

DESIGN OF $\alpha + \alpha_2$ HIGH TEMPERATURE TITANIUM ALLOYS BY THE AID OF THERMODYNAMICS

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ABSTRACT

In order to construct a design method of $\alpha + \alpha_2$ high temperature titanium alloys, a thermodynamic analysis of the α and α_2 phases in the Ti-Al-Sn-Zr system were performed by means of the two sublattice model. From the creep and tensile tests of ten Ti-Al-Sn-Zr alloys, which were designed by the thermodynamic calculation, the $V\alpha_2$ of about 0.1 (at 873K) was proposed as the best design condition for $\alpha + \alpha_2$ high temperature titanium alloys.

INTRODUCTION

The use of the ordered α_2 phase (Ti_3Al , DO_{19}) to strengthen the α phase titanium is one of possible approaches to develop new high temperature titanium alloys [1]. In order to design such alloys, it is necessary to control the compositional and microstructural parameters such as the volume fraction of the α_2 phase ($V\alpha_2$) and the degree of solid-solution strengthening of the α phase.

For this purpose a thermodynamic analysis of the α and α_2 phases in the systems, Ti-Al, Ti-Sn, Ti-Al-Sn, Ti-Al-Zr and Ti-Sn-Zr was performed [2] by means of the two sublattice model developed by Hillert and Staffansson [3]. Obtained parameters were used to thermodynamic calculations of $\alpha - \alpha_2$ phase equilibria in the Ti-Al-Sn-Zr system.

As the next step, effects of the microstructural and compositional factors on creep properties were examined by using Ti-Al-Sn-Zr alloys designed by the above thermodynamic calculations [4].

DESCRIPTION OF THE THERMODYNAMIC PROPERTIES OF THE α AND α_2 PHASES

The free energy of the α phase in the Ti-Al-Sn-Zr-Nb system was represented by the regular solution model as

$$G^\alpha = \sum_i X_i {}^0G_i^\alpha + RT \sum_i X_i \ln(X_i) + \sum_{i,j} A_{ij} X_i X_j \quad (1)$$

where ${}^0G_i^\alpha$ is the Gibbs energy of the pure component i . X_i and A_{ij} are the atom fraction and the interaction parameter for the i - j binary system, respectively.

Table I Interaction parameters for the α phase in Eq. (1).

i-j	A_{ij}		i-j	A_{ij}	J/mol
Ti-Al	-111629 + 38.49·T	*1	Zr-Al	-76366	*1
Ti-Sn	-87780	*2	Zr-Sn	-55967	*1
Ti-Zr	7600	*3	Al-Sn	11704	*2

*1: present work, *2: after Kaufman and Bernstein [5],
*3: after Murray and Wriedt [6].

The interaction parameters for 3 systems Ti-Al, Zr-Al, and Zr-Sn (Table 1) were determined from equilibrium composition data of α and β phases in binary phase diagrams by Hansen. For the other systems, the parameters were taken from the works of Kaufman and Bernstein [5] and Murray and Wriedt [6].

The free energy of the α_2 phase was represented by the two sublattice model developed by Hillert and Staffansson [3].

The α_2 phase in the Ti-rich corner of the binary Ti-Al system was treated as $(\text{Ti})_3(\text{Ti,Al})$. Nandy et al. has reported that Zr occupies Ti sites in the α_2 phase [7]. Sn was assumed to occupy Al sites since Ti and Sn could form the compound Ti_3Sn of DO_{19} structure. The binary α_2 phase models could thus be extended to the quaternary model $(\text{Ti,Zr})_3(\text{Ti,Al,Sn})$ with Gibbs energy expression,

$$G^{\alpha_2} = \sum_{i,j}^1 Y_i^2 Y_j^0 G_{i:j}^{\alpha_2} + 3RT \sum_i ({}^1Y_i \ln {}^1Y_i) + RT \sum_i ({}^2Y_i \ln {}^2Y_i) + \sum_{i,j,k}^1 Y_i^1 Y_j^2 Y_k^L G_{i,j:k}^{\alpha_2} + \sum_{i,j,k}^1 Y_i^2 Y_j^2 Y_k^L G_{i,j:k}^{\alpha_2} \quad (2)$$

where the sY_i is the site fraction of the component i in the sublattice s . ${}^0G_{i:j}^{\alpha_2}$ and $L_{i,j:k}^{\alpha_2}$ are the Gibbs energy of the pure compound i_3j and the interaction parameter, respectively. A comma separates the elements on the same sublattice whereas a colon separates the elements on different sublattices. The unknown parameters ${}^0G_{i:j}^{\alpha_2}$ and $L_{i,j:k}^{\alpha_2}$ were approximated as shown in Table 2 using the data on α/α_2 equilibrium in the systems Ti-Al and Ti-Sn assessed by Murray and Wriedt [6]. For the optimization of the other parameters, we used the α/α_2 phase boundaries in systems Ti-Al-Zr [8], Ti-Al-Sn [9] and Ti-Sn-Zr [9]. The parameters evaluated in this study are summarized in Table II.

The calculated α/α_2 phase boundary in the Ti-Al-Sn-Zr system is compared to the experimental one reported by

Table II Parameters for the α_2 phase in Eq(2).

Gibbs energies of pure compounds (J/mol)

$${}^{\circ}G_{\text{Ti:Al}}^{\alpha_2} = 3{}^{\circ}G_{\text{Ti}}^{\alpha} + {}^{\circ}G_{\text{Al}}^{\alpha} - 104034 + 25.82 \cdot T$$

$${}^{\circ}G_{\text{Ti:Sn}}^{\alpha_2} = 3{}^{\circ}G_{\text{Ti}}^{\alpha} + {}^{\circ}G_{\text{Sn}}^{\alpha} - 95000, \quad {}^{\circ}G_{\text{Zr:Al}}^{\alpha_2} = 3{}^{\circ}G_{\text{Zr}}^{\alpha} + {}^{\circ}G_{\text{Al}}^{\alpha} - 79800$$

$${}^{\circ}G_{\text{Zr:Sn}}^{\alpha_2} = 3{}^{\circ}G_{\text{Zr}}^{\alpha} + {}^{\circ}G_{\text{Sn}}^{\alpha} - 78200$$

$${}^{\circ}G_{\text{Zr:Ti}}^{\alpha_2} = 3{}^{\circ}G_{\text{Zr}}^{\alpha} + {}^{\circ}G_{\text{Ti}}^{\alpha}, \quad {}^{\circ}G_{\text{Ti:Ti}}^{\alpha_2} = 4{}^{\circ}G_{\text{Ti}}^{\alpha}$$

Interaction parameters

$$L_{\text{Ti,Zr:Ti}}^{\alpha_2} = L_{\text{Ti,Zr:Al}}^{\alpha_2} = L_{\text{Ti,Zr:Sn}}^{\alpha_2} = 7600$$

$$L_{\text{Ti:Ti,Al}}^{\alpha_2} = L_{\text{Zr:Ti,Al}}^{\alpha_2} = -11918 + 45.029 \cdot T - 2.248 \cdot (T/10)^2$$

$$L_{\text{Ti:Ti,Sn}}^{\alpha_2} = L_{\text{Zr:Ti,Sn}}^{\alpha_2} = 17000, \quad L_{\text{Ti:Al,Sn}}^{\alpha_2} = L_{\text{Zr:Al,Sn}}^{\alpha_2} = 1170$$

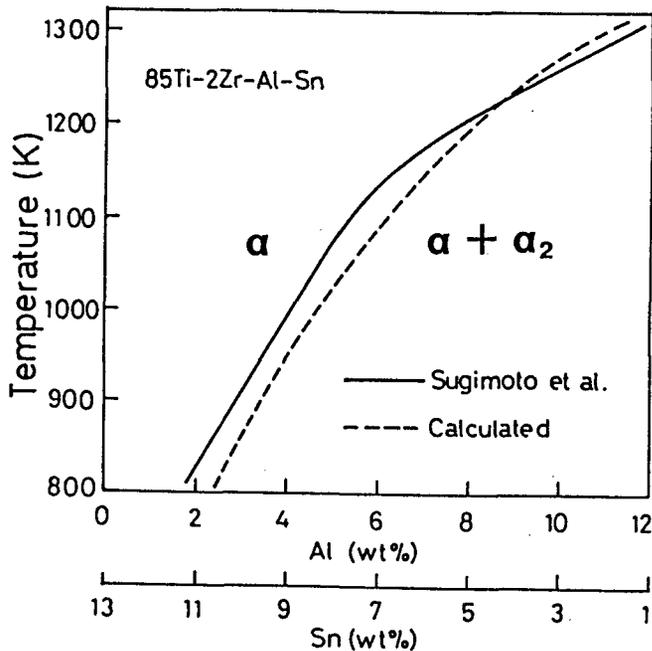


Figure 1 - The $\alpha / \alpha + \alpha_2$ phase boundary of the 85Ti-2Zr - Al-Sn alloys.

Sugimoto et al. [10] in Figure 1. The agreement is very satisfactory, and this supports the present thermodynamic analysis and the evaluated parameters.

DESIGN OF $\alpha + \alpha_2$ TITANIUM ALLOYS

Experimental procedure

In the present study, the solid-solution strengthening of the α phase was estimated by the following Eq.(8).

$$dDE^{\alpha} = 14.40 \cdot X_{Al} + 17.61 \cdot X_{Sn} + 9.69 \cdot X_{Zr} \quad (3)$$

where X_i is the atomic fraction of the element i in the α phase. Eq.(8) was obtained from the work of Sasano and Kimura [11] on the solid-solution strengthening of the α -Ti.

Ten Ti-Al-Sn-Zr alloys (Table III), which had various values of $V\alpha_2$ and dDE^{α} , were designed by the above thermodynamic calculations. Designed values of $V\alpha_2$ and dDE^{α} are shown in Table III. These alloys were arc melted as 2kg double melt ingots. Creep specimens were machined from bars which were rolled to about 70% reduction at 1273K. Creep tests were performed at 823K/274.4MPa. All specimens were β solution treated for 1h and furnace cooled (FC) or water quenched and aged at 873K for 4h (STA). The microstructures of thin foils were examined in a Hitachi H-700 transmission electron microscope.

Results of TEM observations are shown in Table 3. The strength of α_2 reflection in the selected area diffraction pattern (SADP) increases with increasing value of designed

TABLE III Chemical compositions (wt%)* and calculated $V\alpha_2$ and dDE^{α} (at 873K) of designed alloys.

Alloy	Al	Sn	Zr	$V\alpha_2$	dDE^{α}	SAR		$d\beta$ μm
						FC	STA	
GT-78	6.4	-	5.7	0	1.9	X	X	605
GT-79	6.1	2.5	6.9	.10	1.9	Δ	Δ	1300
GT-80	6.0	3.7	3.2	.09	1.8	Δ	X	1100
GT-81	6.2	4.3	5.6	.18	1.9	Δ	X	706
GT-82	7.1	4.1	5.1	.29	1.8	\circ	\circ	940
GT-83	7.8	4.0	6.8	.41	1.9	\circ	\circ	880
GT-84	8.2	3.6	9.8	.48	2.0	\circ	\circ	180
GT-85	6.6	2.1	11.0	.19	2.1	Δ	\circ	700
GT-86	2.6	11.0	5.6	.04	1.8	X	X	590
GT-87	4.6	6.6	5.6	.08	1.8	X	X	640

*: Balance Ti, SAR: The strength of α reflection in the SADP. (\circ : Strong, Δ : Weak, and X : Not observed.)

$V\alpha_2$. These results suggest that the present thermodynamic calculation can predict very well the tendency of the α_2 formation in Ti-Al-Sn-Zr alloys. The average grain size of prior β phase (d_β) was measured for FC materials by linear analysis from optical photographs and listed in Table III.

Creep properties of designed alloys

Creep properties such as the time to each creep strain and the minimum creep rate were obtained for FC and STA materials and summarized in Tables IV and V. As shown in Table IV, rupture lives of FC materials increase in the order of alloys GT-78, 80, 87, 79, 86, 81, 85, 82, 83, and 84. The calculated $V\alpha_2$ (Table III) increases in nearly the same order of alloys. From these results, it seems that the rupture life

Table IV Creep properties of FC materials at 823K and 274MPa.

Alloy	Time to creep strain /h			Minimum Creep Rate %/s	Rupture life h	Total El. %
	0.1%	0.2%	0.5%			
GT-78	2.2	3.8	8.5	7.1×10^{-8}	325	23.5
GT-79	7.5	17.5	88.0	7.3×10^{-7}	1743	11.5
GT-80	5.7	8.5	20.0	3.6×10^{-8}	569	15.5
GT-81	19.5	43.5	157.0	5.2×10^{-7}	2246	10.3
GT-82	89.5	280.0	977.0	1.2×10^{-7}	6757	5.4
GT-83	1260.0	2627.0	5950.0	2.4×10^{-8}	16331	1.9
GT-84	75.0	1879.0	> 5860.0	1.6×10^{-8}	> 5860*	> 0.4
GT-85	24.0	75.0	313.0	2.9×10^{-7}	3391	10.1
GT-86	4.0	28.0	170.0	8.9×10^{-7}	1823	10.1
GT-87	4.5	8.5	50.0	2.4×10^{-8}	1026	18.6

* : Interrupted.

Table V Creep properties of STA materials at 823K and 274MPa.

Alloy	Time to creep strain /h			Minimum Creep Rate %/s	Rupture life h	Total El. %
	0.1%	0.2%	0.5%			
GT-78	1.0	2.2	5.7	1.9×10^{-5}	214	58.9
GT-79	9.0	19.5	46.5	2.4×10^{-6}	828	27.1
GT-80	2.3	5.8	18.2	4.9×10^{-6}	461	25.4
GT-81	2.3	6.4	24.3	3.1×10^{-6}	501	29.3
GT-82	23.0	79.0	311.0	2.9×10^{-7}	4390	13.1
GT-83*	2.7	8.5	30.5	3.6×10^{-6}	376	10.6
GT-84*	7.5	25.5	59.0	4.9×10^{-6}	308	4.5
GT-85	2.7	6.5	21.7	4.7×10^{-6}	414	21.7
GT-86	1.6	5.8	24.1	3.3×10^{-6}	898	36.1
GT-87	1.0	3.0	10.8	9.1×10^{-6}	252	24.0

* : Creep test was performed at 873K and 274MPa.

increases with increasing $V\alpha_2$. The same tendency is seen in Table V for STA materials.

Rupture lives and times to given strain of FC materials are longer than those of STA materials as seen from in Tables IV and V. The morphology of transformation products varies depending on the cooling rate. The microstructure of FC material consists of a basketweave type widmanstatten α in a β matrix with thick α platerets and grain boundary α . That of WQ material consists of fine acicular martensite. Such morphological changes seem to explain this difference in creep performances. P.A. Blenkinsop et al. [12] have reported the same cooling rate dependence for β heat treated IMI685 alloy.

In order to evaluate quantitatively the effect of microstructural and compositional factors (volume fraction of α_2 phase ($V\alpha_2$), grain diameter of prior β phase (d_β), and degree of solid solution strengthening (dDE^α)) on creep strength, multiple regression analyses have been performed. In the present analysis, the following Larson-Miller parameter (LMP) was used in order to treat creep data at different temperatures.

$$\text{LMP} = 10^{-3} \cdot T \cdot \{ 20 + \log(t) \} \quad (4)$$

T : test temperature (K)
t : time (h) to a given creep strain

The creep strength (LMP) in Tables IV and V was analyzed as a linear function of parameters $V\alpha_2$, dDE^α , and d_β . When all variables were used, variables d_β and dDE^α were not 1% significant in t-test. The same tendencies were observed in the analyses for the FC condition and for other creep strains 0.1%, 0.5%, and the rupture life. The best regression equations obtained by neglecting parameters dDE^α and d_β are listed in Table VI. There was a good correlation between the creep strength and $V\alpha_2$ as shown in Table VI. From these results, it can be concluded that the α_2 precipitates play very effectively for improving high temperature strength of the α phase titanium alloys.

The relationship among the total elongation (El.) in Tables IV and V and parameters $V\alpha_2$, dDE^α , and d_β was also examined by multiple regression analysis. When all variables were used, variables dDE^α and d_β were not 1% significant as same as for the creep strength. The best regression equations obtained by neglecting these variables are also listed in Table VI. There was a fairly good correlation between the total elongation and $V\alpha_2$ (C.C.=.84 and .79 for STA and FC materials, respectively). These regression equations suggest that the total elongation decreases with increasing $V\alpha_2$.

Table VI The best regression equations for creep properties.

Heat Treatment	Regression equation LMP for each creep strain and Total elongation (El.)	Correlation Coefficient
STA	LMP(0.1%) = $16.42 + 3.54 \cdot V\alpha_2$.92
	LMP(0.2%) = $16.74 + 3.81 \cdot V\alpha_2$.93
	LMP(0.5%) = $17.16 + 3.82 \cdot V\alpha_2$.94
	LMP(rupture) = $18.42 + 2.71 \cdot V\alpha_2$.88
	El.(%) = $40.00 - 80.12 \cdot V\alpha_2$.84
FC	LMP(0.1%) = $16.80 + 3.83 \cdot V\alpha_2$.89
	LMP(0.2%) = $17.00 + 4.97 \cdot V\alpha_2$.96
	LMP(0.5%) = $17.48 + 4.99 \cdot V\alpha_2$.92
	LMP(rupture) = $18.70 + 3.15 \cdot V\alpha_2$.86
	El.(%) = $19.00 - 47.85 \cdot V\alpha_2$.79

Room temperature tensile properties

Results of room temperature tensile tests for representative alloys are correlated with calculated $V\alpha_2$ in Figure 2. In the FC condition, the tensile strength decreases with increasing $V\alpha_2$. A remarkable decrease in the elongation is observed at around $V\alpha_2$ of 0.1, and premature fracture occurs in alloys GT-83 and 84 containing $V\alpha_2$ of larger than 0.4. On the other hand, solution treated (ST) materials does not show such premature fracture. The 0.2% proof stress and the tensile strength in ST materials increase with increasing $V\alpha_2$. The elongation decreases gradually with increasing $V\alpha_2$. C.G. Rhodes et al. [1] reported that water quenching could avoid α_2 formation in a Ti-8Al-5Nb-5Zr-0.2Si alloy while large amount of α_2 phase were observed in the solution treated and aged condition. Then, it seems that the improvements of ductility in the ST condition seen in Fig.7 are resulted from the suppression of α_2 formation by quenching.

From the results shown in Fig.2, it can be concluded that the available $V\alpha_2$ is less than 0.1 to strengthen α phase titanium alloys without a large decrease in ductility in the FC condition. Furthermore, the present results show that the ST condition can give $\alpha + \alpha_2$ type titanium alloys a good ductility at room temperature. This suggests the possibility to use these alloys in the ST condition. This suggestion seems to be supported by the results of C.G. Rhodes et al. [12] that the good combination of high temperature creep resistance and room temperature ductility has been obtained by a Ti-8Al-5Nb-5Zr-0.2Si alloy in the ST condition, while the STA condition has exhibited brittleness.

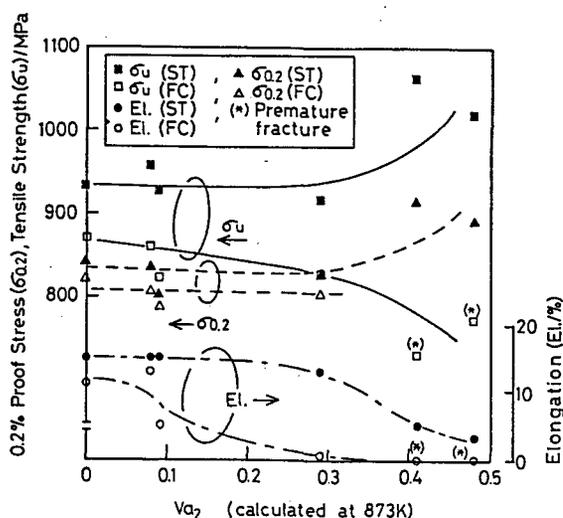


Figure 2 - Room temperature tensile properties of representative alloys in the furnace cooled (FC) and the solution treated and quenched (ST) conditions.

From the present results, the $V\alpha_2$ of about 0.1 (at 873K) seems to be the best condition for designing $\alpha + \alpha_2$ type high temperature titanium alloys having the good combination of the creep properties and the room temperature tensile ductility in the FC condition [4].

CONCLUSION

(1) Thermodynamic analyses of the α and α_2 phases in the systems, Ti-Al, Ti-Sn, Ti-Al-Sn, Ti-Al-Zr, and Ti-Sn-Zr were performed, by means of the two sublattice model proposed by Hillert and Staffansson [2]. The analyses with relevant parameters determined from existing data on $\alpha - \alpha_2$ phase equilibria was able to reproduce the experimentally determined $\alpha / \alpha + \alpha_2$ phase boundary in the Ti-Al-Sn-Zr system.

(2) From creep tests of ten Ti-Al-Sn-Zr alloys which were designed by the above thermodynamic calculations, it was concluded that the α_2 precipitates would be very effective for improving high temperature strength of the α phase titanium alloys.

(3) In the FC condition, a remarkable decrease in the elongation was observed at the calculated $V\alpha_2$ of about 0.1 at 873K in room temperature tensile tests. On the other hand, the 0.2% proof stress and the tensile strength increased with increasing $V\alpha_2$ and good ductility was observed in the solution treated (ST) condition.

(4) As the best design condition for $\alpha + \alpha_2$ high temperature titanium alloys, the $V\alpha_2$ of about 0.1 at 873K was proposed.

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