Microstructures and Properties of Newly Developed Alpha Titanium- Ti_5 Si_3 Alloys

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ABSTRACT

The high melting point titanium silicides, such as Ti_5Si_3 and $TiSi_2$ have been investigated in recent years. Alpha titanium forms with the complex hexagonal Ti_5Si_3 compound (D_8^8-type of crystal structure) an eutectic system with large volume fractions of about 30 vol.% Ti_5Si_3 embeded in the hexagonal α-Ti(Si) solid solution. For the development of high temperature oxidation resistant Ti-based alloys two different processing routes have been considered: One is directional solidification in order to achieve a fibre reinforcement of α-Ti matrices due to the presence of high strenght and elastically stiff discontinuous Ti_5Si_3 fibres which are aligned parallel to the road axes. The other route is to produce a fine grained eutectic or hypoeutectic microstructure consisting of α-Ti with a fine dispersion of Ti_5Si_3 particles of several microns in size.

The present paper describes and discusses the physical and mechanical properties of newly developed α-Ti/T_5Si_3 materials under consideration of their excellent high temperature properties of the refractory intermetallic Ti_5Si_3 compound.

INTRODUCTION

Titanium-base alloys for high temperature applications consist either dispersion or particle strenghtened second phases or fibre reinforcements. In order to explore the feasibility of producing new temperature resistant titanium alloy with sufficient strength, creep properties, and oxidation resistance at medium temperatures up to 650 °C or higher, a material system based on titanium-silicon with additions of aluminium of hypereutectic and eutectic compositions have been prepared and examined. Hypereutectic alloys have not been considered because of the presence of coarse proeutectic Ti_5Si_3 dendrites exhibiting "chinese script" morphologies. These constituents may improve the wear resistance and fretting behaviour. However, the sharp edges of the faceted Ti_5Si_3 crystals might cause severe fatigue problems.

In recent years the physical and mechanical properties of the high melting point intermetallic Ti_5Si_3 compound have been studied by several investigators **[1-3]**. In order to evaluate the choosen alpha titanium - Ti_5Si_3 alloy system with additions of aluminium the important properties of the coexisting intermetallic Ti_5Si_3 compound present in the alpha titanium matrix will be taken into account.

Comprehensive studies on the binary titanium-silicon phase diagram have been carried out by [4, 5]. Gase-phase reaction metallurgy of the titaniuim-silicon system was employed by [6]. The phase diagram reported by MASSALSKI [7] exhibits an eutectic system, containing 9wt% Si, composed of α-Ti and Ti_5Si_3 on the titanium-rich side. The eutectic melting temperature is about 1330 °C, and the melting temperature of the refractory Ti_5Si_3 compound is 2130 °C, which is comparable with that of the oxide ceramic aluminia. Ti_5Si_3 is metastable below 1170 °C, and the stable phase Ti_3Si will occur after long term annealing. The Ti_5Si_3 phase reveals a homogeneity range of about 4at.% around the stoichiometric composition and will be formed congruently from the melt during solidification. The density of Ti_5Si_3 was determined to $\rho = 4.32$ g/cm^3. The Vicker's hardness is about 970 ± 25 HV5. The high melting temperature and high hardness values result from the high binding energy - formation enthalpy $\Delta H^{Ti_5Si_3} = -580$ kJ/mol - and the complex D_8^8 lattice structure. The crystallography of this compound have been described by J. QUARKERNAAT et al. (1974) [8] and K. CENZUAL and E. PARTHÉ (1986) [9].

The unit-cell is presented in figure *1*. The lattice constants of Ti_5Si_3 are: a=0.5143 nm and c=0.7444 nm. This compound possesses two formula units per unit-cell. The D_8^8 structure is built up by two atomic species which occupy three different crystallographic positions. The Ti(I) atoms form columns of octahedrons connected along the c-axis, while the Ti(II) atoms are arranged in chains parallel to each other. The Si atoms surround octahedrally the Ti(II) atoms. The octahedral interstices along the c-axis might be partially or completely filled by interstitials.

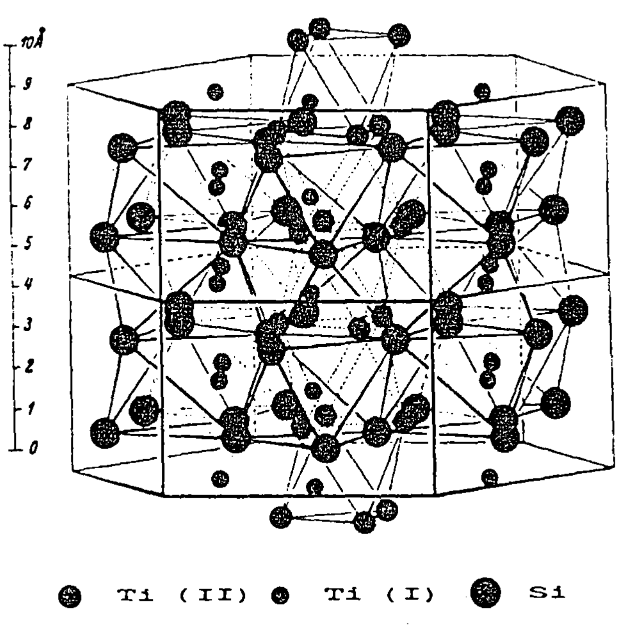

Fig. 1. Crystal structure of the intermetallic Ti_5Si_3 compound (Mn_5Si_3–type, space group $P6_3/mcm$)

EXPERIMENTAL PROCEDURE

The monolithic intermetallic $Ti_5\ Si_3$ compound was prepared by solid state reaction from pure titanium and silicon powders. The conglomerates obtained were ground in argon atmosphere to powder of final grain sizes ranging from 10 to 50 microns. The fine grained alloy powder was precompacted uniaxially at room temperature in mild steel cans using molybdenum foil as inlets. After degassing at 400 °C the cans have been sealed under vacuum and densified by HIP process at T=1250 °C in argon atmosphere at p=2000 bar for 10 hrs. The microstructure of the processed material possessed grain sizes of about 20 to 50 microns.
The finer grained hypereutectic TiSilAl alloys were melted in an argon arc furnace and cast to ingots. The unidirectionally solidified Ti-Ti_5Si_3 eutectic alloy was produced by electron beam zone melting technique using a zone velocity of 60 mm/h and a temperature gradient of about 50 K/mm. As starting material, precompacted rods of 25 mm in diameter and 300 mm in length have been prepared by a mixture of Ti_5Si_3 powder and α-Ti powder (99.9% purity). Test speciments of the monolitic Ti_5Si_3 compound material and the eutectic α-Ti-Ti_5Si_3(Al) alloy were cut by spark erosion and machined using diamond tools.

RESULTS AND DISCUSSIONS

MICROSTRUCTURES

Figure ***2a*** shows the microstructure of the monolithic Ti_5Si_3 compound revealing polygonal grains of the compacted samples. The average size of the randomly distributed grains ranges between 15 to 40 microns. Some grains possess deformation twins. Acute and also reentrant angled grain shapes of the consolidated powder particles are eliminated by diffusion processes during hot isostatic pressing.

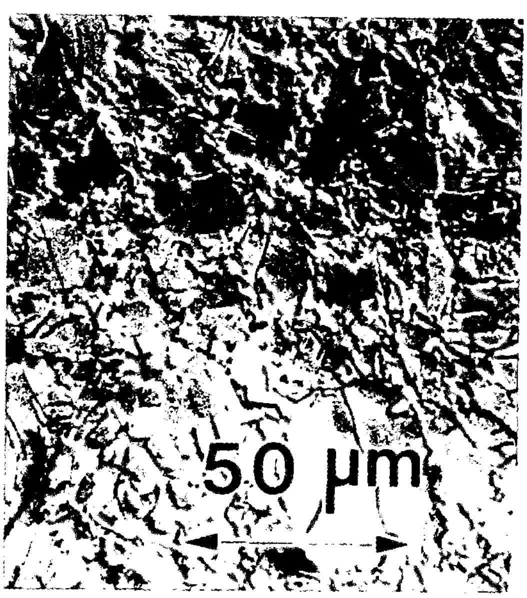

Fig. 2a. *M: 500x*
Optical micrograph of the monolithic Ti_5Si_3 compound revealing deformation twins.

Fig. 2b. *M: 500x*
Microstructure of a fine grained hypo-eutectic TiSi7,5Al1 alloy in the as cast state.

A typical microstructure of the hypereutectic TiSi7.5Al1 alloy is illustrated in Fig. ***2b***. Dendritic α-Ti grains are randomly distributed in the finely dispersed eutectic matrix. With increasing silicon content up to about 9 wt. % the microstructures of the as cast samples consist of a fine dispersion of Ti_5Si_3 silicide particles within the α-Ti(Si) solid solution matrix. This microstructure exhibits microhardness values of 360 to 390 $HV_{0,3}$ and possesses an excellent wear resistance [**10**] Directional solidification leads to a microstructure, which is presented in figures ***3a*** and ***3b***. The SEM images reveal longitudinal (a) and cross (b) sections of discontinuous Ti_5Si_3 fibres of hexagonal shapes with an average thickness dimension of about 3 microns. The crystallographic c-axis of the fibres is oriented parallel to the rod axis. Some perpendicularly oriented microcracks are present in the fibres. Blunted crack tips in the Ti-matrix were detected on both sides of the Ti_5Si_3-fibres. These defects have been caused by thermal stresses acting at the fibre - matrix interfaces.

*longitudinal section (**a**)* *cross section (**b**)*

*Fig.**3a**. and **b**. SEM micrographs showing microstructures of an unidirectionally solidified eutectic Ti-Ti_5Si_3 alloy .*

PHYSICAL PROPERTIES

THERMAL EXPANSION

The temperature dependence of the thermal expansion coefficients α(*T*) of the polycrystalline Ti_5Si_3 compound, of the hypereutectic TiSi7,5Al1, and of the Ti-Ti_5Si_3 composite with fibre structure are shown in Fig. ***4***. With increasing temperature the α(*T*) values of the investigated materials increase steadily in the range from 20 °C to 1000 °C. As expected, the thermal expansion coefficients of the hypoeutectic and of the unidirectionally solidified eutectic alloy are higher than that of the Ti_5Si_3 material in the investigated temperature regime. The hypoeutectic and eutectic alloys exhibit similar expansion coefficients. The deviation of the values is within the experimentally determined limits of the error. In the temperature range between 25 °C and 200 °C the $\alpha(T)$ value of the eutectic Ti-Ti_5Si_3 alloy is α $10.0\times10^{-6}K^{-1}$. For the Ti_5Si_3 compound the expansion coefficient was determined to a somewhat lower value of $\alpha=7.1\times10^{-6}K^{-1}$. At 1000°C the termal expansion coefficient of the directionally solidified eutectic Ti-Ti_5Si_3 increases to $\alpha=13.8\times10^{-6}$ K^{-1}. The monolithic Ti_5Si_3 exhibits an α value of about 9.1×10^{-6} K^{-1}. It should be noted, that the linear thermal expansion coefficient of other titanium silicides (e.g. $TiSi_2$ and TiSi) is also relatively low in the investigated temperature range, because of their high binding energies and the relatively short interatomic distances in the complex crystal lattices [11].

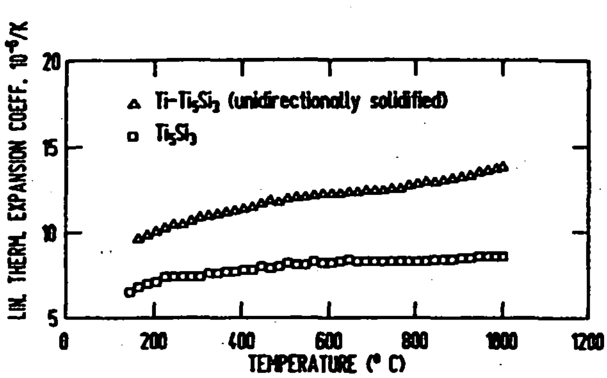

Fig. 4. Temperature dependence of the thermal expansion coefficients of the monolithic Ti_5Si_3 compound, the hypoeutectic TiSi7,5Al1 and the unidirectionally solidified eutectic Ti-Ti_5Si_3 alloy.

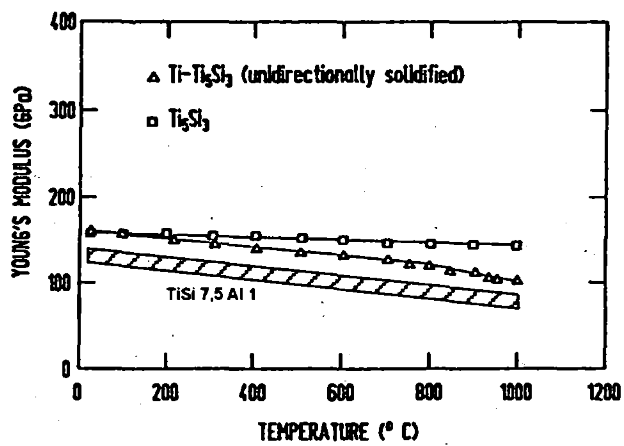

Fig. 5. Young's moduli of the monolithic Ti_5Si_3 compound, the hypoeutectic TiSi7,5Al1 and the unidirectionally solidified eutectic Ti-Ti_5Si_3 allo. as a function of the test temperature.

ELASTIC MODULI

The important property for characterizing the elastic stiffness of a material is the Young's modulus. This was determined in the temperature range from 20 °C to 1000 °C using the resonance frequency method.

Figure *5* represents the temperature dependent Young's moduli curves of the monolithic Ti_5Si_3 compound with randomly oriented grains, of the fine grained hypoeutectic TiSi7Al1, and of the unidirectionally solidified Ti -Ti_5Si_3 eutectic. The Ti_5Si_3 material shows a small decrease of the E-modulus curve with increasing temperature. At room temperature and at 1000 °C the elastic moduli of Ti_5Si_3 are about $E^{25°C}$=156 GPa and $E^{100°C}$=140.5 GPa, respectively. The Ti_5Si_3 alloy exhibits a much higher Young's modulus to density ratio than e.g. nickel-base superalloys do. For the eutectic Ti - Ti_5Si_3 alloy the elastic modulus at room temperature is almost equal to the elastic modulus of the monolithic Ti_5Si_3 compound. With increasing temperature, above 750 °C, a marked decrease occurs. At the maximum of the investigated temperature of about 1000 °C, the composite shows $E \cong 100$ GPa. From the comparison of this value with the relatively low elastic modulus of alpha titanium of about 110 GPa at room temperature it is deduced that the Ti_5Si_3 fibres embedded in the α-Ti matrix are acting as effective stiffening components. The Young's modulus of the hypoeutectic TiSi7Al1 alloy shows a similar temperature dependence as the unidirectionally solidified eutectic one. However, the values are slightly lower than those of the eutectic composition, because of the randomly oriented distribution of the fine Ti_5Si_3 particles.

The Young's modulus of the polycrystalline Ti_5Si_3 compound is a quantitative measure for characterizing its stiffness in the elastic region. This property depends upon the shape of the potential curves and the atomic distances of the corresponding titanium and silicon atoms in the complex hexagonal D_8^8 lattice structure.

From the high lattice stability it can be deduced, that the strong binding force of Ti_5Si_3 might cause large elastic moduli. However, the interatomic distances of silicon and titanium atoms will be relatively large in comparison to the dense packed b.c.c., f.c.c. and h.c.p. metals and alloys.

The elastic properties of the reinforced α-Ti-T_5Si_3 composite at room and elevated temperature up to 600 °C are determined by the stiff Ti_5Si_3 fibres parallel aligned within the titanium matrix. The difference between the Young's moduli of the polycrystalline compound and the composite is very small. Considering the anisotropy and the rule of mixture for reinforced composites with discontinuous fibres, a larger elastic modulus of the oriented Ti_5Si_3 filaments parallel to their c-axis than that of the quasi isotropic material is expected. The elastic modulus was calculated to about $E^{Ti_5Si_3} = 265$ GPa. This value is larger than $E^{Ti_5Si_3} = 240$ GPa, published by Crossman et al. [**12**].

MECHANICAL PROPERTIES

YIELD STRESS

The yield stresses of the investigated materials were determined in compression tests applying the strain rate of $(\varepsilon) = 10^{-4} s^{-1}$. Figure ***6*** illustrates the flow stress $\sigma_{0.2}$ values of the Ti_5Si_3 compound, the hypoeutectic Ti-Si7-Al1 and of the Ti-Ti_5Si_3 composit as a function of the test temperature. The flow stress curves of the investigated materials reveal two regimes. These are: The hypoeutectic and the unidirectionally solidified eutectic alloys show at room temperature flow stresses of the order of 1030 and 1080 MPa, respectively. The amount of plastic deformation in crack-free samples yields to $\varepsilon_{pl} = 10\%$ for the hypoeutectic alloy and about 3.5% for the unidirectionally solidified eutectic material. Here the load axis is aligned parallel to the Ti_5Si_3 fibre axis.With increasing temperature the compressive flow stresses decrease steadily to 200 MPa at 800 °C - hypoeutectic alloy - and 250 MPa at 1000 °C for the unidirectionally solidified eutectic one. At the operation temperature of 650 °C the hypoeutectic alloy shows flow stresses of about 350 to 380 MPa. The reinforcing fibre structure of the eutectic composition leads to higher flow stresses of about 550 MPa. It should be noted that the widely used TiAl6V4 alloy exhibits in the optimal processed state with lamellar two phase $\alpha+\beta$ microstructure a flow stress of 350 MPa. This value is comparable with the flow stress of the hypoeutectic alloy. However the unidirectionally solidified eutectic shows improved strength properties at higher temperature. In comparison the refractory intermetallic $Ti_5\ Si_3$ compound is brittle at deformation temperatures below 950 °C and no macroscopic ductility has been observed under compressive load. At the test temperature of 1000 °C a remarkable high flow stress of about 1050 MPa was achieved. Crack initiation revealed after plastic deformation of $\varepsilon_{pl} \approx 1.5\%$.

In the temperature range between 1000 °C and 1500 °C the flow stress of Ti_5Si_3 drops steeply from 1048 MPa to about 50 MPa. However, at 1300 °C, beyond the maximum application temperature of nickel based superalloys of about 1130 °C to 1170 °C, the Ti_5Si_3 compound shows still a considerable high flow stress of 250 MPa [11].

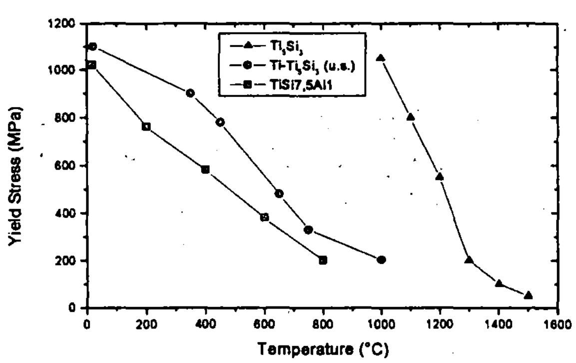

Fig. 6. Yield stresses versus temperature for Ti_5Si_3, the hypoeutectic, TiSi7,5Al1, and the unidirectionally solidified eutectic Ti-Ti_5Si_3 alloy.

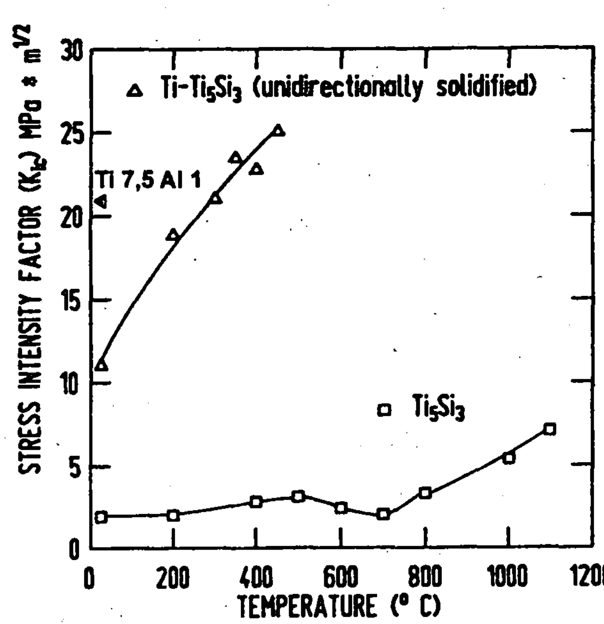

Fig. 7. Stress intensity factors of the Ti_5Si_3 compound, the hypoeutectic TiSi7,5Al1, and the directionally solidified Ti-Ti_5Si_3 alloy as a function of the test temperature.

FRACTURE TOUGHNESS

The fracture toughness of the monolithic Ti_5Si_3 compound, of the hypoeutectic TiSi7Al1, and of the unidirectionally solidified Ti-Ti_5Si_3 alloy have been determined in four-point bend tests. Figure 7 represents the stress intensity factor K_{IC} as a function of the test temperature. The behaviour of the fracture toughness in dependence on the temperature is controversely to that of the flow stress. At room and elevated temperatures up to 700 °C, K_{IC} values between 2.0 and 3.5 MPa $m^{1/2}$ for Ti_5Si_3 and of 11 to 25 MPa $m^{1/2}$ for the Ti-Ti_5Si_3 composite have been measured [12]. The fracture toughness of the hypoeutectic alloy with a fine grained eutectic matrix and primary alpha titanium grains of dentritic morphology is relatively high. At room temperature the K_{IC} – value is about 21 Mpa $\sqrt{m}$ to 23 MPa $\sqrt{m}$. At higher temperature of 600 °C the fracture toughness is increasing to more than 45 Mpa $\sqrt{m}$, respectively. This is caused by the dominating ductile alpha titanium matrix. The relatively low maximum of the fracture toughness of the monolithic Ti_5Si_3 at 500 °C corresponds to SiO_2 precipitations at grain boundaries. Segregated impurities on grain boundaries of selected Ti_5Si_3 test samples have been detected using Auger spectroscopy. The results show that some oxygen is in the bounded state forming silicon oxide. Above 700 °C segregated oxygen goes into solution and consequently the fracture toughness increases. The K_{IC} value of Ti_5Si_3 is about 7 MPa$\sqrt{m}$ and somewhat higher at 1050 °C. A similar brittle to ductile transition in the temperature range from 850 °C to 1000 °C has also been observed for the flow stress of the $Ti_5Si_3(Al)$ material. The unidirectionally solidified Ti-Ti_5Si eutectic behaves more ductile and the stress intensity factor exhibits a strong increase up to 500 °C and at higher temperature. No ductile to brittle transition occurs at temperatures fairly below room temperature. This behaviour is mainly caused by the pronounced ductility of the α-titanium matrix.

CREEP PROPERTIES

Investigations on creep properties of the monolithic Ti_5Si_3 phase have been carried out at different temperatures: 1000 °C and 1200 °C, and stress levels. For determining the creep strength in the high-temperature range ($T >$ 1200 °C) the Ti_5Si_3 specimens were coated with silicon by plasma spraying in order to improve the oxidation resistance of the samples.

In the temperature region between 1000 °C and 1200 °C the creep stress decreases from 240 MPa to 44 MPa at a given strain rate of $\dot{\varepsilon} = 10^{-7}\ s^{-1}$. At the highest test temperature of 1400 °C the creep stress of the Ti_5Si_3 compound drops drastically to about 10 MPa. A stress exponent of n equal 3 for the Ti_5Si_3 compound was determined from the log $\dot{\varepsilon}$ versus log (σ) plot, shown in Fig. ***8***. The value of $n = 3$ refers to the power law creep behaviour controlled by dislocation motion [14]. The activation energy has been determined from the slope of the curves in the semi-logarithmic plot log ($\dot{\varepsilon}$) versus $1/T$ in Fig. ***9*** at constant stress level using the equation:

$$Q = -R\left(\frac{d\log\dot{\varepsilon}}{d(1/T)}\right)_{\sigma}$$

where $\dot{\varepsilon}$ is the strain rate; T describes the absolute test temperature and R is the universal gas constant.

The calculated activation energy for power law creep is Q=350 ± 20 kJ/mol. This value is about 150 to 170 kJ/mol higher than the activation energy for lattice self diffusion of titanium in commercial titanium alloys [15, 16].

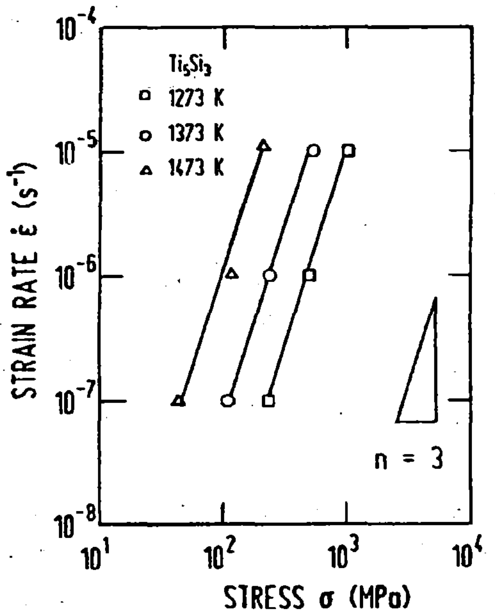

*Fig. 8. Determination of the stress exponent **n** of Ti_5Si_3 from the log. $\dot{\varepsilon}$ versus log σ curves.*

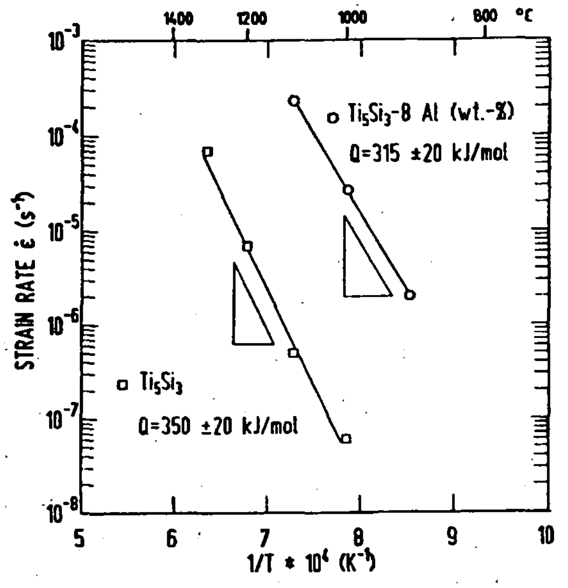

Fig. 9. Creep stress of the monolithic Ti_5Si_3 as a function of the temperature (secondary creep rate $\dot{\varepsilon} = 10^{-7}\ s^{-1}$).

CONCLUSIONS

Titanium silicides are under development as structural materials and coatings for high temperature applications, e.g. turbine airfoiles, burning chamber parts, and missile nozzles. Other applications are wear resistant coatings and thin layers for diverse electronic and surface engineering purposes. The main disadvantage of the silicides is their intrinsic brittleness at room temperature up to the brittle-ductile transition at elevated temperatures of 700 °C to 900 °C. However, alpha titanium-Ti_5Si_3 intermetallic composite material exhibit improved ductility at room temperature and combine the advantages of high flow stresses and improved oxidation resistance at elevated temperatures. Therefore, these materials show considerable potential applications for turbine engines and internal combustion engine parts. It should be noted that the refractory titanium silicides, such as Ti_5Si_3 and $TiSi_2$ have been evaluated as airfoiles in a hybrid design concept for static turbine blades.

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