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Compression plasma flows modification of surface layers in the system "Ti–Si": Phase composition, structure and element redistribution

V.V. Uglov [a,*], N.T. Kvasov [a], R.S. Kudaktsin [b], Yu.A. Petukhou [a], K.F. Ermalitskaya [a], V.M. Astashynski [b], A.M. Kuzmitski [b]

[a] Belarusian State University, Nezavisimosti ave. 4, 220030 Minsk, Belarus
[b] A.V. Lykov Heat and Mass Transfer Institute of National Academy of Sciences of Belarus, P. Brovka Str. 15, 220072, Minsk, Belarus

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ABSTRACT

In the present study Ti_5Si_3/Si layers synthesized by compression plasma flows treatment (treatment time ~100 μs) of the system "titanium coating (1 μm) – silicon substrate" are studied. XRD, SEM and LAES were employed to characterize the phase composition, structure and elemental distribution of these layers. It has been found that plasma energy density (Q) dominates peculiarities of layer structure and elemental distribution. For $Q < 5$ J/cm^2 layers of thickness up to 2 μm with diffusive element distribution form. For 5 J/cm^2 < Q < 8 J/cm^2 layers of thickness up to 10 μm with as convective as diffusive element distribution form. For $Q > 8$ J/cm^2 layers of thickness up to 25 μm with convective element distribution form. Silicon dendrites grow in modified layer and eutectics Ti_5Si_3/Si is localized in interdendritic space. The mechanisms of structure formation and element redistribution are discussed in detail.

1. Introduction

Nowadays particular consideration is given to the search of new materials with high thermal and corrosion stability of electrical, mechanical and chemical properties. Metal silicides possess these properties and are widely studied as materials for nano- and microelectronics ($CrSi_2$, $TiSi_2$, $ZrSi_2$, Ni_2Si), optoelectronics ($FeSi_2$), nanostructure growth (NiSi, $CoSi_2$) and high temperature and mechanical applications ($MoSi_2$, Ti_5Si_3) [1–5].

The present paper focuses on the synthesis of silicide Ti_5Si_3. Ti_5Si_3 is an intermetallic compound which is perspective for high temperature structural applications. It has low density (4.32 g cm^{-3}), high melting point (2130 °C), excellent oxidation and corrosion resistance, excellent creep resistance, good strength at elevated temperature [6–9]. Limitation of monolithic Ti_5Si_3 is its brittleness [10]. Therefore many researchers tend to synthesize some composite material based on the given silicide [5,6,11,12].

Many research works have been done on methods for silicide Ti_5Si_3 synthesis with main focus on technique cost, structure and properties of final products. Generalizing them several different groups of methods for Ti_5Si_3 synthesis can be designated. They are different powder techniques [5,11], heat treatment [13], laser treatment [12], electrochemical synthesis [6–8], chemical vapor deposition (CVD) and other deposition technique [14,15] and etc.

This paper is devoted to another perspective method for synthesis of the given silicide and composite materials based on it. It is compression plasma flows (CPF) [16,17]. CPF are used for pre-surface layer modification of some materials in order to improve their properties or to synthesize some structured layers on their surface.

CPF has smaller treatment time (~100 μs) comparing with electrochemical synthesis (several hours), some kinds of heat treatment (several seconds – hours), powder techniques and deposition methods (several minutes – hours). This method allows obtaining during one pulse modified layer of thickness up to ~25 μm on the area ~1–2 cm^2.

The closest method to CPF is laser treatment. But there are several differences between them. First is that electromagnetic irradiation of laser penetrates into material to some depth and heats whole pre-surface layer. CPF acts as surface heat source because of plasma particles energy is not enough to penetrate into material (~2–3 eV). Therefore great temperature gradient forms during CPF treatment (up to ~50 K/μm). And it conditions differences between laser and CPF in heat and mass transfer processes in materials and as a result in modified layer structure.

Second is that plasma flows are material flows and when they interact with surface melt the latter can be intermixed with plasma substance and forced convection can take place (density of plasma near target is ~10^{17} cm^{-3}, plasma flow pressure on target is ~10 – 30 atm.).

The main aim of our research is to use CPF for synthesis of protective composite layers for high temperature and mechanical applications based on Ti_5Si_3. For this aim it is planning to deposit several coatings on some substrate materials (steels, titanium alloys and etc.) and treat this system by CPF. In order to use CPF effectively it is necessary to

* Corresponding author. Tel.: +375 172095134; fax: +375 172095212.
E-mail address: uglov@bsu.by (V.V. Uglov).

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understand heat and mass transfer processes during CPF treatment. It is easier to do using double system (titanium – silicon) then system with more number of layers.

In previous work we investigated theoretically heat and mass transfer processes in system "titanium–silicon" during CPF treatment [18]. The main result of this work was that varying plasma flow parameters it is possible to synthesize layers with as convective as diffusive element distributions. The present paper is devoted to experimental investigation of mass transfer in the system "titanium coating – silicon substrate". We performed detailed analysis of microstructure, phase composition and element redistribution by means of SEM (scanning electron microscopy), XRD (X-ray diffraction), LAES (laser atomic-emission spectroscopy) and AES (Auger electron spectroscopy).

2. Material and methods

The initial samples were silicon single-crystalline substrate <100> with titanium layer (1 μm thickness). Titanium coating was deposited by vacuum arc deposition method (arc current ~100 A, negative bias potential — 120 V, deposition time — 10 μm). Then these samples were treated by compression plasma flows. 60 samples were treated.

Compression plasma flows are considered to be an effective method to create micro-scaled nanostructured composite layers. One of the main features of this technique is that target is neither cathode nor anode. Schematically CPF treatment is shown in Fig. 1. In vacuum camera (1) electrodes (2–3) and sample holder (4) are placed. Vacuum chamber is filled by plasma forming gas (nitrogen) to pressure ~400 Pa. Voltage 2–5 kV is created between central conic cathode (2) and peripheral rode anodes (3). It causes electrical discharge in gas and plasma flow appears. Time of discharge is ~10 μs, plasma existence time being 100 μs. Plasma flow then acts on sample (5) and its modification occurs. Energy density of plasma was measured by calorimetric method to be $Q = 3–30$ J/cm^2. For silicon substrate it is more appropriate to use values of $Q = 3–12$ J/cm^2. Action time is ~100 μs.

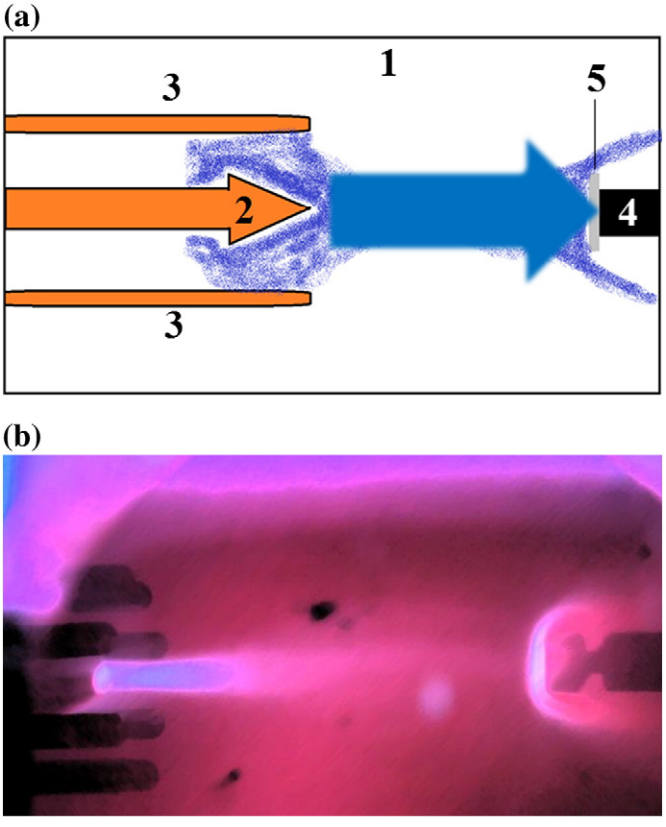

Fig. 1. CPF treatment: (a) schematically represented CPF treatment; (b) edited photo of CPF treatment.

Microstructure investigation was carried out by SEM (microscope LEO 1455 VP of Karl Zeiss, survey was carried out in elemental contrast mode). Samples for cross-section SEM investigations were prepared in the following way. First samples were poured by epoxy resin in order to fix them in vertical position. Then they were mechanically polished in polishing Struers device.

Phase composition was investigated by XRD. Survey was carried out by means of diffractometer DRON 4-13 in Bragg–Brentano focusing with Cu irradiation ($\lambda = 0.154178$ nm) in diffraction angle range $20° < 2\theta < 80°$.

Element concentration profiles were studied by LAES (spectrometer LSS-1, double pulse Nd laser, 1064 nm). LAES is a method for investigation of concentration profiles. It is based on the study of spectrum of plasma produced during material ablation under laser irradiation. Because of properties of plasma depend on plasma composition (component concentrations) it is a complicated task to evaluate absolute concentrations of components in modified layer. But intensity of signal in spectrum is proportional to amount of corresponding atoms. Therefore the given method allows obtaining concentration profiles of every component in modified layer.

To evaluate atomic concentration of components in modified layers we used AES method (spectrometer PHI-660 was used with samples surface sputtering by argon ions with energy 3 keV, etching time is ~45 min, average etching velocity was 0.15 μm/min).

Structure, phase composition and element concentration profiles of initial samples are shown in Fig. 2.

CPF-treated samples with upper layer consisting of solid Ti were studied after etching procedure carried out by H_2O_2:H_2SO_4 = 1:1 solution at temperature 100 °C.

3. Results

The XRD investigation shows that silicide Ti_5Si_3 forms after CPF action. This silicide is present over all range of used energy density.

In Fig. 3 changes of phase composition with increase of CPF energy density is represented. For 3 J/cm^2 < Q < 5 J/cm^2 both Ti and Ti_5Si_3 phases are observed. Beginning from $Q \cong 7$ J/cm^2 only silicide Ti_5Si_3 is observable. Also it is noticeable that there is some halo at diffraction angles $25° < 2\theta < 50°$. This halo corresponds to amorphous phase. In order to define what phase is amorphous chemical etching of titanium and silicide was carried out. It was found that amorphous phase remains (Fig. 3c). Therefore it can be concluded that silicon is partially amorphized.

The cross-section SEM investigations in element contrast mode show that modified surface layer consists of a number of sub-layers. In Fig. 4 three characteristic types of structure after CPF action are shown. Fig. 4a corresponds to energy densities 3 J/cm^2 < Q < 5 J/cm^2, Fig. 4b to 5 J/cm^2 < Q < 8 J/cm^2, and Fig. 4c to Q > 8 J/cm^2 respectively.

For 3 J/cm^2 < Q < 5 J/cm^2 initial titanium coating (1) partially remains not melted and silicon–titanium modified layer (2) is localized under it. Thickness of layer usually varies from 0.3 to 2 μm. In some cases layer can contain vertically oriented silicon dendrites. This layer usually has smooth upper and lower boundaries.

For 5 J/cm^2 < Q < 8 J/cm^2 modified layer consists of two sub-layers (2–3). In sub-layer (3) titanium concentration is more than in sub-layer (2). The latter contains vertically oriented silicon dendrites. Its thickness varies from 1 μm to 5 μm. Sub-layer (3) can also contain silicon dendrites but their orientation is free. Its upper boundary is wavy. This sub-layer usually also contains bubbles (black dots in Fig. 4b). Layer thickness varies from 2 to 10 μm.