Some Predictions Concerning the Configurational Characteristics of the Vanadium—Cobalt Sigma Phase**

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A simple pair-wise interaction energy model has been used to examine the possible configurational characteristics of σ(V—Co) as a function of composition and temperature. Near-maximum order, essentially of classic sigma-phase form, with preferential occupation of sublattices I and IV by cobalt and II by vanadium, is predicted for all compositions at room temperature. The calculations indicate significant disordering on heating, with most rapid changes in the approximate temperature range 800–1 000 K, but with some order remaining up to the melting point. The model results are compared with published experimental indications of transformation in this phase.

(Keywords: Atomic order; Model; Sigma phase)

Einige Voraussagen bezüglich Konfigurations-Charakteristiken der Vanadium-Kobalt sigma-Phase

Es wird ein einfaches paarweises Wechselwirkungsenergiemodell zur Untersuchung möglicher Konfigurations-Charakteristiken von σ(V—Co) als Funktion von Zusammensetzung und Temperatur benutzt. Es wird nahezu maximale Ordnung (im wesentlichen von klassischer sigma-Phasenform) mit bevorzugter Besetzung der Untergitter I und IV durch Kobalt und II durch Vanadium für alle Zusammensetzungen bei Raumtemperatur vorhergesagt. Die Berechnungen lassen signifikante Unordnungen bei Erhitzen erwarten, wobei die raschesten Veränderungen im Temperaturbereich von 800—1 000 K zu erwarten sind, jedoch einige Ordnung bis zum Schmelzpunkt erhalten bleibt. Die Resultate des Modells werden mit experimentellen Hinweisen von Transformationen in dieser Phase verglichen.

Introduction

Indirect experimental evidence suggesting structural changes during heating or cooling has been reported for a few sigma phases [1–3]. In the case of σ(V—Co), for example, *Marcone* and *Coll* [3] have observed anomalous variations in hardness, dilatation and electrical resistivity when these were studied as a function of temperature and from this they have inferred the possibility of an order-disorder transformation. Structural studies of this phase [5] are confined to the establishment of its typical $D8_b$ structure and the composition dependence of its lattice parameters at room temperature; no experimental information is available concerning the distribution of the different atomic species in the structure. Thus it was considered to be of interest to examine the variations of atomic configurations within the phase which might be suggested by applying a simple pair-wise interaction model.

Although the sigma-phase structure consists of five sublattices, characterised by sites having *Kasper-Frank* co-ordination numbers of 12, 15, 14, 12 and 14 respectively, most models make the simplifying assumption that sublattices with the same co-ordination have the same species occupancy [5–7]. Such constrained "three sublattice" treatments have been found to provide an adequate basis for the description of thermodynamic properties [6, 7] and for the prediction of the general pattern of ordering characteristics [8] of the sigma phases. Experimental observations of atomic order in sigma phases generally confirm the tendency for preferential occupation of the C.N. 15 sites by "A" atoms and C.N. 12 sites by "B" atoms, with the C.N. 14 sites being more indifferent to their composition, as originally proposed by *Kasper* and *Waterstrat* [5]. However, acceptance of the detailed results would indicate that the occupancy of different sublattices of the same co-ordination number are not necessarily identical and that deviations representing greater or lesser order than the orthodox description of sigma may occur. This suggests that in any examination of configurational aspects of this structure it is desirable to employ an unconstrained model which permits discrimination between all five sublattices. The generalised version [9] of the pairwise interaction model is therefore used in the present examination of the possible composition- and temperature-dependence of the atomic arrangements in σ(V—Co). The model has been described in detail in previous publications, so only its essential features will be reiterated here.

Theoretical Treatment

Assuming that the different atomic species are randomly distributed *within* their chosen sublattices and that the enthalpy may be described by

the summation of pair-wise interaction energies over nearest-neighbours only, the free energy of the phase may be related to the lattice structure and site occupation parameters by the general expression

$$G = \frac{H_1}{2} \sum_{ij} L_i C_{ij} + \frac{H_2}{2} \sum_{ij} L_i C_{ij} (1 - P_i - P_j) + H_3 \sum_{ij} L_i C_{ij} (1 - P_i) P_j$$
$$+ RT \sum_i L_i [P_i \ln P_i + (1 - P_i) \ln (1 - P_i)] \tag{1}$$

Here L_i is the fraction of the total number of sites comprising the sublattice "i" and C_{ij} the number of "j" sublattice sites occurring in the first co-ordination shell of sublattice "i". In the present case, P_i and P_j are the fractional occupation of the "i" or "j" sublattices by Co. $H_1 = (H_{VV} + H_{CoCo})/2$, $H_2 = (H_{VV} - H_{CoCo})/2$ and $H_3 = H_{VCo} - (H_{VV} + H_{CoCo})/2$ where H_{VV}, H_{CoCo} and H_{VCo} are the pairwise interaction enthalpies for the respective like and unlike interactions. Invariant interaction values appropriate to the *average* co-ordination of the sigma phase are employed and it is assumed that the *variations* of entropy with temperature and composition are predominantly configurational in origin; that is, non-configurational excess entropies are implied to be relatively insensitive to the configurational state of the phase.

    Values for H_{VV} and H_{CoCo} were estimated using the heats of vaporisation [10] of the normal forms of the elements, heats of transformation [11] from their normal to sigma lattices and a weighted average co-ordination number of 13.47 for the sigma structure. H_{VCo} was determined from the experimental enthalpy of formation of $\sigma(V—Co)$ at 40 atom per cent Co and 1 473 K taken from a calorimetric study by *Spencer* and *Putland* [12]. The value of H_{VCo} and the equilibrium values of $P_{i(j)}$ were established by minimising G with respect to these parameters. Thermodynamic properties and configurational states at other compositions and temperatures were then derived assuming H_{VCo} to be independent of T and x.

Results and Discussion

    The composition dependence of the heats of formation and configurational entropies at 1 473 K, yielded by the application of the model, are shown in Fig. 1. Satisfactory working of the model is indicated by the good agreement between the calculated and experimental enthalpies at compositions remote from the input point. The calculated configurational entropies show negative deviations from random mixing values pointing to significant atomic ordering even at the elevated temperature.

    The predicted form of this order is illustrated by the sublattice occupational parameters for 1 473 K plotted in Fig. 2; for reference, the
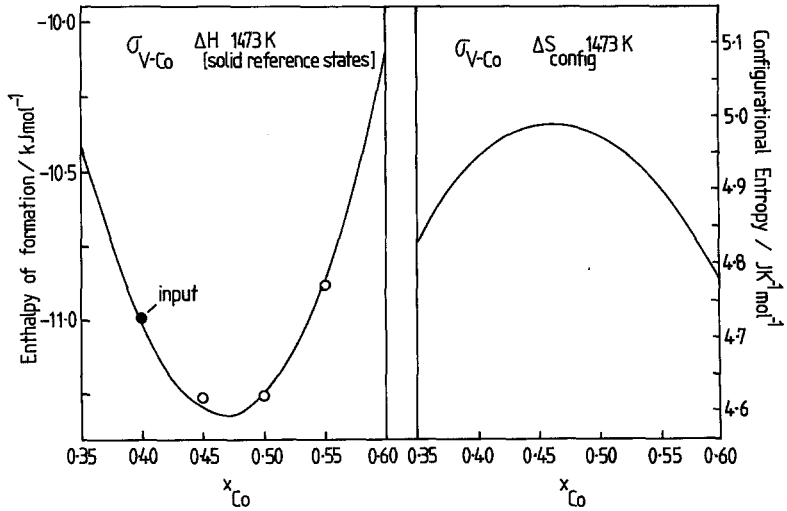
Fig. 1. Computed composition dependence of enthalpy of formation and configurational entropy of $\sigma(V—Co)$ at 1 473 K. ◯ Experimental [● input for H_{VCo} evaluation]
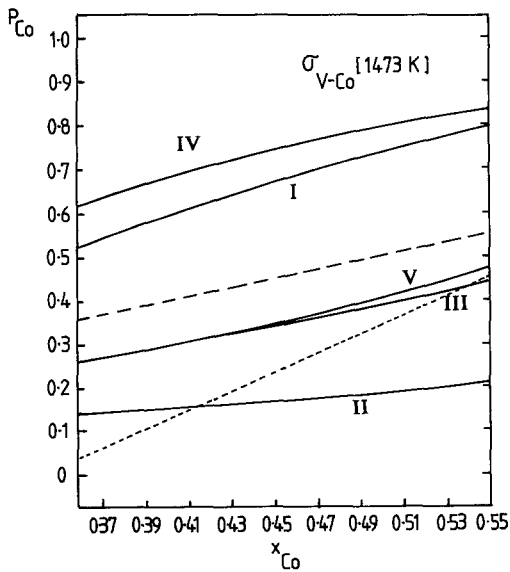

Fig. 2. Computed fractional occupation of sublattices of $\sigma(V—Co)$ by Co at 1 473 K. ——— P_{Co} for totally random distribution; --------- P_{Co} (III + V) random, if I, IV and II fully ordered

lines corresponding to totally random occupation and the average (III + V) sublattice composition required in the case of perfect (I + IV) and II order are also indicated. It will be recalled that the orthodox ordering scheme would, in the present case, correspond to values of $P_{Co} = 1$ for sublattices I and IV and $P_{Co} = 0$ for sublattice II and that maximum order
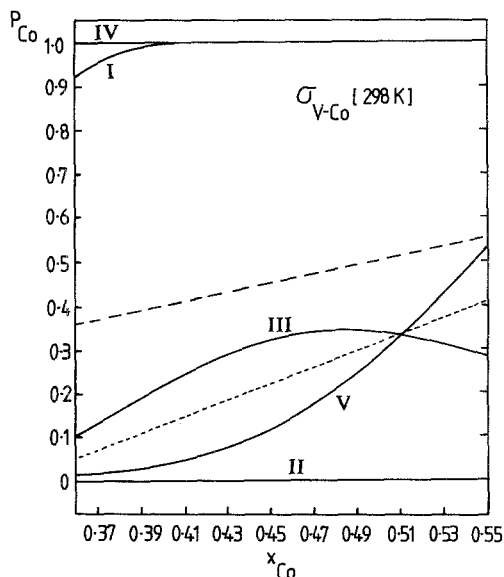

Fig. 3. Computed fractional occupation of sublattices of σ(V—Co) by Co at 298 K. —— —— P_{Co} for totally random distribution; ------- P_{Co} (*III* + *V*) random, if *I*, *IV*, and *II* fully ordered

of this form is in principle achievable at all compositions of σ(V—Co). Preferential occupation is apparent, but the deviations from random composition of sublattices I, II and IV are only approximately half of those required for full orthodox order. Values vary only slightly with overall phase composition, but occupation of the individual Co-preferring sublattices is not identical, with IV showing slightly higher degrees of preferential behaviour; III and V are similarly occupied throughout. If the calculations are repeated with the temperature changed to 298 K, the atomic distributions at room temperature are predicted to be as shown in Fig. 3. Maximum orthodox ordering on I, II and IV is now indicated at most compositions, although the first sublattice appears to become detectably defective at the lowest Co contents of the phase. The model

suggests, however, that at low temperatures preferential occupation may extend to the sublattice III and V which now exhibit Co contents which vary significantly with phase composition and differ from each other, except at approximately 51 atom per cent Co above which, coincidentally, the III : V relative species preference is reversed.
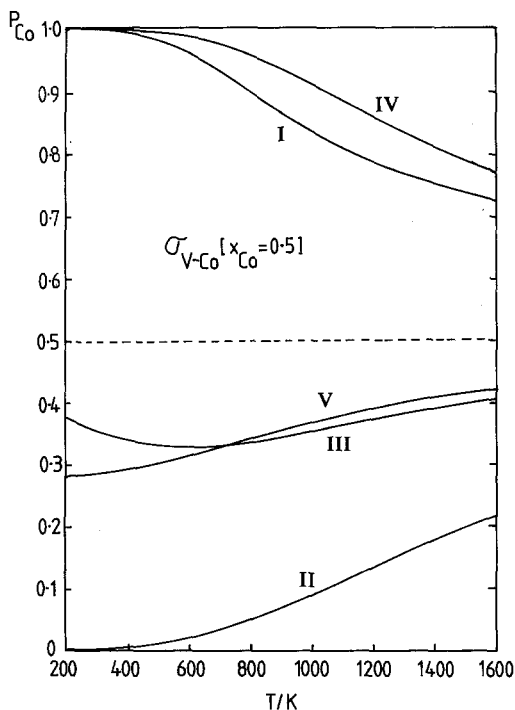

Fig. 4. Computed temperature dependence of occupation of sublattices of σ(V—Co)$_{x_{Co} = 0.5}$ by Co. — — — P_{Co} random distribution

The temperature dependence of configuration was examined in more detail at a fixed composition. Occupational parameters were computed for the σ(V—Co) phase containing 50 atomic per cent Co, which corresponds to the composition studied by *Marcone* and *Coll,* over the range 200–1 600 K and the values obtained are plotted in Fig. 4. The results indicate that the appearance of antistructure defects begins at temperatures only slightly above room temperature. Sublattice I appears most sensitive to temperature, as it was to composition (Fig. 3) and consequently I and IV

exhibit different occupational parameters at all temperatures. The rates of disordering of the strongly ordered sublattices all increase with temperature initially, passing through maxima at different individual temperatures between approximately 800 and 1 000 K.
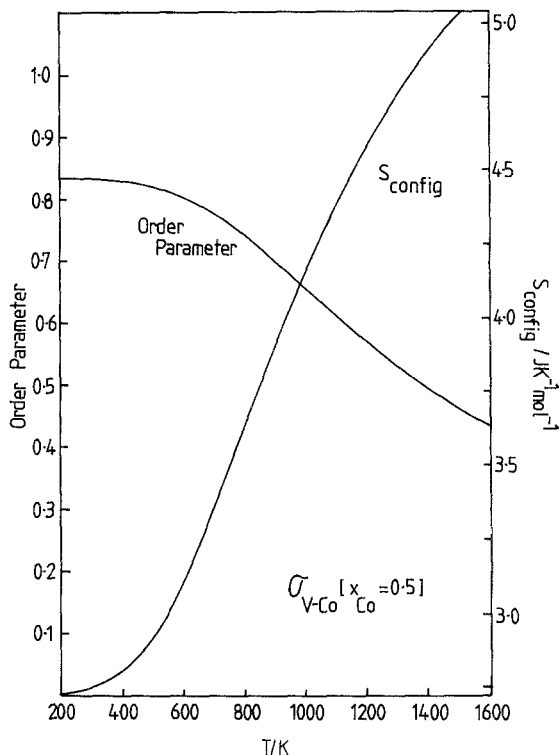

Fig. 5. Computed temperature dependence of overall order parameter and configuration entropy of $\sigma(V—Co)_{x_{Co}=0.5}$

The overall behaviour of the phase is best represented by a single configurational parameter obtained by combining the contributions of the individual sublattices. A convenient approach, which recognises that sigma phases are not characterised by a fixed stoichiometry and avoids the need to presuppose the particular role of any sublattice, is to define an "order parameter" in terms of the weighted sum of the *magnitudes* of the deviation of each sublattice composition from that of the phase, i.e.,

$$\alpha = \frac{1}{30}[2|x^I—x| + 4|x^{II}—x| + 8|x^{III}—x| + 8|x^{IV}—x| + 8|x^V—x|]$$

5*

where x^i and x are, respectively, the atom fraction of Co of the sublattice "i" and of the total alloy. However, since the value of α corresponding to maximum attainable order will vary with phase composition, a normalised order parameter is defined by $\alpha/\alpha_{max(x)}$, where $\alpha_{max(x)}$ refers to
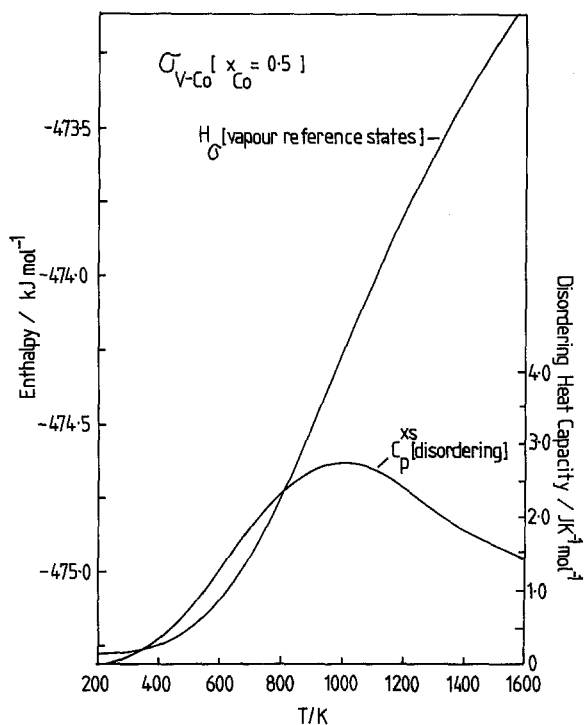

Fig. 6. Computed temperature dependence of enthalpy and heat capacity of disordering of $\sigma(V\text{---}Co)_{x_{Co}=0.5}$

maximum possible order using all five sublattices. The normalised parameter can thus range from 0 to 1 at all compositions.

The values calculated for the present example are shown in Fig. 5. High, although less than maximum possible, values at low temperatures reflect the essentially perfect order of sublattices I, II and IV and weakly preferential behaviour of III and IV. The combined effect of the different rates of disordering of the individual sublattices is now seen to result in a maximum rate of disordering at around 1 000 K for the phase as a whole. The rate, however, varies only slightly after about 700 K and disorder

develops steadily, but is still incomplete, up to the solidus temperature of the phase (approx. 1 520 K). Calculated configurational entropies of the phase are also shown in Fig. 5 for comparison.

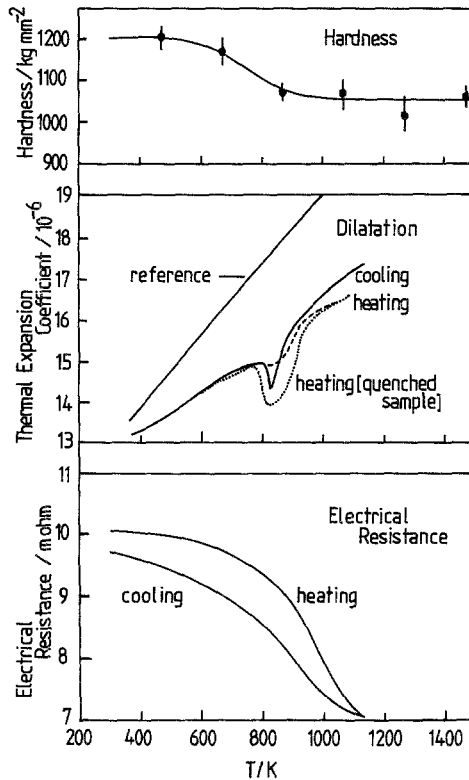The summation of the pairwise interaction enthalpies as represented

Fig. 7. Experimental evidence of transformation in $\sigma(V—Co)_{x_{Co}=0.5}$ (*Marcone* and *Coll* [3]). a) Variation of hardness with temperature. b) Variation of coefficient of expansion with temperature: — — — — Heating; ———— Cooling; ···· Heating, quenched sample. c) Variation of electrical resistivity with temperature

by the first three terms of equation (1) describes the enthalpy of the phase relative to the free atom (vapour) states of the elements at the reference temperature (1 473 K) of the experimental heat of formation input to define H_{AB}. Temperature coefficients of this phase enthalpy will thus represent the heat capacity associated specifically with the disordering process, under the restricted condition of assumed invariant pair-wise

interactions. The computed enthalpy and "transformation" heat capacity values are presented as a function of temperature in Fig. 6.

Experimental indications of transformation in σ(V—Co) are summarised in Fig. 7. The variations of most properties show effects developing over a wide range of temperatures and are suggestive of a second order change such as disordering. The observed low temperature onset and accelerating rate of most of the changes are similar to those of the computed configurational behaviour, but the upper "critical temperatures" indicated experimentally are in most cases lower than that of the maximum disordering rate given by the model. Only the resistivity measurements show their most rapid changes at higher temperatures similar to those suggested by the present calculations.

Nevertheless the present model examination does lend strong support to the earlier suggestion that significant structural changes, probably associated with a disordering process, are to be observed on heating σ(V—Co). It is interesting, however, to note that while the calculated excess specific heats of disordering pass through an obvious maximum, they appears as a broad band extending over a very wide range of temperatures and so contrast markedly with the narrower temperature ranges and sharply defined critical points typical of classic examples of order-disorder transformations [10] in e.g. $L1_0$ (CuAu) or $L1_2(Cu_3Au)$ structures. Such a more diffuse process of disordering is perhaps to be anticipated for phases such as sigma, in view of the multiplicity of sublattices, with their various co-ordinations, and the presence of a large proportion of lattice sites (III and V) which show only weak preference for occupation by a single species. The discrepancy as to the exact temperature at which the structural changes occur most rapidly is doubtless a consequence of the over-simplicity of the model and particularly the assumption of invariant interaction enthalpies. Especially significant in the present context may be the need to allow for their possible variation with temperature, since the observed changes in resistivity, showing a decrease with increasing temperature, cannot be attributed directly to disordering, but must involve electronic structure or bonding changes consequential to it. Further experimental work is being attempted on this phase. Preliminary dilatometric and thermal analysis studies [13] have again indicated transformation effects, but results remain inconclusive as to the critical temperature. It is hoped to obtain structural information from a planned series of electron microscopy measurements.

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