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Current research situation of titanium alloys in China

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Abstract: Titanium and its alloys possess excellent comprehensive properties, and they are widely used in many fields. China pays great attentions to the research on new titanium alloys. This paper mainly reviews the research on new Ti alloys in China, for example, high strength and high toughness Ti alloys, burn resistant Ti alloys, high temperature Ti alloys, low cost Ti alloys and so on. New basic theories on Ti alloys developed in China in recent years are also reviewed.

Key words: titanium alloys; basic theory; near beta forging

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1 Introduction

Titanium and its alloys have been extensively used because of their low density, high specific strength, corrosion resistance, weldability and so on. Through more than 40 years arduous efforts, China forms an integral titanium industry system. At present, there are more than 100 units in researching and manufacturing titanium alloys. Six main researching directions for titanium alloys have been formed, i. e. high temperature titanium alloys, high strength titanium alloys, corrosion resistant titanium alloys, titanium alloys used for shipbuilding, functional titanium alloys and medical titanium alloys. More than 70 titanium alloys were developed, and many alloys have been put into practical uses, which make important economy efficiency. The objective of this paper is to review the new Ti alloys developed in China in recent years.

2 Development of new titanium alloys

The new titanium alloys researched and developed in recent years mainly are high temperature titanium alloys, high strength titanium alloys, titanium composites, burn resistant titanium alloys, high elastic titanium alloys, low cost titanium alloys and corrosion resistant titanium alloys.

2.1 High temperature titanium alloys

Table 1 lists the high temperature Ti alloys that are being researched in China. 600℃ of high temperature Ti alloys are paid more attentions.

Based on the electric density law of Ti_3X precipitates, Ti55 alloy for 550℃[1], was designed. Some typical parts made from Ti55 have successfully gone through trial[2]. Ti60, which is designed on the basis of Ti55, is a near α 600℃ high temperature Ti alloy[3]. It has been carried through industrial trial and application research[1]. Ti600 is also a new near α 600℃ high temperature Ti alloy. Ti60 and Ti600 possess

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good properties at 600℃, especially, the creep property of Ti600 alloy are better than that of famous IMI843[4], as shown in Table 2. Ti600 has wide working window, and it has good promising. As shown in Table 1, there is rare earth element (RE) in the two kinds of high temperature Ti alloys. High temperature Ti alloys with RE are one of the contribution for the development of world Ti alloys made by China.

Table 1 600℃ of high temperature Ti alloys developed in China

Designation	Service temperature/℃	Composition1) /%
Ti60	600	Ti-5.8Al-4.8Sn-2Zr-1Mo-0.85Nd-0.35Si
Ti600	600	Ti-6Al-2.8Sn-4Zr-0.5Mo-0.4Si-0.2Y

Note: 1) Mass fraction

Table 2 Typical properties of high temperature titanium alloys[3]

Alloy	Tensile at RT				Tensile at 600℃				Residual strain1) /%	Corresponding microstructure
	UTS /MPa	YS /MPa	EL /%	RA /%	UTS /MPa	YS /MPa	EL /%	RA /%		
Ti600	1068	1050	11	13	745	615	16	31	0.03	Equiaxed $\alpha+\beta_{trans}$
Ti60	1100	1030	11	18	700	580	14	27	0.1	Equiaxed $\alpha+\beta_{trans}$
IMI834	1070	960	14	20	680	550	15	50	0.1	Equiaxed $\alpha+\beta_{trans}$
Ti1100	960	860	11	18	630	530	14	30	0.1	Lamellar

Note: 1) after creep exposure at 600℃, 150 MPa for 100 h

2.2 High strength titanium alloys

Table 3 shows the high strength titanium alloys researched in China in recent years. β21, developed by Timet in USA, is a metastable βTi alloy, which has a good cold workability. In the past five years, some researchers also paid great attentions to β21s[5,6]. Ti-B19 developed in China is a metastable βTi alloy with high strength and high toughness (K1c≥70 MPa)[7]. Its 3T ingot has been put into use, and semi-finished product of Φ410 mm/Φ230 mm×2000 mm has been made. Ti-26 is a fastener metastable βTi alloy with high strength, and good cold workability[8]. TC21[9] is a new high strength, high toughness and damage tolerance Ti alloy. In the past three years, it has gone through from alloy design to industrial trial. Ti-B 18[10] and Ti-B20[11] are new high strength and high toughness Ti alloys which are just being researched.

Table 3 High strength titanium alloys researched in China and their typical properties

Alloy	Composition1) /%	UTS/MPa	Toughness	
			K1c/MPa $\sqrt{M}$	αk/(J·cm^{-2})
β21S	Ti-15Mo-3Al-2.7Nb-0.2Si	1200	50	
TC21	Ti-Al-Sn-Zr-Cr-Mo-X	1100	70	
Ti-B19	Ti-Al-Mo-V-Cr-Zr	1250	70	
Ti-26	Ti-15-3+Zr+Nb	1250		
Ti-B18	Ti-Al-Mo-Zr-Sn-X	1300		50
Ti-B20	Ti-Al-Mo-Zr-Sn-Fe-X	1300		50

Note: 1) Mass fraction

2.3 Titanium composites

Two kinds of titanium composites are being researched in China. One is TiC particle reinforced Ti which can becomposite, named as TP-650 (Fig. 1), used up to 650℃[12]. Another is SiC continuous fibre reinforced Ti composite (SiC/Ti). TP-650 possesses good comprehensive properties after research more than 10 years (Table 4). In the coming 5 years, more attentions will be still paid to this alloy, hoping it can be put into practical applications. SiC/Ti is just beginning to research. However, SiC fibre is so expensive that research on it does not make breakthrough. Interfacial reactions of SCS-6 SiC fibre reinforced Super α_2[13], Ti_2AlNb[13], IMI834[13], pure Ti[14], Ti-6Al-4V[15] and Ti40 (Ti-25V-15Cr-Si)[15] matrix composites were investigated. The interfacial reaction of SiC/Super α_2 is more severe and up to six layers of reaction products exist. There are only three or four layers of reaction products in the interfacial zone of composite SiC/Ti_2AlNb and SiC/IMI834. The silicide S_2 formed at the interface of SiC/IMI834 is of benefit to the thermal stability of the composite at some temperature. Thermodynamic study on the interfacial reactions was also conducted and it was found that the formation of Ti_3AlC at interface or in matrix is caused by the reaction of $Ti_3Al + C \rightarrow Ti_3AlC$[13].

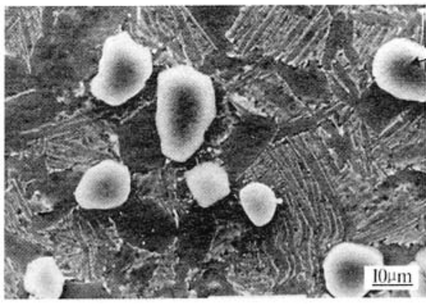

Fig. 1 SEM image of TP650 composite

Table 4 Typical properties of TP-650 alloy

Tensile at RT					Tensile at 650℃				Residual strain1)/%
UTS/MPa	YS/MPa	EL/%	RA/%	E/GPa	UTS/MPa	YS/MPa	EL/%	RA/%	
1330	1280	5	13	130	681	562	24	39	0.2

Note: 1)Residual strain after Creep exposure at 650℃, 100 MPa for 100 h

2.4 Burn resistant titanium alloys

Burn resistant Ti alloys possess good burn resistance and mechanical properties. Table 5 is the burn resistant Ti alloys developed in China. Both Ti40 and TF1b alloys are new β burn resistant alloys developed on the basis of Alloy C (Ti-35V-15Cr). These two alloys have good burn resistance[16], and Ti40 possesses good mechanical properties[17,18], as shown in Table 6. Its bars, sheets, biscuits and rings have been made from Ti40. Ti14 burn resistant alloy, designed and developed in China, is a $\alpha + Ti_2Cu$ alloy[19]. It has good burn resistance and mechanical properties[20] (Table 6).

Table 5 Burn resistant titanium alloys developed in China

Designation	Composition(mass fraction)/%
Ti40	Ti-25V-15Cr-Si
Ti40-1	Ti-25V-15Cr-3Al
TF1b	Ti-V-Cr
Ti14	Ti-Al-Cu-Si

2.5 High elastic titanium alloys

Table 7 lists the high elastic Ti alloys that are being researched in China. The value of elastic modulus of conventional Ti alloys is between 90 GPa and 110 GPa, while that of high elastic Ti alloys is above 125 GPa. HE130, a Ti-Al-V-Mo-Fe-B system alloy, is a $\alpha+\beta$ high elastic Ti alloy[6,21]. Its wide sheets of 0.25 mm×400 mm×1650 mm were made. Ti811ZB[22], a Ti-Al-Mo-Zr-B system alloy, is a near α high elastic Ti alloy. These two alloys have good mechanical properties (Table 7).

Table 6 Typical properties of Ti40 and Ti14 burn resistant titanium alloys

Alloy	Tensile at RT				Tensile at 540℃				Residual strain[1)] /%
	UTS /MPa	YS /MPa	EL /%	RA /%	UTS /MPa	YS /MPa	EL /%	RA /%	
Ti40	1000	980	15	30	800	650	20	40	0.1
Ti14	960	810	11	20	620	486	38	94	Fracture at 10 h

Note: 1) Residual strain after creep exposure at 540℃, 250 MPa for 100 h.

Table 7 High elastic Ti alloys being researched in China and their typical properties

Designation	UTS/MPa	El/%	E/GPa	Composition/%
HE130	1000	6	130	Ti-Al-V-Mo-Fe-B
Ti811ZB	1100	6	125	Ti-Al-Mo-Zr-B

2.6 Low cost titanium alloys

The high cost of Ti alloys limits their extensive applications. In order to expand Ti applications, low cost Ti alloys must be developed. There are mainly two ways to reduce Ti cost. One is to choose cheap alloying elements to replace expensive ones. Another is to improve the processing technology. At present, the first method is used in China. Ti8LC[23] and Ti12LC[24] low cost alloys are being developed. Their alloying system and typical properties are shown in Table 8. Cheap element Fe is used by adopting cheap Fe-Mo master-alloy, which widely used in steel, to replace expensive element V in Ti-6Al-4V for the development of Ti8LC and Ti12LC[25,26]. Their mechanical properties are similar to that of Ti-6Al-4V, and the cost of their small bars is reduced about 30%. These two new alloys are being put into industrial trial. In the next five years, the research group led by the authors will pay great attentions to reduce Ti cost through above-mentioned two ways.

Table 8 Low cost Ti alloys being researched in China and their typical properties

Alloy	Tensile at RT				Tensile at 400℃				Composition /%
	UTS /MPa	YS /MPa	EL /%	RA /%	UTS /MPa	YS /MPa	EL /%	RA /%	
Ti8LC	1050	990	12	30	700	600	15	50	Ti-Al-Fe-Mo-X
Ti12LC	1100	1050	12	40	00	800	15	50	Ti-Al-Mo-Fe-X

2.7 Corrosion resistant titanium alloys

Table 9 lists the corrosion resistant titanium alloys developed in China. Ti31 is a low strength and high plasticity α titanium alloy[12], and Ti75 is a middle strength and high toughness α Ti alloy[12]. Some typical parts made from Ti75 and Ti31 have been put into practical applications as structural parts[27]. Ti91 and Ti70 are middle strength, high plasticity, good cold workability and weld-ability α Ti alloy[27,28]. Ti55C is a low strength, high plasticity, weld-ability and good cold workability α Ti alloy[29] and its typical parts will be put into practical uses in the next 5 years. Ti80[27] is a high strength and weld-ability α Ti alloy. Its tensile properties, fracture toughness, stress-corrosion resistance and low cycle fatigue behavior are better than that of Ti-6Al-4VELI[27].

Table 9 Corrosion resistant titanium alloys developed in China and their typical properties

Designation	Strength scale/MPa	Elongation/%	Composition/%
Ti31	630	18	Ti-Al-Zr-Mo-Ni
Ti75	730	13	Ti-Al-Mo-Zr
Ti91	700	20	Ti-Al-Fe
Ti55C	550	25	Ti-Al-Ta-Zr-Mo
Ti70	700	20	Ti-Al-Zr-Fe
Ti80	850	12	Ti-Al-V-Mo-Zr

3 New basic research on Ti alloys

Basic theory is an important basis to develop new materials. Researchers and engineers engaged in titanium alloys in China pay great attentions to the development of titanium theory. The following gives some basic research results.

3.1 Effects of rare earth elements (RE)

High temperature titanium alloys developed in China almost all have minor RE, as shown in Table 1. RE has important role in high temperature Ti alloys as followings: (1) To refine the microstructure, leading to strengthening and toughening[12]; (2) To form the REyOx second phases, leading to Orowan strengthening[30]; (3) To be inner-oxidation and to retard the precipitation of Ti_3Al phase, resulting in improved properties[30]; (4) To increase β transus with addition of Y, resulting in wide working window[31].

For example, Ti600 alloy with addition of 0.1Y/%(mass fraction) exhibit refined β transformed α platelet structures, which result in the increase of yield stress. The higher tensile ductility of Ti600 is the result of smaller β grain size. Y_2O_3 particles purify α matrix by absorbing O and Sn atom, restrain the precipitation and growth of α_2 phase during thermal exposure. These lead to the improvement of thermal stability of the alloys with Y. The improved creep performance of Ti600 alloy has relation to the shorter dislocation slip length. Small amount of Y oxides and slow growth of α_2 phase have extra contributions to keeping the alloy lower creep deformation. Phases of containing Nd are formed in Ti60 alloy with addition of 1.0%(mass fraction) Nd, resulting in alloying element Sn and O partitioning to it and retarding α_2 phase precipitation. The phases with Nd increase oxidation resistance and fine grains in the oxidation layer lead to difficult formation of cracks. In the mean time, dislocations around it retard crack growth, resulting in improvement of thermal stability.

Different RE has different content in different high temperature titanium alloys. For example, Nd content is greater than 0.8%(mass fraction) in Ti55 and Ti60 alloys, while Y content is not greater than 0.25%(mass fraction) in Ti600 alloy. Phase with Y cannot be detected with optical microscopy in Ti600 alloy, and it can only find with transmission electron microscopy. Its size is less than 0.8 μm. Phase with Nd is very easily found with optical microscopy in Ti60 alloy, and its size is greater than 8 μm. The bigger size of phase with RE has not good effect on fatigue behavior[32].

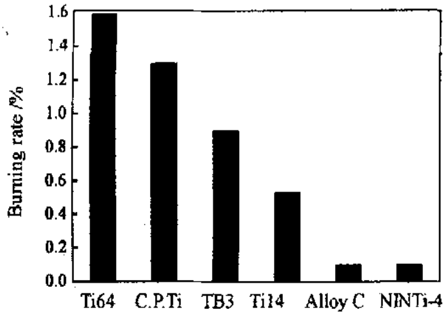

Fig. 2 Burning rate of several Ti alloys (TB3, Ti-3.5Al-10Mo-8V-1Fe)

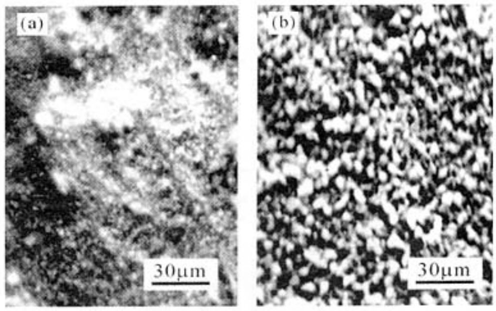

Fig. 4 SEM Interfacial images between the burning products and the matrix
(a)—Ti-6-4; (b)—Ti40

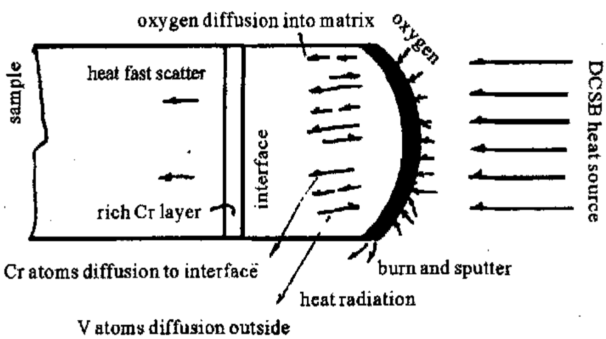

Fig. 3 Burn resistant model of Ti40 burn resistant titanium alloy

3.2 Burn resistant mechanism

The most important characteristic of burn resistant titanium alloy is its burn resistance. The burning behavior and its affecting factors of titanium alloys were deeply and systematically researched by DCSB (direct current simulation burning) method[18] that was invented[33] by the present authors in NIN. Samples of 50 mm×5 mm×2 mm were machined. These samples were ignited by the DCSB method, in which the titanium was ignited for a certain time under a certain direct current (5A direct current was used to ignite titanium in 50 s). After burning, their weight gains were calculated. The burning products were examined by scanning electron microscopy (SEM). Ti40 alloy has good burn resistance compared with conventional Ti alloys, as shown in Fig. 2. Burn resistant model (Fig. 3) was proposed. Tenacious oxidation layer was formed at the interface between burning products and the matrices during burning compared with Ti-6-4, as shown in Fig. 4. Burn resistant mechanisms of fast dispersive heat and suspend oxygen diffusion were put forward[16,34,35], which gave a good explanation on the burn resistant behavior of Ti40 alloy.

Besides DCSB method, there are high-speed friction and laser ignition ones. BIAM uses high-speed friction method to examine the burning behavior of titanium alloys, however, there are not public reports from BIAM. Laser ignition method is not used in China. This method is used in USA to examine the burn resistance of Alloy C (Ti-35V-15Cr) burn resistant alloy. DCSB is a cheap method. It is not need to build new instrument. It just uses the one for chemical composition analysis[33]. High-speed friction and laser ignition method are need to build new equipment. They are expensive.

3.3 Tri-modal microstructure

It is obvious that the mechanical properties of Titanium alloys vary with the variation of the relative volume fraction of equiaxed α and transformed β. It was found that only when the heating temperature was close enough to beta transus, the relative volume fraction of equiaxed alpha and transformed beta varied significantly, and could be effectively controlled by controlling the heat temperature. This is the theoretical and experimental fundamentals of near beta forging[36,37]. That is, the new high-temperature deformation strengthening and toughening process consists of heating at 10—15℃ below beta transus, rapid water quenching after forging, high-temperature toughening and low-temperature strengthening treatment. Titanium alloys forged by this new process do not produce equiaxed microstructure (Fig. 5(a)), lamellar (Fig. 5(b)) or bi-modal one, but do produce a new tri-modal microstructure (Fig. 5(c)), which consists of 10%—20% equiaxed alpha, basket-weave formed by striature alpha and transformed beta matrix, as shown in Fig. 5(c).

In tri-modal microstructures, some equiaxed alpha ensures coherent deformation, which retards the formation and propagation of voids, presenting a higher ductility. The interwoven lamellar alpha, which formed by water quenching after forging and high-temperature toughening treatment, not only retards slip deformation, but also changes the direction of the crack propagation and slows it down. For this reason, tri-modal microstructures have a good combination of strength, ductility and toughness, as shown in Table 10.

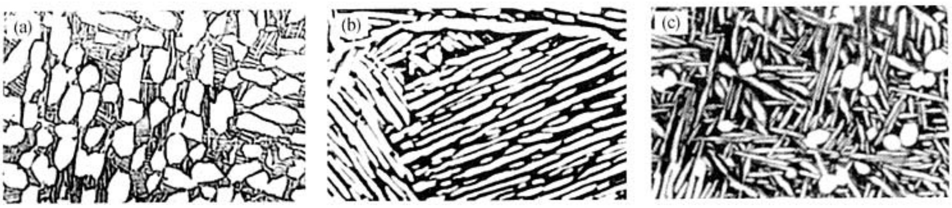

Fig. 5 Optical microstructure developed by conventional forging (a), beta forging (b) and near beta forging (c)

Table 10 Typical properties of Ti-6.5Al-3.5Mo-1.5Zr-0.3Si alloy by near beta forging compared with conventional forging and beta forging[38]

Forging method	Tensile properties at RT				Thermal stability 1)			Fracture toughness
	UTS/MPa	YS/MPa	El/%	RA/%	UTS/MPa	El/%	RA/%	K_{1c}/MPa $\sqrt{M}$
Conventional	1061	1018	15	46	1081	12	32	73
Near beta	1098	1049	17	44	1153	17	36	89
beta	1083	990	13	19	1094	10	16	92

Note: 1) after exposure at 520℃ for 100 h

3.4 Semi-solid oxidation

Ti14 alloy is a $\alpha+Ti_2Cu$ alloy, as shown in Table 5. Fig. 6 shows the weight gain curves of Ti14 alloy after semi-solid oxidation at various temperatures for different times. The weight gain increases obviously as the increase of time oxidation at 1000℃, which is 10℃ above the Ti_2Cu melting point. A linear relation between the weight gain and time is found when time is over 30 s at 1000℃. With oxidation at 1100℃, which is 110℃ above the melting point, the weight gain increases rapidly from 10 s to 60 s, while the weight gain decreases clearly from 60 s to 90 s, and then increases slightly with time. With oxidation at

1150℃, which is 160℃ above the melting point, the weight gain increases rapidly from 10 s to 30 s, while the weight gain then drops gradually.

For the oxidation temperatures of more than 10℃ above the melting point, the curves first reach a maximum and then gradually decrease while remaining above the melting point. The decrease in weight gain is due to the vaporization of oxidized products of CuO. The melting point of CuO is 1065℃. With the oxidation at 1100℃ and 1200℃, which is over 1065℃, CuO vaporizes, resulting in no CuO in the oxidation layers, as shown in Fig. 3. This leads to a decrease in weight gain (Fig. 2), which is similar to that of burn resistant Ti40 alloy oxidation over 700℃ where oxidized products of V_2O_5 vaporize[38]. With semi-solid oxidation of Ti14 alloy, the melting positions of Ti_2Cu on the grain boundary and within grains is the fast diffusion path for oxygen diffusion into the matrix, especially the selective diffusion of oxygen diffusion into the matrix along the melting grain boundaries.

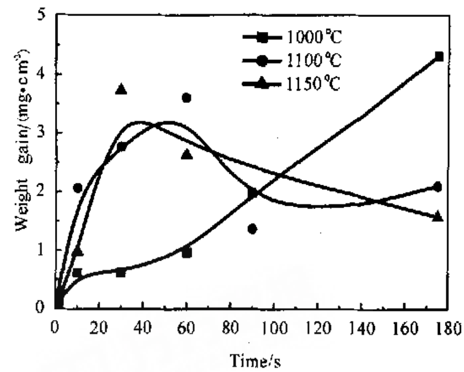

Fig. 6 Weight gain curves of Ti14 alloy after semi-solid oxidation at different temperatures

3.5 Semi-solid deformation

Fig. 7(a) shows the true stress vs true strain curves of Ti14 alloy after deformation at 1050℃ with different strain rates. The true stress-strain behavior is similar to that of conventional solid deformation, in which an increase in strain rate results in an increase of flow stress and the flow stress becomes smoothly when it reaches the maximum. Fig. 7(b) gives the true stress vs true strain curves of Ti14 alloy deformation at different temperatures with a strain rate of 5/s, which is also similar to the conventional one: the higher the temperature the lower the deformation resistance. With the semi-solid deformation of Ti14 alloy, the existence of low Ti_2Cu melting point phases causes the co-existence of liquid and solid on the grain boundary and within grains, leading to very low deformation resistant stress. The semi-solid deformation of Ti14 alloy cannot achieve this result, which means they still contain coarse grains (α and Ti_2Cu) after semi-solid deformation and the grain boundary is wide. The growth of Ti_2Cu phase on the grain boundary is the main reason for the increase in grain boundary width. The wide grain boundaries connect with each other to

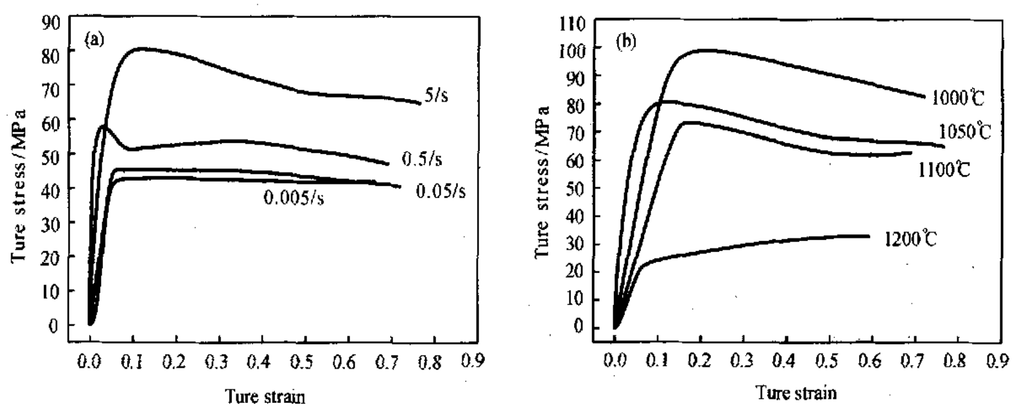

Fig. 7 True stress-true strain curves of Ti14 alloy
(a)—fixed temperature 1050℃; (b)—fixed strain rate 5/s

form network structures. The new fine grains are not a result of dynamic recrystallization, but of a fast cooling of the alloy after semi-solid deformation. The grain boundary and grain flow vertically to the forced direction during semi-solid deformation. The growth of the liquid Ti_2Cu phase on the grain boundary and within grains form wide grain boundaries and network structures, which is the main result of the semi-solid deformation.

4 Summary

After more than 40 years arduous efforts, titanium alloys developed in China achieved great development. Many achievements have been gotten from the research on new titanium alloys and basic theories, for example high temperature Ti alloys, burn resistant Ti alloys, low cost Ti alloys, high strength & high toughness Ti alloys, semi-solid deformation, semi-solid oxidation, burn resistant mechanism and so on. However, the cost of titanium alloys is still high, we should pay great attentions to reduce their cost and enlarge their applications by developing new technology and new equipment.

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