

[Article ID] 1003- 6326(2001) 05- 0644- 05

# Effect of grain size reduction on high temperature oxidation of binary two-phase alloys<sup>①</sup>

LI Yuan-shi(李远士)<sup>1</sup>, NIU Yan(牛焱)<sup>1,2</sup>, FU Guang-yan(付广艳)<sup>1</sup>,  
WU Wei-tao(吴维叟)<sup>1</sup>, F. Gesmundo<sup>2</sup>

(1. State Key Laboratory for Corrosion and Protection, Institute of Metal Research,  
Shenyang 110016, P. R. China;

2. Dipartimento di Ingegneria Chimica e di Processo, Università di Genova,  
Genova 16129, Italy)

**[Abstract]** The effect of grain size reduction on the high temperature oxidation of binary two-phase alloys was discussed based on the recent research progress. The results show that for those two-phase alloys with coarse grain prepared by the conventional methods, complex oxide scales are easily formed after oxidation under high oxygen pressure or under oxygen pressure below the stability limit of the less reactive component oxides. On the contrary, for the nano-sized alloys, an exclusive external oxidation of the most reactive component usually occurs during oxidation in air or pure oxygen even for much lower content of the most reactive component. So the grain size reduction is not always beneficial to improve the oxidation resistance of the materials, but exhibits different effects depending mainly on the protective feature of the scales. The transition mechanisms between the different oxidation modes are discussed with respect to the thermodynamic and dynamic aspects.

**[Key words]** two-phase alloy; nanocrystallization; oxidation mode; oxidation resistance

**[CLC number]** TG 174.44

**[Document code]** A

## 1 INTRODUCTION

Metallic materials for high temperature applications often contain more than one phase, and elements Al, Cr and Si are mainly introduced to improve their mechanical properties, such as strength and creep resistance. The corrosion resistance of these alloys depends on their ability to form stable and slowly growing protective oxides, normally  $\text{Cr}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$ , formed by selective oxidation of the corresponding alloy components<sup>[1]</sup>. Basic oxidation behavior of binary two-phase alloys shows that the exclusive external oxidation of the most reactive component is more difficult for these materials than for solid-solution alloys<sup>[2~6]</sup>. As for those simple solid-solution alloys, such as some stainless steels or Ni-based alloys, it has been demonstrated that nanocrystallization can decrease the critical concentration of the most reactive component required for the transition from the internal to the external oxidation, and the main effect of the grain size reduction is to increase the rate of transport of the metal components through the alloy by producing large densities of grain boundaries<sup>[7,8]</sup>. However, for two-phase alloys, the effects of microstructural parameters, such as grain or particle size, and the spatial distribution of each phase, have drawn less attention so far<sup>[9]</sup>. Recently, the oxidation behaviors of a series of binary two-phase alloys,

prepared by different methods<sup>[10~12]</sup>, have been studied thoroughly and the results are reviewed in this study.

## 2 EXPERIMENTAL FUNDAMENTAL

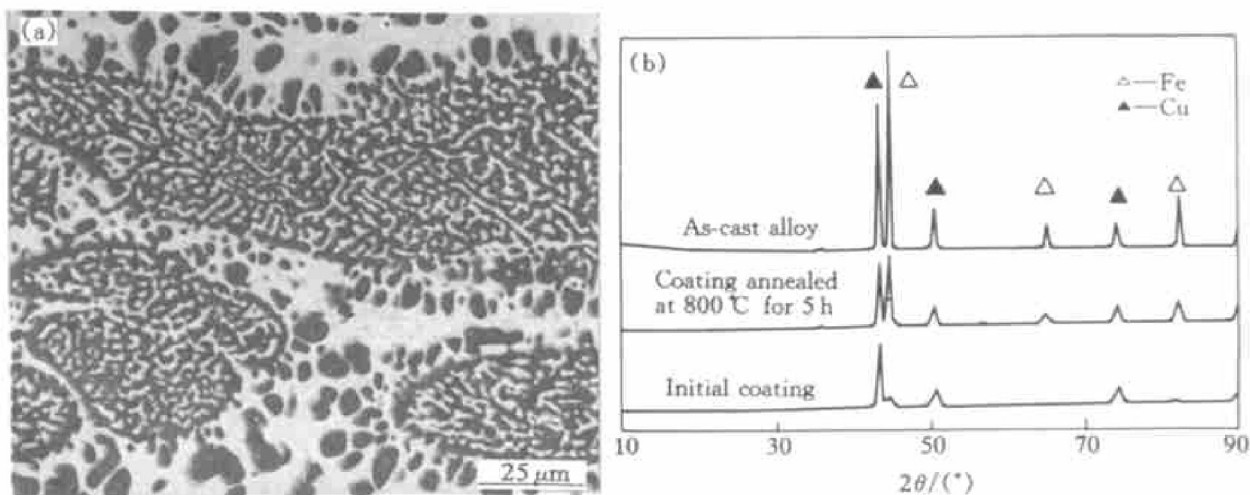
Several Cu-50% M (mass fraction) alloys (M is Cr, Fe, and Co respectively), were chosen as model materials in this study. All the alloys prepared by the conventional casting are composed of two-phase with quite big grains (as shown in Fig. 1a), while local compositions may present very strong deviation from their average bulk values. However, mechanical alloying or magnetron sputtering alloys have fine grain with size of 20~30 nm and quite excellent thermal stability and more homogeneous composition distribution (as shown in Fig. 1b). The air oxidation of those conventional alloys usually produces composite scales containing mixtures of the Cu and M oxides as well as their duplex oxides (as shown in Fig. 2a). A region of internal oxidation of M in a copper matrix is also present in most cases<sup>[12~14]</sup>. Even under low oxygen pressure that only M can be oxidized, a simultaneous internal oxidation and external oxidation of M will readily occur rather than exclusive external oxidation (as shown in Fig. 2b). On the contrary, nano-sized alloys such as Cu-Cr<sup>[10]</sup> and Cu-Fe<sup>[12]</sup> allow to obtain an exclusive external oxidation of the most reactive

① **[Foundation item]** Project (59725101) supported by the National Outstanding Youth Foundation of China

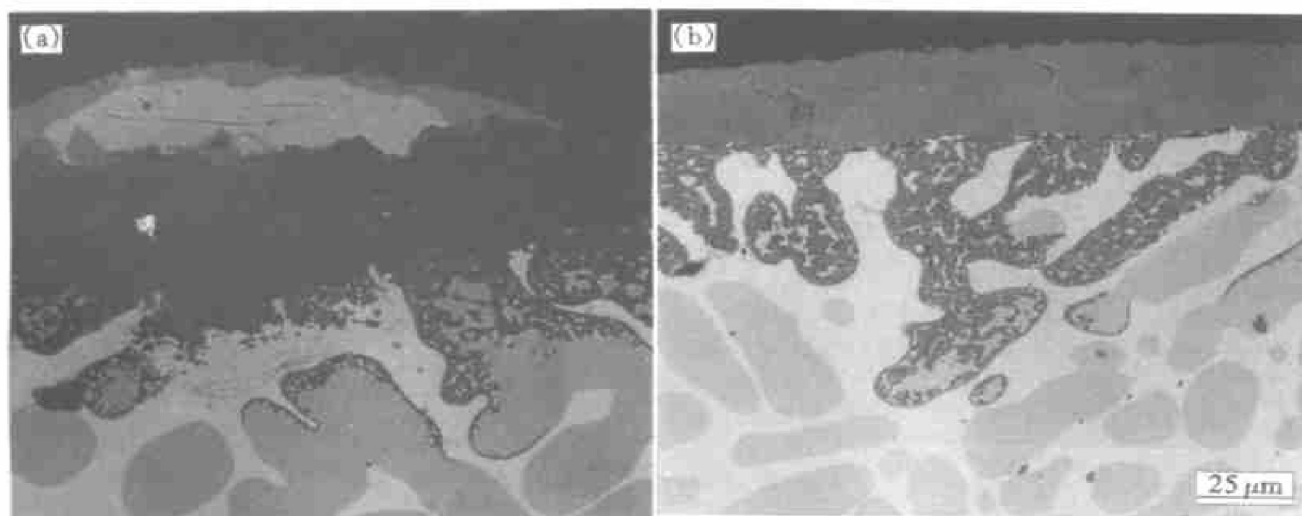
**[Received date]** 2001- 02- 19; **[Accepted date]** 2001- 06- 01

component during air oxidation (as shown in Fig. 3), even for much lower content of Cr or Fe (down to 25%), while the large reduction of the grain size is

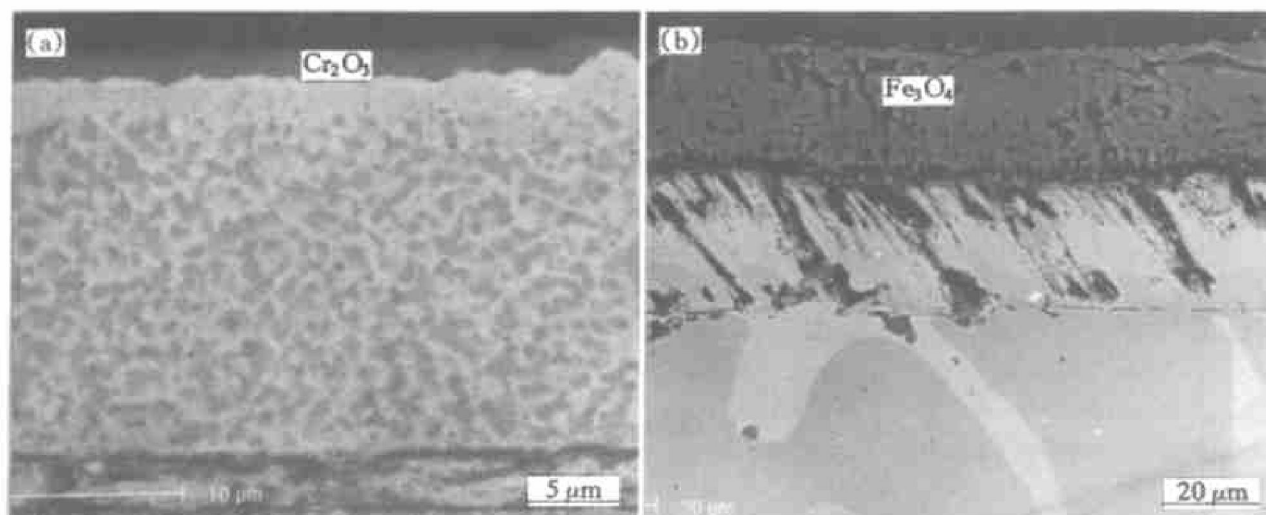
insufficient for Cu-Co alloy to promote an exclusive oxidation of cobalt, and a mixed oxide scale is still formed after air oxidation<sup>[11]</sup>. As a partial conclud-



**Fig. 1** Microstructure of as-cast Cu-Fe alloy (a) and corresponding XRD patterns (b)



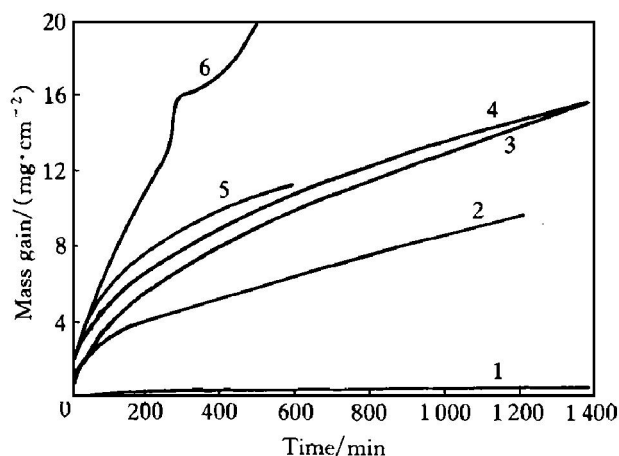
**Fig. 2** Cross-sectional morphologies of as-cast Cu-50Fe alloy oxidized at 800 °C  
(a) —In air, for 20 h; (b) —Under  $10^{-5}$  MPa  $O_2$ , for 10 h



**Fig. 3** Cross-sectional morphologies of sputtered nanocrystalline coatings oxidized in air at 800 °C  
(a) —CuCr, for 24 h; (b) —CuFe, for 1 h

sion, grain size reduction has effectively promoted the exclusive external oxidation of the most reactive component for those two-phase alloys with limited mutual solubility.

On the other hand, the grain size reduction of the alloy may also result in different effects on the oxidation resistance for different alloy systems (as shown in Fig. 4). In Cu-Cr system, for example, the oxidation rate can be reduced significantly once an external  $\text{Cr}_2\text{O}_3$  scale forms. But it is not the same case for Cu-Fe system, in which the oxidation rate increases remarkably by nanocrystallization compared with that of the conventional alloy with the same compositions. The oxidation rate of Cu-Co alloy with largely reduced grains was also much higher than that of the conventional alloy. Therefore the results imply clearly that the grain size reduction is not always beneficial to improve the oxidation resistance of the materials.



**Fig. 4** Oxidation kinetics of as-cast and

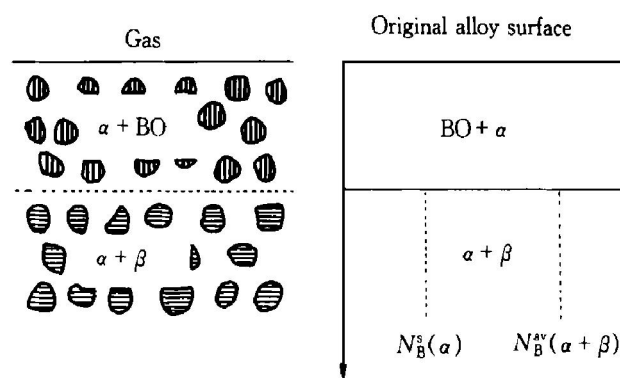
grain size reduced Cu-M alloys in air at 800 °C

- 1—Grain size reduced Cu-Cr alloy; 2—As-cast Cu-Co alloy;  
3—As-cast Cu-Cr alloy; 4—Grain size reduced Cu-Fe alloy;  
5—As-cast Cu-Fe alloy; 6—Grain size reduced Cu-Co alloy

### 3 DISCUSSION

As for binary two-phase A-B alloys (B is the more reactive component), the formation of the stable B oxide as an exclusive external scale over the alloy surface is usually more difficult than that in single-phase alloys under similar condition. In fact, the preferential or exclusive oxidation may occur, producing a depletion of that component in a subsurface layer of the alloy, so that the same component will diffuse from the bulk alloy towards the surface, while the components consumed at lower rates will diffuse oppositely. The depletion degree of the more reactive component at the alloy/scale interface will depend on a combination of the consumption rate due to the oxidation and the diffusion rate of the same component from the bulk to the surface. For two-phase A-B al-

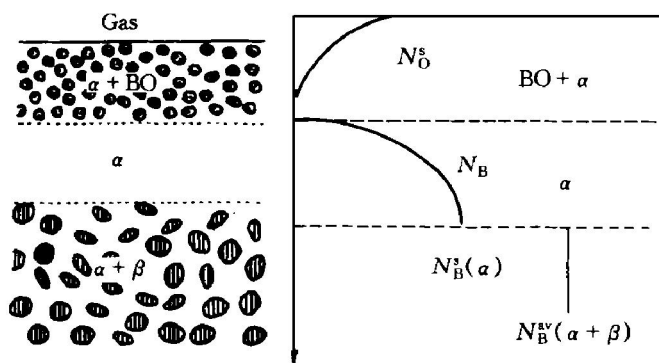
loys with quite limited mutual solubility, the diffusion of B from the matrix towards the surface can hardly occur or very difficult as long as the two phases are in equilibrium thermodynamically. As a direct consequence, the insufficient supply of the reactive element B from the alloy in the presence of two phases will not favor the formation of the most stable oxide at the alloy surface with respect to solid solutions. Furthermore, a stronger super-saturation of oxygen also occurs in two-phase alloys than in solid solutions, therefore an "in-situ" or "diffusionless" type internal oxidation of B will easily occur, which is completely different from that observed in solid solutions, as shown clearly in Fig. 5.



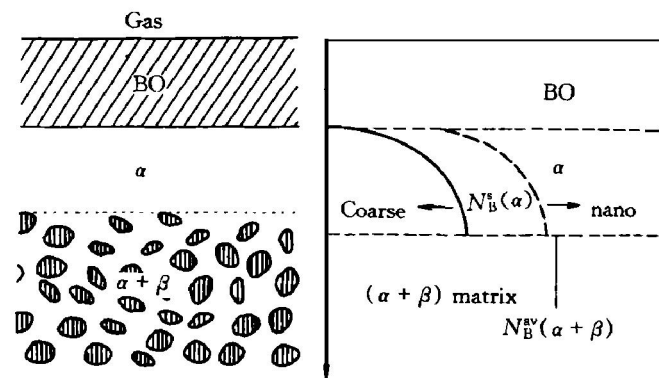
**Fig. 5** Schematic structure of corrosion-affected region formed on binary two-phase A-B alloy in absence of diffusion processes of metal components

Even under conditions that the diffusion of B in A can not be neglected, an external B oxide scale can form as well as B-depleted single-phase layer beneath the internal oxidation area. The actual solubility of B in the single-phase region is still much smaller than in those binary solid solution alloys, since it is determined by its effective solubility in the noble element-rich phase, but not the overall content in the alloy. So the concentration gradient of B in the single phase region is still not large enough to force B transport outward rapidly in order to support the continuous growth or stability of the external oxide scale, as observed in Cu-Ag system and shown in Fig. 6 here. In any case, the critical concentration required for the transition from the internal oxidation of B to an exclusive oxidation will be much higher in two phase alloys than in solid solution alloys, and the difference even increases with the decrease of the solubility of B in A<sup>[15, 16]</sup>.

As observed in Cu-Fe and Cu-Cr systems, a large reduction of the grain size promotes the formation of the most stable oxide as an exclusive external scale on the alloy surface. The change of the oxidation modes is actually due to a sum of different factors involved. One of them is related to an increased diffusivity of the metal components through the bulk al-



**Fig. 6** Schematic structure of oxide scale formed on binary two-phase A-B alloy (in which diffusion of metal components can not be neglected)



**Fig. 7** Schematic structure of oxide scale formed on binary two-phase A-B alloy (in which metal components exhibit high solubility and diffusivity)

loy. This occurs because the diffusion coefficient of any species in fine-grained materials, especially through grain boundaries, is clearly much larger than that through the bulk. The second effect is related to the change in the solubility of the two components<sup>[10, 17]</sup>. This is a grain-size effect related to the open and distorted structure of the grain boundaries, which can accept larger concentrations of impurities than the bulk. In particular the solubility of the reactive component in the noble component is one of the factors which play important roles in affecting the critical content of the reactive component required for its exclusive external oxidation. Another factor is that small particles of the B-rich phase will dissolve more rapidly than large particles in a matrix of the A-rich phase, especially in the case of particles with nanometer size. In fact, the dissolution of the B-rich phase in a B-depleted A-rich matrix is a prerequisite for supplying a flux of B to the B oxide layer. Because those two-phase alloys obtained by casting are frequently homogeneous, the presence of large composition variations in the local area results in a non-uniform scaling behavior of the same alloy. While the grain size reduction provides the maximum possibility to produce materials in which the two phases can distribute more uniformly.

These results imply that the critical average B content needed for the exclusive external oxidation in two-phase alloys depends strongly on the size of the two phases. And the phase size can be reduced quite effectively when the alloy grain size decreases. The faster the reactive element is supplied from the alloy with very small grain size, the easier the most-stable oxide at the alloy surface forms, as shown in Fig. 7. In fact, the oxidation behaviors of the nano-sized two-phase alloys are similar significantly to those of solid-solution alloys.

Finally, the grain size reduction also exhibits complex effects on the oxidation resistance in different alloy systems, which depends mainly on the pro-

TECTIVE feature of the oxide scales. In fact, when more stable oxide formed in the alloy with small grains is both thermodynamically stable and able to grow sufficiently slowly, such as  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ , the oxidation resistance can be improved significantly. On the contrary, the decrease of the grain size does not change the feature of the external scale at all, as shown in Cu-Co system, and the external scale is still composed of the mixed oxides. Even though a direct relationship between the grain size of an alloy and that of the scales growing on its surface has not been found at present, in many cases fine-grained alloys usually produce oxide scales with smaller grain size. In turn, the reduction of the oxide grain size increases the rate of transport through the scale. The same mechanism applies to Cu-Fe system, in which an exclusive iron oxide scale forms, yet the oxidation rate still increases due to the poor protective properties of the iron oxide.

## 4 CONCLUSIONS

- 1) For those binary two-phase alloys with conventional coarse grains, mixed oxide scales can be easily formed due to the limited mutual solubility and the diffusion restriction of the most reactive component.
- 2) Grain size reduction can significantly promote the exclusive external oxidation of the most reactive component in two-phase alloys, because both the mutual solubility and diffusivity among the system are enhanced.
- 3) Grain size reduction is not always beneficial to improve the oxidation resistance, and it may show quite different effects depending on the protective feature of the final oxide scales.

## [ REFERENCES ]

- [ 1 ] Doychak J, Smialek J L, Barrett C A. Oxidation of high-temperature intermetallics [ A ]. Grobstein T, Doychak J

- Eds. Proceedings of the Workshop on the High-temperature Intermetallics [C]. Warrendale: TMS, 1988: 41–45.
- [2] Gesmundo F, Gleeson B. Oxidation of multicomponent two-phase alloys [J]. *Oxid Met*, 1995 (1/2): 211–237.
- [3] LI Y S, NIU Y, Gesmundo F. High temperature scaling of binary Fe-Y alloys in pure oxygen [J]. *High Temperature Material and Processes*, 1999, 18: 185–195.
- [4] NIU Y, LI Y S, Gesmundo F. High temperature scaling of two-phase Fe-Cu alloys under low oxygen pressures [J]. *Corros Sci*, 2000, 42: 165–181.
- [5] NIU Y, LI Y S, Gesmundo F. Oxidation of Binary Two-phase Co-15Y alloy in 0.1 MPa O<sub>2</sub> at 600~800 °C [J]. *Intermetallics*, 2000, 8: 293–298.
- [6] LI Yuan-shi, NIU Yan, WU Wei-tao. Oxidation behavior of two-phase Cu-Ni-Fe alloy under low oxygen pressure at 800~900 °C [J]. *The Chinese Journal of Nonferrous Metals*, (in Chinese), 2000, 10(Suppl. 1): 160–164.
- [7] LI Yuan-shi, NIU Yan, WU Wei-tao, et al. Effect of grain size on the high temperature oxidation of Cu-10Ni alloy [J]. *Acta Metall Sinica*, (in Chinese), 1999, 35 (11): 1171–1174.
- [8] WANG F H. The effect of nanocrystallization on the selective oxidation and adhesion of Al<sub>2</sub>O<sub>3</sub> scales [J]. *Oxid Met*, 1997, 48: 215–224.
- [9] Gesmundo F, Viani F, Niu Y, et al. An improvement treatment of the conditions for the exclusive oxidation of the most reactive component in the corrosion of two-phase binary alloys [J]. *Oxid Met*, 1994, 42: 465.
- [10] FU Guang-yan, GUAN Heng-rong, NIU Yan, et al. Oxidation behavior of sputtered Cu-Cr microcrystalline coatings [J]. *Acta Metall Sinica*, (in Chinese), 2000, 36(3): 279–282.
- [11] Song J, Frarne G, Niu Y, et al. Air oxidation at 600~800 °C of two nanophase Co-50% Cu alloys prepared by mechanical alloying [J]. *High Temp Mater Proc*, 2001, 20(1): 25–37.
- [12] LI Yuan-shi, NIU Yan, WU Wei-tao. Preparation of Fe-50Cu nanocrystalline coating and its oxidation performance [J]. *Acta Physica Chimica Sinica*, (in Chinese), 2000, 16(10): 912–917.
- [3] NIU Y, SONG J, Gesmundo F. Air oxidation of two-phase Co-Cu alloys at 600~800 °C [J]. *Corros Sci*, 2000, 42: 799–815.
- [14] NIU Y, Gesmundo F, Viani F, et al. The air oxidation of two-phase Cu-Cr alloys at 700~900 °C [J]. *Oxid Met*, 1997, 48(5/6): 357–380.
- [15] NIU Y, Gesmundo F, Viani F, et al. The air oxidation of two-phase Cu-Ag alloys at 650~750 °C [J]. *Oxid Met*, 1997, 47(1/2): 21–52.
- [16] Gesmundo F, Viani F, Niu Y. The internal oxidation of two-phase binary alloys beneath an external scale of the less stable oxide [J]. *Oxid Met*, 1994, 42: 465–483.
- [17] Jiang J Z, Gente C, Bormann R. Mechanical alloying in the Fe-Cu system [J]. *Mater Sci Eng*, 1998, A242: 268–277.

(Edited by YANG Bing)