Influence of the processing on the ordering process in the Al-Ti binary system with composition close to Al$_3$Ti

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Abstract. The phases and their stability in Al$_{70}$Ti$_{30}$, Al$_{75}$Ti$_{25}$ and Al$_{80}$ Ti$_{20}$ planar flow cast ribbons and their master alloys have been studied. Analyses are based on the XRD and DTA measurements. In all samples the high-temperature Al$_{11}$Ti$_5$ and Al$_5$Ti$_2$ superstructures (1d-APSSs) have been present. The stable low-temperature phases Al$_2$Ti, Al$_3$Ti and Al have been identified, too. The 1d-APSSs being formed as first during the quenching persist for considerable time also at low temperatures. During heating in reverse, only the 1d-APSSs remain before melting, being formed after large superheating from all low-temperature phases in Al$_{70}$Ti$_{30}$ and Al$_{75}$Ti$_{25}$ alloys. The phase Al$_{11}$Ti$_5$ is reported in the Al$_3$Ti and more Al-rich alloys for the first time.

1. Introduction
AlTi-based intermetallics due to their low specific weight, high specific strength especially at elevated temperatures, good hardness, excellent creep strength and good oxidation/corrosion resistance are promising materials for high temperature applications particularly in automotive and aerospace industries [1]. However their brittleness as well as the anomalous strengthening seems to be closely related with the formation of superstructural phases such as the Al$_5$Ti$_3$-type or Al$_5$Ti$_2$ ordering with increasing Al composition [2].

In the Al-Ti phase diagram (see figure 1), the formation of various long-period superstructures has been reported in the Al-rich region deviating from the stoichiometry. Also the wide solubility to the Al-rich side in the case of AlTi, the peritectic reaction accompanying the formation of Al$_3$Ti and the high-temperature (h) and low-temperature (l) modifications of Al$_3$Ti exist. In the vicinity of 65 at% of Al the formation of the equilibrium r-Al$_2$Ti often does not follow the phase diagram however firstly the metastable phases Al$_5$Ti$_3$ and the orthorhombic Al$_5$Ti$_2$ nucleate, grow and dissolve in the quenched alloys [4]. Concerning the glass-forming ability, amorphous phase has been observed only in the composition range of 40-65 at% Al in the Al-Ti alloys prepared by sputtering [5]. Concluding, due to the difficulty in reaching equilibrium state at low temperatures within a limited time certain confusion might accompany the process of formation and thermal stability of the individual phases especially in the case of quenched, sputtered or mechanically alloyed samples. Simultaneously certain considerable confusion in the experimental data exists as has been critically analysed in the review of Schuster and Palm [3]. Particularly, that would be related to the processing techniques.

In our previous work [6], the synthesis of the initially elemental nanoscaled Al/Ti multilayers has been investigated. Foils with the overall chemical composition Al$_{50}$Ti$_{50}$ and with a wide variety of individual number and thickness of layers were obtained by plasma-assisted magnetron layer-by-layer
sputtering. Due to the diffusion of Ti through the Al/amorphous interface the synthesis between Ti and Al, when is controlled by slow heating rate (in DSC), completes already below 700 °C. Being a complex solid-state reaction, it is a sequence of gradual changes; it starts by amorphisation, then (metastable) c-Al$_3$Ti is formed, and is progressively changed to tetragonal Al$_3$Ti, Al$_2$Ti and finally AlTi and also Ti$_3$Al phases (see also figure 3).

![Figure 1. Al-Ti phase diagram according to the current assessment [3].](image)

The thermodynamic stability and the eventual evolution of individual phases in the mechanically milled Al$_3$Ti powder have also been studied [7]. The powder (nominal chemical composition Al$_3$Ti) was prepared by grinding the compound Al$_3$Ti and its subsequent milling in H$_2$ atmosphere using a magnetically controlled planetary-ball mill. Thus the Al$_3$Ti structure was broken and the nanostructured products of solid solution fcc-Al(Ti) and Al$_{1+x}$Ti$_{1-x}$ (x = 0.3) were formed. In such material, firstly the massive structural relaxation superimposed by the endotherm of H$_2$ desorption and then spontaneous crystallization of the intermediate Al$_5$Ti$_2$ is realized isothermally or in the regime of continuous heating in DSC up to 600 °C. Afterwards at higher temperatures, no melting of Al however the small exothermal effects representing the further formation of Al$_5$Ti$_2$ and also Al$_{1+x}$Ti$_{1-x}$ can be observed (see also figure 3). Finally above 700 °C, also the Al$_3$Ti$_2$ phase dissolves and nearly total transformation into the equilibrium h-Al$_3$Ti (DO$_{22}$) phase is realized.

The thermodynamic stability of the rapidly solidified Al-rich AlTi alloys has not yet been systematically investigated. Recently the ordering processes of Al$_5$Ti$_3$, h-Al$_5$Ti and r-Al$_5$Ti have been investigated in ribbons containing up to 62.5 at % Al [8]. In these quenched alloys as well as in our multilayers and milled powders the metastable non-equilibrium or unexpected phases as Al$_5$Ti$_3$, Al$_{1+x}$Ti$_{1-x}$ or Ti$_3$Al (in alloys with above 50 at % of Al) have been obtained.

In the present work these aspects are addressed including also the rapidly quenched ribbons prepared from the Al$_3$Ti-like master alloys (containing 70-80 at % Al).

2. Experimental details
The master alloys (nominal composition Al$_{80}$Ti$_{20}$, Al$_{75}$Ti$_{25}$ and Al$_{70}$Ti$_{30}$, at. %) were prepared by melting, homogenization and quenching in the arc melting furnace using high purity components: Al(5N) and Ti(4N5). Ribbons approx. 25µm thick and 3 mm wide were produced by planar flow
casting from the melt under protective atmosphere of high-purity Ar. Inductively coupled plasma spectroscopy was used to check the chemical composition of the as-quenched ribbons.

Figure 2. X-ray diffraction patterns of specific Al-Ti ribbons (R) and master alloys (MA).
The thermodynamic stability and the process of structural transformations due to temperature-controlled reactions were studied by differential scanning calorimetry (Perkin-Elmer DSC7) and high temperature differential thermal analysis (Perkin-Elmer DTA7) during continuous heating. Flowing argon atmosphere and opened alumina sample pans were used. Each effect giving a DSC or DTA peak has been characterized by its onset, peak and end temperatures, $T_x$, $T_p$ and $T_e$, respectively, (all ±0.5 °C) and transformation enthalpy $\Delta H$ (±4 J g$^{-1}$). X-ray diffraction patterns were obtained by standard Bragg-Brentano method using CuKα radiation and carbon monochromator in the diffracted beam.

3. Results and discussion

The DSC measurements did not show any effect. It means that the as-quenched ribbons do not contain any amorphous phase and they are stable up to 600 °C.

The structure of the as-quenched ribbons was examined by X-ray diffractometry. (figure 2). Phases identified in the investigated Al-Ti (Al-rich) system are: fcc-Al, tetragonal h-Al$_3$Ti (high-temperature phase with DO$_{22}$ structure, no. 139 with lattice parameters $a = 0.3844-0.3849$ nm, $c = 0.8596-0.8610$ nm), tetragonal Al$_{11}$Ti$_5$ (no. 139, $a = 0.39230$nm, $c = 1.65349$ nm), tetragonal Al$_5$Ti$_2$ (no. 123, $a = 0.3905$nm, $c = 2.9196$nm) and tetragonal r-Al$_2$Ti (no. 141, $a = 0.3971$ nm, $c = 2.432$ nm).

Alloy Al$_{80}$Ti$_{20}$ master alloy contains only Al$_3$Ti and fcc-Al phases. The ribbon prepared from this master alloy contains Al$_3$Ti, however, in higher amount than in the master alloy, fcc-Al but in significantly lower quantity than in the master alloy. Definite presence of Al$_{11}$Ti$_5$ phase has been observed (figure 2).

In the case of Al$_{75}$Ti$_{25}$ ribbon almost pure Al$_3$Ti, small traces of fcc-Al and small traces of Al$_{11}$Ti$_5$ were found.

Alloy Al$_{70}$Ti$_{30}$ exhibits no traces of pure fcc-Al. Its master alloy contains Al$_{11}$Ti$_5$ probably together with small amounts of Al$_{5}$Ti$_2$ (similar reflections as for Al$_{11}$Ti$_5$ - figure 2), Al$_3$Ti and Al$_2$Ti. The ribbon contains larger amount of Al$_{11}$Ti$_5$ and Al$_2$Ti than in the master alloy and smaller quantity of Al$_3$Ti; no presence of Al$_2$Ti was observed.

Another characterization of the as-quenched ribbons is their thermal stability. This has been inspected by the DTA measurements. Thus in figure 3, the lower temperature range of the DTA plots is shown (being related to the alternative properties of AlTi multilayers or the Al$_3$Ti mechanically alloyed powder). Thus in the case of Al$_{80}$Ti$_{20}$ ribbon, the endothermal effect, $R_l$, of $\Delta H_l = 46$ J g$^{-1}$ at $T_{x,l} = 657.7$ °C is assigned to the melting of ~12 wt % of Al-based solution (660.1 °C and 400 J g$^{-1}$ for pure fcc-Al[9]). Similar, however much smaller, DTA peak of 2 J g$^{-1}$ at $T_{x,l} = 643.4$ °C presents a minimal quantity of Al also in the Al$_{75}$Ti$_{25}$ ribbon. The straight line excludes any pure Al in the Al$_{70}$Ti$_{30}$ ribbon.

High-temperature parts of the DTA plots obtained from the Al$_{70}$Ti$_{30}$, Al$_{75}$Ti$_{25}$ and Al$_{80}$Ti$_{20}$ ribbons in (figure 4) present the typical melting peaks. Thus the Al$_{80}$Ti$_{20}$ ribbon shows a broad endotherm, Rh, of $\Delta H_h = 474$ J g$^{-1}$ at $T_{x,h} = 1373.2$ °C ($T_{p,h} = 1394.2$ °C, $T_{c,h} = 1403.1$ °C), which however might begin already at $T_{x,l}$. Then both effects Rl and Rh might be attributed to the solidus and liquidus (~1395 °C, [3]) of the Al$_3$Ti + Al (eventually Al(Ti)) hypoeutectic alloy.

In the case of Al$_{75}$Ti$_{25}$ ribbon, a relatively narrow and sharp endotherm, Rh, of $\Delta H_h = 526$ J g$^{-1}$ at $T_{x,h} = 1420.4$ °C ($T_{p,h} = 1428.8$ °C, $T_{c,h} = 1433.7$ °C), which has no counterpart Rl at lower temperatures, is observed. Such effect correlates with the melting of a single phase and following the Al-Ti phase diagram it might be the solidus (~1420 °C) and liquidus (~1437 °C) of a 1d-APS “one dimensional antiphase domain structure” as Al$_{11}$Ti$_5$ or/and Al$_2$Ti$_2$ [3]. However, in the second measuring cycle which followed immediately after the DTA heating to 1500 °C and cooling down, another small endothermal pre-effect, Rh’, of $\Delta H_{h'} = 7$ J g$^{-1}$ at $T_{p,h'} = 1406.9$ °C ($T_{p,h'} = 1409.9$ °C) is superimposed on the initial parts of Rh. The significantly stronger pre-effect, Rh’, of $\Delta H_{h''} = 27$ J g$^{-1}$ at $T_{x,h''} = 1409.3$ °C ($T_{p,h''} = 1415.9$ °C) and less intensive main effect, Rh, of $\Delta H_h = 397$ J g$^{-1}$ ($T_{p,h} = 1426.8$ °C, $T_{c,h} = 1431.0$ °C) are the principal variations which characterize the Al$_{70}$Ti$_{30}$ master alloy.
The ribbon Al\textsubscript{75}Ti\textsubscript{25} has the stoichiometric composition. Surprisingly, its melting is similar to that of the Al\textsubscript{70}Ti\textsubscript{30} master alloy. Both intensity and temperature of the main peak, Rh, of $\Delta H_{h} = 473 \text{ J g}^{-1}$ at $T_{x,h} = 1404.0 \degree \text{C}$ ($T_{p,h} = 1412.2 \degree \text{C}$, $T_{c,h} = 1417.1 \degree \text{C}$) lies between those of the preceding two samples. Generally, this Rh is slightly softer than that in the case of the Al\textsubscript{70}Ti\textsubscript{30} ribbon; it contains the characteristic pre-peak Rh' at $T_{x,h'} = 1374.4 \degree \text{C}$ already in the as-quenched state; however as it has already been said, it is related also with the particular low temperature effect, RI (see figure 1). Following the phase diagram and the X-rays analysis, the Rh effect correlates well with the melting of the particular 1d-APS also in this case.

Generally it is known that eutectoid, peritectoid and first-order polymorph transitions in Al-Ti alloys need not to be observed by DTA due to their sluggishness [3]. Also, the DTA effect connected with the crossing of the boundary line between one-phase and two-phase fields might be very weak and may strongly depend on the steepness of the phase boundary [10]. Then our Rh’ endothermal pre-peaks might be connected with the delayed transformation of the Al\textsubscript{11}Ti\textsubscript{5} $\leftrightarrow$ Al\textsubscript{11}Ti\textsubscript{5} + Al(l) in the Al\textsubscript{75}Ti\textsubscript{25} and Al\textsubscript{70}Ti\textsubscript{30} ribbons and also Al\textsubscript{5}Ti\textsubscript{2} + Al\textsubscript{3}Ti $\leftrightarrow$ 1d-APSs in the Al\textsubscript{70}Ti\textsubscript{30} master alloy.

Our results show that the high temperature phases as Al\textsubscript{11}Ti\textsubscript{5} and Al\textsubscript{5}Ti\textsubscript{2} (and also Al\textsubscript{3}Ti and h-Al\textsubscript{3}Ti), which are closely related to the L1\textsubscript{0} AlTi crystal structure, are frequently observed also at room temperatures in Al\textsubscript{3}Ti-like planar flow casted ribbons and in the quenched master alloys. The prior nucleation of the 1d-APSs in the Al\textsubscript{70}Ti\textsubscript{30} melt correlates with the phase diagram [3] and their preservation at low temperatures after quenching reflects the strong decrease of the mobility of diffusing species with decreasing temperature. The presence of the 1d-APSs in the stoichiometric Al\textsubscript{13}Ti\textsubscript{25} and even in the hypoeutectic Al\textsubscript{50}Ti\textsubscript{20} alloy is documented for the first time. It might predicate about the preferential ordering and the cluster structure already in the aluminium-rich Al-Ti melt.
4. Conclusions
The phases and their thermodynamic stability in the Al-Ti binary system with chemical composition close to Al₃Ti were investigated using planar flow casted ribbons and their master alloys. The following conclusions were reached. (1) The 1d-APSs can be formed in the wide compositional range around Al₃Ti composition at least up to 80 at % Al. (2) Upon quenching of the melt first the superstructures as Al₁₁Ti₅ or Al₅Ti₂ are formed. (3) The high-temperature 1d-APSs, though being unstable, persist also at room temperatures coexisting with the eventual low temperature phases. (4) The low temperature phases as Al₂Ti and Al₃Ti could be formed only after a certain time at elevated temperatures, thus they are more feasible in a master alloy than in a ribbon. (5) Contrariwise during the heating, the already existing low temperature phases as Al₂Ti or Al₃Ti need considerable time and extensive temperatures to reform back into the high temperature 1d-APSs. So they transform after being overheated. (6) The melting, because it represents the 1d-APSs ↔ liquid (or Al₃Ti + Al ↔ liquid in the case of Al₈₀Ti₂₀), is in accord with the equilibrium phase diagram.

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