Characterization of Ti-Al surface alloy formed by pulsed electron-beam melting of film-substrate system

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Abstract. This paper presents our first results of an ongoing research dedicated to the analysis of Ti-Al surface alloy obtained by a new duplex electron-beam treatment. The crack-free Ti₃Al-based surface alloy was synthesized by cyclic pulsed melting/mixing of pre-deposited Al film (100nm) on Ti substrate with a low-energy (10–20keV) high-current electron beam (3µs, 3.5J/cm²) followed by additional pulsed e-beam melting (100µs, 15keV, 15J/cm²). The surface analysis has revealed the complexity of the local transformation paths associated with this synthesis mode. A fairly good surface chemical homogeneity was obtained but a duplex microstructures formed because of local changes in the primary phase under rapid solidification and the subsequent modifications of the solid state transformation paths.

1. Introduction
Bulk Ti₃Al/TiAl-based alloys have been studied for a long time owing to their attractive mechanical properties like high specific strength and stiffness at high temperatures as well as good oxidation resistance. These properties of Ti-Al intermetallics make them suitable for use as structural protective coatings. Unfortunately, they also possess certain disadvantages such as poor ductility and low toughness at room temperature. Several techniques have been used to fabricate Ti-Al surface layers or coatings: thin-film deposition/annealing [1], ion implantation [2], laser melting deposition [3]. The present work shows the first results on the surface characterisation of Ti-Al surface alloy formed by pulsed e-beam liquid-phase mixing of the film-substrate system [4]. This processing route consists of cyclic liquid-phase mixing of pre-deposited Al film with Ti-substrate by Low-Energy High-Current Electron Beam (LEHCEB) of microsecond duration followed by pulsed melting Ti-Al surface alloy by sub-millisecond (100µs) e-beam [5, 6] Low energy (10-20keV) high-current electron beam of microsecond duration is a fairly recently developed method for surface treatments [4, 5-8]. The pulsed electron irradiation induces (i) a rapid heating and cooling of the surface together with (ii) the formation of thermal stress and stress waves [4, 6-10]. As a result, improved surface properties of the material, often unattainable with conventional surface treatment techniques, can be obtained fairly easily. This is particularly true for tribological [6, 8, 11-13]
and corrosion properties [4, 7, 12-16]. Generally present at the top surface is a zone that has been melted and subsequently solidified rapidly that is often a few µm in thickness [4, 7, 8, 17]. The repeated melting and rapid solidification sequences imparted to the material surface often leads to the dissolution of second phases precipitates (carbides, intermetallics) and the formation of a fairly homogeneous melted layer as was observed for the 316L [12, 18] and D2 [19] steels as well as NiTi shape memory alloys [20]. The so-formed homogeneous layers were demonstrated to improve the corrosion properties of these dual phase alloys. The treatment also often induces the formation of nano-scale structures formed by rapid solidification in the melted layer [19-25]. These ultra fine grains are not the only reason for the generally observed surface hardening and improved wear resistance. Surface strain hardening is also witnessed by the observation of slip traces [7, 26] or, in some cases depending on the stacking fault energy of the material, by the observation of deformation twins [27]. In addition, significant sub-surface hardening is generally observed and witnesses by the presence of two distinct hardness peaks [8, 10, 12, 28, 29]. The first hardness peak - extending generally over about 30/50µm – has been attributed essentially to the quasi-static thermal stress and the repeated action of the beam induced the formation of micro-deformation bands. The second peak -of lower intensity but extending over more than 100µm- was related to deeper hardening induced by the thermal stress wave [12].

As already mentioned, in addition to the previously listed advantages of the LEHCEB process for surface modification, it is also possible to use this electron beam technique for surface alloying by liquid-phase mixing of previously deposited layers [4, 7, 8, 24, 30]. In the present work, a Ti₃Al-based surface alloy has been synthesized by pulsed liquid-phase mixing of pre-deposited Al film on a Ti substrate. As it is also well established that the mechanical behavior of these TiAl-based alloys strongly depends on their microstructure and crystallographic texture [31], a special attention is paid here to the characterization of the microstructure that is expected to form from the melt at cooling rates of about 10⁶K/s.

2. Experimental

An apparatus combining a dual stage device has been used for the preparation of the sample. In the first rig, an Al film has been deposited on a polycrystalline Ti substrate using a high-current pulsed vacuum arc evaporator [32]. The deposition rate was 0.8nm per pulse. The sample was then transferred in the second part of the chamber where the LEHCEB treatment was applied for melting and inter-mixing of the Al-Ti system. Further information on the LEHCEB source and it description can be found elsewhere [6, 7]. The working chamber was evacuated with a turbo-molecular pump to a pressure of 10⁻⁴Pa. The irradiation of the sample was carried out in argon at partial pressure of 3×10⁻²Pa. Prior to the Al film deposition, the Ti substrates were irradiated with LEHCEB (pulse duration of ~3µs, energy density of 5÷6J/cm², pulse number n=10) in order to avoid a local delamination of the thin film at pulsed melting because of potential surface cratering [4, 8, 19, 33]. The thickness of the deposited Al film in each synthesis cycle was 100 nm. After each film deposition the coated sample was subjected to pulsed melting with the same electron beam energy (3÷4J/cm²). The number of cycles N of the Al film deposition followed by pulsed melting was 50; leading to a maximum total thickness of the deposited Al coating of ~5µm. The surface-alloyed sample was subjected to an additional pulsed multiple (n=9) e-beam melting under a stronger energy density level (10÷15J/cm²) for a longer duration (100µs) to avoid surface cracking.

The surface morphology was examined using a JEOL 6500F FEG scanning electron microscope (SEM). The chemical composition of the surface layer was determined by EDS in the SEM. The SEM images were done under the secondary electron imaging (SEI) or backscattered electron imaging (BSE) conditions. The electron backscattering diffraction (EBSD) analysis was carried out with a step size of 0.05µm using the FEG-SEM equipped with the HKL-channel. The X-ray diffraction (XRD) measurements for the analysis of the present phases were carried out with a CPS 120 INEL diffractometer using the Cu-Kα radiation.
3. Results and discussion

3.1. Structure and chemical composition
As shown by the XRD diffractogramme obtained from the sample surface (figure 1), the analyzed surface layer was essentially composed of $\alpha_2$ (Ti$_3$Al) phase. EDS analysis have revealed that this layer contain ~ 34at.% Al rich (balance Ti) with traces of oxygen and carbon. As shown in figure 2, despite the presence of significantly different microstructure features, and figure 3, the repartition of Ti and Al over the entire surface was fairly homogeneous. This is illustrated by the SEM image in Figure 2a that shown two types of microstructure while the concentration maps given in figure 2(b) (Al) and 2(c) (Ti) are rather homogeneous. The slight changes, in particular in the Al map, are clearly not related to the differences in microstructure but more likely to the surface topology. A more detailed microstructure analysis is given in the following section, in particular in figure 3.

![XRD diffractogramme](image1.png)

**Figure 1.** XRD diffractogramme obtained from the sample surface.

![SEM images](image2.png)

**Figure 2.** SEM images under secondary electron imaging condition (a) and corresponding composition maps of the same zone with Al (b) and Ti (c) repartitions.
3.2. Microstructure of the surface and local phase transformation paths.
The general surface topology is presented in figure 3(a) where grains having different height are clearly revealed. Higher magnification images of this zone are presented in figure 3(b) and 3(c). Two types of grains have been observed: grains containing nodular sub-micrometer domains (noted N) and larger grains containing lamellar structures (noted L). The N grains have sizes ranging from about 5 to 10µm while the L grains have sizes in the range 10 to 30µm. Quantitative manual image analysis using the intercept method indicated the fraction of L grains at the surface is about 85%. In order to gain more insights on the microstructure formation, a detailed EBSD analysis has been carried out and is detailed in the following section.

Figure 3. SEM images of the surface microstructure observed under SEI (a-c) and BSE imaging conditions (b).

3.3. Analysis of EBSD maps.
Figure 4 shows an example of EBSD map measured using the hexagonal α (α₂) indexing. About 46% of the pixels were indexed. The missing fraction corresponds to non-indexed points but no other phases were detected. The colour key of the map is given by the all euler orientation legend. The white domains in the map correspond to the non-indexed pixels. It is clear that the grains of type N have a fairly homogeneous colour indicating thereby that they present little internal misorientation. Comparatively, the lamellar domains in the grains of type L correspond to martensitic variants. The presence of martensitic variant is confirmed by the data given in table 1. In table 1 are presented the calculated misorientation obtained between each type of lamellar variant for the domain labelled L₁ in figure 4. As described in [34-35], the misorientations calculated from the inherited α₂ orientations correspond to the β α transformations and these variants are issued from the same parent β phase. In many titanium and zirconium alloys, the high temperature (BCC) β phase transforms upon cooling into the (HCP) α phase with respect to the Burgers orientation relations [36]. The Burgers orientation was also obtained here (Table 1).
Thus, it is clear that the different microstructures obtained at the surface of the sample can be explained by different phase selection from the melt during the rapid solidification and the subsequent solid state transformation paths. The grains of N type have solidified directly as from the melt. Comparatively, the grains of type L come from the primary $\beta$ phase that subsequently followed the $\beta \to \alpha$ martensitic transformation.

Table 1. Misorientation between two considered variants present in the $L_1$ grain.

| Variant1 | Variant 2 | Variant3 | Variant 4 |
|----------|-----------|----------|-----------|
| Variant1 | X         | 60° [1-210] | 10°[-110-3] | 90°[1-210] |
| Variant2 | 60° [1-210] | X        | 60°[-3210] | 60°[-4-483] |
| Variant3 | 10°[-110-3] | 60°[-3210] | X         | 90°[-12-10] |
| Variant4 | 90°[1-210] | 60°[-4-483] | 90°[-12-10] | X         |

4. Conclusion

A Ti$_3$Al–based surface alloy has been synthesized by cyclic LEHCEB melting and mixing of a pre-deposited Al film on a Ti substrate followed by pulsed melting with submilsisecond e-beam to obtain microstructure without microcracks. For the investigated experimental conditions, the top surface chemistry was fairly homogeneous and contained about $34\%$ Al. Despite the absence of significant chemical gradient at the top surface, two types of microstructure were revealed. This is the result of local changes in the transformation paths due to a local modification of the primary phase in solidification. While some grains (N type) have solidified directly as a hexagonal phase from the melt, other domains solidified as $\beta$ and subsequently followed the $\beta \to \alpha$ martensitic transformation.

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