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On the ternary Laves phases $\{Sc,Ti\}_2M_3Si$ (M = Cr, Mn, Fe, Co, Ni) with $MgZn_2$-type

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Abstract

$\{Sc,Ti\}_2M_3Si$ alloys (M = Cr, Mn, Fe, Co, Ni) were investigated by X-ray powder and single crystal diffraction, optical microscopy and electronic density-functional theory. Structure determination from X-ray CCD-data from a single crystal of Ti_2Co_3Si and Rietveld refinements of X-ray powder diffraction data for Sc_2M_3Si (M = Fe, Co) and Ti_2M_3Si (M = Cr, Mn, Fe, Co, Ni) revealed in all cases isotypism with the C14 $MgZn_2$-type Laves phase: Sc (or Ti) atoms fully occupy the 4f sites, whereas M and Si atoms share the 6h and 2a sites in various ratios, in good agreement with ab inito results. Furthermore, the series of enthalpies of formation for these compounds as well as for the two binary intermetallics, $ScFe_2$ and Sc_5Si_3, have been calculated to compare with available calorimetric data for multicomponent-alloys design. The enthalpy of formation of Ti_2Fe_3Si of -55.9 ± 1.6 kJ/mol of atoms measured in an isoperibolic calorimeter agrees well with the calculated value of -52.6 kJ/mol of atoms. The chemical instability of "Sc_2Cr_3Si" with the $MgZn_2$-type structure was theoretically confirmed by the calculation considering the competing phases in equilibrium. The general trends of thermodynamic stabilities versus atomic number of M were discussed for $\{Sc,Ti\}_2M_3Si$. Our structural models confirm the fact that M/Si substitution of 16.7 at.% Si in the binary Laves phase stabilizes for all these ternary compounds a $MgZn_2$-type structure irrespective of the crystal structure of the binary parent Laves phase. Finally, spin-polarized calculations for four selected compounds ($ScFe_2$, Sc_2Fe_3Si, $TiFe_2$, Ti_2Fe_3Si) indicate a significant drop of the local magnetic moment of Fe upon substitution of Fe by Si.

Keywords: Transition metal alloys and compounds; Crystal structure; Enthalpy; Calorimetry; Computer simulations

1. Introduction

The technological and scientific importance of silicon containing Laves phases serves as a basis for continuous scientific interest. A number of early studies [1–12] are concerned with the Laves phases in the ternary systems {Sc,Ti}–M–Si (M = Cr, Mn, Fe, Co, Ni). The stabilization of the Laves phases with $MgZn_2$-type structure by metal–silicon substitution was attributed to a reduction of the effective electron concentration [12]. Particular interest was devoted to the composition $\{Sc,Ti\}(M_{0.75}Si_{0.25})_2$ for which an ordered variant of the $MgZn_2$-type structure (Mg_2Cu_3Si-type) was frequently reported [4,11,10]. Recently, excellent mechanical characteristics [13], magnetic and electrical properties [14,15] of $\{Sc,Ti\}(M_{1-x}Si_x)_2$ Laves phases provided a stimulus for material researchers for detailed investigation of the phase diagrams and the crystal structure of these phases [14,16–18]. Despite of the achievements obtained, some contradictions can be found. For example, Ti_2Ni_3Si with $MgZn_2$-type was found in alloys annealed at 750 [5], 1000 [1] and 1100 °C [2,17], as well as in specimens prepared by a laser cladding process, but no Laves phase was claimed to exist in the 900 °C isothermal section of Ti–Ni–Si [16]. Early studies of the scandium silicides report that Sc_2Co_3Si [10] and Sc_2Fe_3Si [11] crystallize in the Mg_2Cu_3Si-type structure, which is a superstructure of $MgZn_2$ with an ordered distribution of Fe and Si in the 2a and 6h sites, respectively. But a recent detailed reinvestigation of Sc_2M_3Si (M = Fe, Co, Ni) shows that M and Si atoms are randomly distributed in the 6h and 2a sites [14]. Sc_2Fe_3Si is the only compound for which all crystallographic properties are reported [14]. However, crystallographic data on Laves phases

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$\{Sc,Ti\}_2M_3Si$ (M = Cr, Mn, Fe, Co, Ni) are still incomplete as in most cases only lattice parameters were reported. Therefore, the purpose of the present work is to provide a detailed structural investigation of $\{Sc,Ti\}_2M_3Si$ (M = Cr, Mn, Fe, Co, Ni) in order to establish the crystallographic parameters and the atom site preference. Furthermore, phase stabilities will be evaluated by first principles ab initio ground-state energy calculations backed by drop calorimetry providing heat of formation for Ti_2Fe_3Si.

2. Experimental details

Alloy specimens (1 g each) were prepared by argon arc melting on a water-cooled copper hearth in Ti-gettered argon from elemental ingots with a minimal purity of 99.9 wt.%. Each alloy was re-melted twice or three times to homogenize the composition. Weight losses were less than 0.1%. For Ti_2Mn_3Si, a slight excess of Mn was used to allow for evaporation during fusion. A part of each alloy was sealed in a quartz tube under vacuum and was annealed at 800 °C (for 14 days, Sc_2M_3Si), 900 °C (for 10 days, Ti_2M_3Si), 950 °C (for 7 days, Ti_2M_3Si) or 1000 °C (for 4 days, Ti_2M_3Si) prior to quenching in cold water. X-ray powder diffraction data from as-cast and annealed alloys were collected employing a Guinier–Huber image plate system with Cu $K\alpha_1$ ($8° < 2\theta < 100°$). Precise lattice parameters were calculated by least-squares fits to the indexed 4θ-values employing Ge as internal standard ($a_{Ge} = 0.5657906$ nm). X-ray powder diffraction data for the determination of structural parameters were collected on a Siemens D5000 instrument with Cu $K\alpha_{1,2}$ ($10° < 2\theta < 110°$, step $\Delta 2\theta = 0.02°$) equipped with a secondary monochromator. For Rietveld refinements, we employed the FULLPROF program [19]. A single crystal fragment was isolated from the as cast alloy of Ti_2Co_3Si. Inspection on an AXS-GADDS texture goniometer assured high crystal quality, unit cell dimensions and Laue symmetry of the specimens prior to X-ray intensity data collection on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite monochromated Mo Kα radiation (λ = 0.071073 nm). Orientation matrix and hexagonal unit cell parameters were derived using the program DENZO [20]. No special absorption corrections were necessary because of the rather regular crystal shape and small dimensions of the investigated specimen. The structure was determined and refined with aid of the SHELXS-97, SHELXL-97 programs [21].

The heat of dissolutions of the alloys $Ti_{0.33}Fe_{0.50}Si_{0.17}$ as well as of pure Fe and Ti were measured using an isoperibolic calorimeter by dropping the solid samples at room temperature (i.e. 298 K) into liquid aluminium at a temperature of 1409 ± 5 K. Experimental techniques and the method of evaluation of the integral enthalpy of formation of liquid dilute alloys (referring to standard temperature, 298.15 K) were described in our previous paper [22]. The value for the enthalpy change upon heating of pure aluminium from room temperature to 1409 ± 5 K ($\Delta H^{1409}_{298,Al}$) was taken from the SGTE data for pure elements [23]. Note, that this value is required for determination of a calibration factor (heat equivalent) of the calorimeter used as well as for evaluation of standard heat of formation of intermetallics investigated.

For ab initio density functional theory calculations of the compounds Sc_2M_3Si and Ti_2M_3Si (M = Cr, Mn, Fe, Co, Ni) we used the Vienna ab initio simulation package (VASP) [24–26] with the projector augmented wave potential (PAW) [27,28] construction. An overall energy cutoff of 400 eV was chosen. For the exchange correlation functional, the generalized gradient approximation (GGA) of Perdew and Wang [29] was applied. Brillouin-zone integrations were performed for suitably large sets of special k points according to Monkhorst and Pack [30]. In all calculations, structural parameters are optimized. For some selected cases, spin-polarized calculations were performed by the approach of Vosko et al. [31]. Enthalpies of formation have been calculated by the standard procedure described in our previous publication [32] as the difference between the total energy of the considered compounds and the sum of the energies of the equilibrium bulk phase of the pure constituents at their specific ground states. Therefore, the equilibrium ground-state energy of the pure bulk phases of diamond Si, hcp-Sc and α-Ti, bcc-Cr, ferromagnetic bcc-Fe, ferromagnetic hcp-Co and ferromagnetic fcc-Ni were also calculated. It should be noted that the derived DFT data correspond to 0 K. Because of the complicated magnetic ground state of bulk Mn (γ-Mn), we apply a correction of 1.6 kJ/mol of atom [33] to our calculated energy of antiferromagnetic γ-Mn [34] to obtain the true ground-state energy of α-Mn.

3. Experiment results and discussion

3.1. Formation, crystal structure and site preference in Sc_2M_3Si

In agreement with earlier data [35], no Laves phase was found in an annealed alloy Sc_2Cr_3Si by X-ray powder diffraction. The existence of a Laves phase with $MgZn_2$-type structure was confirmed in annealed (800 °C) specimens Sc_2M_3Si for M = Mn, Fe, Co, Ni, however, samples with Mn and Ni were found to be multiphase and therefore no quantitative crystallographic analysis was performed. Although the isothermal section of Sc–Mn–Si at 800 °C [35] reports a single-phase Sc_2Mn_3Si, our alloy "Sc_2Mn_3Si", annealed at 800 °C, consists of $MgZn_2$-type Laves phase ($a = 0.50079(2)$ nm; $c = 0.81770(8)$ nm) and secondary Sc_5Si_3 (space group: $P63/mcm$, $a = 0.78643(4)$ nm; $c = 0.5743(1)$ nm). The lattice parameters obtained are close to those reported by Ref. [36] for $Sc(Mn_{0.75}Si_{0.25})_2$ (see Table 1; Fig. 1). Sc_2Ni_3Si is a ternary Laves phase [10,11,14]. X-ray diffraction and EPMA of the alloy annealed at 800 °C revealed that this composition is a mixture of Laves phase with $ScNi_2$ ($MgCu_2$-type; space group: $Fd\bar{3}m$, $a = 0.69404(1)$ nm) and G phase (Th_6Mn_{23}-type; space group: $Fm\bar{3}m$, $a = 1.22265(2)$ nm).

Sc_2Fe_3Si and Sc_2Co_3Si annealed at 800 °C were found to be single phase with $MgZn_2$-type structure in good agreement with previous investigations [10,11,14]. Rietveld refinements (Table 2) confirm for both compounds the $MgZn_2$-type structure with a complete occupancy at the 4f sites by Sc atoms and a random distribution of Fe (or Co) and Si atoms at the 2a and 6h sites. Results on the lattice parameters and site preference for Sc_2Fe_3Si agree well with data in literature [10,11,14], and reasonable agreement was obtained for positional parameters (see Tables 1 and 2). In contrast to that, the crystallographic model with ordered distribution of the M and Si atoms in the 2a and 6h sites yielded high residual values and negative temperature factors (values in square brackets, Table 2) and thus was rejected.

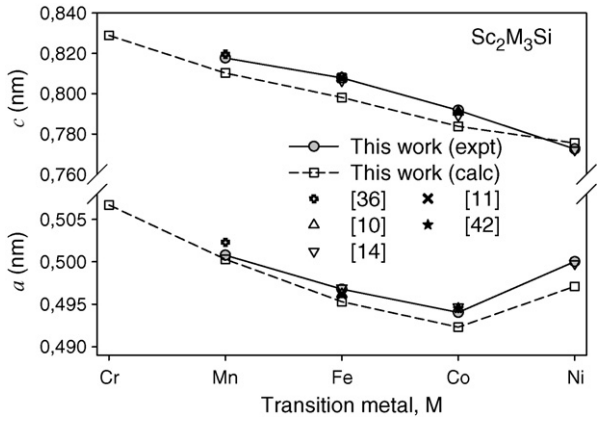

Fig. 1. Trends of calculated lattice parameters in Sc_2M_3Si (for configuration (ii)) vs. 3d transition metal M (M = Cr, Mn, Fe, Co and Ni) as compared to available experimental data.