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Rietveld refinement of the A_3B ($D0_{19}$) and A_2B ($B8_2$) phases in Ti–Sn and Ti–Ga alloys

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ABSTRACT

The structures of A_3B ($D0_{19}$) and A_2B ($B8_2$) phases have been investigated using Rietveld refinement of XRD data. The analyzed chemistry of individual phases has been used to determine the site occupancy of initial models. The shifts in Ti atoms corresponding to 6(h) Wyckoff positions have been calculated in both the Ti_3Sn and Ti_3Ga phases. This is related to the presence of symmetry elements in $D0_{19}$ structure which in turn allows local shift due to different site occupancies resulting in different potentials. The nature of atomic shift is opposite in Ti_3Sn and Ti_3Ga phases. The site occupancy patterns of A_3B (Ti_3Sn, Ti_3Ga) and A_2B (Ti_2Sn and Ti_2Ga) are different due to unlike chemical compositions.

1. Introduction

Intermetallic compounds have been subject of intense study spurred by the demands of aerospace and automobile industries for the materials that are usually strong at elevated temperatures [1]. They belong to a class of materials that present special opportunities for unusual combination of lightness and high temperature strength. On the other hand, they lack room temperature ductility and toughness. The initial alloy development programmes have been focused to address these issues. For example, Nb has been identified as most effective alloying addition to improve the ductility of Ti_3Al ($D0_{19}$) intermetallic by changing the slip behavior and also stabilizing the ductile β (or its ordered form B2) phase into the structure [2,3].

Both the Ti–Sn and Ti–Ga systems exhibit the presence of A_3B (Ti_3Sn and Ti_3Ga) and A_2B (Ti_2Sn and Ti_2Ga) intermetallic phases [4]. The A_3B is typical $D0_{19}$ phase exhibited by prototype Ni_3Sn while the A_2B phase is represented by Ni_2In ($B8_2$) prototype. The details of these structures are given in Table 1. It is to be noted that the first principle calculations based on density functional theory have been used to predict structural stability of Ti–Sn system [5]. It has been shown that the electronic structures of the Ti–Sn intermetallics exhibit a strong hybridization between Ti 3d and Sn 5p states. This plays dominant role in the bonding mechanisms of Ti_3Sn and Ti_2Sn compounds. Stability of both the Ti_3Sn and Ti_2Sn phases along with constitutional and thermal defects has been investigated as function of composition and extension of one phase domain of the phases are discussed [6,7]. However, similar studies are rather lacking for Ti–Ga system.

It is clear from the Table 1 that the 6(h) Wyckoff positions of A_3B phase are variable although one of the regular close packed hexagonal (cph) corresponds to a position (1/6, 2/6, 1/4). It has been assumed in most of the studies that atoms in $D0_{19}$ type phases are located at regular cph positions as given by Pietrokowsky for Ti_3Sn phase [8]. Gehlen [9] has reported first time that the position of titanium atoms in a single crystal of the Ti_3Al phase is slightly displaced from the sites they would occupy in regular cph lattice. This has resulted in very large changes in the intensities of some of the superlattice peaks. Later, Banumathy et al. [10] have observed displacement of titanium atoms in a series of binary Ti–Al alloys (Ti–20Al, Ti–25Al and Ti–30Al) having single Ti_3Al phase. They have related this to the presence of symmetry elements in the $D0_{19}$ structure, which in turn allow local shift due to different site occupancies resulting in different atomic potentials. The shift in Ti positions changes the Ti–Ti and Ti–Al first neighbor bond lengths within and out of the plane and also the size of tetrahedron.

The presence of small shift may affect the physical properties of the A_3B alloys [11]. As an example, the sudden drop in the magnetic susceptibility in the Ti_3Al composition range may be explained by the presence of clusters [12]. The tighter bonding of titanium atoms in tetrahedron may result in broadening of titanium band. This in turn introduces a large change in the density of states corresponding

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Table 1
Structure of A_3B ($B8_2$) ($D0_{19}$) and A_2B phases.

A_3B phase: hexagonal (prototype Ni_3Sn)					
$P6_3/mmc$ or D^4_{6h}; 8 atoms per unit cell					
hP8					
Atomic positions					
Atoms	Wyckoff notation	Symmetry	*x*	*y*	*z*
Sn	2(c)	$\bar{6}$m2	1/3	2/3	1/4
Ni	6(h)	mm2	x	2x	1/4
A_2B phase: hexagonal (prototype Ni_2In)					
$P6_3/mmc$ or D^4_{6h}; 6 atoms per unit cell					
hP6					
Atomic positions					
Atoms	Wyckoff notation	Symmetry	*x*	*y*	*z*
Ni1	2(a)	$\bar{3}$m	0	0	0
In	2(c)	$\bar{6}$m2	1/3	2/3	1/4
Ni2	2(d)	$\bar{6}$m2	1/3	2/3	3/4

to the drop in magnetic susceptibility. In addition, the determination of the small shift along with the site occupancy will be helpful to calculate accurately the energy of planar faults in these alloys. On the other hand, the Wyckoff positions of A_2B (Ti_2Sn and Ti_2Ga) phase are fixed and no such shift is possible. The site occupancy can vary according to the individual phase composition. However, the degree of order and corresponding site occupancy in turn affect the mechanical properties [13].

Thus the aim of present work is to study the structure of $D0_{19}$ phase and related atomic shift of titanium atoms in Ti–Sn and Ti–Ga systems in the presence of A_2B phase using Rietveld refinement of X-ray diffraction (XRD) data [14]. The site occupancies of both the A_3B and the A_2B intermetallics in Ti–Sn and Ti–Ga systems have also been refined using analyzed individual phase compositions in the initial models.

2. Experimental

600 g pancakes of two alloys with nominal compositions Ti–25Sn and Ti–25Ga were prepared by non-consumable vacuum arc melting technique under a partial pressure of argon (400 mm Hg) with a tungsten electrode. The melting was repeated six times to ensure chemical homogeneity. The analyzed compositions of Ti–25Sn and Ti–25Ga were found to be Ti 73.2, Sn 26.8 and Ti 72.4, Ga 27.6 (atom%), respectively. The small pieces of the alloys were homogenized at 1000 °C for 24 h and water quenched. The powders of homogenized alloys were made by filing and then subjected to stress relieving treatment at 400 °C for 100 h.

The microstructures of the as-cast and homogenized alloys were initially examined using an optical and scanning electron microscopes (OM and SEM). The specimens for OM and SEM observations were prepared following standard metallographic techniques used for titanium and its alloys and etched with Kroll's reagent (5 ml HF, 10 ml HNO_3 and 85 ml H_2O). The chemical compositions of the constituent phases were obtained by the electron probe microanalyser (EPMA; model: SX100, Ms Cameca) and given in Table 2. The X-ray diffraction (XRD) patterns of as-cast (bulk) and powders (homogenized) specimens were recorded by a Philips PW3020 diffractometer equipped with a graphite monochrometer operated at 40 kV and 25 mA in a step size of 0.015° (2θ) and counting time of 5 s/step. XRD data of powders were subjected to the Rietveld refinement program using Philips XPert plus software. The volume fractions of the corresponding phases have also been obtained from XPert plus software after Rietveld refinement.

Table 2
Chemical compositions of individual phase in homogenized condition.

Alloy	Stoichiometry	Ti–Sn (atom%)		Ti–Ga (atom%)	
		Ti	Sn	Ti	Ga
Dark phase	A_3B	74.1	25.9	75.1	24.9
Bright phase	A_2B	66.4	33.6	67.9	32.1

3. Results and discussion

The optical and back scattered electron (BSE) SEM micrographs of the both the binary alloys in as-cast condition are shown in Fig. 1. This clearly displays the presence of two phase microstructure. The XRD patterns of these alloys also reveal the presence of two phases namely Ti_3Sn, Ti_2Sn and Ti_3Ga, Ti_2Ga in Ti–Sn and Ti–Ga samples, respectively (Fig. 2). This indicates that the compositions of the experimental alloys have shifted to two phase field which is in agreement of the analyzed overall compositions.

The optical and BSE SEM micrographs of homogenized alloys are shown in Fig. 3 that also exhibit the presence of two phases as observed in as-cast alloys. The chemical compositions of the individual phases in homogenized condition are given in Table 2. XRD patterns of the powders of the homogenized and stress relieved alloys also confirm the presence of above mentioned two phases (Figs. 4 and 5). These XRD patterns have been subjected to Rietveld refinement using Philips XPert plus software. The analyzed chemistry of individual phases in experimental alloys has been used to model site occupancy. No vacant sites are allowed during refinement.

The analyzed composition of Ti_3Sn phase indicates only one possibility of site occupancy. The 2(c) sites are occupied by Sn and 6(h) sites are occupied by Ti atoms. Since the composition of Sn is higher than 25 atom% in Ti_3Sn phase, the excess Sn atoms tend to occupy on 6(h) sites. The analyzed chemistry of Ti_2Sn displays Sn atoms more than 33.3 atom%. As a result, this exhibits following three possibilities of site occupancies.

(1) The 2(a) and 2(d) sites are occupied by Ti atoms while 2(c) sites are occupied by Sn atoms. The excess Sn atoms are occupied on 2(a) sites.
(2) The 2(a) and 2(d) sites are occupied by Ti atoms while 2(c) sites are occupied by Sn atoms. The excess Sn atoms are occupied on 2(d) sites.
(3) The 2(a) and 2(d) sites are occupied by Ti atoms while 2(c) sites are occupied by Sn atoms. The excess Sn atoms are equally distributed on both the 2(a) and 2(d) sites.

The refinement has been carried out for both the Ti_3Sn and Ti_2Sn phases by fixing the space groups and corresponding Wyckoff positions. The occupancies of Ti and Sn atoms are used for the initial model of Ti_3Sn and three models of Ti_2Sn phases as mentioned above. The results show that a combination of initial model of Ti_3Sn phase with the structure model 3 of Ti_2Sn phase exhibits smallest value of goodness of fit (GOF) indicating best solution for refinement. It is to be mentioned here that a smallest value of GOF with the correct chemistry of constituent phases results in best solution of the refinement. Hence, this represents the right choice of site occupancy for both Ti_3Sn and Ti_2Sn phases in present experimental alloy. This also indicates that models 1 and 2 of the Ti_2Sn phase do not result in best solution for refinement. Consequently, these models do not have the right choice of site occupancy. The important refinement parameters such as residual profile (Rp), residual weighted profile (Rwp), residual expected profile (Rexp), GOF and corresponding lattice parameters of both the phases for the best solution are given in Table 3. The volume fractions of Ti_3Sn and Ti_2Sn phases are approximately 84.0% and 16.0%, respectively.

The analyzed chemistry of Ti_3Ga phase of the present alloy also indicates only one possibility of site occupancy. The 2(c) and 6(h)