# High temperature oxidation of powder metallurgy two-phase Cu-Cr alloys under low oxygen pressure ①

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**Abstract :** The oxidation of two-phase Cu-Cr alloys containing 25 % and 50 % Cr prepared by powder metallurgy ( PM) with a rather uniform two-phase microstructure has been studied at 700 ~ 900 ℃ under oxygen pressure below the stability of the copper oxides . The two PM alloys oxidized very slowly and formed only external $Cr_2O_3$ scales rather than undergoing an internal oxidation of chromium . This result is attributed mainly to a supply of chromium from the small Cr-rich particles dispersed within the Cu-rich phase . The oxidation kinetics of the two PM Cu-Cr alloys approximately followed the parabolic rate law . The scaling rates are of the same order as those measured for pure chromium under the same oxygen pressure , but smaller than those for the alloys of similar composition prepared by normal arc melting techniques , whose compositions were largely non-uniform . The results are interpreted in terms of the two-phase nature of these alloys .

**Key words :** two-phase Cu-Cr alloys ; oxidation ; low oxygen pressure                    **Document code : A**

## 1   INTRODUCTION

Many structural materials for high temperature applications contain two or more metallic phases , such as Ni- or Co-base superalloys , and have different corrosion behaviors with respect to the common single-phase alloy[1] . Cu-Cr alloys are ideal systems to study high-temperature corrosion of binary two-phase materials because the two metals have very small mutual solubility and do not form intermediate phase . Moreover , the thermodynamic stability and the growth rates of their oxides are largely different[2] , so that the two phases are expected to exhibit quite different scaling behaviors when the oxidant pressure is sufficient to oxidize both alloy components . However , the volume fraction and spatial distribution of the two phases of these alloys prepared by normal arc melting techniques changed considerably from sample to sample of the same alloy , and even quite distinctly from one region to another within the same sample , while the uniformity of their microstructure could not be improved even by repeated melting as well as annealing treatments at high temperatures . The large deviations of the local composition of these alloys from the average value had significant effects on their oxidation behaviors[3] . This paper examines the scaling behaviors of two powder metallurgy Cu-Cr alloys containing 25 % and 50 % Cr with a uniform microstructure under low oxygen pressure , below the stability of the copper oxide , to compare the alloys of similar composition prepared by normal melting processes considered previously[3] .

## 2   EXPERIMENTAL

Two binary Cu-Cr alloys with nominal chromium contents of 25 % and 50 % were prepared by powder metallurgy technique ( denoted as PM Cu-25Cr and PM Cu-50Cr , respectively) . Both PM alloys are two-phase , as shown in Fig .1 , and contain a dispersion of isolated-phase particles composed of practically pure chromium ( dark) in a matrix of copper-rich phase ( light) . The alloys are still composed of a number of small chromium particles dispersed within the copper matrix which contains an average content of chromium up to 2 % . The volume fraction and the spatial distribution of the two phases are rather uniform , at variance with the Cu-Cr alloys studied previously[3] , even though the chromium particles tend to form dendritic clusters in PM Cu-25Cr .

Samples of about 2 .5 $cm^2$ surface area were oxidized for 24 h using $H_2$-$CO_2$ gas mixtures containing 92 .9 % , 33 .0 % and 4 .2 % $CO_2$ at 700 , 800 and 900 ℃ , balance $H_2$ , which under equilibrium conditions provide $10^{-20}$ MPa $O_2$( below the stability of $Cu_2O$) . The kinetics was measured continuously by a model 2 000 Cahn thermobalance . Oxidized samples were examined by X-ray diffraction and scanning electron microscopy with energy dispersive spectrometer ( SEM/ EDX) to study the scale microstructure .
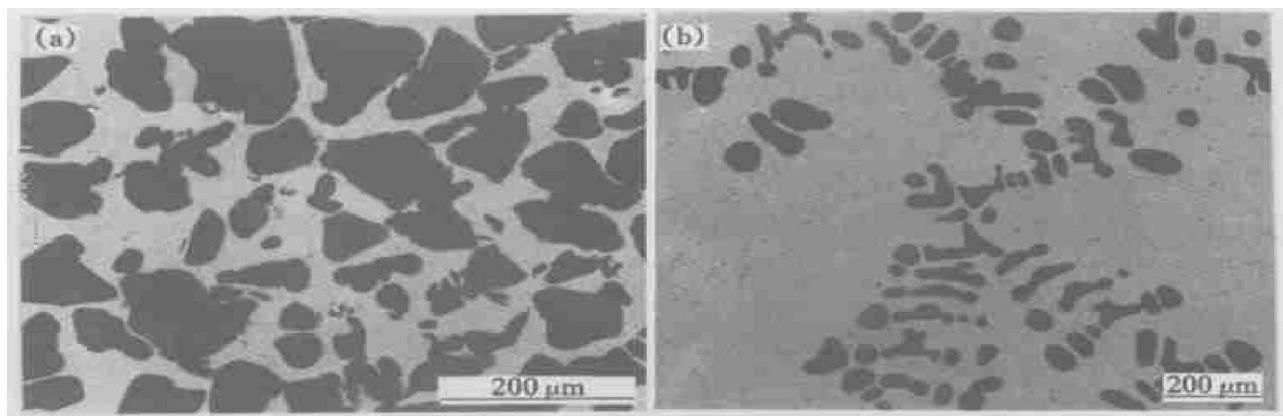
**Fig .1**  Microstructures ( SE M/ BEI) of binary two-phase alloys
(a) —P M Cu-25Cr ; ( b) —P M Cu-50Cr

## 3  RESULTS

The oxidation kinetics of the two P M Cu-Cr al-
loys and of pure chromium at the three temperatures
is shown in Figs .2( a) ~ ( c) , respectively . The oxi-
dation kinetics followed parabolic rate law for both al-
loys at 900 ℃ and for P M Cu-25Cr at 800 ℃ , while
in other cases the rates were parabolic only during an
initial stage and then became linear . At all tempera-
tures P M Cu-50Cr oxidized more rapidly than P M
Cu-25Cr and the scaling rates are of the same order as
those measured for pure chromium under the same
oxygen pressure . Approximate values of the rate con-
stants calculated from appropriate sections of the ki-
netic curves are reported in Table 1 .

In fact , effective mass gains can be used to com-
pare the oxidation rate between the present two P M
alloys under $10^{-20}$ MPa $O_2$ and those measured for
the normal Cu-25Cr and Cu-50Cr alloys prepared by
melting technique[4] under the same experimental
conditions , in view of their generally irregular kinet-
ics . Fig .2( d) shows an example for the temperature
of 800 ℃ : the results for the other two temperatures
are similar and thus are not shown for brevity . P M
Cu-25Cr oxidizes at rates slightly lower than those of
Cu-25Cr , while P M Cu-50Cr oxidizes significantly
more slowly than Cu-50Cr .

The scale structure grown on the two P M alloys
after 24 h oxidation at 700 ~ 900 ℃ is shown in Figs .
3 and 4 , respectively . Both alloys formed only an ex-
ternal chromia layer ( as determined by means of
SE M/ EDX and XRD) , as a fact that the oxygen
pressure in the gas was below the dissociation pressure
of $Cu_2O$ ( equal to 1 .8 × 10$^{-12}$ , 8 .2 × 10$^{-11}$ and 1 .9
× 10$^{-9}$ MPa $O_2$ at 700 , 800 and 900 ℃ , respective-
ly) and also of the double oxide $Cu_2Cr_2O_4$[3] . The
thickness of the chromia layer is not completely uni-
form for each sample . The external oxide scale
formed on P M Cu-25Cr at 700 ℃ is too thin to be ob-
served by SE M . Occasionally , some zones of the sam-

ple surface oxidized at higher temperatures are also
free from an oxide layer . However , the absence of in-
ternal oxidation of chromium behind the surface re-
gions suggests that an external scale was present over
the whole sample during exposure at high tempera-
tures and then spalled off during cooling . Only after
oxidation at 900 ℃ , some degree of internal oxidation
of chromium and/ or of interphase boundary attack ,
possibly formed before the external chromia layer was
established , is observed over some regions of both P M
alloys ( Figs .3( b) and 4( d)) . Besides producing an
external layer , chromia tends also to form deeper in
the alloy along the interfaces between the two phases .

## 4  DISCUSSION

The most important difference between the scal-
ing behaviors of the P M Cu-Cr alloys under low oxy-
gen pressure and in air[5] is their ability to form exter-
nal chromia scales under the present conditions , as
observed previously for the cast Cu-Cr alloys[4] . In
fact , the oxidation of the normal and P M Cu-Cr ma-
terials with similar chromium contents in air or in
pure oxygen produces complex scales containing a
mixture of the oxides of the two metals with a double
Cu-Cr oxide ( $Cu_2Cr_2O_4$ )[3,5] . This difference is
mainly a consequence of the low value of the oxygen
pressure used here . In fact , the critical content of the
most-reactive component B of binary solid-solution A-
B alloys required for its exclusive external oxidation is
significantly lower , when the oxygen pressure is be-
low ( low oxidant pressures) , than that above ( high
oxidant pressures) the dissociation pressure of the ox-
ide of the more noble component ( AO)[6] .

If these alloys are considered to be solid-solution
systems , the critical chromium content needed for the
transition at 900 ℃ under 10$^{-20}$ MPa $O_2$ is calculated
as 1 .7 × 10$^{-2}$( mole fraction)[7~9] . Thus , if the Cu-
rich solid-solution behaved independently of the Cr-
rich phase , its chromium content would be insuffi-
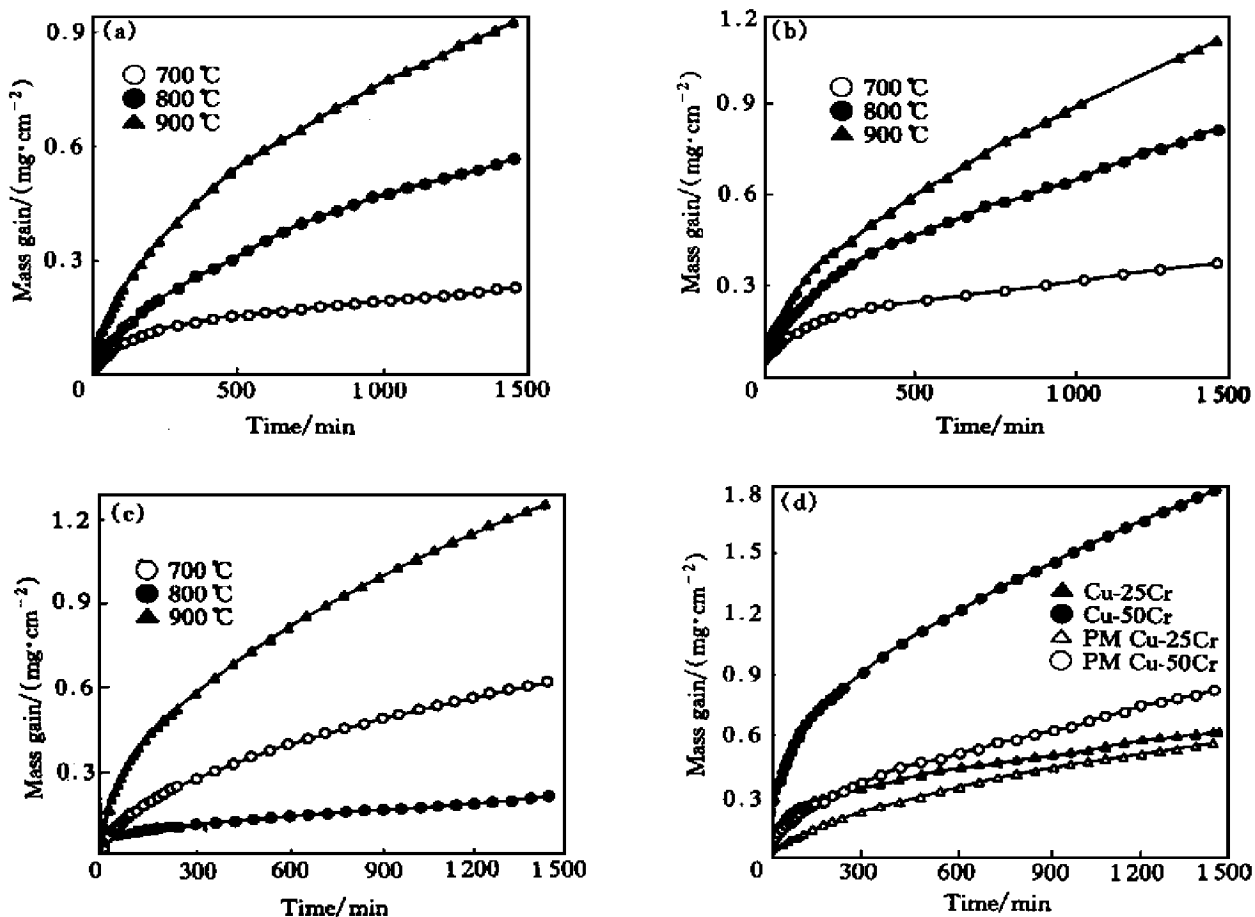cient to form continuous chromia scales .

Fig .2    Oxidation kinetics of P M Cu-25Cr ( a) , P M Cu-50Cr ( b) and pure chromium ( c) under $10^{-20}$ MPa $O_2$ at 700 ~ 900 ℃ as well as comparison with two cast Cu-Cr alloys at 800 ℃ ( d)

Table 1    Approximate parabolic rate constants for oxidation of pure chromium and two P M Cu-Cr alloys under $10^{-20}$ MPa $O_2$ at 700 ~ 900 ℃ for 24 h ( $g^2 \cdot cm^4 \cdot s^{-1}$ )

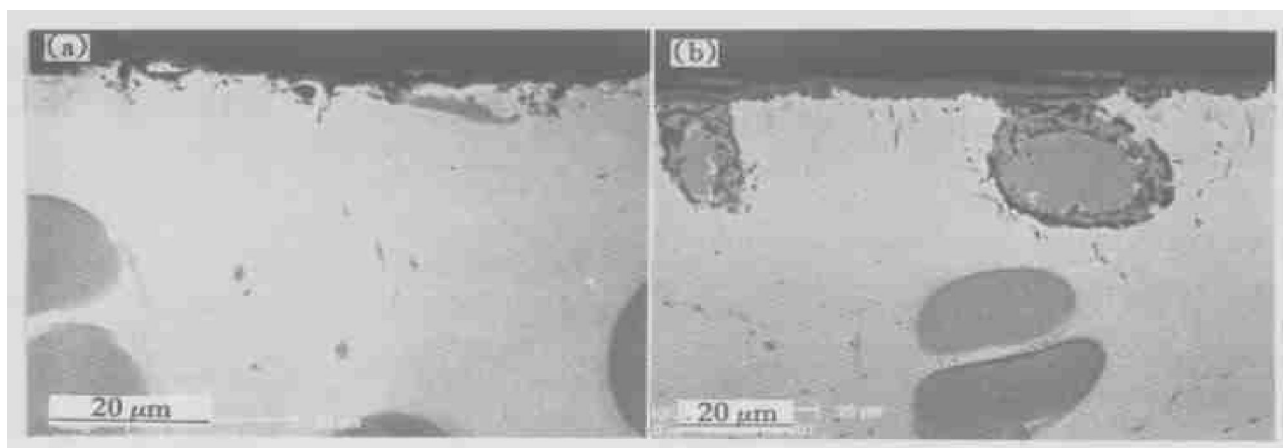| Material | 700 ℃ | | 800 ℃ | | 900 ℃ | |
|---|---|---|---|---|---|---|
| | Initial | Final | Initial | Final | Initial | Final |
| Cu-25Cr | $1.3 \times 10^{-12}$ | Linear | $4.8 \times 10^{-12}$ | $4.6 \times 10^{-12}$ | $1.1 \times 10^{-11}$ | $1.1 \times 10^{-11}$ |
| Cu-50Cr | $2.8 \times 10^{-12}$ | Linear | $7.8 \times 10^{-12}$ | Linear | $1.1 \times 10^{-11}$ | $2.0 \times 10^{-11}$ |
| Cr | Irregular | Linear | $4.3 \times 10^{-12}$ | $4.3 \times 10^{-12}$ | $1.7 \times 10^{-11}$ | $1.7 \times 10^{-11}$ |



Fig .3    Scale micrographs ( SE M/ BEI) of P M Cu-25Cr oxidized for 24 h under $10^{-20}$ MPa $O_2$ at 800 ℃ ( a) and 900 ℃ ( b)
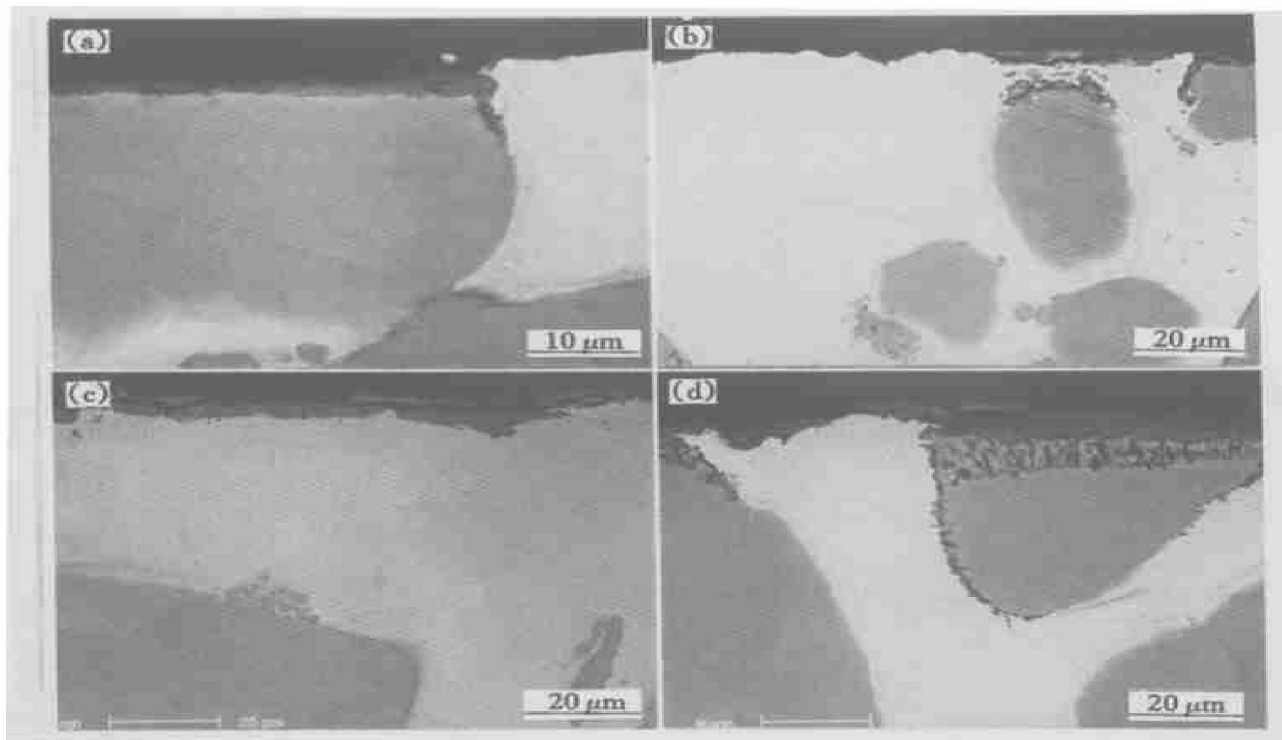
**Fig .4**   Scale micrographs ( SE M/ BEI) of P M Cu-50Cr oxidized for
24 h under 1 0$^{-20}$ MPa O$_2$ at 700 ℃ ( a) , 800 ℃ ( b) and 900 ℃ ( ( c) , ( d) )

The formation of an external chromia layer even over the islands of the Cu-rich phase and the absence of internal oxidation of chromium , are very likely due to the presence of the small chromium particles dispersed within the $\alpha$ phase , which act as reservoirs of chromium, dissolving when the surrounding matrix becomes undersaturated . In this way the $\alpha$ phase behaves as a Cu-base solid solution with a chromium content larger than its solubility in copper , allowing the growth of chromia scales over the Cu-rich regions . This is particularly effective when the chromium particles are very small , as already pointed out[10] . Finally, the diffusion of chromium from the surrounding $\beta$ phase regions , even in directions parallel to the alloy surface , may also contribute to increasing the chromium flux through the $\alpha$ phase required to sustain the growth of the outer chromia scales at the rates observed over these regions .

The oxidation under high oxygen pressures of the present alloys[5] produces external scales containing a mixture of copper and chromium oxides as well as a double Cu-Cr oxide , as recalled above , showing that their chromium contents are insufficient for its exclusive external oxidation , at variance with what is observed under low oxygen pressures . This result agrees with the fact that in the oxidation of solid-solution A-B alloys under high oxygen pressures , when external AO scales are stable , the critical B content required for the transition from the internal to the external oxidation of B is higher than the predicted above for low oxygen pressures[6] . The corrosion rates of these alloys change with their chromium con-

tent under constant temperature and are larger for P M Cu-50Cr than for P M Cu-25Cr and are also different with respect to those of pure chromium .

According to a previous model of the defect structure of Cr$_2$O$_3$[11] , the main transport process through chromia should be by metal interstitial . So, in the presence of compact and adherent scales , the parabolic rate constant for the oxidation of chromium expressed in terms of thickness of metal consumed , $k_c^0$, under an oxygen pressure in the gas , $p_g($ O$_2)$ , is given by[11]

$$k_c^0 = \theta\{ \ p_{eq}( O_2)^{-3/16} - \ p_g( O_2)^{-3/16}\} \qquad (1)$$

where   $p_{eq}($ O$_2)$ is the oxygen pressure for the Cr/ Cr$_2$O$_3$ equilibrium and $\theta$ an appropriate constant .

In the oxidation of Cu-Cr alloys forming external chromia scales , as observed here , the activity of chromium at the alloy-scale interface is smaller than 1 , so that the oxygen pressure prevailing in the scale at its interface with the alloy is higher than that prevailing at this site in the oxidation of pure chromium at the same temperature . In principle , this should produce a decrease of the parabolic rate constant of the alloy with respect to pure Cr under the same oxygen pressure in the gas , because the rate constant for the oxidation of the alloys , $k_c( a)$ , is given by

$$k_c( a) = \theta\{ \ p_i( O_2)^{-3/16} - \ p_g( O_2)^{-3/16}\} \qquad (2)$$

where   $p_i($ O$_2)$ is the oxygen pressure for the equilibrium between chromia and chromium under the activity prevailing at the alloy/ scale interface , $a_i($ Cr) . The two latter parameters are related by

$$p_i( O_2) = [ \ K( Cr_2O_3) \ a_i( Cr)^2 ]^{-2/3} \qquad (3)$$

where $K(Cr_2O_3)$ is the equilibrium constant for the chromia formation. Moreover, since the chromium depletion at the alloy-scale interface is more serious for alloys poor in chromium, the rate constant for the alloy oxidation should increase with their chromium content. The dependence of the rate constant for the oxidation of Cu-Cr alloys on the chromium activity at the alloy-scale interface, $a_i(Cr)$, calculated assuming the formation of external $Cr_2O_3$ scales using Eqs.(2) and (3), is shown in Fig.5.
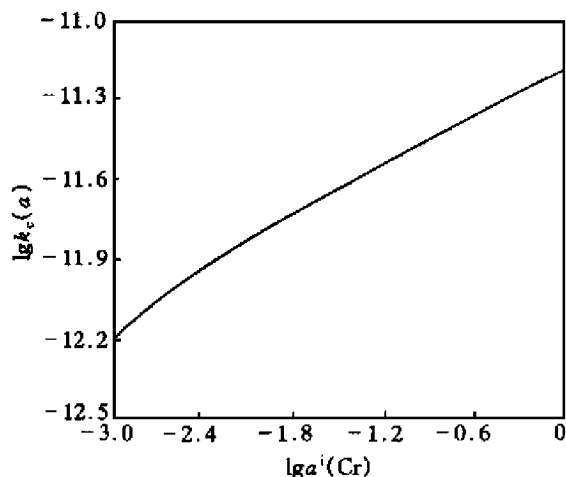


**Fig.5**  Parabolic rate constant for growth of external chromia scales on binary alloys (in terms of thickness of metal consumed) as a function of Cr activity at alloy-scale interface at 900 ℃

These predictions correspond only partly to the sequence of kinetic data observed in the present system. According to the rate constants (Table 1) and the mass gain in Fig.2, the rate of PM Cu-50Cr is slightly higher than that of PM Cu-25Cr under each testing condition, while both alloys oxidize more or less at the same order of rates as pure chromium under $10^{-20}$ MPa $O_2$ at all temperatures, which could be a consequence of the doping of chromia by copper, as examined elsewhere[4].

Another possible reason for the observed difference between the rates of growth of chromia over the present alloys and pure chromium may be that the thickness of the scales grown on the alloys is not uniform, while a significant degree of attack along the interphase boundaries is also present, at variance with the case of oxidation of pure chromium. This may contribute to producing larger mass gains than those in the case of growth of uniform scales, even though a quantitative estimate of these effects does not seem possible. Therefore, no simple analysis of the effect of the alloy composition on the scaling kinetics appears possible for these systems, due to their complex structure and behavior. In any case, their rates of scaling under low oxygen pressures are substantially in agreement with those for the corrosion of pure chromium under both low and high oxygen pressures at the same temperature.

The scaling rates of the present two PM Cu-Cr alloys under $10^{-20}$ MPa $O_2$ are lower than those measured for normal Cu-Cr alloys of similar compositions, as shown in Fig.2(d). The difference is quite small for PM Cu-25Cr, but much larger for PM Cu-50Cr. A possible reason of this difference is that the chromium activity at the interface between the Cu-rich $\alpha$ phase and the external chromia layer is higher for the PM alloys than that for normal alloys of similar composition due to the smaller content of chromium in this phase in the form of small $\beta$ phase particles.

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