EFFECT OF ALLOYING ELEMENTS ON PROPERTIES OF PM Ti-Al-Si ALLOYS

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Abstract

This work was devoted to the description of the effect of alloying by transition metals (Cr, Cu, Fe) on the structure and properties of TiAl15Si15 alloy. Alloying elements does not form separate phases, being dissolved in titanium silicide or aluminide. Cu was found predominantly in aluminide phase, while iron was found to bethe silicide-former. Chromium dissolved in both aluminide and silicide in almost comparable amounts. All applied alloying elements increased the wear resistance, but reduced the room-temperature compression strength. The addition of iron and chromium strongly increase the thermal stability at 1000°C by stabilizing the silicide phase.

Keywords: reactive sintering; mechanical properties testing; intermetallic compounds; oxidation

1 Introduction

Alloys based on titanium aluminides (Ti_3Al and TiAl) are modern materials for high-temperature applications. Due to low density, good mechanical properties and oxidation resistance at high temperatures, these alloys already found its application in the aerospace industry. The application limits of Ti_3Al phase are 760°C in inert atmosphere (creep limit) and approx. 600°C in air (oxidation limit) [1]. Application range of TiAl phase is 750°C in air and approx. 900°C in inert atmosphere or vacuum [1]. It shows that the temperature range of application of all Ti-Al phases is strongly limited by their high-temperature oxidation. To improve the high-temperature oxidation behaviour of these materials, additions of various alloying elements are applied. Previously, it was reported that niobium and tantalum increase the high-temperature oxidation resistance [2] and creep behaviour [3] of Ti-Al alloys. It led to the development of new generation of Ti-Al alloys [4]. However these heavy and expensive elements undesirably increase the density and cost. Other possibility how to improve high-temperature behaviour is alloying with silicon. When Ti-Al-Si alloys are produced by conventional melting metallurgy techniques, coarse sharp-edged particles of Ti_5Si_3 silicide are formed, having negative impact on mechanical properties such as ductility or fracture toughness. Simple production route leading to the fine structure is a reactive sintering powder metallurgy. In our previous works [5], [6], production route for Ti-Al-Si alloys with aluminium content between 8 and 20 wt. % and silicon in the range of 10-20 wt. % was developed and room-temperature properties were described [5].

There are many papers dealing with the influence of various alloying elements on the structure and selected properties of Ti-Al and Ti-Si binary alloys. In addition to the effect of Nb and Ta,

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positive effect of chromium on the oxidation resistance of Ti-Al alloys was reported [7]. Copper [8] and iron [9] were found to improve the reactive sintering behaviour of Ti-Si alloys. Iron also reduces the grain size of titanium silicides produced by this process [9]. With the exception of the papers dealing with the niobium addition [10], there is a lack of information about the possibilities of the improvement of Ti-Al-Si alloys' properties by the addition of quaternary alloying element. This paper aims to describe the effect of selected transition metals (Cr, Cu, Fe) on microstructure, phase composition, mechanical properties and thermal stability of Ti-Al-Si alloys prepared by reactive sintering. Thermal stability was evaluated above the common applicability limit (at 1000 °C).

2 Experimental materials and conditions

This work aimed to describe the effect of alloying elements (Fe, Cr, Cu) on the structure, phase composition and properties of Ti-Al-Si alloys was studied. The alloys were produced by reactive sintering of titanium, silicon, AlSi30 alloy and alloying elements' powders. Powders (fine chips) of titanium and AlSi30 with a particle size of 200 – 600 μm were prepared by mechanical machining. Silicon powder with the particle size up to 50 μm was obtained by mechanical milling. Chromium, copper and iron as alloying elements were utilized in the form of commercial powders (purity >99.5 wt. %) and particle size < 10 μm. Powders were blended to produce Ti-Al-Si-X powder mixtures containing 15 wt. % of aluminium, 15 wt. % of silicon and 15 wt. % of alloying element. Powders were pressed at the laboratory temperature by a pressure of 320 MPa using LabTest 5.250SP1-VM universal loading machine. The green bodies had a cylindrical shape of 12 mm in diameter and 10 mm in height. Pressureless reactive sintering was carried out at a temperature of 900°C for 15 min in an electric resistance furnace in evacuated and sealed silica ampoules. Heating rate of the sample to the reactive sintering temperature was approx. 400 °C/min which was achieved by placing of the sample to the preheated furnace.

Microstructure of prepared materials was observed by an Olympus PME3 light microscope and a TESCAN VEGA 3 LMU scanning electron microscope equipped with OXFORD Instruments INCA 350 EDS analyser (SEM-EDS). Phase composition of the samples was determined by X-ray diffraction analysis (XRD) using PANalyticalX'Pert Pro X-ray diffactometer and by SEM-EDS. Silicide grain size was measured on the light micrographs by the means of image analysis (LUCIA 4.8 image analysis software). Hardness of the prepared materials was tested by Vickers method with a load of 10 kg (HV 10). The abrasive wear resistance was evaluated by using a modification of the "pin-on-disc" method, where "pin" was the tested material and "disc" was a P1200 grinding paper. The applied load was 5.8 N and the sliding distance was defined as 2.5 km. The wear rate was calculated from the measured weight losses by the equation (1.) [11]:

$$w = \frac{\Delta m \cdot 1000}{\rho \cdot l} , \qquad (1.)$$

where: w[$mm^3m^{-1}N^{-1}$] - wear rate, Δm[g] - weight loss, ρ [$g.cm^{-3}$] – density, l [m] - sliding distance on the grinding paper.

The density of samples was determined by the measurement of the samples' volume and weight.

Compressive strength was measured on the samples prepared by reactive sintering using LabTest 5.250SP1-VM universal testing machine at the room temperature.

Thermal stability of Ti-Al-Si-X alloys was evaluated by hardness measurement and microstructure observation after annealing at 1000°C for 400 h.

3 Results and discussion

Fig.1 shows the microstructure of the studied materials obtained by reactive sintering. Materials were prepared according to our previous experiments [5] to achieve the lowest possible porosity together with the absence of residual unreacted components. The TiAl15Si15 reference alloy is formed by Ti_5Si_3 grains surrounded by TiAl (**Fig.1a**). Thealloy with the addition of Cr is composed of the $(Ti,Cr)_5Si_3$ and (Ti,Cr)Al. Copper-containing alloy comprises Ti_5Si_3 and (Ti,Cu)Al (**Fig.1b,c**). The aluminide phase in Ti-Al-Si-Cu alloy appears darker than in the other material after the same etching time. It indicates lower corrosion resistance of (Ti,Cu)Al aluminide phase. Iron-alloyed material is formed by $(Ti,Fe)_5Si_3$ a mixture of TiAl and Ti_3Al phases, see **Fig.1d**. The above presented results show that the applied alloying elements do not form detectable amounts of their own phases during reactive sintering, being dissolved in the above mentioned silicide and/or aluminide.

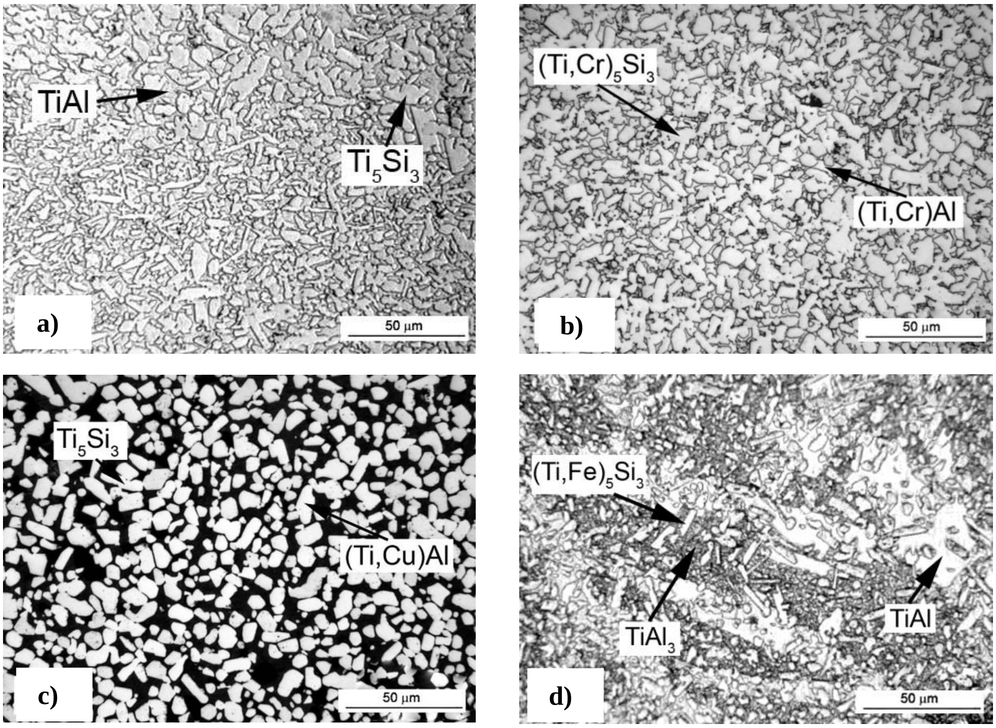

Fig. 1 Microstructure of a) TiAl15Si15, b) TiAl15Si15Cr15, c) TiAl15Si15Cu15, d) TiAl15Si15Fe15 produced by reactive sintering at 900°C for 15 min

The average size of $(Ti,X)_5Si_3$ silicide particles reaches 6 – 13 µm in dependence on the alloy composition (**Fig. 2**). The highest value (13 µm) is achieved in the reference ternary TiAl15Si15 alloy, while all alloying elements refine the silicides. Additions of Cr and Cu lead to the silicide particle size decrease to 7 - 9 µm, while alloying by iron reduces this parameter down to the approximately 6 µm.

Porosity of the reference ternary TiAl15Si15 alloy is approx. 6 vol. %. The effect of copper is on the porosity is negligible. Alloying by chromium slightly increases the amount of pores to 8 - 9 vol. %. Iron effect is strongly detrimental, leading to the porosity of 16 vol. %. As proved in our previous works, reaction of aluminium or silicon with iron produces usually highly porous materials [12]. The porosity increase in the case of iron aluminides was found to be connected with volume changes when the crystal lattice changes from iron to more complex structures of aluminides or silicides. In addition, Kirkendall effect was reported to play an important role [13]. The pores in all alloys are almost spherical and located predominantly in the centre of the sample. This behaviour was already described in our previous work dealing with the preparation of Ti-Al-Si alloys [5]. In reactive sintering process, the reactions are initiated firstly on the surface of the green body. After that, the reaction front propagates throughout the body of the reactants. In the centre of the sample, residual air can be trapped, forming rounded pores [5]. In addition, aluminium evaporation due to local enormous increase of temperature in the reaction mixture can be one of the reasons for increased porosity. This behaviour is completely different from the formation of porosity during annealing in e.g. ECAP process [14, 15].

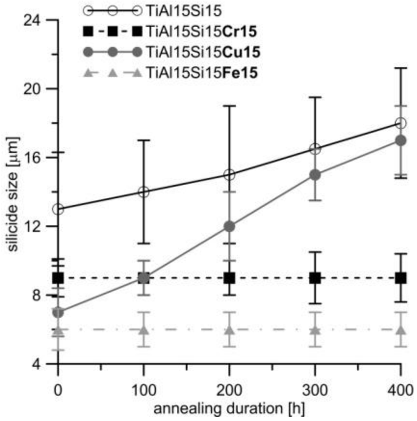

Fig. 2 Equivalent diameter of $(Ti,X)_5Si_3$ particles vs. duration of annealing at 1000°C

The hardness of the ternary TiAl15Si15 is 1180 HV 10 (**Fig.3**). The effect of Cr and Cu on the hardness is negligible. Iron strongly increases the hardness to approx. 1450 HV 10. In this case, higher hardness can be attributed to the presence of harder $TiAl_3$ phase. The presence of $TiAl_3$ phase is probably a result of lower solubility of aluminium in $(Ti,Fe)_5Si_3$ mixed silicide than in the unalloyed titanium silicide.

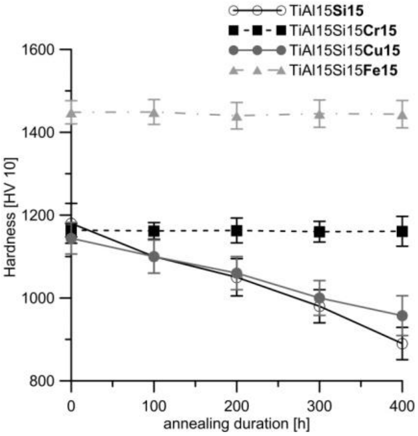

Fig. 3 Hardness of Ti-Al-Si-X alloys vs. duration of annealing at 1000°C.

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All alloying elements have positive effect on the abrasive wear resistance (**Fig.4a**). The strongest reduction of the wear rate was found in the case of iron, followed by chromium. These alloys are also characterized by high hardness, see **Fig.3**. The improvement of wear resistance and hardness is probably connected with the refinement of the hard silicide particles by all alloying elements. Porosity and the pores geometry can also play important role in wear mechanism [16, 17]. Sharp-edged isolated pores were reported act as stress concentrators, leading to the nucleation and propagation of microcracks. However, in the tested materials, the majority of the pores were spherical, being located mainly in the central area of the sample. The near-surface area was almost pore-free. Therefore, the porosity was not taken into the account when explaining the wear behaviour.

On the contrary to the wear resistance, the effect of the alloying elements on mechanical properties in compression is almost negative (**Fig.4b**). Except for the copper-alloyed material, the ultimate compressive strength reduced due to alloying. The lowest values were measured for iron-containing alloy. Addition of copper had no effect on the ultimate strength. The most probable reason for the reduction of compressive strength by alloying is higher porosity of Cr- and Fe-alloyed materials.

The fracture areas after the compression test indicate the brittle fracture in all tested alloys, see **Fig.5**. In the Cr and Fe-containing alloys, the fracture area seems to exhibit the areas of the cleavage fracture. However, this appearance is caused by the fact that the fracture surface follows the silicide-aluminide interface, indicating weaker bonding between these phases (**Fig.5b**). Pores can be also seen on the fracture area in **Fig.5b** which confirms the explanations for poor mechanical properties of Cr- and Fe-containing alloys by the increase of porosity.

After annealing of the investigated alloys at 1000°C, hardness decrease can be observed. Softening during annealing strongly depends on the alloy composition. The smallest hardness changes with the annealing time were detected in alloys containing Cr and Fe (**Fig.3**). The hardness of reference Ti-Al-Si alloy and copper-alloyed material degraded substantially stronger than the other alloys.

As it is evident from **Fig.2**, the hardness decrease during annealing is caused by coarsening of $(Ti,X)_5Si_3$ grains. Silicide particle size during annealing can be stabilized by the addition of the elements that dissolve in silicide phase (Cr, Fe). The effect of aluminide stabilizer (Cu) on both hardness reduction and silicide coarsening is detrimental.

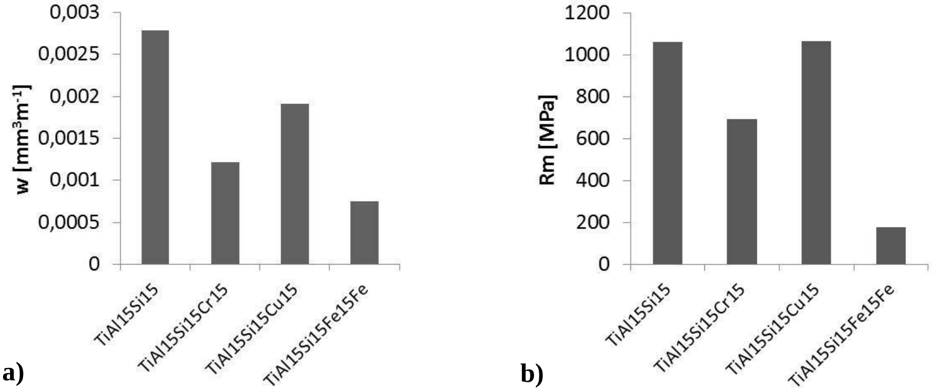

Fig. 4 Abrasive wear rate (a) and ultimate compressive strength (b) vs. alloy composition

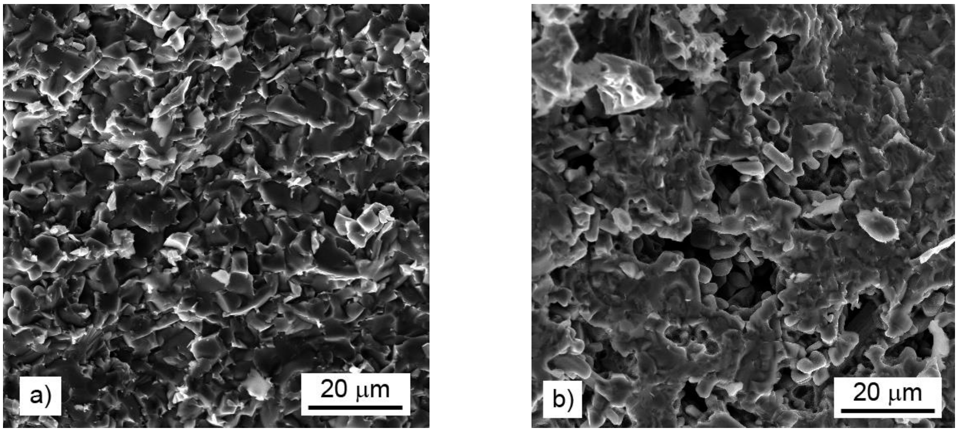

Fig. 5 Fracture area after compression test in a) TiAl15Si15, b) TiAl15Si15Fe15

4 Conclusions

In this work, the effect of chromium, copper and iron on the structure and selected properties of TiAl15Si15 alloy was studied. It was found that these elements dissolve in titanium silicide or aluminide. Copper was found in the aluminide phase, while iron was detected predominantly in the silicide phase. Chromium dissolves in both aluminide and silicide. All applied alloying elements increase the wear resistance, but reduce the room-temperature compressive strength. Iron and chromium improve the thermal stability at 1000 °C.

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