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Reaction behavior and evolution of phases during the sintering of Ta–Al powder mixtures

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ABSTRACT

Intermetallic compounds based on tantalum aluminides are of considerable interest in various industrial applications. In this work, the formation of tantalum aluminides has been studied in elemental powder mixtures containing 25, 50 and 66.7 at% Ta. A differential scanning calorimeter (DSC) was used to heat the samples up to 1500 K at 15 K min^{-1}. Phase evolution was studied by heating a few samples to temperatures below and above the observed DSC peaks. The heat treated samples were analyzed using scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction. The results suggest an exothermic reaction between tantalum particles and molten aluminum, which leads to the formation of Al_3Ta compound as the initial product. This reaction reached completion for the aluminum-rich samples and the corresponding DSC peak was very broad, containing two distinct steps which indicated the effect of a diffusion barrier during the reaction. In these samples, the Al_3Ta product was stable upon further heating. A different behavior was observed for the equiatomic and tantalum-rich samples, an incomplete reaction with a considerable amount of unreacted tantalum. These samples were associated with a narrower reaction peak in the DSC plots, followed by a mildly exothermic peak at higher temperatures. The latter was found to correspond to the formation of $Al_{69}Ta_{39}$ phase in the solid state, together with minor amounts of σ (Ta-rich) and φ (near equiatomic) phases. The $Al_{69}Ta_{39}$ phase showed a tendency to disappear on prolonged heating. The σ and φ phases were observed to dominate as the major phases in tantalum-rich and equiatomic samples, respectively.

Increasing the heating rate shifted the reaction peak for Al_3Ta formation to higher temperatures and the apparent activation energies were estimated as 383 ± 13 kJ mol^{-1} and 439 ± 22 kJ mol^{-1} for the initial and final stages of this reaction. The heat of formation of Al_3Ta was also estimated as −36 ± 7 kJ mol^{-1} in the interval 1050–1350 K. Studies on the effect of particle sizes of the reactants showed that, in most cases, the reaction peak shifted to lower temperatures on decreasing the tantalum particle size. A similar behavior was observed for aluminum in the tantalum-rich samples, while an inverse effect was seen in equiatomic and aluminum-rich samples.

1. Introduction

Intermetallic compounds based on transition metal aluminides have been regarded as suitable candidates for advanced structural applications. These compounds exhibit an attractive combination of properties such as high melting points and enhanced resistance against corrosion and oxidation at elevated temperatures. This group of materials, including Al–Ta compounds, offers a variety of applications in different fields such as thin films and coatings [1,2], microelectronics, resistors and capacitors [3,4], diffusion barriers [5,6] and structural materials which can serve at high temperatures [7,8]. Amorphous Al–Ta alloys have been employed in applications requiring high thermal and chemical stability [1,4]. However, low ductilities of intermetallic compounds, particularly at ambient temperatures, may limit their use in some applications.

Despite extensive studies on the Al–Ta system [3,4,7–12], uncertainties are still associated with some phase relations and the binary phase diagram is not yet fully established. However, there is agreement in literature on the existence, stabilities and

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compositions of several phases in the system. For example, it is generally agreed that the compound Al_3Ta, which has shown good potential for advanced applications at elevated temperatures [2,7,13], is an almost stoichiometric (24–25 at %Ta) phase [7,11,12] with a tetragonal $D0_{22}$ structure and melts incongruently at 1814 K [8]. This compound has been reported as the first phase to form in Al–Ta diffusion experiments [5,6].

In addition to Al_3Ta, a non-stoichiometric σ-phase has also been identified in the Al–Ta system [4,7,8,10–12]. According to a recent experimental and thermodynamic study performed by Witusiewicz et al. [8], the σ-phase has a homogeneity range of 65–81 at % Ta [12]. This phase has a topologically close packed structure with a tetragonal unit cell [8,10], and has been mainly designated as $AlTa_2$ [3,4,7,10,11]. However, deviations in the phase composition and the stability range for this phase have been reported in some studies [3,4,10].

As seen in the Al–Ta phase diagram (Fig. 1), the σ-phase is in equilibrium with phase φ which is stable around the equiatomic composition (52.2–57.3 at % Ta) [12]. In some references, the phase φ has been designated as AlTa [3,9,10]. However, this phase is assumed to be a line compound at lower temperatures [8]. It has been suggested that the phase φ has a complex monoclinic unit cell representing a topologically close-packed structure [10]. According to the Al–Ta phase diagram, the Ta-rich σ-phase decomposes to φ (equiatomic) and an intermediate phase which was initially reported as Al_3Ta_2 or Al_2Ta [3,8]. However, further studies by Mahne and Harbrecht [14] revealed that this intermediate phase corresponds to the $Al_{69}Ta_{39}$ compound exhibiting a face centered cubic structure with a giant unit cell. The eutectoid transformation at 1371 K [8] leads to the decomposition of $Al_{69}Ta_{39}$ phase into Al_3Ta and φ phases.

Several researchers [5,6] have studied the formation of aluminides through solid-state diffusional reactions in the Al–Ta system. In these experiments, the Al_3Ta compound was observed to form at temperatures below the melting point of aluminum. In the temperature range 723–848 K, Howard et al. [6] reported the growth of a Al_3Ta layer with an irregular interface. They suggested a non-parabolic growth rate for the Al_3Ta compound, which was thought to be due to the selective penetration of diffusing species through the grain boundaries where the lattice diffusion was negligible. This led to the conclusion that high melting compounds like Al_3Ta exhibit a lower lattice diffusivity compared to those with relatively lower melting points such as Al_7Cr that showed parabolic growth during annealing [6]. Chung et al. [1] studied the thermal

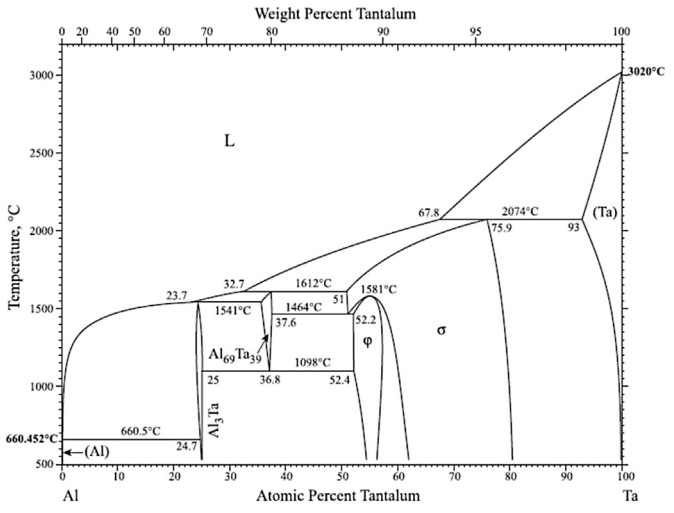

Fig. 1. Aluminum-tantalum phase diagram [12].

stability of Al–Ta compounds and found that it is strongly related to the composition of the mixture and increased with tantalum content.

Intermetallic compounds can be produced using different techniques, but methods based on powder metallurgy are considered to be advantageous. Most powder metallurgical routes for synthesizing intermetallic compounds use pre-alloyed powders as starting materials. However, premixed elemental powders have been successfully used to produce high strength alloys and compounds [15,16]. Premixed powders are generally softer than pre-alloyed powders, resulting in higher compact densities and an increased die life. Reactive synthesis or combustion synthesis is a well-suited technique to produce intermetallic compounds from elemental powders. A reaction occurs between the reactant powders upon heating and such reactions are usually exothermic. A self-sustaining process is thus possible provided enough heat is generated during the reaction. This method is recognized as an efficient route through which a wide range of materials like intermetallic compounds, ceramics, functional materials and composites can be produced [17]. Compared to conventional production techniques such as melting and casting, reactive synthesis offers some advantages like simplicity, energy savings and higher productivity. Further, near-net-shape products can be fabricated through this method [6]. However, controlling the exothermic reactions and limiting porosity formation are critical in this process [18].

Tantalum aluminides have been synthesized using combustion synthesis. Yeh and Wang [19] produced tantalum aluminides through thermite-based reactions between tantalum oxide (Ta_2O_5) and aluminum powder mixtures. In their study, the effect of sample stoichiometry on the combustion behavior and the degree of phase conversion was investigated. Alumina-tantalum carbide composites have also been synthesized using a thermite-based combustion process [20].

Aydelotte et al. [21] performed a mechanistic study on impact-initiated reactions in explosively consolidated Ta + Al powder mixtures. Significant plastic deformation of both constituents was found to play a key role in decreasing the energy required for the initiation of reactions in Ta + Al samples, as compared to those observed in Ni + Al and W + Al systems.

A scan of literature shows a number of studies on the reactive synthesis of nickel, cobalt, titanium and iron aluminides [22–25], but the studies devoted to the Al–Ta system are very few. Although these studies focus on the production of tantalum aluminides, the reaction behavior and phase evolution during heating have not been investigated in detail. Information on the effect of processing parameters such as reactant particle size and heating rate on the reaction behavior in Ta–Al system is not available in literature. This has prompted the present study on the reactive synthesis of tantalum aluminides using elemental powder mixtures. In this work, binary tantalum-aluminum powder mixtures with selected Ta/Al ratios were chosen for study in a differential scanning calorimeter (DSC) in order to identify the reactions governing the process. It may be noted that calorimetric studies have been effectively employed in powder different metallurgical processes to optimize the sintering regime [26,27].

2. Materials and methods

Pure elemental powders of tantalum (<75 μm) and aluminum (<60 μm) were used as the starting materials to prepare the samples. The powders were thoroughly mixed to get three sets of specimens with nominal compositions of Ta+3Al, Ta + Al and 2Ta + Al, corresponding to the constituent phases in Al–Ta system. Compacted discs (4 mm in diameter and <1 mm in thickness) were