Mechanical alloying of Mo-Si-Fe powders [①]

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[Abstract] Mechanical milling behavior of Mo-Si-Fe powders was investigated using XRD, SEM and TEM techniques. The mixtures of elemental molybdenum (> 99%), silicon (> 99%) and iron (> 98%) powders with a stoichiometry of $Mo_{5-x}Fe_xSi_3$(x = 0.5, 1, 2) were milled in a planetary mill for up to 195 h. For all three powder mixtures, high-energy milling of 60 h led to formation of the Mo(Fe, Si) supersaturated solid solution (Mo_{ss}); and to a remarkable expansion of the solubility of Fe, Si in molybdenum. The transformation of Mo_{ss} to an amorphous phase was identified after longer time milling. In the milling process, the grain size of Mo(Fe, Si) decreased gradually and the internal stress increased linearly. After 40 h milling, the grain size was reduced to about 11 nm. SEM analysis of milled powders showed that the particle size increased initially with milling time. After 195 h milling, particles exhibited a spherical morphology and the particle size were reduced to about 100 nm.

[Key words] silicides; mechanical alloying; structure refinement; alloying effect

[CLC number] TG 146.4　　　　　　　　　[Document code] A

1　INTRODUCTION

Metallic silicides are a category of intermetallic compounds, whose properties are between metals and ceramal. Among silicides with technological importance, $MoSi_2$ has been most extensively studied as structural materials for elevated temperature applications due to its good combination of high elastic modulus, intermediate strength, low density, and excellent oxidation and corrosion resistance[1~4] Mo_5Si_3 is another compound with technological interest in the Mo-Si system. It is known that the melting point of Mo_5Si_3 is higher than that of $MoSi_2$ and the creep resistance of $MoSi_2$-Mo_5Si_3 eutectic alloy is better than that of single phase $MoSi_2$[5]. Mo_5Si_3 is thus supposed to be used as a matrix or a reinforcing phase in high temperature structural materials. Major problems impeding engineering applications of Mo_5Si_3 are its low-temperature brittleness and lack of sufficient oxidation resistance at high-temperature. Much effort has been devoted to solve these problems. It is expected that alloying might contribute to a certain extent to the improvement in the properties of Mo_5Si_3 because its presence over a composition range gives a room for alloying process. Previous work showed that the level of boron in $Mo_{5+y}Si_{3-y}$ at 1 800 ℃ reaches a maximum value of approximately 2% (mole fraction) in a narrow region within the homogeneity range of $-0.08 \leqslant y \leqslant 0.04$[6]. Recently it is reported that the oxidation resistances of Mo_5Si_3 can be substantially improved with less than 2% boron(mass fraction) ad-

ditions[7]. In addition, the boron doped materials possess creep resistance comparable to that of undoped $Mo_{5+y}Si_{3-y}$ alloy. It is known that Fe, W, Ti, V and Nb exhibit a certain solid solubility in Mo_5Si_3[8, 9] and Fe addition results in crystal structure modification[10]. Likely because of a large complex united cell, semi-covalent bonding and larger barrier to dislocation motion, the increased symmetry of hexagonal Mo_5Si_3C does not result in improved toughness or plasticity at room temperature[11]. How the other element influence Mo_5Si_3 is of great interest.

Mo_5Si_3 can be prepared by many ways, such as traditional vacuum arc melting and powder metallurgy processes. Mechanical alloying (MA) is a unique method of the preparation for composite, amorphous or quasicrystalline phases, intermetallic compounds etc. It is relatively simple for materials synthesis and its output is efficient. Mechanical alloying of $MoSi_2$ has been studied extensively[12~14]. It is known that crystalline compound can be formed from pure component with a stoichiometry of $MoSi_2$ after being milled for hours. But crystalline compound cannot be formed from pure component with a stoichiometry of Mo_5Si_3 after being milled for same periods of time. It was found that amorphous phase is obtained after longer time high-energy milling[5].

Recently, preparation of nanocrystal has received great attention in material science. The successful example of nanoceramics TiO_2 that can be deformed eas-

ily at low temperature provides a useful way for solving the brittleness of intermetallic compound. Can we prepare nanocrystalline Mo_5Si_3 by MA? Can we improve the property of Mo_5Si_3 by microstructure refinement and alloying strategies? The purpose of this work is to characterize mechanical milling behavior of Mo-Si-Fe powder mixtures and prepare nanocrystalline $(Mo, Fe)_5Si_3$ powders for further treatment.

2 EXPERIMENTAL

Starting materials used in this study were pure molybdenum powder (purity of 99%, 1~2 μm), pure silicon powder (purity of 99%, 2~3 μm), and pure iron powder (purity of 98%, 1~2 μm). The nominal composition of powder mixtures is shown in Table 1.

Table 1 Composition of powder mixtures

Sample	Composition
1	$Mo_{4.5}Fe_{0.5}Si_3$
2	Mo_4FeSi_3
3	$Mo_3Fe_2Si_3$

A laboratory high-energy planetary mill (QM-1SP) was used in the mechanical milling of the powders. The chosen processing parameters were as the following: stainless steel milling bowl and balls, rotation speed of 400 r/min and the ball to powder mass ratio of about 20:1. To avoid oxidation, the loaded stainless vial was sealed in a glovebox filled with argon after being evacuated. In order to study the mechanical milling behavior of powder mixtures, a small amount of powder was extracted from vial for analysis after being milled for a certain time. The above operations were also carried on in the glovebox.

Phase evolution of powder mixtures, grain size and microstrain of (Mo) during MA were characterized using Rigaku 3014 X-ray diffractometer with CuK_α radiation ($\lambda = 1.5406$).

Scherres equation was used to estimate grain size of (Mo):

$$D = 0.91 \lambda / (B\cos\theta) \qquad (1)$$

where D is grain size, λ is X-ray wavelength, θ is Bragg angle, B is pure diffraction breadth (half-maximum line breadth) due to crystallite-size effect.

Using the following equation to calculate the micro strain of (Mo) caused by the second internal stress.

$$\Delta d / d = n / 4\tan\theta \qquad (2)$$

where d is distance of crystallite plane, Δd is deviation from distance of crystallite plane, n is pure diffraction breadth due to internal stress.

Powder Morphology and structure were investigated by SEM (type JSM-5600LV) and TEM (type H-800).

3 RESULTS AND DISCUSSION

3.1 Grain size and micro-strain of (Mo) during mechanical alloying

Fig. 1 shows the milling time dependence of grain size at room temperature. In general, grain size of (Mo) decreased gradually with milling time. Initially, the grain size decreased rapidly, then the change in grain size became smaller. The final grain size after 40 h milling, for instance, is as small as 11 nm. Microstrain is also varied with time, as shown in Fig. 2. From 0 to 40 h milling, the magnitude of micro-strain increased with time linearly.
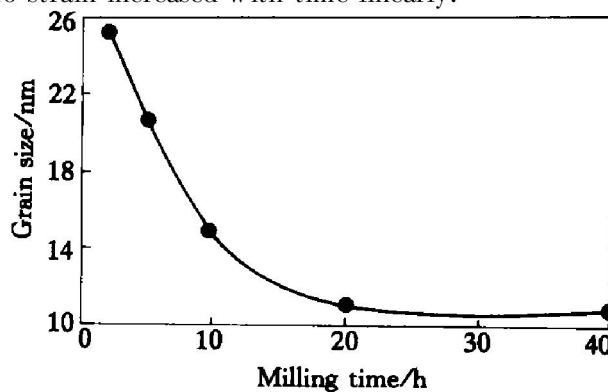

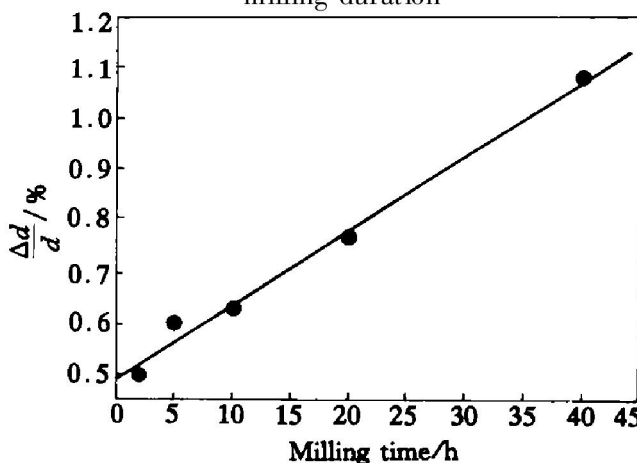**Fig. 1** Grain size of (Mo) as a function of milling duration

Fig. 2 Micro strain of (Mo) as a function of milling duration

In the process of mechanical milling, powder deformed plastically. As a result, dislocations grew in number quickly and took on a cell structure. There might be small orientation difference between cells. With milling intensity further enhanced, the density of dislocation making up cell walls is supposed to increase, the size of cells decreased and the average orientation difference between cells would increase gradually. When the amount of the deformation in powders became large enough, cell walls would transform to grain boundary and grain got refined, i.e. grain boundary grew in number. So the effect of orientation difference and hindrance of the grain boundary could be enhanced. The resistance to dislocation movement

increased correspondently. As a result, the slope of the curve (Fig. 1), which represents the rate of grain refinement, became small.

3.2   Phase change during mechanical alloying

X-ray diffraction patterns after different milling durations of samples are shown in Fig. 3 to Fig. 5. Three kinds of powder mixtures showed the same trend. The broadening peaks were due to the very strong strain in the powders during the mechanical collision and the decrease of grain size in the particles. After milling for up to 30 h, Fe and Si peaks still show up in the XRD patterns. The scanning electron micrograph of sample 2 after 10 h milling is shown in Fig. 6. There exists a block-like particle with straight edges and flat surfaces. EDS analysis showed it is Si particle. The intensity of Fe and Si peaks decreased continuously as the milling time increased. After 60 h, Fe and Si peaks disappeared and Mo(Si, Fe) supersaturated solid solution was formed. High-energy milling could remarkably extend the solubility limit of Si and Fe in Mo. There was conventional solid solution in which solute atoms went into the crystal lattice of solvent to change the lattice parameter. Further
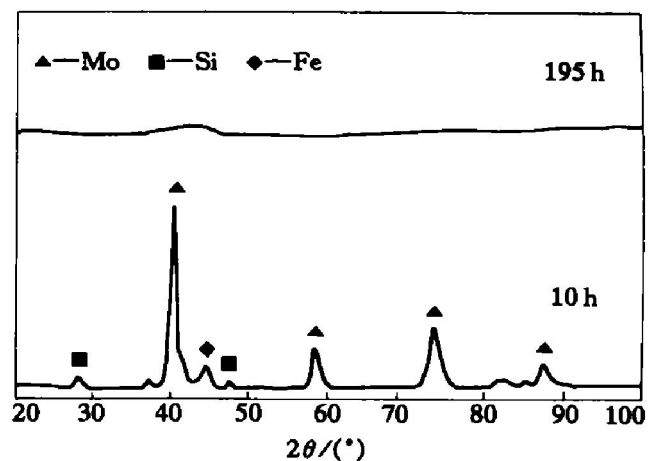

Fig. 3   X-ray diffraction pattern of sample 2

Fig. 4   X-ray diffraction pattern of sample 3

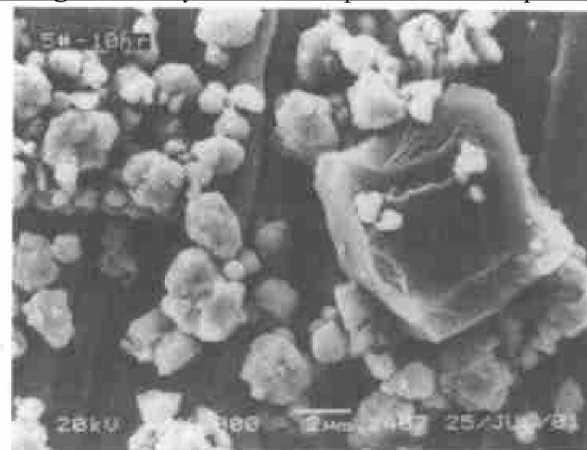**Fig. 5**   X-ray diffraction pattern of sample 1

Fig. 6   SEM micrograph of sample 2 milled for 10 h

more, nanocrystal provided a large number of grain boundary. Many solute atoms accumulated there and lost feature of diffraction. So X-ray diffraction patterns displayed single phase. On this occasion, solute atoms and solvent atoms did not contact closely with each other, so it was a sub-solution.

From the viewpoint of thermodynamics, the fact that MA remarkably enlarged the solubility may be attributed to several reasons. Firstly, at the early stage of MA, a large number of dislocations were generated. Part of mechanical energy of deformation was stored in the form of elastic energy of dislocations, resulting in a considerable increase in free energy of element powder mixtures. This was the main driving force of alloying. Secondly, formation of nanoscale crystallites by MA significantly increased the fraction of grain boundary, to which an extra surface energy was related. This was also one type of driving force of alloying, which should not be ignored. Thirdly, the two most important events involved in MA were the repeated welding and fracturing of the powder mixtures. So the surface energy related to phase boundary played an important role in alloying.

Kinetically, mechanical milling made diffusion between different components easy and fast. Firstly, microcracks may appear on the surface of powder particles in the MA process, thus providing a large
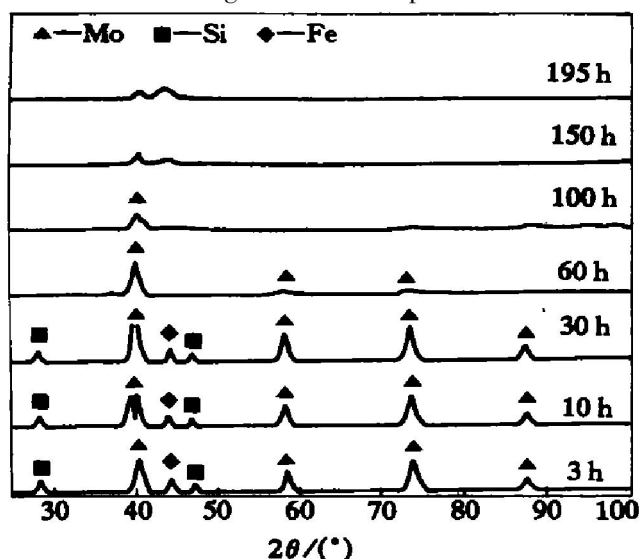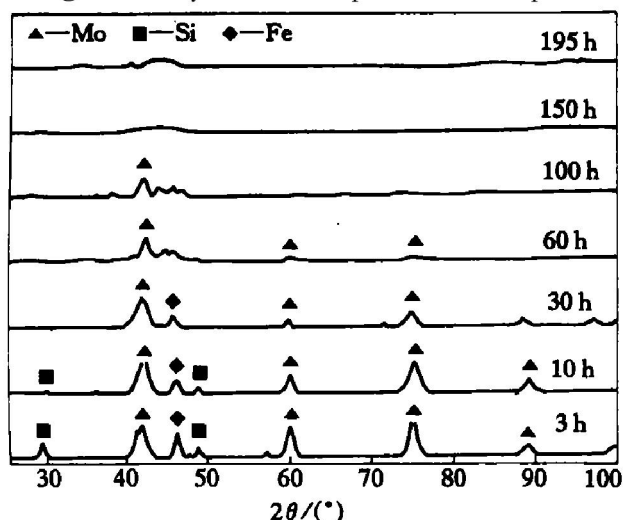
amount of free surfaces. Secondly, grain refinement led by MA infers that more short-cuts for diffusion were available. So diffusion along grain boundary (GB) and surface (S) would be dominant in the process of MA. It is well known that at certain temperature, diffusion coefficient D_{GB} and D_S are larger than D_L (for the lattice). Thirdly, as a result of large amount of defects due to high-energy collision of the powder particles, the total activation energy required by diffusion is lower. It causes enhancement of the diffusion process too. Furthermore, the balance of atom concentration at the interface between two different components might be destroyed by subsequent fracturing of the powder particles. Consequently, new surfaces with very different composition met each other to form new diffusion couples when different particles were cold welded together. The concentration of the species was important in that it affected their diffusivity. Large difference in composition at the interface therefore promoted interdiffusion. Mechanical alloying is controlled by diffusion. Therefore, the atom of Si and Fe entered the inside or boundary of grain easily to form conventional solution or sub-solution.

After 150 h milling, a diffraction peak with wide and round shape appeared on X-ray diffraction patterns, indicating that Mo (Si, Fe) supersaturated solid solution was transformed to amorphous phase. With longer time milling, on one hand, nanoscale crystallites were formed by grain refinement. The system possessed excess Gibbs free energy because of large fraction of grain boundary. On the other hand, the lattice deformed seriously and the internal stress increased because of the deformation of the powders

and the size difference among different element components in supersaturated solid solution. As a result of these factors, the free energy of supersaturated solid solution with nanocrystal structure became larger and might be bigger than that of correspondent amorphous phase. The lattice of (Mo) lost its stability and transformed to an amorphous structure. Electron diffraction pattern of sample 2 is shown in Fig. 7(a). There were no spot or ring, which represents crystal structure. This illustrated the presence of amorphous phase.

3.3 Evolution of particles morphology

Powder morphology after different milling durations of samples is shown in Fig. 7 and Fig. 8. After 5 h milling, the size of particles was reduced on the whole (as shown in Fig. 8(a)). The particle size increased with milling time because of cold welding (as shown n Fig. 8(b)). Powder particles with irregular shape and rough surface were composed of some sub-particles. After 40 h milling, the particle size decreased slightly (as shown in Fig. 8(c)). After 100 h milling, the shape of powder particles began to sphericize and the surface became smooth (as shown in Fig. 8(d)). After 195 h milling, spherical particles were obtained and their size was about 100 nm (as shown in Fig. 7(b)).

4 CONCLUSIONS

1) The studied Mo-Fe-Si powder mixtures exhibit the same trend of phase evolution in the process of mechanical milling.

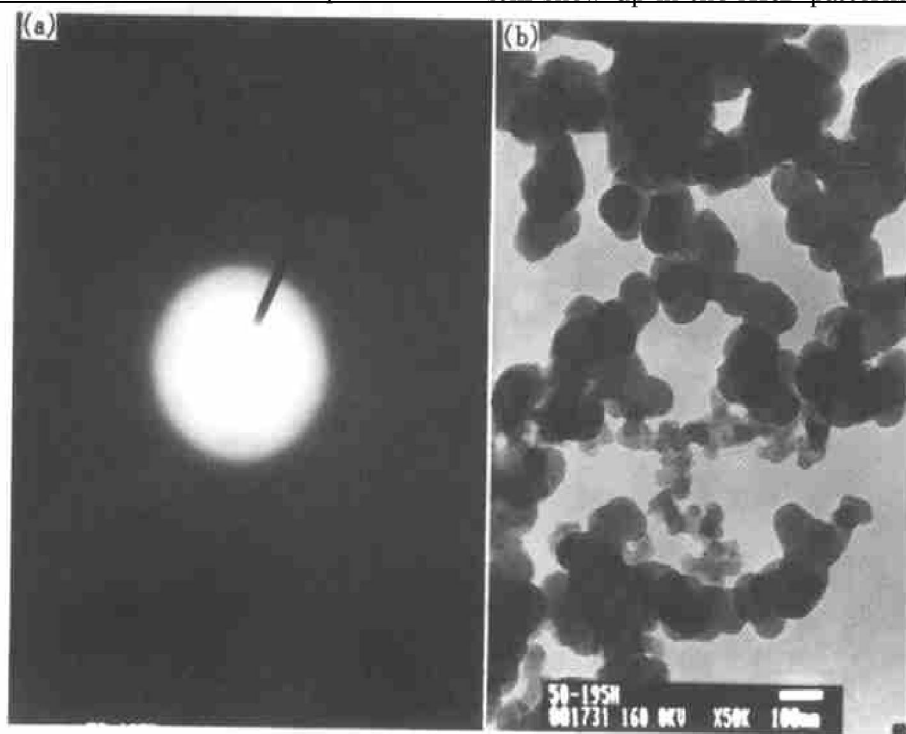2) After milling for up to 30 h, Fe and Si peaks still show up in the XRD patterns. Single-phase solid

Fig. 7 Electron diffraction pattern(a) and powder morphology (b) of sample 2 milled for 195 h
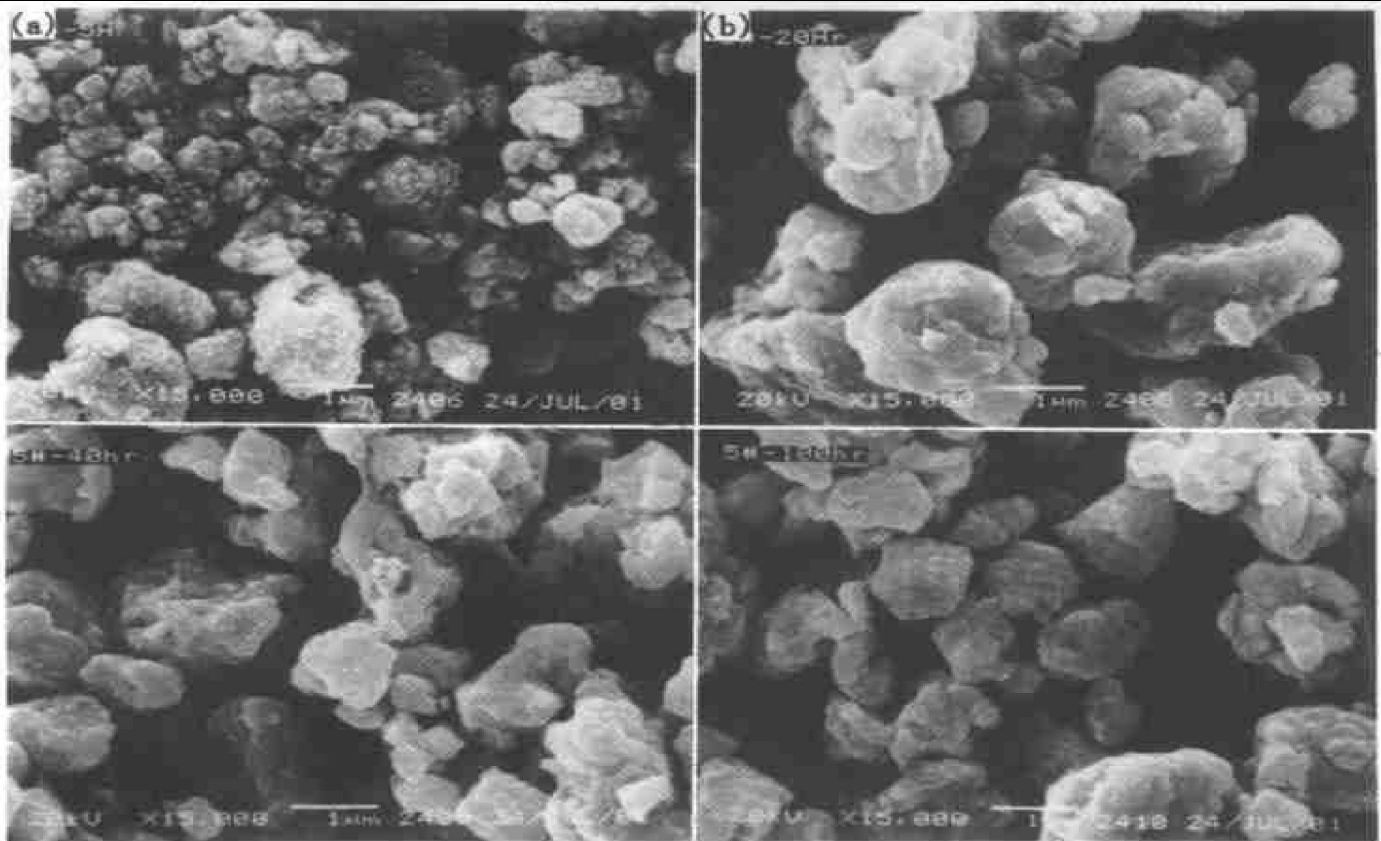
Fig. 8   SEM micrographs of sample 2 milled for different time
(a) —5 h; (b) —20 h; (c) —40 h; (d) —100 h

solution, Mo(Fe, Si), was formed after being milled for up to 60 h. High-energy milling could remarkably extend the solubility limit of Si and Fe in Mo.

3) Long-time (60~ 195 h) high-energy milling gradually led to the phase transformation from the supersaturated solid solution to amorphous phases.

4) With increasing milling time (from 0 to 40 h), the grain size of (Mo) decreased gradually and the final size was about 11 nm. Meanwhile, the internal stress increased linearly.

5) SEM analysis of milled powders shows an increase → decrease variation in the particle size with milling time. TEM analysis indicates that the particle shape was modified to be spherical and the particle size is about 100 nm after 195 h milling.

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(Edited by YANG Bing)