than that for binary two-phase Cu–Cr alloys and ternary two-phase Cu–Ni–Cr alloys under similar conditions.

Acknowledgments

Financial supports by the National Natural Science Foundation of China under contact no. 50771068 and Liaoning Province Education Committee of China under contact no. 2007T166 are gratefully acknowledged.

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