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ARTICLE *in* JOURNAL OF MATERIALS SCIENCE · JANUARY 1991

Impact Factor: 2.37 · DOI: 10.1007/BF00545549

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JOURNAL OF MATERIALS SCIENCE 26 (1991) 2637–2644

Microstructural changes induced by ternary additions in a hypo-eutectic titanium–silicon alloy

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Hypo-eutectic Ti–6.5 wt % Si alloy modified by separate additions of misch metal and low surface tension elements (Na, Sr, Se and Bi) has been examined by microscopic study and thermal analysis. Addition of third element led to modification of microstructure with apparently no significant enhancement of tensile ductility, with the exception of bismuth. Bismuth enhanced the ductility of the alloy by a factor of two and elastic–plastic fracture toughness to 9 MPa m$^{-1/2}$ from a value of almost zero. The improved ductility of bismuth modified alloy is attributed to the reduced interconnectivity of the eutectic silicide, absence of significant silicide precipitation in the eutectic region and increase in the volume fraction of uniformly distributed dendrites. These changes are accompanied by a decrease in the temperature of eutectic solidification.

1. Introduction

Severity of metal-mould reaction, low castability and high energy consumption are major inherent problems in casting titanium alloys. These difficulties can be minimized by the development of low melting cast eutectic alloys with useful mechanical properties. The majority of binary eutectic alloys of titanium are formed at high concentration (~25–40 wt %) with most of the elements. Two elements with low density, Si and Be, form binary eutectics with titanium at lower concentrations (~8 wt %). In view of the toxic nature of Be, Ti–Be system has not received much attention. The Ti–Si system has been studied in some detail. The system exhibits a eutectic reaction [1]

$$(\mathrm{Ti{-}Si})_l \longrightarrow \mathrm{Ti} + \mathrm{Ti_5Si_3} \qquad (1)$$

at a temperature of 1603 K and 8.5 wt % Si. The limited studies [2, 3] on Ti–Si alloys have demonstrated that tensile strength increases with an increase in Si content and attains a maximum value of 750 MPa at 2 wt % Si. Further addition of Si (upto 3 wt %) resulted in a decrease in tensile strength to 540 MPa. The alloys exhibited very low ductility (< 0.1%) when Si addition exceeded 2 wt %. The decrease in tensile strength and fracture resistance were attributed to coarse grains and silicide precipitation at grain boundaries. These observations discouraged further exploration of the Ti–Si system for almost three decades. More recently, a directionally solidified Ti–8.5 wt % Si alloy [4] with a tensile strength of ~ 1000 MPa and elastic modulus of 190 000 MPa but with almost zero ductility has been reported. Preliminary research by the authors [5] on Ti–Si alloys showed that the tensile properties (upto 3 wt % Si) were similar to those reported in the literature. However, there was significant enhancement in tensile strength at higher concentration of Si (Table I). Cast alloys having near eutectic composition (Ti–6.5 wt % Si) yielded a tensile strength of 834 MPa and ductility of 0.8%.

It is a common practice to modify the microstructure and improve the ductility of eutectic alloys by minor additions of a third element. The modification of Al–Si alloys by minor additions of a Na or Sr is a good example [6]. Additions of a third element were made to Ti–6.5 wt % Si alloy with the aim of modifying structure for increased ductility. An attempt was made to modify the microstructure by minor addition of misch metal or low surface tension elements (Na, Sr, Se, Te and Bi).

2. Experimental procedure

The Ti–Si alloy pancakes (110 mm dia × 15 mm) were prepared by melting the charge in a water-cooled copper crucible of non-consumable vacuum arc melting furnace under argon atmosphere. Virgin metals of high purity (99.5%) were used in the preparation of the alloys. Each pancake was melted four times to ensure uniform chemistry of the alloy. After melting samples were taken from the cast alloy pancake for chemical analysis and evaluation of mechanical properties.

The tensile tests were conducted using an Instron Universal Testing Machine of 10 metric ton capacity at a crosshead speed of 1 mm min^{-1}. A minimum of

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TABLE I Tensile properties of Ti–Si alloys

Si (wt %)	Ultimate tensile strength (MPa)	0.2 % Yield strength (MPa)	Elongation (%)
0.0	315	207	30
0.6	535	423	21
1.0	686	608	18
2.0	780	726	1.0
3.0	589	–	< 0.1
4.5	711	687	0.7
6.5	834	736	0.8
8.5	775	726	0.4

three samples were tested in each condition to evaluate tensile strength and fracture toughness. Fracture toughness was calculated from the energy absorbed during impact test using Charpy V-notch samples. The impact test was performed at room temperature on Model 84 Tinius-Olesen Universal Pendulum Impact System. The on-line test data were obtained, analysed and recorded with the help of an IBM personal computer. The data acquisition was done at intervals as low as 5–10 μs for a total of 1036 events. The real time data record includes deflection and energy absorbed as a function of event time. Charpy V-notch specimens were prepared according to ASTM standard, E-230.

Metallographic specimens were prepared from tensile samples after testing. The samples were polished using diamond paste and etched with dilute aqueous solution containing 1–3 ml l^{-1} HF and 2–6 ml l^{-1} HNO_3 (Kroll reagent). The volume fraction of dendrite was measured by the point count method. A number of measurements were made from different areas of the sample. Microstructural and fractrographic studies were carried out in a scanning electron microscope (JSN 840A), equipped with energy dispersive spectroscopy (EDS). The Si and Bi content in the dendrite and eutectic regions was determined with a scanning electron probe microanalyser (CAMEBAX MICRO). Differential thermal analysis (DTA) was used to measure the transformation temperature during cooling of modified and unmodified Ti–6.5 wt % Si alloys. A Dupont 1090 thermal analysis system was employed. Heating and cooling of the samples during DTA was done in an argon stream to avoid oxidation of samples. The heating rate of the sample was controlled at 20 K min^{-1} whereas the cooling rate was estimated to be $\sim$ 70 K min^{-1}.

3. Results and discussion

3.1. Minor addition of low surface tension elements

The low surface tension elements used in this study to modify Ti–6.5 wt % Si alloys were Na, Sr, Se, Te and Bi. Microstructures resulting from the addition of Na and Sr to Ti–6.5 wt % Si alloys are shown in Fig. 1. Fig. 1a and b show the microstructure of Ti–6.5 wt % Si alloy exhibiting distribution of dendrites and morphology of eutectic silicides, respectively. The silicide rods in the Ti matrix of eutectic regions are interconnected as shown in Fig. 1b. Sodium additions provide much finer and uniform distribution of dendrites as compared to Sr addition (Fig. 1c and e). The silicides in the eutectic region in both cases are cylindrical rods and are not interconnected (Fig. 1d and f). The dendrite distribution is finer and the eutectic silicides have lower aspect ratio in Na modified alloys. There also appears to be a considerable amount of secondary silicide precipitation in the eutectic region between the eutectic silicide rods, which is absent in case of Ti–6.5 wt % Si alloy. However very small amounts of secondary silicide precipitation is noted in the dendrite region. The microstructures for the Ti–6.5 wt % Si alloy with Se and Te additions are given in Fig. 2. Se or Te (Fig. 2) give rise to needle type interconnected eutectic silicides with almost no secondary silicides in contrast to microstructural changes observed with Na and Sr.

A change in the mode of precipitation and morphology of silicides in the eutectic region was also observed with addition of 0.06 wt % Bi to the Ti–6.5 wt % Si alloy. The silicides in the eutectic region were more cylindrical in nature, similar to those observed with Na and Sr (Fig. 1). The microstructure indicated uniform distribution of dendrites and near absence of interconnectivity of eutectic silicides (Fig. 3). No evidence of secondary silicide precipitation in the eutectic regions was observed. A summary of microstructural modifications obtained by the addition of third element to Ti–6.5 wt % Si alloy is presented in Table II.

3.2. Minor additions of rare earth elements (misch metal)

Misch metal of normal commercial grade having 25–35% La, 40–50% Ce, 5–10% Pr, 5–10% Nd was added to Ti–6.5 wt % Si alloy. The microstructures exhibited finer distribution of dendrites with increase in misch metal from 0.02 to 0.08 wt %. The silicides in the eutectic region change to more pronounced rod-like morphology (Fig. 4) and as compared to that in Ti–6.5 wt % Si alloy (Fig. 1b) appear to be finer and interconnected.

The influence of different ternary additions on the tensile properties of Ti–6.5 wt % Si alloy is presented in Table III. The data presented in Table III clearly shows that minor additions of misch metal or low surface tension elements do not lead to improvement in tensile ductility, although the microstructure is modified appreciably. Bismuth was the only element that displayed a beneficial effect on ductility. Therefore a detailed examination of Ti–Si–Bi alloys was undertaken to determine the correlation between the microstructure and ductility.

3.3. Microstructure property correlation in Bi modified Ti–6.5 wt% Si cast alloy

To establish the role of Bi in enhancing the ductility of Ti–6.5 wt % Si alloy, varying additions of bismuth (0.02–0.5 wt % Bi) were made to this alloy. The tensile properties obtained are listed in Table IV. It is seen

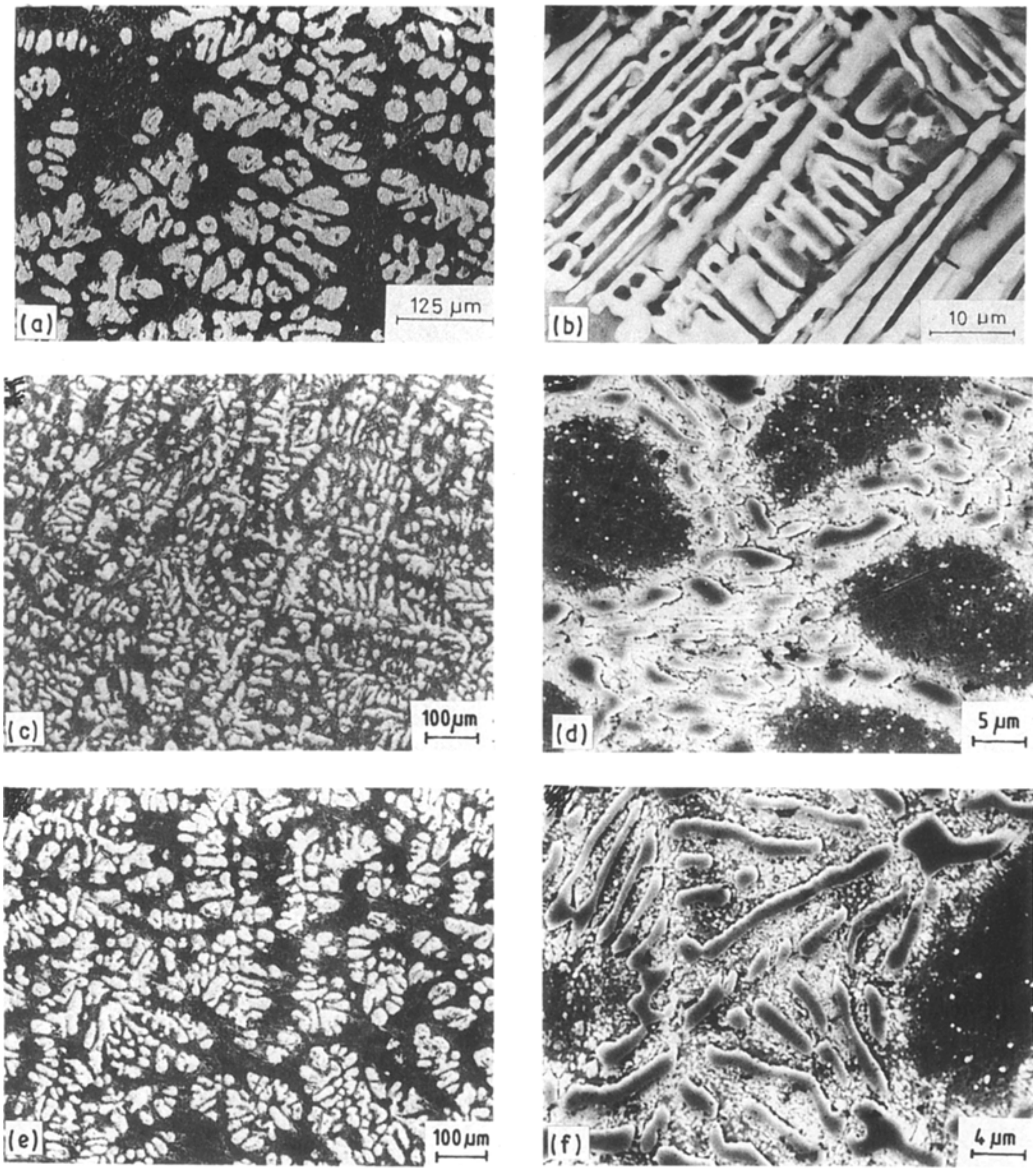

Figure 1 Micrographs of Ti–6.5 wt % Si alloy; (a), (b) No ternary addition, (c), (d) with 0.06 wt % Na, (e), (f) with 0.06 wt % Sr.

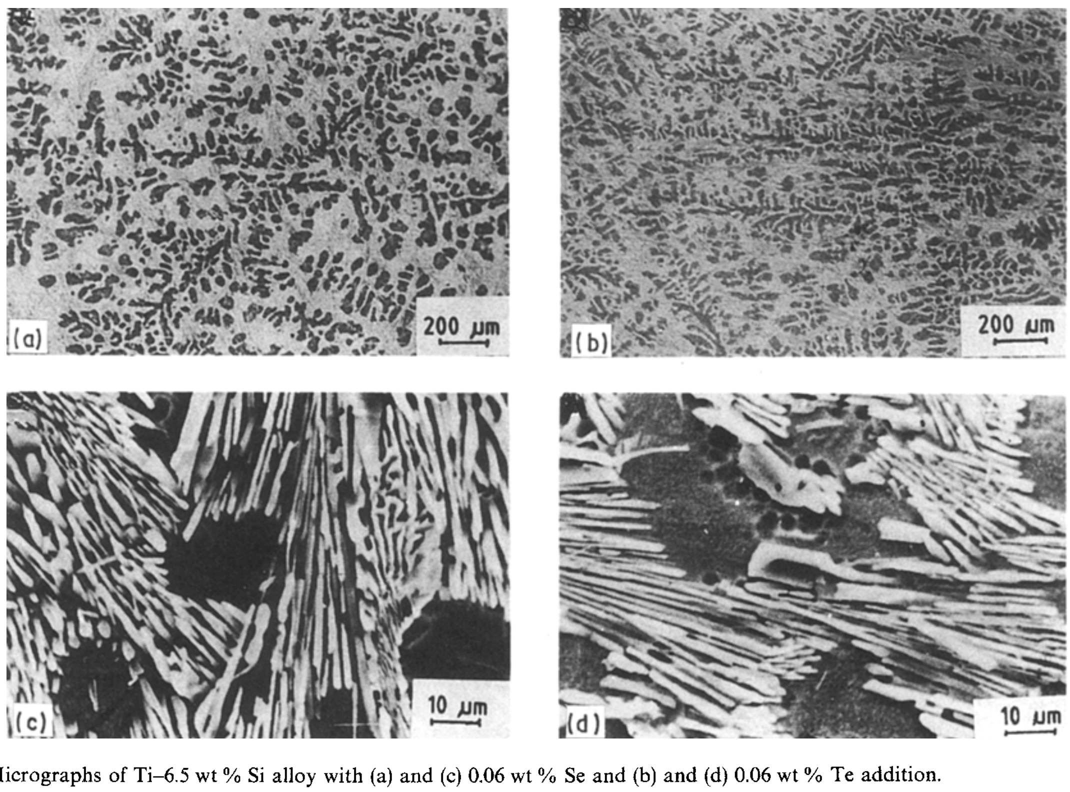

Figure 2 Micrographs of Ti–6.5 wt % Si alloy with (a) and (c) 0.06 wt % Se and (b) and (d) 0.06 wt % Te addition.

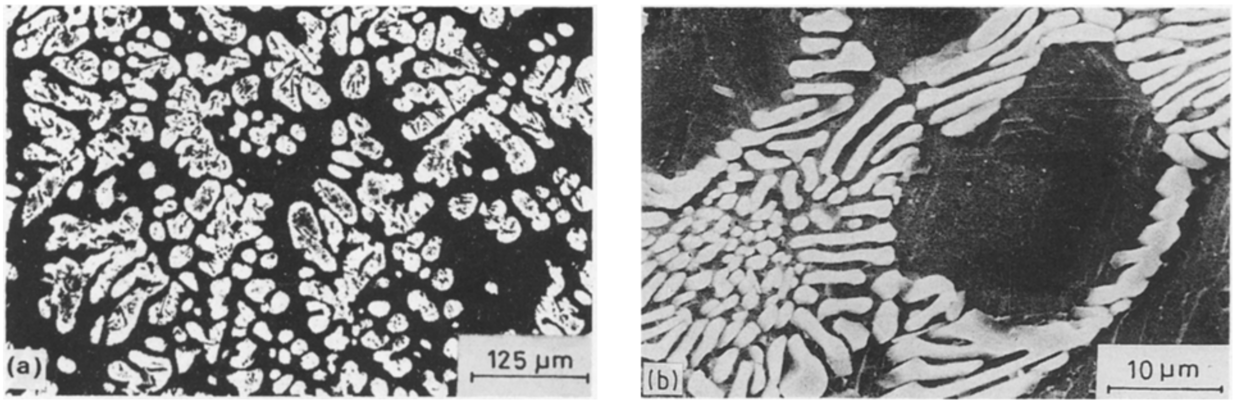

Figure 3 Micrographs of Ti–6.5 wt % Si alloy with addition of 0.06 wt % Bi.

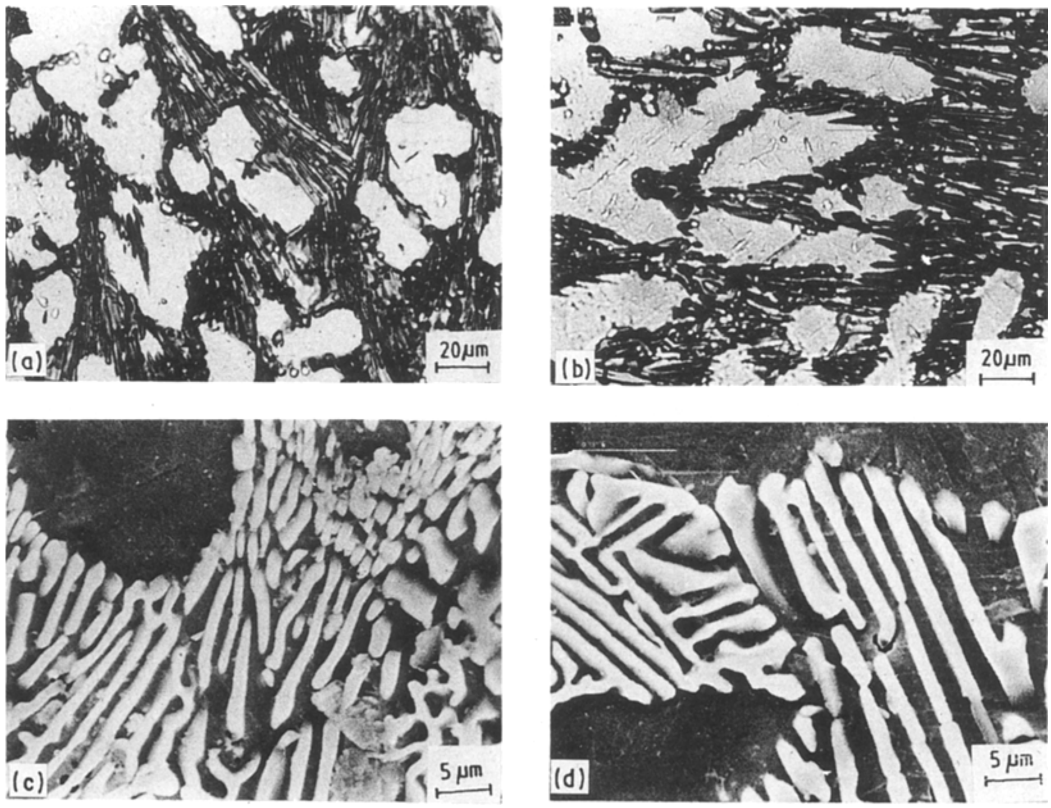

Figure 4 Microstructure of Ti–6.5 wt % Si with (a) and (c) 0.02 wt % and (b) and (d) 0.06 wt % of misch metal addition.

TABLE II Summary of microstructural details of Ti–6.5 % Si–*X* alloys in the eutectic region

Ternary addition	Morphology of silicides	Interconnectivity of silicides	Extensive and secondary silicide precipitation
Na/Sr	Cylindrical rods	absent	present
Se/Te	Needle-like	present	absent
Bi	Cylindrical rods	absent	absent
Misch metal	Rod-like	present	absent

TABLE III Effect of minor additions (0.06 wt %) of misch metal and low surface tension elements on tensile properties of Ti–6.5 wt % Si alloy

Elements	Surface tension ($\mathrm{n\,m^{-1}}$)	UTS (MPa)	0.2% YS (MPa)	El (%)
–	–	834	736	0.8
Na	0.191	746	657	0.85
Sr	0.303	814	783	1.0
Se	0.106	849	797	0.75
Te	0.180	873	770	0.6
Bi	0.376	834	741	1.7
Misch metal	–	791	698	0.86

that there is no appreciable effect on strength (UTS) upto about 0.1 wt % Bi. At higher Bi contents the strength is reduced considerably. However, tensile ductility increases by almost a factor of two (i.e. from 0.8–1.8%) for Bi additions upto 0.1 wt %. At higher Bi content (0.5 wt %) the tensile ductility drops to 0.5%. The stress–strain curves are shown in Fig. 5, the increased plastic zone is apparent in the curves corresponding to lower Bi additions.

The impact toughness data for Ti–Si and Ti–Si–Bi

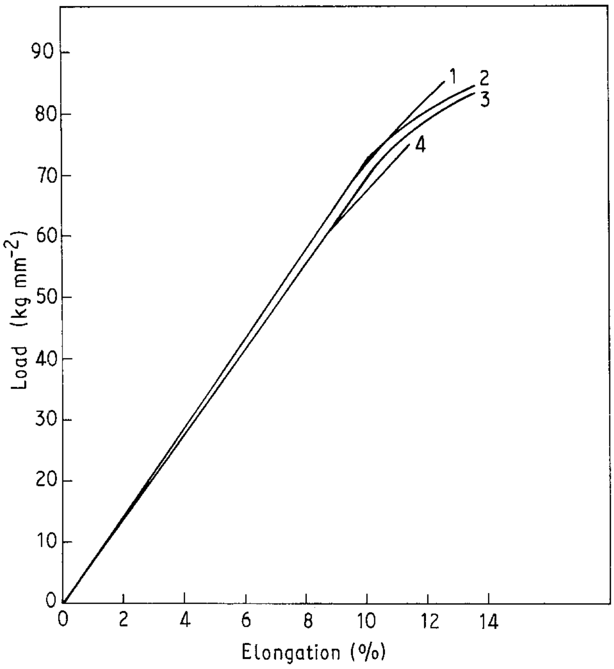

Figure 5 Stress–strain curves for Ti–6.5 wt % Si alloy with varying additions of bismuth; (1) 0 wt %, (2) 0.06 wt %, (3) 0.1 wt %, (4) 0.5 wt % Bi.

TABLE IV Tensile properties and volume fraction of dendrites in Ti–6.5wt% Si alloy with varying bismuth additions

Bi (wt%)	UTS (MPa)	0.2% YS (MPa)	El (%)	Volume fraction of dendrites (%)
0	834	736	0.8	38
0.02	814	716	1.4	–
0.04	834	736	1.7	49
0.06	824	736	1.8	45
0.10	814	716	1.6	42
0.20	795	628	0.9	–
0.50	765	628	0.5	37

alloys are listed in Table V. Both alloys exhibit predominantly brittle fracture. The addition of 0.06 wt % of Bi was found to increase the load to fracture and absorbed energy. The data were analysed to derive dynamic fracture toughness properties *via* dynamic elastic fracture toughness (K_D) and dynamic elastic–plastic fracture toughness (K_{JD}) using the equations [7].

$$K_D = \rho_f L/BYw^{3/2} \qquad (2)$$

where ρ_f is the fracture initiation load, L is the span, B is the thickness, w is the width and Y is a geometrical factor (approximated at 1.175 for $a/w = 0.2$, where a is the notch depth).

$$K_{J_D} = [E_{JD}/(1 - \nu)^2]^{1/2} \qquad (3)$$

where E is the Young's modulus, ν is the Poisson's ratio and J_D is the J-integral fracture toughness calculated as

$$J_D = 2E_{fl}/B(w - a) \qquad (4)$$

where a is the notch depth and E_{fl} is the fracture energy absorbed by the specimen, derived as the difference between total absorbed energy (E_f) and machine absorbed energy (E_m). The fracture toughness values thus determined are given in Table VI. It is clearly evident that there is 60% increase in the elastic–fracture toughness (K_D) in the case of Bi modified Ti–6.5 wt % Si alloy. It is also interesting to note that Ti–Si–Bi alloy shows evidence of elastic–plastic fracture toughness ($K_{JD} \simeq 9.0$ MPa m^{-1}), although it is significantly lower than that for engineering alloys.

The distribution of dendrite and eutectic regions in the alloy is altered by Bi. In Fig. 6a there are large areas of eutectic region corresponding to bismuth-free Ti–6.5 wt % Si alloy. With the addition of Bi upto 0.1 wt % dendrite and eutectic regions are uniformly distributed (Fig. 6b and c). However, on the addition of higher percentages of Bi (0.5 wt %) larger areas of eutectic regions are again observed (Fig. 6d). The volume fraction of dendrites, evaluated at a magnification of 160 using the point count method, are listed in Table IV. The volume fraction of the dendrite phase was found to increase with the Bi content (upto 0.1% Bi). The trend is reversed at higher Bi concentrations (0.5% Bi). As regards the morphology of silicides, Ti–6.5 wt % Si alloy exhibits interconnected silicide needles (Fig. 7a). The interconnectivity is reduced considerably with a small addition of bismuth (Fig. 7b and c). However, at higher Bi contents (0.5 wt %) the interconnectivity again appears (Fig. 7d). It seems that the effect of Bi at the optimum level is to refine the distribution of the eutectic region and alter the morphology of the eutectic silicides by rendering them finer with appreciably reduced interconnectivity or branching. These microstructural changes are expected to bring about improvement in the ductility of the alloy, consistent with the observed mechanical properties. The eutectic silicides in modified Ti–Si alloys grow in an anisotropic manner in contrast to the behaviour of modified Al–Si or Fe–C systems where growth is isotropic. If the brittle phase is interconnected, the crack is expected to propagate at a faster rate after initiation. Thus the absence of interconnectivity may be one of the reasons for enhanced ductility of Ti–Si–Bi alloys.

TABLE V Fracture load and absorbed energy for Ti–6.5 wt % Si and Ti–6.5 wt % Si–0.06 wt % Bi alloys obtained from impact tests

Specimen	Event Time (mm s) Max load	Total	Max load (kN)	Absorbed Energy (j) Max load	Total
Ti–Si No. 1	0.10	0.15	5.6	0.841	1.330
Ti–Si No. 2	0.10	0.15	5.2	0.819	1.262
Ti–Si–Bi No. 1	0.07	0.10	8.0	0.986	1.529
Ti–Si–Bi No. 2	0.07	0.10	8.5	1.071	1.651

TABLE VI Estimated values of fracture toughness for Ti–6.5 wt % Si and Ti–6.5 Si–0.06 Bi Alloys, (Normalized energy = Absorbed energy/$B(w - a)$, Poisson's ratio = 0.3, Young's modulus = 147 000 MPa)

	Normalized energy ($\mathrm{J\,mm^{-1}}$)		Fracture toughness ($\mathrm{MPa\,m^{-1/2}}$)	
	Initial	Total	Elastic K_D	J Integral K_{J_D}
Ti–Si No. 1	0.011	0.017	26.2	–
Ti–Si No. 2	0.010	0.016	24.2	–
Ti–Si–Bi No. 1	0.012	0.019	37.4	8.90
Ti–Si–Bi No. 2	0.013	0.021	40.1	8.97

The variation in tensile ductility of Bi containing Ti–6.5 wt % Si alloy (Table IV) appears to follow the same behaviour as that of microstructural variation (Fig. 6) implying that the presence of fine silicides (in the eutectic region), reduced/eliminated interconnectivity in eutectic silicides and higher volume fraction of dendrites favour relatively improved ductility of bismuth containing alloys. The fine distribution of dendrite and eutectic region is more likely to take place if there is an increase in the number of nucleation events, which may be possible in the event of under-cooling. An increase in the volume fraction of dendrites is expected to result from an increase in the Si content at the eutectic composition. To check the validity of the aforementioned statement and confirm if there is an increase in the silicon content in the eutectic region DTA and electron microprobe analysis (EPMA) of the eutectic and dendrite regions was carried out.

The results of DTA obtained under identical conditions of cooling for Bi containing alloys are presented in Fig. 8. The start of the exothermic peak on the right hand side represents the beginning of solidification (liquidus) whereas the eutectic horizontal (solidus) is represented by the end of the peak on the left hand side. Small variations in Si composition will appreciably alter the beginning of solidification (liquidus) but will have no effect on the solidus temperature (eutectic horizontal). The exact temperature of eutectic horizontal was determined by drawing a tangent to the base line identified by the arrows in Fig. 8. It may be noted that on the addition of small amounts of Bi upto about 0.1 wt % to the Ti–6.5 wt % Si alloy, the eutectic horizontal is shifted to a slightly lower temperature. However, at 0.5 wt % Bi the solidus temperature is similar to that of non-bismuth containing alloy. There is a maximum of 10 K decrease in the temperature for the completion of solidification in a Ti–Si alloy containing 0.04 wt % Bi. This decrease in temperature for eutectic solidification may be one of the reasons for obtaining finer and homogeneous distribution of dendrites in the matrix as indicated in Fig. 6. This observation is similar to the case of Na– modified Al–Si alloys whereas a decrease in the temperature for eutectic solidification by 5–7 K was observed [8, 9].

The microstructural examination of Bi containing Ti–Si alloys indicated an increase in the volume fraction of dendrites (Table IV) with Bi concentration (upto 0.1 wt % Bi). This suggests an incremental shift in Si content of the eutectic composition. Electron probe microanalysis data (Table VII) supports this hypothesis. The increase in Si wt % in the eutectic and dendrite region is indicative of shift in Si composition at the eutectic horizontal. It is interesting that the increase in Si in the dendrite and eutectic regions with Bi concentration in the alloy is accompanied by an increase in microhardness (Table VII). Efforts to

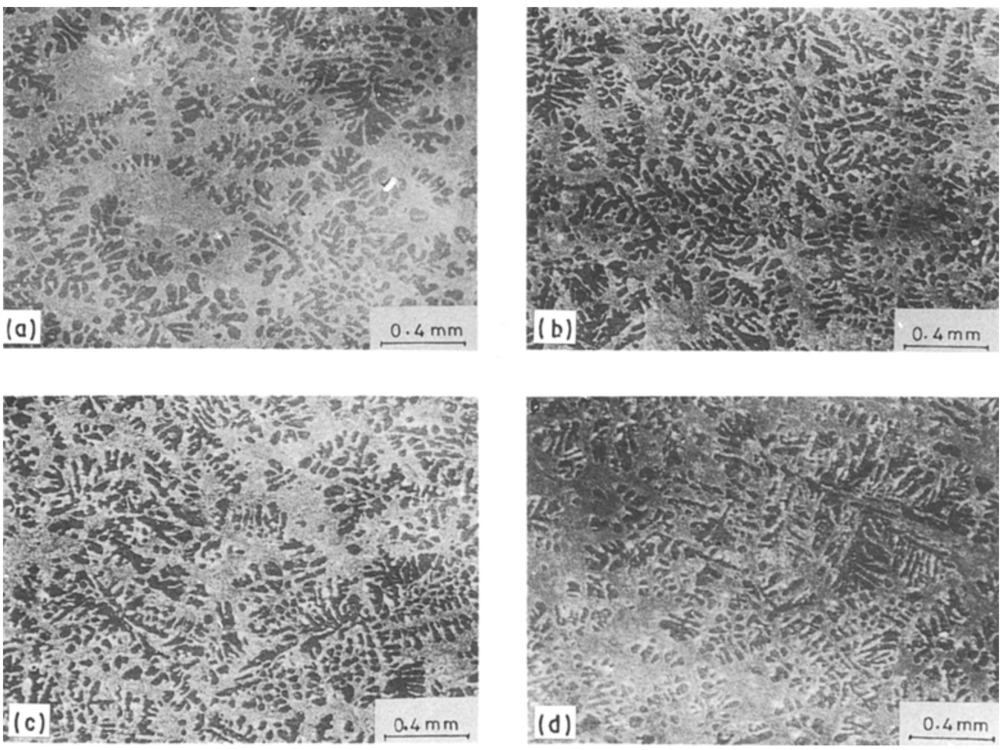

Figure 6 Micrographs showing the effect of bismuth addition on the distribution of eutectic and dendrite regions in Ti–6.5 wt % Si alloy; (a) 0 wt % (b) 0.04 wt % (c) 0.08 wt % and (d) 0.5 wt % Bi.

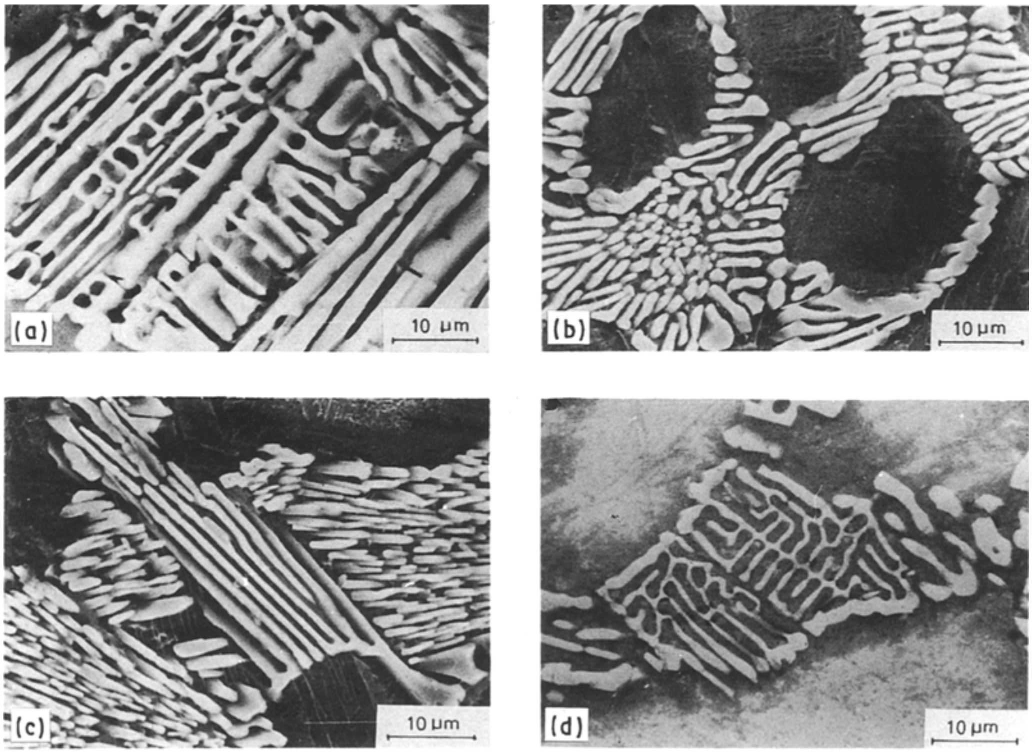

Figure 7 Scanning electron micrographs illustrating the effect of bismuth on the morphology and interconnectivity of eutectic silicides; (a) 0 wt % (b) 0.04 wt % (c) 0.08 wt % and (d) 0.5 wt % Bi.

TABLE VII Si per cent in dendrite and eutectic region and their corresponding microhardness in Ti–6.5 wt % Si alloy having varying per cent of Bi added

Wt % Bi in alloy	Dendrite		Eutectic		Depression in eutectic horizontal (K)
	Si (wt %)	Microhardness (VHN)	Si (wt %)	Microhardness (VHN)	
0	1.77 ± 0.234	342	8.82 ± 0.251	393	–
0.04	1.93 ± 0.235	362	9.03 ± 0.252	455	10
0.08	2.26 ± 0.236	360	9.49 ± 0.233	453	8
0.5	1.73 ± 0.233	–	8.99 ± 0.250	–	2

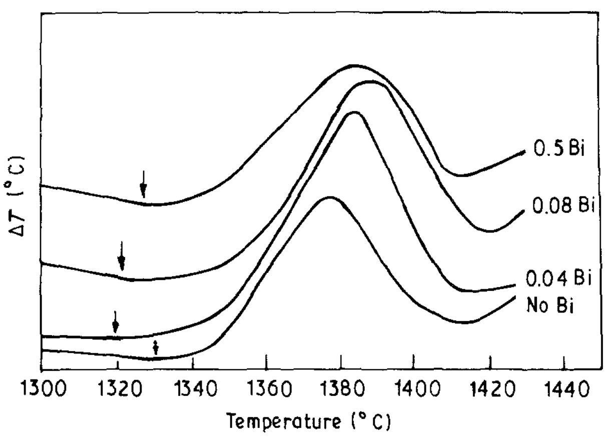

Figure 8 Results of DTA illustrating the effect of bismuth on the eutectic solidification temperature of Ti–6.5 wt % Si alloy; cooling rate = 70 °C min^{-1}.

identify possible preferential distribution of Bi in Ti–Si alloys using electron probe microanalyser were unsuccessful within the spatial resolution of EPMA and the distribution was found to be uniform.

4. Conclusions

1. Minor additions of misch metal or low surface tension elements (Na, Sr, Se, Te and Bi) led to modification of microstructure with apparently no improvement in tensile ductility, with the exception of Bi.
2. Addition of small amounts of bismuth to Ti–6.5 wt % Si alloy improved the ductility and yielded elastic–plastic fracture toughness (K_{J_D}) of 9 MPa m$^{-1/2}$ from a value of zero.
3. The improved ductility in Ti–Si–Bi alloy is attributed to the change in the morphology of eutectic silicides which were finer and displayed reduced interconnectivity. The increase in the volume fraction of dendrites may also contribute to the enhanced ductility of the alloy.
4. The microstructural changes induced on the addition of bismuth to Ti–6.5 wt % Si alloy can be attributed to the decrease of the eutectic solidification temperature (eutectic horizontal) and marginal increase in Si content in dendrite and eutectic regions.
5. The effect of Bi in Ti–6.5 wt % Si alloys is similar to the effect of Na in Al–Si alloy as far as shift in Si composition and lowering of the eutectic horizontal

on cooling are concerned. However, instead of isotropic growth of Si in the case of Na– modified Al–Si alloy, the growth of eutectic silicides in bismuth modified Ti–Si alloy is anisotropic in character.

Acknowledgements

The authors thank Mr N. Eswara Prasad for his valuable help in fracture toughness evaluation. The authors wish to express their sincere gratitude to Dr P. Rama Rao, Director, DMRL, for encouragement and permission to publish this work.

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Received 10 January
and accepted 16 May 1990