JOURNAL OF MATERIALS SCIENCE **32** (1997) 229–234

Characterization of silicides in high-temperature titanium alloys

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Different types of silicides precipitate in high-temperature titanium alloys depending upon the composition and heat treatment of the alloys. However, there are inconsistencies and lacunae with respect to the chemical and crystallographic characteristics of the silicides and these are pointed out here. Hexagonal silicides s_1 ($a = 0.780_4$ nm; $c = 0.544_7$ nm) and s_2 ($a = 0.70_1$ nm; $c = 0.36_8$ nm) coexist in the ternary alloy Ti–5Zr–Si; however, only the s_2 silicide exists when the addition of β stabilizing element is made. In addition, there is no common agreement about the space group of s_2 silicide while the space group of s_1 silicide was found to be $P6_3/mcm$ (hP16). The $(TiZr)_6Si_3$ stoichiometry of s_2 silicide is based on the experimental findings; however, the $(TiZr)_5Si_3$ stoichiometry of s_1 silicide is simply deduced. Also the orientation relationships of silicides with α and β phases of the matrix are discussed.

1. Introduction

Near α and (α + β) titanium alloys have been designed for high-temperature components in jet engines. The development of such alloys has been reviewed [1]. It is well established that addition of a small amount of silicon to these alloys leads to significant improvement in their creep resistance [2–9]. However, there are differing views regarding the mechanism of creep strengthening from silicon which are based on dynamic strain ageing [5, 8] and pinning of dislocations by silicide precipitates [7]. Silicon is also known to affect the microstructure and static strength of titanium alloys [6, 10–31]. Different types of silicides [11–20, 24–36] precipitate depending upon the composition of the alloys and the heat treatments. The type, size and distribution of silicides affect mechanical properties of these alloys. Silicide precipitation has been found to embrittle the titanium alloys 685 [22–24], 684 [6] and 829 [27–30]. Silicon in solution and in the form of silicides was observed also to affect the low-cycle fatigue behaviour of these alloys [33–35]. The effect of silicides in high-temperature titanium alloys has been reviewed [36] systematically.

The purpose of this paper is to present and highlight some of the discrepancies and lacunae regarding the chemical and crystallographic characteristics of the silicides in the high-temperature silicon-bearing titanium alloys. The orientation relationships of s_2 with α and β phases, are also presented.

2. Chemical and crystallographic characteristics

Different types of silicides, identified in various high-temperature silicon-bearing titanium alloys, subjected to different heat treatments, are presented in Table I. In the ternary alloy Ti–5Zr–1Si, ageing of the β solution-treated and water-quenched specimens at 823–1073 K resulted in the precipitation of silicides [11]. Coarse silicides extracted from the specimen aged at 1073 K were examined [11] by X-ray diffraction. A few selected-area electron diffraction patterns were also recorded from the silicides. After a careful analysis of the diffraction data, it was concluded that only one type of hexagonal silicide (designated) s_1 [12] with lattice parameters $a = 0.780_4$ nm; $c = 0.544_7$ nm; resulted from the ageing at 823 K. However, another hexagonal silicide (designated) s_2 [12] with lattice parameters $a = 0.70_1$ nm; $c = 0.36_8$ nm was observed to coexist with s_1 on ageing in the temperature range 923–1073 K. No attempt was made to determine experimentally the stoichiometry of these two silicides s_1 and s_2.

Antony [13] established, using X-ray diffraction, that the silicide resulting from annealing of the complex alloy Ti–6Al–3Sn–3Zr with varying content of silicon (0.1–1.0 wt %), in the temperature range 1143–1303 K had hexagonal crystal structure but the lattice parameters ($a = 0.773$ nm and $c = 0.5323$ nm) were significantly different from those of s_1 and s_2. This silicide is designated s′.

Qualitative X-ray fluorescence analysis of this silicide indicates that it is of the type (Ti, Zr, Sn) Si; however, the concentration of tin in the silicide was quite low. Based on the X-ray diffraction and X-ray fluorescence analysis, the silicide was identified as a complex silicide, intermediate in composition and structure to the hexagonal silicides Ti_5Si_3 ($a = 0.787$ nm; $c = 0.555$ nm) [14] and Zr_5Si_3 ($a = 0.747$ nm; $c = 0.516$ nm). Antony [13] argued

TABLE I Silicides in high-temperature titanium alloys

No.	Alloy	Heat treatment		TD[a]	Type of silicide	Lattice parameter		Lattice space group	Remarks	Reference
		Solution treatment	Ageing			*a* (nm)	*c* (nm)			
1.	Ti–5Zr–1Si	1473 K, 24 h water quench (WQ)	823 K, 3000 h	–	s_1	0.780_4	0.544_7	Hexagonal	X-ray and electron diffraction	[11]
			923 K, 5 h	–	s_1 s_2	0.780_4 0.70_1	0.544_7 0.36_8	–	–	
			1073 K, 150 h	–	s_1 s_2	0.780_4 0.70_1	0.544_7 0.36_8	–	–	
2.	Ti–5Zr–5Al–1Si	1473 K, 24 h	823 K, 1667 h	–	s_1	0.780_4	0.544_7	Hexagonal	X-ray and electron diffraction	[11]
3.	Ti–6Al–3Sn–5Zr–0.1 to 1.0Si	Annealed at 1143 K to 1303 K	–	–	s′	0.773	0.532	Hexagonal	X-ray diffraction; qualitative chemical analysis using X-ray fluoroscence	[13]
4.	Ti–5Al–5Sn 2Zr–0.8Mo–0.7Si	As-received	–	–	s′	0.773	0.532	Hexagonal	Electron diffraction	[14]
5.	Ti–4.5Al–2Sn–3Zr–3Ga–3Mo–0.5Si	1298 K, 1 h, (AC)	868 K, 4 h	–	s′	0.773	0.532	Hexagonal	Electron diffraction	[14]
6.	IMI-685 (Ti–6Al–5Zr–0.5Mo–0.25Si)	1323 K, 1 h, slow cooling ($0.1\ K\ s^{-1}$)	–	–	s_2	0.698 ± 0.010	0.365 ± 0.010	P321 (no. 150) (hexagonal)	Electron diffraction energy dispersive X-ray analysis (EDAX)	[15]
		1323 K, $\frac{1}{2}$ h, WQ	923 K, 24 h	WQ-A1	s_1 s_2	0.780_4 0.70_1	0.544_7 0.36_8	–	Electron diffraction	[12]
			973 K, 24 h	WQ-A2	s_2	0.70_1	0.36_8	–	–	
			1073 K, 24 h	WQ-A3	s_2	0.70_1	0.36_8	–	–	
7.	VT9 (Ti–6Al–1.6Zr–3.3Mo–0.3Si)	1323 K, 1 h, WQ	873–1073 K, 24 h	– –	s_2	0.70_1	0.36_8	Hexagonal	Electron diffraction	[17] [18]
8.	IMI-829 (Ti–5.5Al–3.5Sn–3Zr–0.5Mo–1Nb–0.3Si)	1323 K, 1 h, WQ	898–1223 K, 24 h	–	s_2	0.70_1	0.36_8	Hexagonal	Electron diffraction	[27]
		1293 K, $\frac{1}{2}$ h, slow cooling		–	s_2	0.696	0.365	Hexagonal P6/*mmm* (no. 191) or $P6_3/mcm$ (no. 193)	Convergent beam electron diffraction (CBED) and EDAX	[28]
		1323 K, 1 h, (AC)	848 K, 1000 h	–	s_2	0.714 ± 0.004	0.374 ± 0.006	Hexagonal $P\bar{6}2m$ (no. 189)	CBED and EDAX	[30] [31]
		1323 K, 1 h, oil quenched (OQ)			s_2	0.714 ± 0.004	0.374 ± 0.006	Hexagonal, $P\bar{6}2m$ (no. 189)	–	[30] [31]
9.	IMI-834 (Ti–6Al–4Sn–4Zr–0.70Nb–0.50Mo–0.40Si)	1353 K, 30 min, WQ	973 K, 24 h	WQβ-A2	s_2	0.70_2	0.36_8	Hexagonal	Electron diffraction	[19]
		1303 K, 30 min, WQ	873 K, 24 h	WQαβ-A1	s_2	0.70_2	0.36_8	Hexagonal	–	
			973 K, 24 h	WQαβ-A2	s_2	0.70_2	0.36_8	Hexagonal	–	
10.	Beta-C (Ti–3Al–8V–6Cr–4Zr–4Mo–0.04Si)	Annealing between 1144 and 1325 K	–	–	s_2	0.698	0.365	Hexagonal P6/*mmm* (no. 191)	CBED	[38]

[a] Treatment designation. Stoichiometry of s_1 deduced to be $(TiZr)_5Si_3$, stoichiometry of s_2 experimentally confirmed as $(TiZr)_6Si_3$.

that the stoichiometry of the complex silicide, s′, could be approximated to $(Ti_{0.4}, Zr_{0.6})_5Si_3$ as the lattice parameters of this silicide are intermediate to those of the hexagonal silicides Ti_5Si_3 and Zr_5Si_3. Further, the s′ silicide also had the same hexagonal crystal structure as the Ti_5Si_3 and Zr_5Si_3. These silicides are isomorphous. Recently, Ramachandra and Singh [37] have reanalysed the X-ray diffraction data of Antony [13] and ruled out the possibility of the existence of s′ silicide; on the other hand, the presence of s_2 silicide was established.

Using Antony's [13] observations and arguments, Flower *et al.* [11] deduced that s_1 in the ternary alloy Ti–5Zr–1Si is of similar stoichiometry, $(TiZr)_5Si_3$. Kotval and Calder [14] characterized the silicides in alloys Ti–5Al–5Sn–2Zr–0.8Mo–0.7Si and Ti–4.5Al–2Sn–3Ga–2Mo–0.5Si, using selected-area diffraction patterns, as s′. The analysis of their selected-area diffraction patterns suggests that the silicides in the alloy Ti–4.5Al–2Sn–2Zr–3Ga–2Mo–0.5Si could be indexed either as s_1 or s′. However, the electron diffraction patterns of the silicide in the alloy Ti–5Al–5Sn– 2Zr–0.8Mo–0.7Si can be indexed only as s′ silicide. The findings of Kotval and Calder [14] require detailed investigations using both X-ray as well as electron diffraction techniques to resolve fully these controversies.

Barbier *et al.* [15] studied precipitation of silicides in alloy 685 in the slow-cooled condition. Electron diffraction analysis revealed that these silicides have hexagonal structure and lattice parameters of $a = 0.698 \pm 0.01$ nm and $c = 0.365 \pm 0.01$ nm. This silicide could be considered the same as the s_2 silicide observed in the ternary Ti–5Zr–1Si alloy. Its stoichiometry based on X-ray micro-analysis was established as $(TiZr)_6Si_3$ [15]. In the same alloy, Ramachandra and Singh [12] found the co-existence of both s_1 and s_2 silicides in the water-quenched specimen, aged at 923 K. However, only s_2 was found to exist when the water-quenched specimen was aged in the temperature range 973–1073 K. In alloy VT9 [16–18] only s_2 silicide was found to exist when the water-quenched specimen was aged in the lower temperature range of 873–1073 K.

Ramachandra *et al.* [19] reported precipitation of s_2 silicide in the different heat-treatment conditions of the near α titanium alloy 834 (Table I). Sridhar and Sarma [26, 27] reported precipitation of only s_2 silicide in the alloy 829 (Table I) heat treated to different conditions. Banerjee *et al.* [28] examined silicide precipitation in the alloy 829 in the slow-cooled condition. Electron diffraction analysis showed that the silicides are hexagonal with the lattice parameters, $a = 0.696$ nm, and $c = 0.365$ nm. These values are marginally different from those of s_2; however, the deviations are within the range of experimental error. Woodfield *et al.* [30] reported slightly higher values of the lattice parameters ($a = 0.714$ nm ± 0.004 and $c = 0.374 \pm 0.006$ nm) for the silicide in the same alloy 829, than those of s_2 [28]. They attributed it to the presence of 1 at % Sn in the silicide and described the stoichiometry as $(TiZr)_6Si_3$. The discrepancy in the lattice parameters of the silicide in the alloy 829 in the two investigations [28, 30] could, therefore, be attributed to either the effect of microalloying elements (such as tin) or experimental error.

Ankem *et al.* [38] studied silicides in Beta-C (Ti–3Al–8V–6Cr–4Zr–4Mo–0.4Si) alloy annealed at 1144 K for 1 h and water quenched. The silicide was found to have hexagonal crystal structure with lattice parameters $a = 0.696$ nm, $c = 0.365$ nm. Based on a qualitative X-ray EDS analysis of silicide, Ankem *et al.* [38] assumed the stoichiometry of the silicide to be $(TiZr)_5Si_3$. However, the lattice parameters mentioned above are in good agreement with those of the s_2 silicide ($(TiZr)_6Si_3$). It should be pointed out that X-ray EDS analysis of silicon requires caution, owing to (a) its low atomic number ($Z = 14$), (b) overlapping of Al ($Z = 13$) and Si ($Z = 14$) peaks and the consequent difficulties encountered in the background correction [39]. Therefore, the above discrepancy can be explained on the basis of difficulties observed in quantifying silicon, in the presence of aluminium, using EDS.

In the light of the above facts, it may be concluded that silicides s_1 and s_2 or only s_2 form in the ternary and even in complex titanium alloys, under different heat-treatment conditions. It is important to point out that s_1 and s_2 coexist at lower ageing temperature. A higher content of β stabilizing elements, such as in alloys VT9 and 829, leads to precipitation of only s_2 silicide. In view of this it is reasonable to deduce that with the addition of β stabilizing elements to these silicon-bearing high-temperature titanium alloys, only the s_2 silicide precipitates. This deduction is further strengthened by the precipitation of only the s_2 silicide in a β alloy [38]. Although the above observation is true with in the majority of investigations, Kotval and Calder's [14] identification of s′ silicides instead of s_2 in the alloys Ti–4.5Al–2Sn–3Ga–2Mo–0.5Si and Ti–5Al–5Sn–2Zr–0.8Mo–0.7Si, which are similar in composition to alloys VT9 and 829, respectively, is surprising. Clearly, further investigations are needed for the characterization of silicides in these systems.

It may also be pointed out that while there is strong experimental evidence for the stoichiometry of s_2, the stoichiometry of s_1 needs to be established unambiguously. It is relevant to mention that in a β alloy, the silicide phase with lattice parameters comparable to s_2 was loosely described as having a stoichiometry of $(TiZr)_5Si_3$ without any quantitative chemical analysis. This also requires a detailed investigation. The morphologies of s_1 and s_2 precipitates, as observed in the TEM, are distinctly different. While s_1 precipitates have rod-like morphology [11], s_2 appears to be elliptical [12, 16–19, 26, 27].

It is important to mention that a few attempts have been made to determine the space group of the silicide s_2 (Table I). Barbier *et al.* [15] analysed s_2 in 685 by using selected-area diffraction and energy dispersive X-ray analysis and reported the structure as trigonal with the space group P321 (number 150); Ankem *et al.* [38] and Banerjee [40] used convergent-beam electron diffraction analysis and deduced the structure of s_2 in 829 to be hexagonal with the space group P6/*mmm* (number 191) and Woodfield and Loretto

[31] found by convergent-beam electron diffraction technique, that s_2 is hexagonal with space group P62*m* (number 189). This shows that there is no agreement between the various workers regarding the space group of the silicide s_2. Thus it is necessary to resolve this controversy.

3. Identification of silicides s_1 and s_2 using electron diffraction technique

In alloy 685, it was reported [12] that the silicides s_1 and s_2 coexist when the β solution-treated and water-quenched specimen is aged at 923 K for 24 h (WQ-A1). However, only s_2 silicide was found to exist on ageing in the temperature range of 973–1073 K. The electron diffraction data obtained to establish the above findings which would be quite useful in similar studies, are presented in this section.

The silicide precipitates were too small (~ 50 nm) in the WQ-A1 condition to give well-developed zones of electron diffraction patterns. However, the interplanar spacings were obtained from various diffraction spots. The interplanar spacings were confirmed to originate from the precipitates via the dark-field technique and are listed in Table II and show good agreement with those reported by Flower *et al.* [11] in the ternary alloys. Ageing of the water-quenched specimens at higher temperatures of 973–1073 K resulted in the coarse silicide particles (Fig. 1) with size in the range 100–250 nm. This enabled well-developed zones of electron diffraction patterns to be obtained from several individual particles. They could be indexed as s_2 silicide. Table II shows that the agreement between the observed (from X-ray and electron diffraction) and calculated interplanar spacings is excellent. The measured angles between different planes, indicated in the diffraction patterns are within $\pm 0.5°$ with the calculated angles. Thus the silicides could be easily identified.

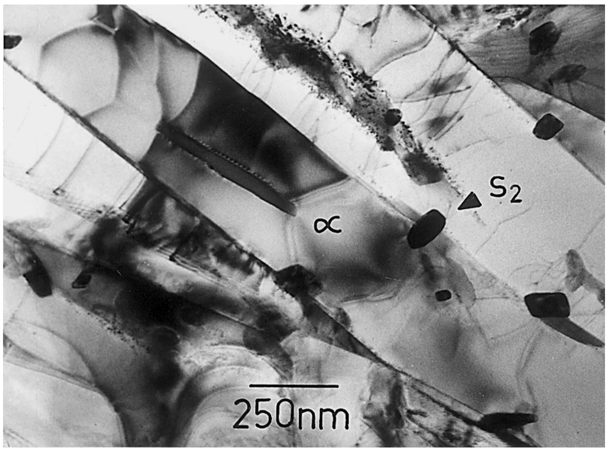

Figure 1 Bright-field transmission electron micrograph showing silicides at the interplatelet boundaries of α.

TABLE II Electron diffraction analysis of silicides in WQ-A1 and WQ-A3 conditions of the titanium alloys 685

Observed electron diffraction *d* values (nm)			Silicide s_1		Silicide s_2	
(WQ-A1) [12]	[11]	(WQ-A3) [12]	Calculated *d* values[a] (nm)	*hkil*	Calculated *d* values[b] (nm)	*hkil*
–	–	0.605	–	–	0.6079	$10\bar{1}0$
–	0.3855	–	0.3904	$11\bar{2}0$	–	–
0.365	0.3678	0.365	–	–	0.3680	0001
–	0.3517	0.350	–	–	0.3510	$11\bar{2}0$
–	0.3370	–	0.3381	$20\bar{2}0$	–	–
–	0.3155[c]	0.3152	0.3172	$11\bar{2}1$	0.3147	$10\bar{1}1$
0.310	0.3038	0.305	–	–	0.3039	$20\bar{2}0$
–	0.2810	–	0.2723	0002	–	–
0.260	0.2592	–	–	–	–	–
0.255	0.2541[c]	0.255	0.2555	$21\bar{3}0$	0.2539	$11\bar{2}1$
0.235	0.2338	0.235	–	–	0.2342	$20\bar{2}1$
0.230	0.2293[c]	0.230	0.2306	$21\bar{3}1$	0.2297	$21\bar{3}0$
–	0.2243	–	–	–	–	–
0.220	0.2127	–	0.2121	$20\bar{2}2$	–	–
0.205	0.2023	–	–	–	0.2026	$30\bar{3}0$
0.195	0.1945[c]	0.195	0.1952	$22\bar{4}0$	0.1948	$21\bar{3}1$
–	0.1863	–	0.1863	$21\bar{3}2$	–	–
–	0.1840	–	0.1838	$22\bar{4}1$	0.1840	0002
0.160	0.1690[c]	0.170	0.1690	$40\bar{4}0$	0.1686	$31\bar{4}0$
0.155	0.1584[c]	0.160	0.1586	$22\bar{4}2$	0.1584	$22\bar{4}1$
–	0.1531[c]	0.155	0.1551	$32\bar{5}0$	0.1532	$13\bar{4}1$
0.145	0.1436[c]	–	0.1436	$40\bar{4}2$	0.1436	$12\bar{3}2$
–	0.1374	–	0.1362	0004	–	–
–	0.1360	–	0.1352	$50\bar{5}0$	–	–
–	0.1301	–	–	–	0.1303	$32\bar{5}1$
–	–	–	–	–	0.1269	$22\bar{4}2$
–	–	–	–	–	0.1774	$30\bar{3}1$
–	–	0.175	–	–	0.1761	$10\bar{1}2$
–	–	–	–	–	0.1755	$22\bar{4}0$
–	–	0.165	–	–	0.1629	$11\bar{2}2$

[a] Assuming that for s_1, $a = 0.780$ nm, $c = 544$ nm.
[b] Assuming that for s_2, $a = 0.70_2$ nm, $c = 0.36_8$ nm.
[c] Interplanar spacings common to both the silicides s_1 and s_2.

4. Orientation relationships between the silicides and α, β phases

Orientation relationships obtained between the silicides and α, β phases using electron diffraction techniques in different high-temperature titanium alloys are listed in Table III.

The orientation relationships between α and s_2, β and s_2 reported in alloys 685 [41], 829 [26] and VT9 [42] (Table III) do not agree with each other. There is disagreement even within each alloy system. Those reported in alloy VT9 [42] indicate that s_2 does not hold a consistent orientation relationship with α as well as β phase. The non-existence of an orientation relationship between s_2 and the matrix phase could probably be understood as due to the precipitation of s_2 either in α or β phases and subsequent migration of the α/β interface to relocate particles in either of the phases α or β. It may be stated that limited studies have been carried out to establish the orientation relationships between α and s_1. The majority of the studies have been performed to establish orientation relationships between α and s_2. In order to resolve the above issue, systematic studies are required on these alloys.

TABLE III Orientation relationships of silicides with α and β Ti in high-temperature titanium alloys

No.	Orientation relationships	*d* spacings (nm)		$\frac{n d_{\alpha'/\beta} - ds}{n d_{\alpha'/\beta'}} \times 100$	*n*	References
		α/β	Silicide			
(a)	Ternary Ti–Zr–Si alloys					[11]
	(between α′ and s_1)					
1.	$(0001)_{\alpha'} \parallel (0001)_{s_1}$	$0.4683_{\alpha'}^{a}$	0.5447_{s_1}	− 16.3	1	
	$(1\bar{1}00)_{\alpha} \parallel (12\bar{3}0)_{s_1}$	$0.2557_{\alpha'}^{a}$	0.2555_{s_1}	+ 0.07	1	
	$(3\bar{2}\bar{1}0)_{\alpha'} \parallel (0\bar{1}\bar{1}0)_{s_1}$	$0.0966_{\alpha'}^{a}$	6.762_{s_1}	0	7	
(b)	IMI-685					[15]
	(between α, β and s_2)					
2.	$[01\bar{1}1]_{\alpha} \parallel [001]_{\beta} \parallel [0001]_{s_2}$	$0.2234_{\alpha'}^{b}$	0.2297_{s_2}	− 2.82	1	
	$\{\bar{1}011\}_{\alpha} \parallel \{110\}_{\beta} \parallel \{12\bar{3}0\}_{s_2}$	0.2321_{β}^{c}	0.2297_{s_2}	+ 1.03	1	
3.	$[0001]_{\alpha'} \parallel [\bar{1}2\bar{1}6]_{s_2}$					[41]
	$(01\bar{1}0)_{\alpha'} \parallel (\bar{1}2\bar{1}\bar{1})_{s_2}$	$0.2544_{\alpha'}^{b}$	0.2539_{s_2}	+ 20	1	
	$(21\bar{3}0)_{\alpha'} \parallel (12\bar{3}\bar{1})_{s_2}$	$0.09616_{\alpha'}^{b}$	0.1948_{s_2}	− 1.29	2	
	$(2\bar{1}\bar{1}0)_{\alpha'} \parallel (10\bar{1}0)_{s_2}$	$0.1469_{\alpha'}^{b}$	0.6079_{s_2}	− 3.45	4	
(c)	IMI-829					
	WQ-aged at 898 K					
4.	$[01\bar{1}\bar{1}]_{\alpha'} \parallel [0001]_{s_2}$					[27]
	$(2\bar{1}\bar{1}0)_{\alpha} \parallel (1\bar{1}00)_{s_2}$	$0.1469_{\alpha'}^{b}$	0.6079_{s_1}	− 3.45	4	
	WQ-aged at 973 K					
5.	$[1\bar{1}0\bar{4}]_{\alpha'} \parallel [1\bar{2}13]_{s_2}$					[27]
	$(11\bar{2}0)_{\alpha} \parallel (10\bar{1}0)_{s_2}$	$0.1469_{\alpha'}^{b}$	0.6079_{s_1}	− 3.45	4	
	WQ-aged at 1073 K					
6.	$[1\bar{1}0\bar{1}]_{\alpha'} \parallel [0001]_{s_2}$					[27]
	$(01\bar{1}\bar{1})_{\alpha} \sim 2^{\circ}\ (10\bar{1}0)_{s_2}$	$0.2234_{\alpha'}^{b}$	0.6079_{s_2}	+ 9.29	3	
7.	$[001]_{\beta} \parallel [1\bar{2}1\bar{3}]_{s_2}$					[28]
	$(101)_{\beta} \parallel (10\bar{1}0)_{s_2}$	$0.2321_{\alpha'}^{c}$	0.6079_{s_2}	+ 12.69	3	
	$(200)_{\beta} \parallel (2\bar{1}\bar{1}1)_{s_2}$	0.1641_{β}^{c}	0.2539_{s_2}	+ 22.63	2	
(d)	VT9					
	WQ-aged at 973 K					[42]
8.	$[4\bar{5}16]_{\alpha'} \parallel [1\bar{2}1\bar{6}]_{s_2}$					
	$(01\bar{1}1)_{\alpha'} 2^{\circ} \parallel (2\bar{2}01)_{s_2}$	$0.2234_{\alpha'}^{b}$	0.2342	− 4.83	1	
	$(\bar{2}203)_{\alpha'} 1^{\circ} \parallel (1\bar{2}11)_{s_2}$	$0.0985_{\alpha'}^{b}$	0.2539	− 14.10	3	
9.	$[4\bar{5}16]_{\alpha'} \sim \parallel (4\bar{5}16)_{s_2}$					[42]
	$(01\bar{1}1)_{\alpha} \parallel (21\bar{3}0)_{s_2}$	$0.2234_{\alpha'}^{b}$	0.2297_{s_2}	− 2.82	1	
	$(\bar{2}203)_{\alpha'} \parallel (20\bar{2}1)_{s_2}$	$0.09853_{\alpha'}^{b}$	0.2342_{s_2}	− 18.84	2	
10.	$[01\bar{1}1]_{\alpha'} \parallel (\bar{1}\bar{1}29)_{s_2}$					[42]
	$(\bar{1}10\bar{1})_{\alpha} \parallel (1\bar{1}00)_{s_2}$	$0.2234_{\alpha'}^{b}$	0.6079	+ 9.29	3	
	$(\bar{1}011)_{\alpha} \parallel (21\bar{3}1)_{s_2}$	$0.2234_{\alpha'}^{b}$	0.1948	+ 12.80	1	
11.	$[001]_{\beta'} \parallel (0001)_{s_2}$					[42]
	$(200)_{\beta}^{3^{\circ}} \parallel (10\bar{1}0)_{s_2}$	0.1641_{β}^{c}	0.6079_{s_2}	+ 7.38	4	
	$(110)_{\beta}^{3^{\circ}} \parallel (12\bar{3}0)_{s_2}$	0.2321_{β}^{c}	0.2297_{s_2}	+ 1.03	1	
12.	$[012]_{\beta} \parallel [1\bar{2}1\bar{3}]_{s_2}$					[42]
	$(200)_{\beta} \parallel (10\bar{1}0)_{s_2}$	0.1641_{β}^{c}	0.6079_{s_2}	+ 7.38	4	
(e)	IMI-834					
13.	$[01\bar{1}1]_{\alpha'} \parallel [1\bar{2}16]_{s_2}$					[19]
	$(\bar{2}110)_{\alpha'}^{5^{\circ}} \parallel (2\bar{2}0\bar{1})_{s_2}$	$0.1469_{\alpha'}^{b}$	0.2342_{s_2}	+ 20.28	2	
	$[01\bar{1}1]_{\alpha'} \parallel [2\bar{1}\bar{1}0]_{s_2}$					
	$(\bar{2}110)_{\alpha'} \parallel (01\bar{1}0)_{s_2}$	$0.1469_{\alpha'}^{b}$	0.6079_{s_2}	− 3.45	4	

[a] ASTM values for unalloyed titanium.

[b] Calculated with lattice parameters [43] $a = 0.29379$ nm and $c = 0.46732$ nm; c calculated assuming $a = 0.3283$ nm.

5. Conclusions

1. Hexagonal silicides s_1 ($a = 0.780_4$ nm; $c = 0.544_7$ nm) and s_2 ($a = 0.70_1$ nm; $c = 0.36_8$ nm) coexist in silicon-bearing high-temperature α titanium alloys free of β stabilizing elements.

2. The addition of even small amounts of β stabilizing elements to near-α alloys as well as $(\alpha + \beta)$ alloys, leads to only precipitation of the s_2 silicide.

3. Identification of hexagonal silicide s' in two alloys, Ti–5Al–5Sn–2Zr–0.8Mo–0.7Si and Ti–4.5Al–2Sn–3Ga–2Mo–5Si needs further characterization.

4. While the stoichiometry of s_2 as $(TiZr)_6Si_3$ has been determined quantitatively, the stoichiometry of s_1 as $(TiZr)_5Si_3$ is based on qualitative experimental evidence and arguments in these alloys.

5. Limited studies have been carried out regarding the orientation relationship of s_1 with α-Ti. s_2 does not hold any consistent orientation relations with either α or β.

Acknowledgements

A. K. S. acknowledges the financial support of the Defence Research and Development Organisation, Government of India. The authors thank Professor Shrikant Lele, Department of Metallurgical Engineering, Banaras Hindu University, Varanasi and Dr D. Banerjee, Defence Metallurgical Research Laboratory, Hyderabad for many helpful discussions. The permission of the Director, Defence Metallurgical Research Laboratory, Hyderabad to publish these results is gratefully acknowledged.

References

1. D. EYLON, S. FUJISHIRO, P. J. POSTANS and F. H. FROES, *J. Metals* **1** (1984) 55.
2. S. R. SEAGLE and H. B. BOMBERGER, in "The Science, Technology and Application of Titanium", edited by R. I. Jaffee and N. E. Promisel (Pergamon Press, New York, 1970) pp. 1001–8.
3. H. M. FLOWER, P. R. SWANN and D. R. F. WEST, in "Titanium Science and Technology", Vol. 2, edited by R. I. Jaffee and H. M. Burte (Plenum Press, 1973) pp. 1143–53.
4. M. KEHOE and R. W. BROOMFIELD, *ibid.* Vol. 4 (1973) pp. 2167–78.
5. M. R. WINSTONE, R. D. RAWLINGS and D. R. F. WEST, *J. Less-Common Metals* **39** (1975) 205.
6. Y. IMBERT, *ibid.* **37** (1974) 71.
7. N. E. PATON and M. W. MAHONEY, *Metall. Trans.* **7A** (1976) 1685.
8. A. T. K. ASSADI, H. M. FLOWER and D. R. F. WEST, *Metals Technol.* **6** (1979) 16.
9. M. W. MAHONEY and N. E. PATON, *Metall. Trans.* **9A** (1978) 1497.
10. H. M. FLOWER, P. R. SWANN and D. R. F. WEST, *J. Mater. Sci.* **7** (1972) 929.
11. *Idem*, *Metall. Trans.* **2** (1971) 3289.
12. C. RAMACHANDRA and V. SINGH, *ibid.* **13A** (1982) 771.
13. K. C. ANTONY, *Trans. TMS-AIME* **242** (1968) 1454.
14. P. C. KOTVAL and R. W. CALDER, *Metall. Trans.* **3** (1972) 1308.
15. F. BARBIER, C. SERVANT, C. QUESNE and P. LACOMBE, *J. Microsc. Spectrosc. Electron.* **6** (1981) 299.
16. C. RAMACHANDRA, PhD thesis, Banaras Hindu University, Varanasi, India (1985).
17. A. K. SINGH, C. RAMACHANDRA, M. TAVAFOGHI and V. SINGH, *J. Alloys Compounds* **179** (1992) 125.
18. A. K. SINGH, T. ROY and C. RAMACHANDRA, *Metall. Mater. Trans. A* (1994) **6** in press.
19. C. RAMACHANDRA, A. K. SINGH and G. M. K. SARMA, *Met. Trans.* **24A** (1993) 1273.
20. A. T. K. ASSADI, H. M. FLOWER and D. R. F. WEST, *Metals Technol.* **6** (1979) 8.
21. H. M. FLOWER, K. LIPSCOBE and D. R. F. WEST, *J. Mater. Sci.* **17** (1982) 1221
22. C. RAMACHANDRA and V. SINGH, *Metall. Trans.* **16A** (1985) 227.
23. *Idem*, *J. Mater. Sci.* **23** (1988) 835–841.
24. *Idem*, *Metall. Trans.* **19A** (1988) 389.
25. D. F. NEAL and P. A. BLENKINSOP, in "Titanium 80, Science and Technology", edited by H. Kimura and O. Izumi (Transactions of the Metallurgical Society, AIME, NY, 1980) pp. 1287–94.
26. G. SRIDHAR and D. S. SARMA, *Metall. Trans.* **19A** (1988) 3025.
27. *Idem*, *ibid.* **20A** (1989) 55.
28. D. BANERJEE, J. E. ALLISON, F. H. FROES and J. C. WILLIAMS, in "Titanium Science and Technology", Vol. 3, edited by G. Lutjering, U. Zwicker and W. Bunk (Deutsche Gesellschaft fur Metallkunde, Oberursel, FRG, 1985) pp. 1519–26.
29. A. P. WOODFIELD, M. H. LORETTO and R. E. SMALLMAN, *ibid.*, pp. 1527–34.
30. A. P. WOODFIELD, P. J. POSTANS, M. H. LORETTO and R. E. SMALLMAN, *Acta Metall.* **36** (1988) 507.
31. A. P. WOODFIELD and M. H. LORETTO, *Scripta Metall.* **21** (1987) 229.
32. W. B. PEARSON, "Lattice Spacings and Structures of Metals and Alloys" (Pergamon press, New York, 1958).
33. C. RAMACHANDRA, V. K. VERMA and V. SINGH, *Int. J. Fatigue* **10** (1988) 21.
34. C. RAMACHANDRA and V. SINGH, *Scripta Metall.* **21** (1987) 633.
35. W. J. PLUMBRIDGE and M. STANLEY, *Int. J. Fatigue* **8** (1986) 209.
36. C. RAMACHANDRA, V. SINGH and P. RAMA RAO, *Defence Sci. J.* **36** (1986) 207.
37. C. RAMACHANDRA and V. SINGH, *Metall. Trans.* **23A** (1992) 689.
38. S. ANKEM, D. BANERJEE, D. J. McNEISH, J. C. WILLIAMS and S. R. SEAGLE, *ibid.* **18A** (1987) 2015.
39. D. B. WILLIAMS, "Practical analytical Electron Microscopy in Materials Science" (Verlag Chemie International, USA, 1983).
40. D. BANERJEE, *Scripta Metall.* **21** (1987) 1615.
41. C. RAMACHANDRA and V. SINGH, *Metall. Trans.* **16A** (1985) 453.
42. A. K. SINGH, C. RAMACHANDRA and VAKIL SINGH, *J. Mater. Sci. Lett.* **11** (1992) 218.
43. T. MANOUBI, C. SERVANT and P. LACOMBE, *J. Less-Common Metals* **69** (1980) 219.

Received 22 February 1995
and accepted 21 May 1996