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Ordering effects in the Re–W and Re–Ta sigma phases

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Abstract

The site occupancy in the Re–W and Re–Ta sigma phases is studied using a first-principles statistical thermodynamics approach. The factors which govern the stability of the sigma phase were analysed using selected supercells for total energy calculations. Cluster variation calculations in the tetrahedron approximation were performed to study the effect of composition and of finite temperature on the ordering phenomena in the sigma phase. The difference between the site occupancy of both Re–W and Re–Ta sigma phases is discussed.

Introduction

It is well known that the so-called Frank–Kasper (FK) phases can be geometrically described in terms of the basic coordination polyhedra CN12, CN14, CN15 and CN16 originally discussed by Frank and Kasper [1]. Among the FK phases, the Laves phases [2] are known to display a high degree of atomic order which is usually the result of a dominant size factor in driving their stability. Conversely, other FK phases like A15 or sigma phases satisfy the Goldschmidt–Hume Rothery’s rule, which makes their formation mostly electronically driven [2]. For these phases, it seems therefore of particular interest to investigate ordering processes which may take place as a function of temperature and composition. Moreover, we think that the existence of crystallographically inequivalent sites in the FK phases leads to ordering phenomena which are much more complex than those observed in simple underlying crystalline structures (such as fcc, bcc or hcp).

Among these complex phases, the sigma phase is known to have no definite stoichiometric composition and then one would not expect a complete atomic ordering in the sigma-phase alloys. The unit cell of this sigma structure contains 30 atoms; its space group is $P4_2/mnm$ and the corresponding Pearson symbol is tP30. In this tetragonal structure, there are five crystallographically different sites, commonly designated as A, B, C, D and E. The coordination shells around the various sites are either icosahedral (around A and D sites) or are of CN14 (around C and E sites) or CN15 (around B site) type. An empirical analysis based on x-ray

and neutron diffraction studies in many transition metal binary and ternary alloys [3] indicates that the elements to the left of the Mn column in the periodic table prefer the CN15 positions. The elements to the right of Mn prefer the CN12 positions, and either kind or mixtures occupy the CN14 positions.

Very recently [4] we showed that for a pure transition metal, the percentage of icosahedral sites of the most stable FK structures is related to the d-band filling. This result was obtained by comparing first-principles calculated total energies for bcc, fcc, hcp, A15, sigma and chi structures and for Nb, Mo, Tc, Ru, Ta, W, Re and Os metals.

To attack the alloying problem and the effect of partial disorder on the stability of the sigma phase, one of us [5] has proposed to couple first-principles total energy calculations with a thermodynamic variational method. More particularly this approach allows us to study the site occupancy of the sigma phase as a function of temperature and composition.

We decided to apply this theoretical approach to the Re–W and Re–Ta sigma phases. The main motivation is that the Re–W sigma phase displays a wide range of composition in the Re–W system while the Re–Ta sigma phase exists only at high temperatures and in a very narrow range of composition (see figure 1). Then one can wonder if ordering phenomena which take place in the sigma phase as a function of composition and temperature are similar in the two systems.

In the following pages, we briefly review the formalism to compute the site occupancy in the sigma phase (section 1). Then in section 2 we show the results and an interpretation of these results is given.

1. General method

For a theoretical phase stability study, we can use an Ising model for which the energetics associated with changing local atomic configurations is parametrized by a set of effective cluster interactions (ECIs). Total energies of a large number of configurations are used to extract these ECIs following the Connolly–Williams method (CWM) [6]. The five inequivalent sites of the sigma phase make $2^5 = 32$ possible distributions of Re and W (or Ta) atoms. As reported previously [5], these 32 configurations are not superstructures of the sigma phase because they all have the same space group symmetry. In addition, 10 sigma superstructures were considered that allowed us to determine the pair interactions between sites of the same type (i.e. B–B, C–C, D–D and E–E type pairs).

1.1. Total energy calculations

Total energies of the 42 configurations were computed using the Vienna *ab initio* simulation program (VASP) [7] which is based on the following principles.

A finite-temperature density-functional approximation is used to solve the generalized Kohn–Sham equations with an efficient iterative matrix diagonalization scheme based on a conjugate gradient technique and optimized density mixing routines. Within this framework, the free energy is the variational functional and a fractional occupancy of the eigenstates is allowed, which eliminates all instabilities resulting from level crossing and quasi-degeneracies in the vicinity of the Fermi level in metallic systems.

The exchange-correlation functional given by Ceperley and Alder is used in the parametrization of Perdew and Zunger [8]. Non-local exchange-correlation effects are considered in the form of generalized gradient corrections (GGCs). We use the Perdew–Wang functional [9]. The GGCs are applied self-consistently in the construction of the pseudopotentials as well as in the calculations of the Kohn–Sham ground state. The calculations

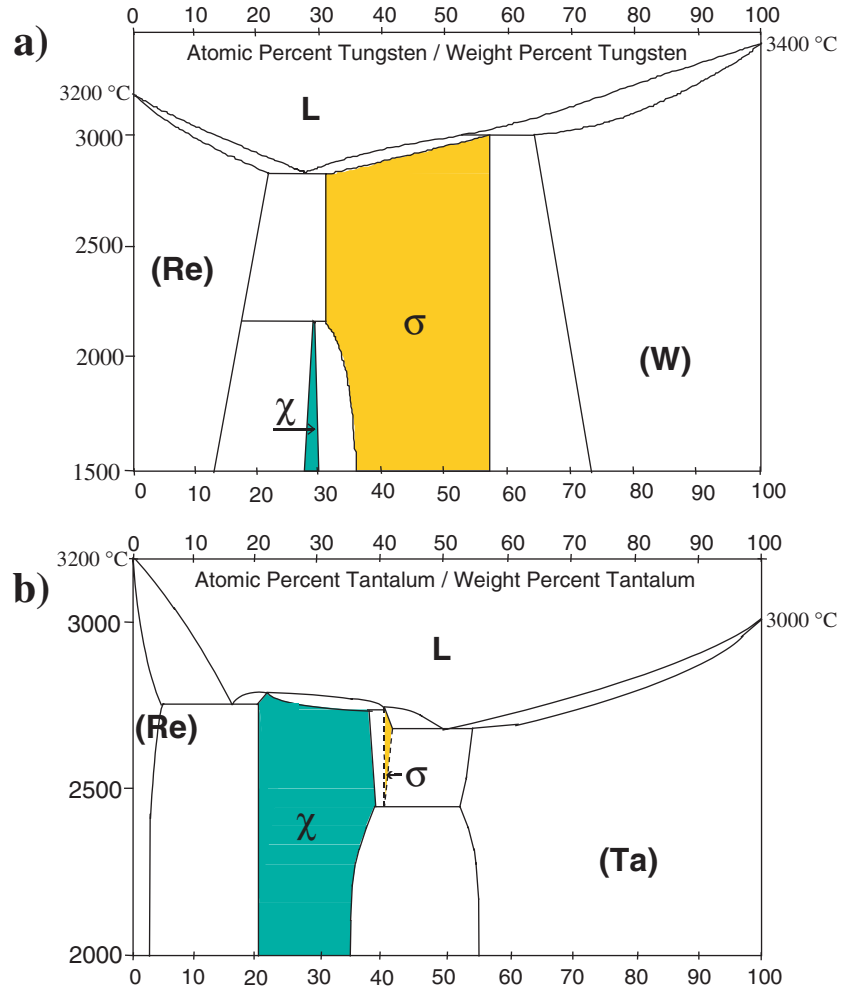


Figure 1. Phase diagrams of (a) Re–W and (b) Re–Ta systems.

are performed using fully non-local optimized ultra-soft pseudopotentials [10] allowing small energy cut-offs which are 193.9, 174.6 and 188.2 eV for Re, Ta and W, respectively. Integrations in reciprocal space use 18k points in the irreducible Brillouin zone.

The a and c parameters of the tetragonal unit cell and the internal coordinates of the five inequivalent sites were optimized for all configurations using a conjugate gradient method [7].

1.2. Effective cluster interactions

Formation energies E_{form} are extracted from the total energies E_{tot} by subtracting the concentration weighted total energies of pure Re and W (or Ta) with the sigma structure. Thus, the formation energies of the 42 configurations are used to obtain ECIs by means of a Connolly–Williams procedure [6]. The ECI V_i for a cluster i is calculated with

$$\sum_{\alpha} \omega^{\alpha} \left(E_{\text{form}}^{\alpha} - \sum_{i=1}^n V_i \xi_i^{\alpha} \right)^2 = \min \quad (1)$$

where ξ is the cluster correlation function as defined in equation (10) of [11], ω represents the weight assigned to each structure. Equation (1) was solved using a singular value decomposition (SVD) procedure. As in the spirit of [12], the sets of equations corresponding to thermodynamically stable structures were given more weight than the equations pertaining to unstable structures. The weighting in the SVD procedure provides an alternative to the linear optimization technique for ensuring that the cluster expansion reproduces the proper sequence of the energy of structures. An additional benefit of weighting the lowest energy states more heavily in the CWM method is that a much more rapid convergence of the cluster expansion is obtained.

At finite temperatures, the configurational entropy and the associated Helmholtz free energy are calculated as a function of composition and temperature within the tetrahedron approximation of the CVM. The site occupancy of the five inequivalent sites is also determined in this calculation. The tetrahedron approximation is a natural choice since the sigma phase is tetrahedrally close packed. For this structure, the tetrahedron approximation gives 17 tetrahedron maximal clusters and a total of 71 correlation functions.

2. Results and discussion

2.1. Determination of the effective cluster interactions

The formation energies of the 42 configurations were calculated with a full geometry relaxation including the optimization of the a and c parameters of the tetragonal unit cell as well as the optimization of the internal atomic coordinates. In table 1 are given the optimized a , c and internal coordinates for pure Re, W and Ta. All these values are very close together showing that the relaxation effects are very weak in these systems and will have no consequence on the study of the thermodynamically stable configurations as discussed in [13].

Table 1. Optimized internal coordinates and cell parameters in the sigma phase for pure Re, W and Ta. Sites are given by their Wyckoff position and the corresponding general coordinates.

Site	Coordinates	Relaxed Re- σ values	Relaxed W- σ values	Relaxed Ta- σ values
A 2(a)	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0
B 4(f)	$x, x, 0$	$x = 0.405$	$x = 0.400$	$x = 0.395$
C 8(i)	$x, y, 0$	$x = 0.463, y = 0.135$	$x = 0.467, y = 0.133$	$x = 0.466, y = 0.128$
D 8(i)	$x, y, 0$	$x = 0.738, y = 0.066$	$x = 0.742, y = 0.060$	$x = 0.740, y = 0.067$
E 8(j)	x, x, z	$x = 0.183, z = 0.251$	$x = 0.188, z = 0.252$	$x = 0.182, z = 0.251$
Cell parameters		$a = 9.558 \text{ \AA}$ $c = 4.970 \text{ \AA}$	$a = 9.779 \text{ \AA}$ $c = 5.085 \text{ \AA}$	$a = 10.175 \text{ \AA}$ $c = 5.291 \text{ \AA}$

As explained in section 1, a singular value decomposition was used to extract 29 and 27 effective interactions for the Re–W and Re–Ta systems, respectively. These interactions are the empty cluster, five single-site terms, 18 pair terms, four triplet terms and one quadruplet term for Re–W system. For Re–Ta system, pair terms and triplet terms are 17 and 3 in number, respectively. For multi-site terms, we used A, B, C, D and E site labels to indicate what kind of sites belong to the multiplet. In table 2 are given the values of these interactions, a positive sign of a single-site term means a Re preference on this site while positive pair interactions favour Re–W or Re–Ta heteroatomic pairs. These interactions reproduced the formation energies with a root mean square error of 0.06 kJ mol^{-1} . This error is well within the precision of the total energy calculations and is much smaller than the smallest difference between the

Table 2. Values of the 29 and 27 effective cluster interactions (in K) for Re–W and Re–Ta systems, respectively; degeneracy is given in parentheses.

Sites	A (2)	B (4)	C (8)	D (8)	E (8)	
Re–W	111	–491	–736	100	–900	
Re–Ta	60	–1375	–2231	–236	–1801	
Pairs	AD (8)	AE (8)	AB (8)	DD (4)	DC (8)	DC (8)
(distance)	(2.94 Å)	(3.14 Å)	(3.26 Å)	(3.01 Å)	(3.06 Å)	(3.07 Å)
Re–W	70	95	51	128	194	135
Re–Ta	293	–15	300	158	258	257
Pairs	DC (16)	DE (16)	DE (16)	BC (8)	BB (2)	BD (16)
(distance)	(3.10 Å)	(3.15 Å)	(3.18 Å)	(3.02 Å)	(3.19 Å)	(3.35 Å)
Re–W	342	499	–138	210	–53	79
Re–Ta	948	–219	619	642.10	–155	304
Pairs	CC (4)	CE (16)	CE (16)	CC (16)	EE (4)	BE (8)
(distance)	(2.89 Å)	(3.45 Å)	(3.50 Å)	(3.54 Å)	(2.84 Å)	(3.53 Å)
Re–W	71	332	–45	–65	353	–14
Re–Ta	349	843	–268	85	882	—
Triangles and tetrahedron	ABD (16)	BDE (16)	BDC (16)	DEC (16)	AEBD (16)	
Re–W	39	50	–106	–194	–74	
Re–Ta	6	155	49	—	144	

formation energies of any of the 42 configurations used in the CWM (see figure 2). Further proof that these interactions accurately represent first-principles calculated formation energies is obtained by computing the predictive error [12]. The predictive error was found to be about 0.3 kJ mol^{-1} , which is very small (see figures 1 and 2) in comparison to the range of the formation energies which are about $15\text{--}25 \text{ kJ mol}^{-1}$.

2.2. Site occupancy

The interactions were used to compute the site occupancy, entropy and Helmholtz free energy of the sigma phase as a function of temperature and composition within the tetrahedron approximation of the cluster variation method.

Figure 2 shows also the site preference at zero temperature. Following the most stable configurations from pure Re towards pure W (or Ta) composition, it is seen that first the B site takes W (or Ta) content, followed sequentially by the E and C sites and finally by the A and D sites. However, some differences exist between Re–W and Re–Ta systems; they are more evident in figures 3 and 4 which show the site preference for both the systems at a low temperature, namely $T = 500 \text{ K}$.

The first difference is that the site occupation sequence is much more pronounced in the Re–Ta system than in the Re–W system. In Re–Ta, the C and D sites start to take Ta content when the B site is fully filled while in the Re–W system, a non-negligible overlap exists especially between the filling of the B site and the E site.

The second difference concerns the filling of the A and D sites. In the Re–W system, this filling increases monotonically for both sites. However, in the Re–Ta system, towards the Ta side, the A site reverses its occupancy with the D site. This curious composition-dependent behaviour was also found in the Fe–Cr system. It can be explained in the context of the Ising-type Hamiltonian by a competition between the single-site and multisite interactions.

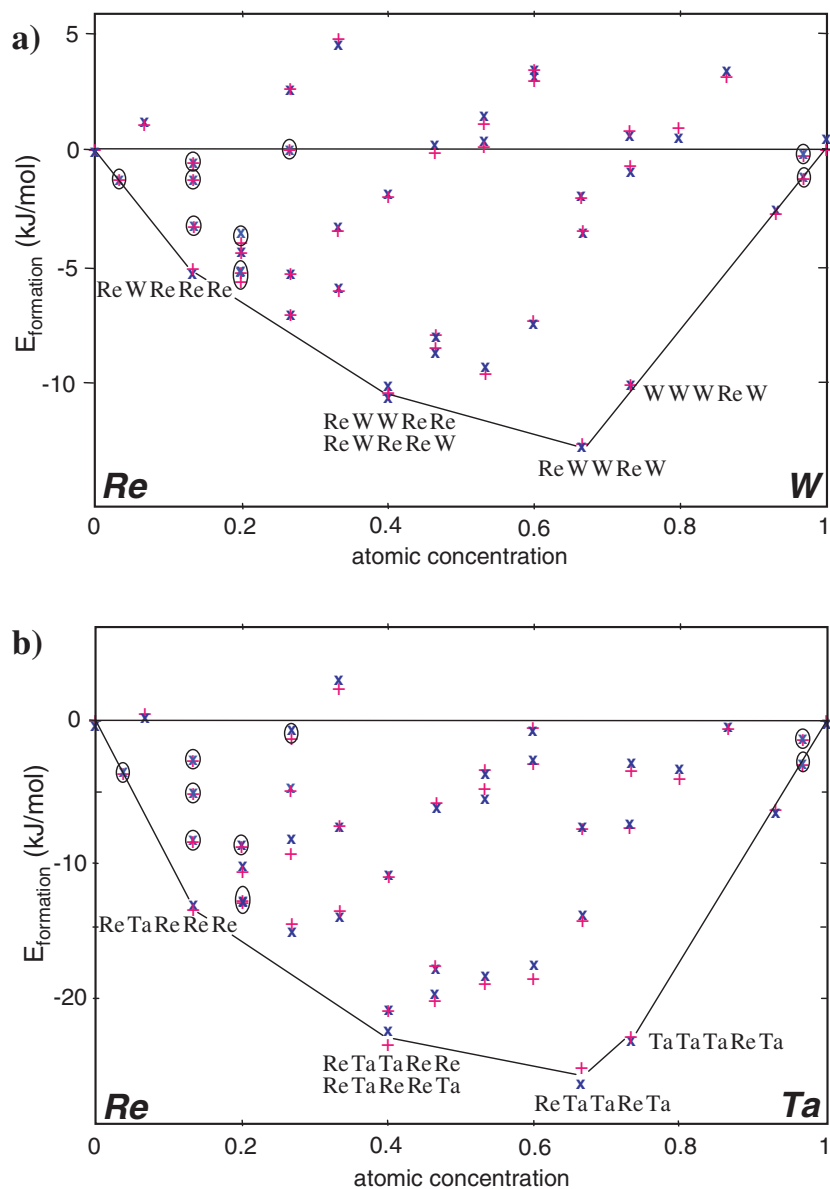


Figure 2. Formation energy (in kJ/atom) of (a) Re–W and (b) Re–Ta relaxed atomic configurations with the sigma structure as computed with VASP (+); as computed from the effective interactions (x). Circles indicate the 10 configurations that are sigma superstructures. The most stable configurations have been connected with a solid line and the occupancy of the A, B, C, D and E sites has been indicated.

In the Re–W system, the positive values of the single-site terms are similar for the A and D sites indicating a Re preference for both sites; in the Re–Ta system, the negative value of the single D site indicates a Ta preference while the positive value of the single A site indicates a Re preference. Thus, first the A sites take Ta content and once all the A sites are filled up the D sites must be filled. At this point, pair interactions play an important role because the

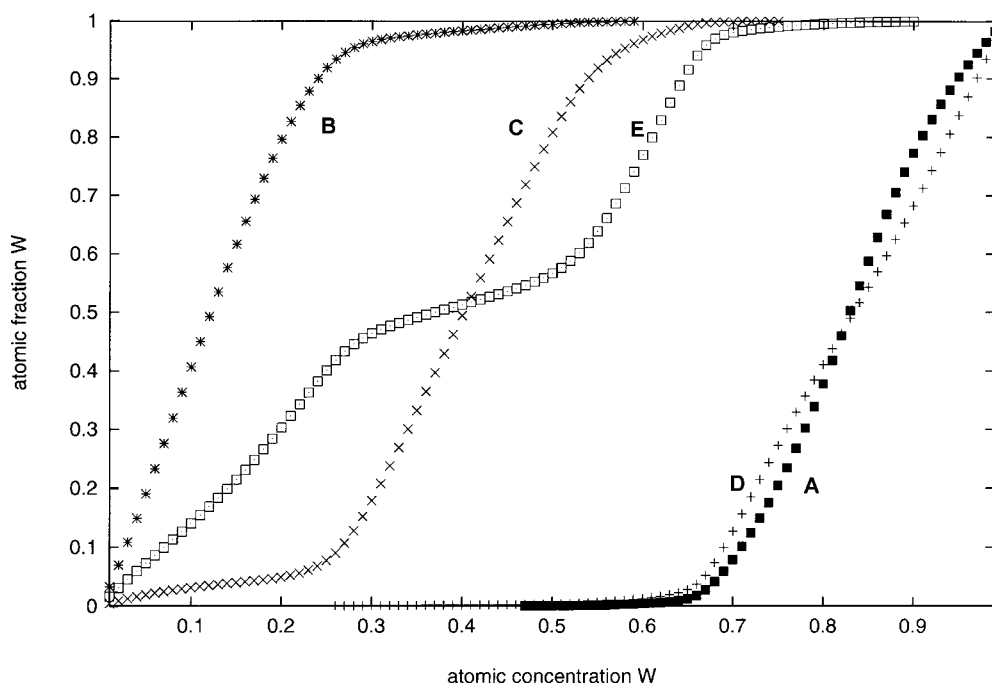


Figure 3. Computed occupancy of the inequivalent sites in the Re-W sigma phase at $T = 500$ K.

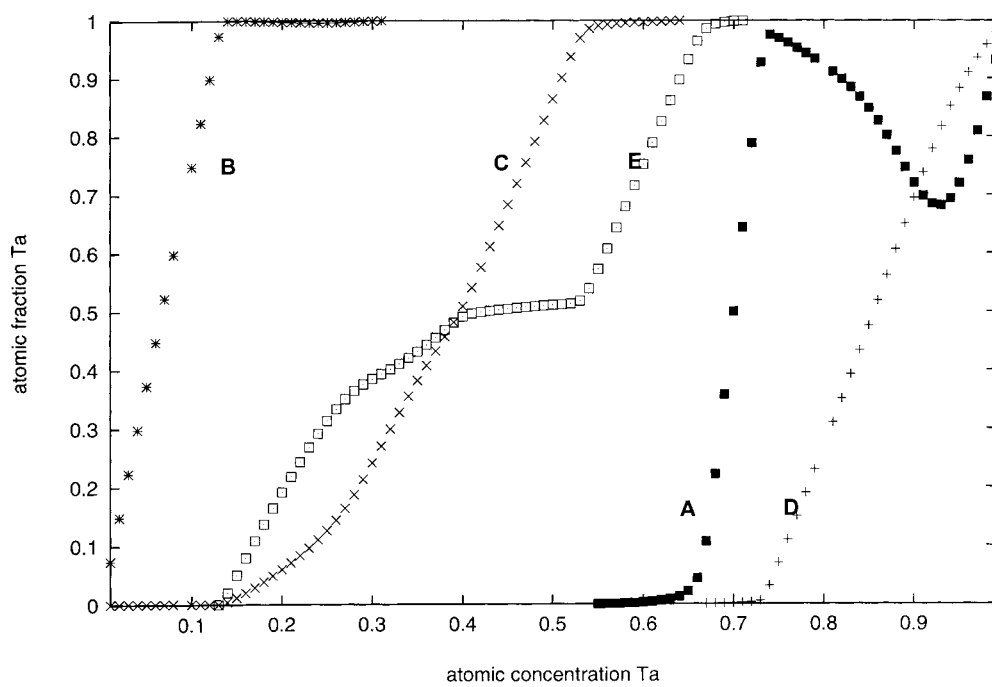


Figure 4. Computed occupancy of the inequivalent sites in the Re-Ta sigma phase at $T = 500$ K.

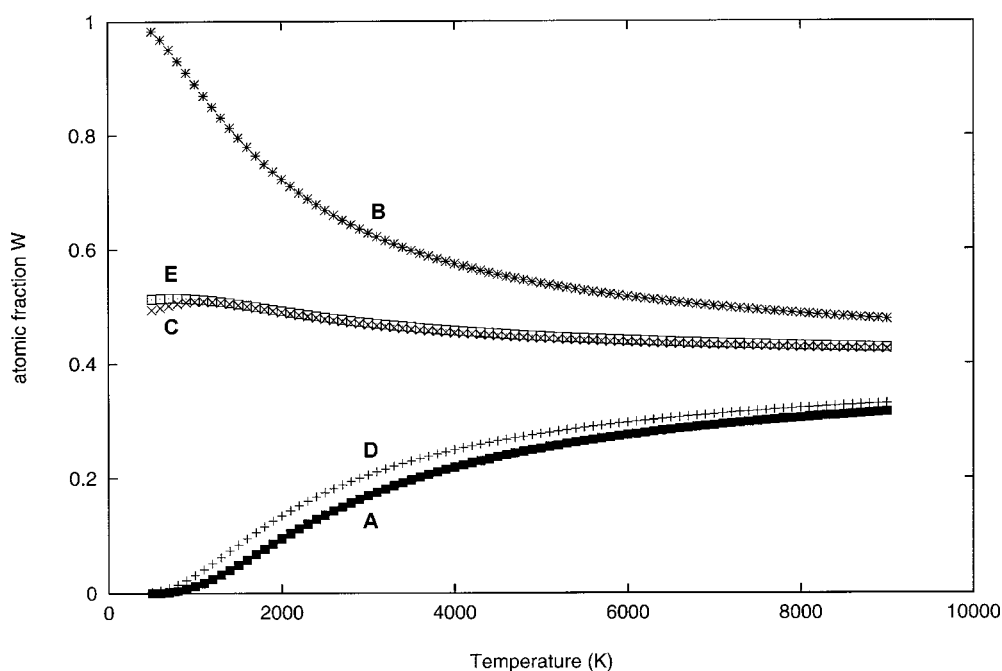


Figure 5. Computed occupancy of the inequivalent sites in the $\text{Re}_{0.6}\text{W}_{0.4}$ sigma phase as a function of temperature.

A site has four D nearest neighbours whereas the D site has only one A and one D nearest neighbour. From table 2, it is clear that Re–Re type pairs between A and D sites and D and D sites are energetically less favourable than Re–Ta type pairs. Thus, as Re occupation of the D sites leads to fewer Re–Re type pairs, this site becomes energetically more favourable than the A site. While the D sites get filled with Re, the A sites are reclaimed by Ta. Only when all the D sites have been filled can Re occupancy of the A sites increase again.

In the same way, the B–C–E sequence results from a competition between single-site and multisite interactions. Table 2 shows that the single-site interaction does not favour the B site occupation by W or Ta with respect to the C and E sites while it is the first one to take W or Ta occupancy according to figures 3 and 4. However, the pair interactions between two identical sites favour the B site occupancy by W or Ta while it is the opposite case for the E sites. The CC pairs are of mixed attractive and repulsive for Re–W system and have the same behaviour as EE pairs for Re–Ta system. Thus, both single-site and pair interactions contribute to the filling of the B site by Ta or W atoms while single-site and pair interactions have an opposite effect in the filling of the E sites by Ta or W atoms.

In figures 5 and 6, the site occupancy of both $\text{Re}_{0.6}\text{W}_{0.4}$ and $\text{Re}_{0.6}\text{Ta}_{0.4}$ alloys as a function of temperature is shown. At high temperatures, the site occupancy very slowly reaches the value corresponding to the random composition. This limit occupancy being determined purely by the alloy composition, in this case, the limit of each site is 60% Re. However, as already discussed previously [6], this limit is not reached because no order–disorder transformation due to the removal of symmetry elements in going to the chemically randomized configuration takes place.

The occupancy of B, A and D sites reaches the high temperature limit more rapidly in Re–W than in Re–Ta which is due to weaker effective interactions in Re–W system. In this

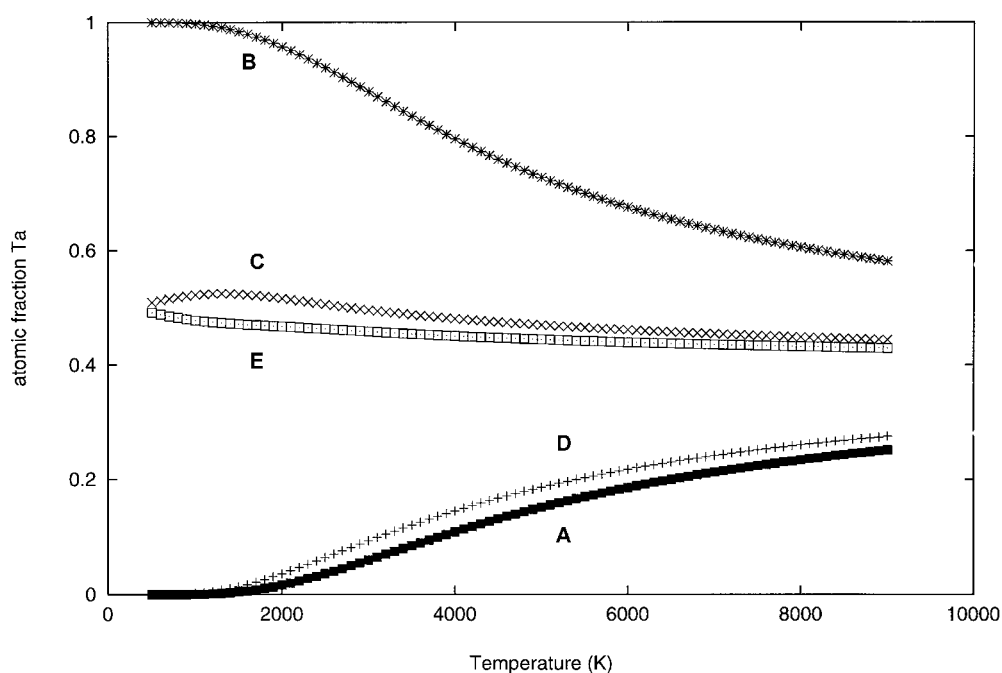


Figure 6. Computed occupancy of the inequivalent sites in the $\text{Re}_{0.6}\text{Ta}_{0.4}$ sigma phase as a function of temperature.

case the temperature effects on the ordering configuration are more pronounced. When the temperature is lowered, the fraction of W (Ta) on B sites increases to reach a total occupancy around 500 and 2000 K for Re–W and Re–Ta, respectively (see figures 5 and 6). Around the same temperatures, the A and D sites display an opposite behaviour which makes a Re occupancy of 100% on these sites.

For both alloys the C and E sites have the most mixed occupancy which is more or less independent of the temperature. These results may be used to predict composition limits for Re–W and Re–Ta sigma alloys.

2.3. Stability range

Since the C and E sites are half occupied in $\text{Re}_{0.6}\text{Ta}_{0.4}$, an ordered sigma phase might exist at sufficiently low temperature. The interactions in table 2 indicate that a structure which minimizes Ta–Ta nearest neighbours of E–E and C–C types would be favoured. Such a sigma structure can be easily found. However, even in the case of Re–Ta where the ECIs are strongest, the CVM indicates that such ordered structures can be more stable than the sigma phase itself at temperatures below 300 K only. As the Re–Ta sigma is not stable at such low temperatures, and as the ECIs in Re–W are weaker and would therefore give an even lower transition temperature, ordered sigma superstructures can be ignored safely.

At very low temperatures, for both systems, one may assume that the A and D sites are occupied only by Re, B sites only by W (or Ta) while C and E sites by a mixture of Re and W (or Ta); in this case the predicted limits of sigma phase existence are 13–66 at% W (or Ta). Thus, from these simple arguments it seems to be difficult to explain the different stability ranges observed in Re–W and Re–Ta systems. In fact, when addressing this problem it is

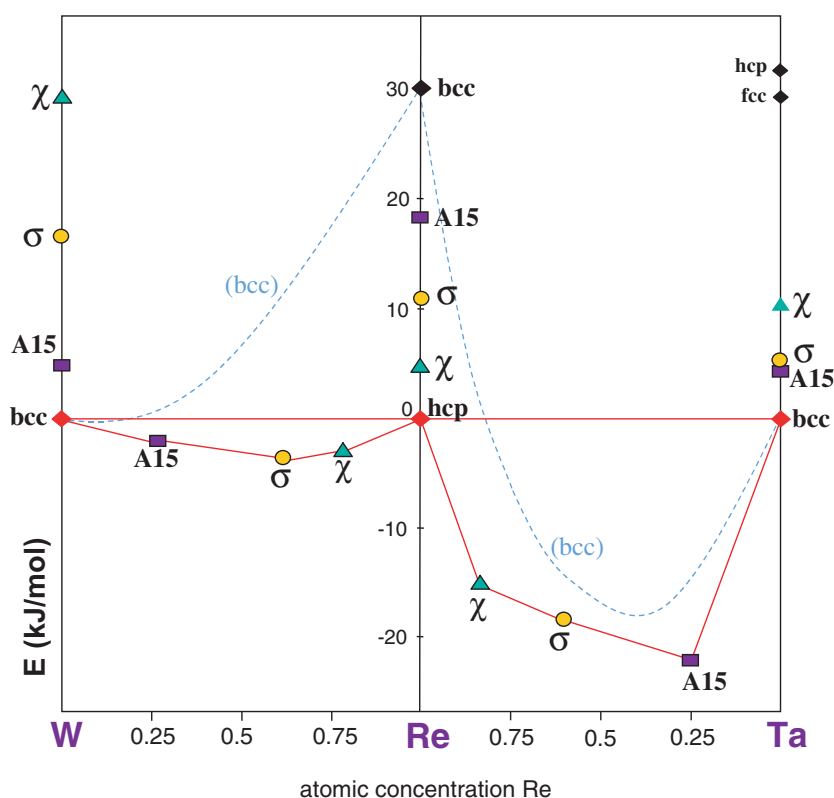


Figure 7. Calculated structural energy of sigma, chi, A15 phases and bcc solid solutions in the Re-W and Re-Ta systems.

necessary to study the competition between all the phases which occur in these systems and thus to calculate the phase diagram.

In the present work, we propose a first answer based on the analysis of the ground states in these systems as reported in figure 7. The first comment is that the obtained sequence for both the systems, namely bcc-A15-sigma-chi-hcp is in excellent agreement with the arguments of [4]. The second point is that the formation energies are markedly more negative in Re-Ta than in Re-W; note that this result could already be extracted from the data of table 2 and figure 2 which show that the alloying effects are much more important in Re-Ta than in Re-W. In addition, the disordered bcc solid solution derived from *ab initio* calculations [14] is also reported in figure 7 since the W (or Ta) rich part of the binary phase diagram is due to a strong competition between the bcc phase and the sigma phase at high temperatures (above 1000 K). For both the systems the disordered bcc solid solution is found less stable than the ground state structures at $T = 0$ K; in fact its range of stability in the equilibrium diagram is due to configurational entropy effects which can be approximated by $RT(x \ln x + (1-x) \ln(1-x))$. The sigma phase tends to have a lower configurational entropy than the bcc phase because the A, B and D sites have a strong site preference so that randomness is limited to the C and E sites, i.e. about half the total number of sites only.

Without performing a complete calculation of the phase diagram in both systems, we can already study the competition between the bcc solid solution and the sigma phase using these qualitative arguments. Indeed for the Re-Ta system, at 50% Ta the difference between

the solid solution and the sigma phase is very weak at $T = 0$ K, around 2 kJ/atom^{-1} . At high temperatures this difference is easily compensated by the entropic term which leads to a stabilization of the bcc solid solution. For Re–W, the situation is quite different since at 50% W, the difference between the solid solution and the sigma phase is roughly equal to 13 kJ/atom which cannot be compensated by entropic effects. Therefore, in the Re–W system, the sigma phase still exists at high temperature and in a wide range of composition.

3. Conclusion

We have investigated the site occupancy in the Re–W and Re–Ta sigma alloys using a first-principles statistical thermodynamics approach. In the context of this approach, the site occupancy of the five crystallographically inequivalent sites results from a competition between single-site and multisite interactions. A reversal in the site preference as a function of composition was observed in Re–Ta but not in Re–W. This peculiar behaviour was already found in Fe–Cr sigma alloys. Although this phenomenon might be common in complex FK structures, it depends also on the alloying effects displayed in these phases. Finally, the site occupancy is also used to determine the composition limits of the sigma alloys.

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