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Site occupancy and lattice parameters in sigma-phase Co–Cr alloys

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Neutron powder diffraction was used to study the distribution of Co and Cr atoms over different lattice sites as well as the lattice parameters of sigma-phase compounds $Co_{100-x}Cr_x$ with $x = 57.0$, 62.7 and 65.8. From the diffractograms recorded in the temperature range of 4.2–300 K it was found for the five crystallographically independent sites that A ($2a$) and D ($8i$) are predominantly occupied by Co atoms, while sites B ($4f$), C ($8i$) and E ($8j$) mainly accommodate Cr atoms. The lattice parameters a and c exhibit linear temperature dependencies, with different expansion coefficients in the temperature ranges of 4.2–100 and 100–300 K.

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1. Introduction

A sigma-phase (σ) in the Co–Cr alloy system is one of ~ 50 known examples of σ phases in binary alloys (Hall & Algie, 1961; Joubert, 2008). According to the binary-alloys phase diagram (Ishida & Nishizawa, 1990), the σ-phase in Co–Cr can be formed at Cr concentrations between ~ 54 and ~ 67 at%, and a transformation of the original body-centred cubic (b.c.c.) phase (α) into the σ-phase can be done by isothermal annealing over the temperature interval ~873–1553 K. The existence and properties of the σ-phase in this alloy system are of great scientific interest and technological importance. The former because the σ-phase in a $Co_{0.435}Cr_{0.565}$ alloy was reported – based on an indirect method – to be (ferro)magnetic (Nevitt & Beck, 1955; Martin & Downie, 1983). If this were true it would be only the third example known of a magnetic σ-phase in a binary alloy system. As the magnetic structure of the σ-phase is still not fully explained, any new information on the issue is of importance as it may help to better understand the magnetism of this phase. The technological significance of σ-CoCr follows (among other applications) from the fact that the Co–Cr alloys are used as dental and surgical material (Karaali *et al.*, 2005; Kilner *et. al*, 1982) as well as a high-density magnetic recording medium (Smits *et al.*, 1984; Fujii *et al.*, 1984; Pundt & Michaelsen, 1995). The σ-phase is known for its extreme brittleness and hardness, and its precipitation causes significant deterioration of mechanical properties of materials. A better knowledge of its properties may help to fabricate materials in which its precipitation does not occur.

The principal aim of this study was to determine the site populations of Co and Cr atoms in a series of σ-CoCr samples with different compositions, as well as lattice parameters. The σ-phase, originally found and identified in the Fe–Cr system, has a tetragonal structure. Its unit cell contains 30 atoms distributed over five non-equivalent crystallographic sites with high (12–15) coordination numbers. For that reason, the σ-

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phase is regarded as a member of the family of the so-called Frank–Kasper phases. Its physical properties are characteristic of a given alloy system, but its common features (as mentioned above) are high hardness and brittleness. The latter makes a precipitation of the σ-phase in various materials of technological importance (*e.g.* stainless steels) a very unwanted phenomenon, as it causes significant deterioration of their useful mechanical and corrosion properties.

Knowledge of the actual distribution of the constituting atoms over the sites is important not only *per se* but also because it helps to properly interpret measurements performed with microscopic methods such as NMR (Dubiel *et al.*, 2010) or Mössbauer spectroscopy (Cieślak, Tobola *et al.*, 2008; Cieślak, Tobola & Dubiel, 2010). It is also very useful as input to performing theoretical calculations of the electronic structure of the σ-phase (Cieślak, Tobola *et al.*, 2008; Cieślak, Tobola & Dubiel, 2010). The distribution of Co/Cr atoms over the lattice sites (as available in the literature) is ambiguous. According to Dickins *et al.* (1956) as well as Yang & Bakker (1994), sites *A* and *D* are exclusively populated by Co atoms, sites *B* and *C* only by Cr atoms, while *E* sites are mixed, *i.e.* both Co and Cr atoms occupy them. On the other hand, following Algie & Hall (1966) all five sites are populated by both types of atoms, and the most populated sites by Co atoms are *A* and *D*. The latter agrees qualitatively with the results found for this phase in Fe–Cr and Fe–V alloy systems, where all five sites have mixed occupancies (Cieślak, Reissner *et al.*, 2008). In light of the above-described situation, studying the issue of atom distribution in the Co–Cr alloy system again was justified.

This paper presents the results obtained for σ-phase samples of $\mathrm{Co}_{100-x}\mathrm{Cr}_x$ alloys with three different compositions by means of polycrystalline neutron diffraction (ND) techniques. It will be shown that they are consistent with those reported earlier for Fe–Cr and FeV compounds (Cieślak, Reissner *et al.*, 2008) as far as the sites population is concerned.

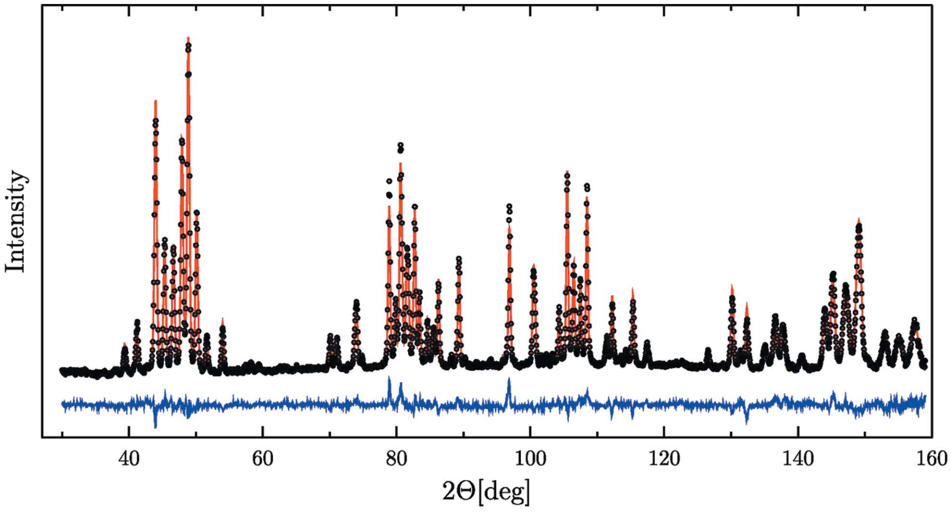

Figure 1
Neutron diffractogram recorded at 300 K on the σ-phase sample of $\mathrm{Co}_{34.2}\mathrm{Cr}_{65.8}$. The solid line represents the best-fit obtained with the procedure described in the text. A difference diffractogram is also marked.

2. Experimental

Master alloys of α-$\mathrm{Co}_{100-x}\mathrm{Cr}_x$ with x = 57, 61 and 65 nominally, were prepared by melting appropriate amounts of Co (99.95% purity) and Cr (99.5% purity) in an arc furnace under a protective argon atmosphere. The melting process was repeated several times to ensure a better homogeneity of the alloys. The product ingots (*ca* 5 g), were next vacuum annealed at 1273 K for 6 d. Their chemical composition was determined by electron probe microanalysis, which gave x = 57.0, 62.7 and 65.8. For neutron diffraction measurements the samples were powdered by a mechanical attrition in an agate mortar and pestle.

The occupation numbers of particular sites and lattice parameters *a* and *c* of the unit cell were derived from neutron diffraction patterns obtained with measurements performed at ILL Grenoble (D1A). The diffractograms recorded using neutrons with λ = 1.91127 Å, an example of which is shown in Fig. 1, were measured in the temperature range between 4.2 and 300 K. They were analysed by the Rietveld method (*FULLPROF* program) assuming the pseudo-Voigt profile function (Rodriguez-Carvajal, 1993). There were 29 refined parameters; nine of them related to the background and position of the spectrum; nine parameters were connected with the scale parameter, line-widths and lattice constants; seven parameters described atom positions in the unit cell; and four parameters were relevant to the Co/Cr occupation numbers of the five different lattice sites. The displacement parameters have been refined using one parameter for all 30 atoms in the unit cell. Attempts were made to fit the spectrum assuming different values of these parameters for Co and Cr atoms, but they did not lead to improving the quality of the fit, while a larger scattering of the results was noticed.

The alloy concentration, x, was held fixed to the values obtained by the microprobe analysis in the analysis of diffractograms, while concentrations related to the particular sublattices were treated as free parameters. The inaccuracies of the occupation numbers were determined assuming they were mainly caused by a chemical inhomogeneity of the samples as well as the limited accuracy of the determined composition, x. For that reason, for each spectrum the full fitting procedure was repeated for two additional compositions: $x + \Delta x$ and $x - \Delta x$ (Δx = 0.3 at% being the maximum expected error of the composition determination). The differences between the results of these two calculations, which did not exceed 0.5%, can be treated as errors of the particular occupation numbers. This protocol for determining the effect of the chemical composition uncertainty on the accuracy of the sites occupation was also used previously for sigma-phase Fe–Cr and Fe–V alloys (Cieślak, Reissner *et al.*, 2008) leading to smooth and systematic behaviour *versus* composition.

3. Results and discussion

3.1. Site-occupation probability

In the following only the average values are discussed. The data displayed in Fig. 2 give evidence that all five sites are occupied by both types of atoms. This observation is in qualitative agreement with that of Algie & Hall (1966): all five sites are populated by both types of atoms, and the most populated sites of Co atoms are *A* and *D*. However, the data do not agree quantitatively with those reported earlier (Algie & Hall, 1966). In particular, the highest probability of finding Co atoms at sites *A* and *D* ranges between ~ 95% at $x = 57.0$ and ~ 75% at $x = 65.8$ for the former, while the corresponding values for site *D*, being weakly concentration dependent, range between ~ 90% and ~ 80% for the extreme values of x. The values determined by Algie & Hall (1966) for $x = 61$ were 65% for *A* and 62.5% for *D*, hence significantly less than ours.

The probability of site *B* is concentration independent and is ~ 20%. The other sites (*C* and *E*) are mostly occupied by Cr atoms as the probabilities of finding Co atoms on these sites range between ~ 20% for $x = 57.0$ and ~ 10% for $x = 65.8$. It could be seen that, in general, there was no significant difference between the results determined from the diffractograms recorded at 4.2 and 295 K. This observation can be regarded as evidence that the analysis of the experimental data measured at two different temperatures was correctly done.

It is easily noticed that the distribution of atoms over the sites is correlated with their atomic volumes and mean interatomic distances, $\langle d \rangle$, and also with coordination numbers, CN. Namely, sites *A* and *D* with the smallest $\langle d \rangle$ values (2.50 and 2.49 Å; Dickins *et al.*, 1956), and the smallest CN values (12), are predominantly occupied by Co atoms (atomic volume 6.7 Å^3), while *B*, *C* and *E* sites with $\langle d \rangle$ values equal to 2.71, 2.66 and 2.64 Å (Dickins *et al.*, 1956), and CN values equal to 15, 14 and 14, respectively, are mostly populated by Cr atoms (atomic volume 7.23 Å^3). These findings are similar to those revealed earlier for the σ-phase in Fe–Cr and Fe–V alloy systems (Cieślak, Reissner *et al.*, 2008).

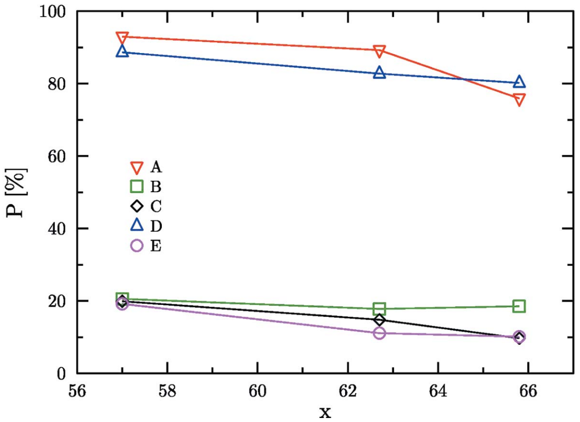

Figure 2
The probability of finding Co atoms at different lattice sites in the σ-phase $Co_{100-x}Cr_x$ compounds, *P versus* chromium concentration x. Solid lines connect the points obtained as the average over the 4.2 and 300 K measurements. They are marked as a guide to the eye.

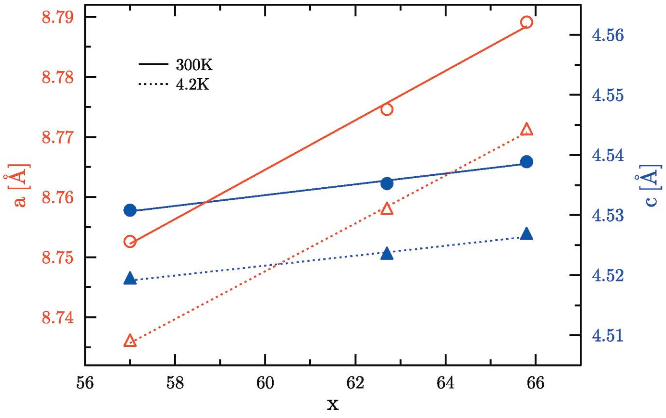

Figure 3
Dependence of the lattice parameters *a* (open symbols) and *c* (full symbols) on chromium content, x as determined from the neutron diffractograms recorded at 4.2 and 300 K.

3.2. Atomic positions

Atomic positions are presented in the Table 1 of the supplementary material.[1] Since the values measured for different compositions and temperatures varied slightly, only the average values are displayed. They can be compared both with the previous experimentally obtained data with which they are in accordance (Dickins *et al.*, 1956), and with theoretically calculated ones (Pavlů *et al.*, 2010) with which they are rather at variance. The discrepancy in the latter case likely follows from the fact that the relevant theoretical calculations were carried out for the σ-phase of pure elements *viz.* σ-Co and σ-Cr only. From the view-point of these calculations, our experimental results can be seen as weighted values obtained for σ-Co and σ-Cr cases.

3.3. Lattice parameters

Lattice parameters *a* and *c* of the unit cell as obtained from the diffractograms recorded at 4.2 and 300 K are presented in Fig. 3 *versus* Cr concentration, x. Both of them increase linearly with x, however, the rate of increase is different for *a* and *c*. Namely, the increase rate of the former equals 4.0×10^{-4} and 4.1×10^{-4} Å/Cr at% at 4.2 and 300 K. The increase rates of the latter are more temperature dependent, and they are equal to 8.3×10^{-4} for 4.2 K, and 9.0×10^{-4} Å/Cr at% at 300 K. Using the 300 K values for *a* and *c*, those of the unit-cell volume, *V*, were calculated and are displayed in Fig. 4. For comparison, the *V* values previously obtained for the sigma-phase Fe_xCr_{100-x} and Fe_xV_{100-x} compounds are also

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: KD5058). Services for accessing these data are described at the back of the journal.

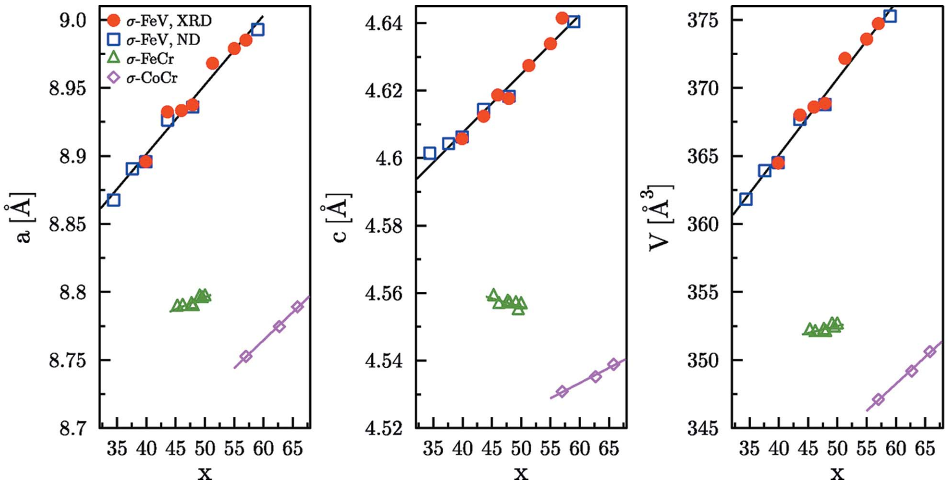

Figure 4
Composition dependence of the lattice parameters *a* and *c*, and that of the unit-cell volume, *V*, at 300 K for the σ-phase in $Fe_{100-x}Cr_x$, $Fe_{100-x}V_x$ (Cieślak, Tobola & Dubiel, 2010), and $Co_{100-x}Cr_x$ alloy systems. The lines are the best linear fits to the data..

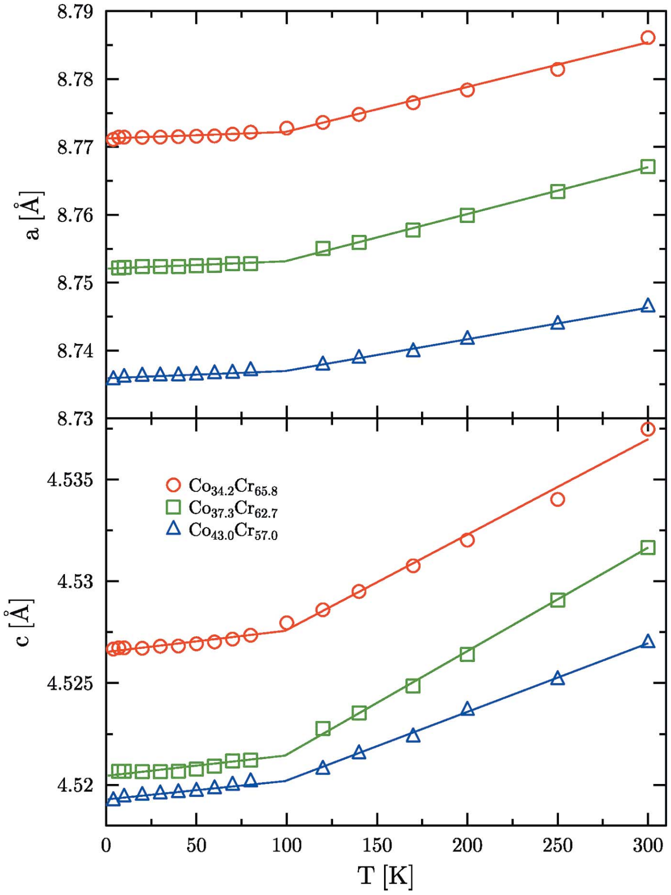

Figure 5
Temperature dependence of the lattice parameters *a* (top panel) and *c* (bottom panel) for the σ-phase Co–Cr samples. The solid lines are the best linear fits to the data.

presented (Cieślak, Reissner *et al.*, 2010). It is evident from that figure that all three structure parameters are characteristic of a given alloy system, and they show a quasi-linear compositional dependence. It is also clear that the structural parameters are correlated with the atomic size of atoms constituting a given compound. In particular, for the Co–Cr system they increase with increasing Cr concentration which reflects the fact that the atomic radius of Cr is greater (1.30 Å) than that of Co (1.25 Å).

Finally, the measurements of the diffractograms over the temperature interval 4.2–300 K enabled the determination of the effect of temperature, *T*, on the lattice constants. As illustrated in Fig. 5, both *a* and *c* show a monotonic dependence on *T* with two characteristic ranges:

(i) < 100 K, where the dependence is weak, and

(ii) > 100 K, where the dependence is strong.

The $a(T)$ and $c(T)$ dependences in both ranges can be well approximated by a linear function $Y(T) = a + bT$. The best fit-paramters obtained by this procedure for all three samples are displayed in Table 2 of the supplementary material. Although Fig. 5 indicates a change of the lattice parameters at $T \simeq 100$ K, we did not find evidence for a phase transition at this temperature.

4. Conclusions

The results obtained and presented in this paper can be summarized as follows:

(i) Co/Cr atoms are present on all five crystallographic sites; *A* and *D* sites are mostly populated by Co atoms with a probability between ~90 and ~70%, whereas Cr atoms predominantly reside on sites *B*, *C* and *E* with the probability between ~90 and ~80% depending on the composition.

(ii) Lattice parameters *a* and *c* increase linearly with the chromium content, *x*, the increase rate being different for *a* than that for *c*.

(iii) The temperature dependence of the lattice parameters *a* and *c* is linear but with different slopes for $T < 100$ and $T > 100$ K.

(iv) No evidence on magnetism was found.

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