Materials Today Communications 3 (2015) 43–51

Contents lists available at ScienceDirect

Materials Today Communications

journal homepage: www.elsevier.com/locate/mtcomm

Design and laser cladding of Ti–Fe–Zr alloy coatings

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ARTICLE INFO

Article history:
Received 9 February 2015
Accepted 23 February 2015
Available online 25 April 2015

Keywords:
Laser cladding
Composition design
Titanium alloy
Cluster formula
Cluster-plus-glue-atom model

ABSTRACT

Ti–Fe–Zr alloys were designed using a "cluster-plus-glue-atom" model, and the alloy coatings were prepared by laser cladding on TA15 titanium substrate. When the Zr content is less than 7.1 at.%, the cladding layers mainly consist of TiFe dendrites and β-(Ti,Zr) + TiFe + Zr_2Fe eutectics. With the increase of the Zr content, the grain is refined, and the volume fraction of the eutectics has increased dramatically. Single eutectic structure has been obtained as the Zr content increases to 7.1 at.%. When the Zr content is higher than the critical point, the cladding layers are mainly composed of β-(Ti, Zr) dendrites and β-(Ti,Zr) + TiFe + Zr_2Fe eutectics. Compared with the cladding layers with Zr content less than 7.1 at.%, the grain is coarse, and the volume fraction of the eutectics has decreased significantly. The results suggest that the cladding layer with 7.1 at.% Zr has the highest hardness value and the best tribological properties.
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1. Introduction

Titanium alloys as important structural materials are widely used in the fields of aerospace, biomedicine and automobile due to their low density, high specific strength, and good corrosion resistance [1–3]. However, their low tribological properties limit their further applications to some extent. Therefore, it is important to improve the mechanical properties of the titanium alloys in order to expand their applications.

Previous research has proved that laser cladding is one of the most effective ways to improve the surface properties of titanium alloys [4–19]. But it has some limitations in selecting cladding materials. Ni-based, Fe-based and Co-based alloys are commonly used as laser cladding materials on titanium alloy substrate to improve the tribological properties. However, they can be hardly used in severe abrasion conditions. To solve the problem, some hard particles had been introduced to form particle-reinforced composites and ceramics had been used to replace the Ni-based, Fe-based, and Co-based alloys. But the big differences in the thermo-physical properties between the cladding materials and the titanium alloy substrates induce inevitably cracking and porosity of the cladding layers, especially the cladding of large surfaces. Although a two-step method had been used to solve the problem of physicochemical compatibility, it is not practical because of its complicated process and high cost. Therefore, the key lies in how to design and select the cladding materials.

Recent research showed that a binary Ti–Fe eutectic alloy, consisting of a eutectic mixture of β-Ti and TiFe phases, has high mechanical properties and good cladding formability [20,21]. Meanwhile, it also exhibits the capability of further strengthening through alloying with Co, Sn, Cu, and B elements, etc. [22–24]. Zr has an unlimited solid solution in β-Ti, acting as solution hardening element. It can also react with Fe forming intermetallic compounds that is helpful for further improving the mechanical properties of the Ti–Fe eutectic alloy. In the present work, Ti–Fe–Zr alloys were designed using a "cluster-plus-glue-atom" model, and then the alloy coatings were prepared by laser cladding on TA15 titanium alloy substrate. The influences of Zr content on the microstructure and the properties of the coatings were investigated.

2. Composition design of Ti–Fe–Zr alloys

In crystalline phases consisting of elements with strong negative mixing enthalpies and large atomic size differences, dissimilar atoms tend to form the nearest neighbor coordination polyhedral clusters, which represent the most pronounced local short-range order features of the formed phases. In terms of a recently proposed cluster-plus-glue-atom model, any structure can be dissociated into a cluster part and a glue atom part so that the phase composition is always described by the cluster formula [cluster](glue)x [25]. In the Ti–Fe binary alloy, for instance, as shown in Fig. 1, there is a Fe-centered CN12–Ti_9Fe_4 icosahedral cluster derived from phase Ti_2Fe. A cluster formula $[Ti_9Fe_4](Ti)_1 = Ti_{71.4}Fe_{28.6}$ (atomic percentage) falls close to the binary $Ti_{70.5}Fe_{29.5}$ eutectic point. According to the cluster close-packing principle, the cluster is the nearest-shell polyhedron centered by any non-equivalent atomic site in the unit

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http://dx.doi.org/10.1016/j.mtcomm.2015.02.005
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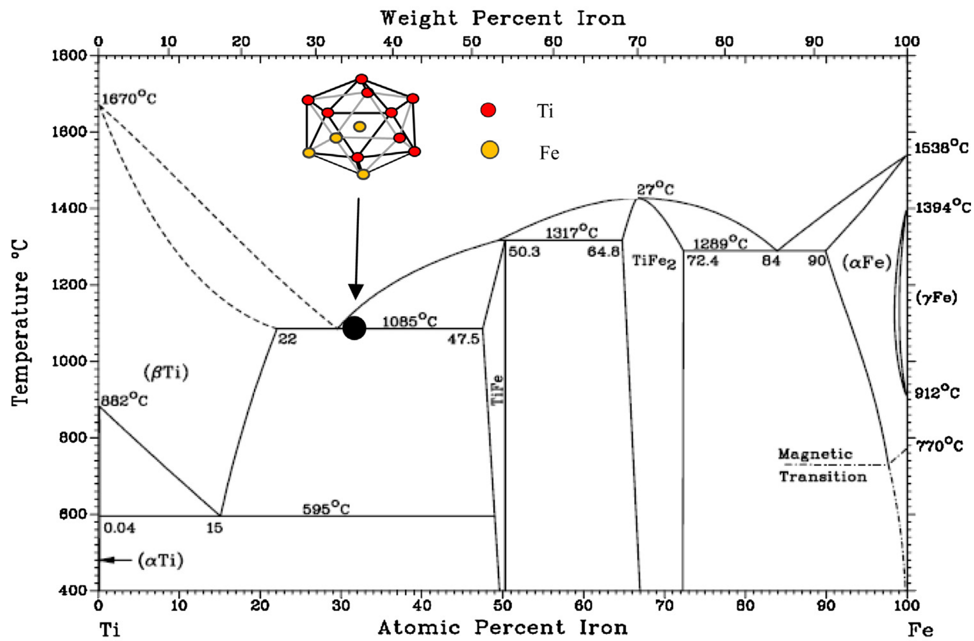

Fig. 1. Ti–Fe binary phase diagram and Ti_9Fe_4 cluster structure.

Table 1
Cluster formulae and chemical compositions of Ti–Fe–Zr alloys used for laser cladding (at.%).

Cluster formula	Chemical composition		
	Ti	Fe	Zr
$[Ti_9Fe_4]3(Zr)$	67.5	30	2.5
$[Ti_9Fe_4]2(Zr)$	66.7	29.6	3.7
$[Ti_9Fe_4](Zr)$	64.3	28.6	7.1
$[Ti_9Fe_4](Zr)_2$	60	26.7	13.3
$[Ti_9Fe_4](Zr)_3$	56.2	25	18.8

cell of the alloy phase, which generally consists of elements having strong negative mixing enthalpies, while glue atoms that are used for filling vacancies between clusters, are composed of elements having weak negative mixing enthalpies. Because Zr has similar properties to Ti, and the mixing enthalpy between them is zero, Zr atoms can substitute Ti atoms directly. Since the Ti_9Fe_4 cluster is already densely packed, the only site for Zr to occupy is to replace the Ti atom at the glue site: $[Ti_9Fe_4](Zr)_1$. For the sake of comparisons, $[Ti_9Fe_4]_3(Zr)$, $[Ti_9Fe_4]_2(Zr)$, $[Ti_9Fe_4](Zr)_2$, and $[Ti_9Fe_4](Zr)_3$ cluster formulae were also taken into account with their detailed compositions listed in Table 1.

3. Laser cladding of Ti–Fe–Zr alloys

TA15 alloy was chosen as a substrate material with its composition listed in Table 2. Elemental powders of Ti (99.99% purity, −200mesh), Fe (99.90% purity, −200mesh), and Zr (99.90% purity, −200mesh) were blended by ball grinder according to the composition listed in Table 1, and then the powder mixtures were pre-placed on the TA15 alloy forming a 1 mm thick layer. A 5 kW continuous wave CO_2 laser system was used as a heat-generating source for producing single-track cladding layer. The optimum parameters of laser cladding were: laser power of 3.0 kW, scanning speed of 6 mm/s, and laser beam diameter of 4 mm. Argon gas was blown into the melt pool to provide shielding during the laser cladding process.

Table 2
Chemical composition of TA15 alloy (wt.%).

Al	Zr	Mo	V	Ti
6.5	2	1	1	Bal

Phase identification of these coatings was carried out using an XRD-6000 X-ray diffraction, equipped with a Ni filtered, Cu K_α radiation operating at 40 kV and 30 mA. The micro-structural characteristics and composition of these coatings were analyzed using a JEOL-5600LV scanning electron microscopy (SEM) and an EPMA-1720 electron probe microanalyzer (EPMA). Vickers hardness of these coatings was measured with a DMH-2LS micro-hardness tester under a load of 0.981 N and a dwell time of 15 s. The specimens with 10 mm × 10 mm × 5 mm were cut out from the laser cladding samples for the wear test. The specimens were ground on 1500 grit size emery paper to obtain the same surface finish. The ball-and-disk friction wear tests for all these coatings were performed using a CETR UMT-2 testing machine. An Al_2O_3 ball with a diameter of 5 mm was selected as the wear couple. The experiment was performed at a normal load of 5 N, a sliding speed of 1.0 mm/s, and a wear time of 30 min.

3.1. Microstructure

Fig. 2 shows an X-ray diffraction pattern of the cladding layer with nominal composition of $Ti_{64.3}Fe_{28.6}Zr_{7.1}$, corresponding to the cluster formula $[Ti_9Fe_4](Zr)_1$. It can be found that the cladding layer consists of disordered bcc β-(Ti,Zr) solid solution, ordered simple cubic TiFe and end-centered orthorhombic Zr_2Fe intermetallic phases. The disordered bcc β-(Ti,Fe) solid solution is an A2 phase in which Fe and Zr atoms randomly substitute Ti ones. The two intermetallic phases TiFe and Zr_2Fe have B_2 CsCl- and Al_2Cu-type structures, respectively.

Fig. 3 shows a cross-sectional SEM micrograph taken from the above cladding layer. The surface zone of the cladding layer exhibits typical morphological characteristics of a eutectic structure (Fig. 3a). Although the ternary Ti–Fe–Zr phase diagram is not available, it can be inferred from the above fact that the surface zone undergoes a eutectic reaction at the initial stage of solidification, resulting in the formation of a eutectic mixture of β-Ti, TiFe and Zr_2Fe phases. On further cooling, the transformation of the

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