

A Ternary Sigma Phase in the System Cr-Ni-P

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The metal-rich part of the ternary phase diagram Cr-Ni-P at 1050°C has been described briefly. The l.p. variations for the sigma phase have been studied.

A study has also been made of the possible occurrence of sigma phases in other Cr-Ni-X systems (where X = Al, Si, Ge, Sn, As) and also in the systems Mo-Pd-Si and W-Pt-Si. Only phosphorus has been found to have an effect comparable to silicon in stabilizing sigma phases.

Following the work of Jette and Foote in 1936¹, several investigators have studied the influence of silicon on the formation of sigma phases²⁻⁴. The indications are that silicon shows an extensive solid solubility in binary sigma phases of 3d elements and that silicon extends the stability range of the sigma phase both as regards the metal-metal ratio and as regards the temperature.

The effect of carbon, nitrogen or boron on the sigma phase formation⁵⁻⁷ is quite different from that of silicon. These elements do not show any appreciable solubility in the sigma phase. Instead, they form carbides, nitrides and borides with the element having the lower atomic number (in a given transition series)⁷. The effect of aluminium is similar⁴, the sigma field in Fe-V-Al and Cr-Co-Al being very limited. On the other hand the formation rate of the sigma phase is accelerated by the addition of small amounts of aluminium (< 0.3 at %) and retarded by somewhat larger amounts⁸.

The aim of this investigation has been to study the effect of aluminium, silicon, germanium, tin, phosphorus and arsenic on the sigma phase formation in the Cr-Ni system. Only phosphorus and silicon were found to give a ternary sigma phase. Since Gupta, Rajan and Beck published their results for the Cr-Ni-Si system while the present work was in progress, the detailed study was confined to the Cr-Ni-P system.

EXPERIMENTAL

Chemicals. The samples were prepared from chemicals of the following purity. Chromium (electrolytic) found on analysis to contain 99.97 % Cr.

Nickel powder from Mond Nickel Co., Ltd., claimed purity 99.9 %.

Red phosphorus with purity 99 % or better.

Germanium (zone-melted) better than 99.9 %.

Aluminium (rod), tin (rod) and arsenic (powder) from Johnson, Matthey & Co., London, claimed purity better than 99.9 %.

Silicon from Pechiney, Paris, claimed purity better than 99.9 %.

Platinum and palladium from Hereaus, Hanau, Germany with claimed purity better than 99.9 %.

Vanadium, found on analysis 99.7 %.

Molybdenum 99.7 %.

Tungsten of unknown purity.

Iron powder with approximately 2 % oxygen.

Preparation. Samples in the Cr-Ni-P system were prepared in the following way. Initially a master alloy of Ni₃P was prepared according to a method used by Haughton¹⁰, Hägg¹¹ and by Rundqvist¹². By this technique, pellets of red phosphorus are dropped into a melt of nickel under an argon atmosphere.

Samples, low in phosphorus (< 12 at %) were obtained by arc-melting pellets of metal and master alloy powder. They were subsequently heat-treated at 1050°C for 20–30 days in evacuated and sealed silica tubes. The samples with higher phosphorus contents were given this heat-treatment only. For the heat-treatments the alloys were put into small tubes of recrystallized alumina inside the silica tube. Arc-melted alloys were found to reach equilibrium faster than those not arc-melted.

In each of the systems Cr-Ni-X (X = Al, Si, Ge, Sn, As) five samples were prepared with a Cr-Ni ratio of 65:35 and an X-concentration ranging from 2 at % to 20 at %. The samples were heat-treated at 950°C for 10–30 days. In several instances this was preceded by cold working, since this is known to accelerate the sigma phase formation^{1,12,13}. The samples in the Cr-Ni-Ge system were also heat-treated at 750°C and 1150°C.

X-Ray work. The phase analysis was performed with powder photographs taken with a Guinier focussing camera using CrK α_1 radiation ($\lambda_{\text{CrK}\alpha_1} = 2.2896 \text{ \AA}$) and with silicon ($a = 5.4306 \text{ \AA}$) as internal standard. The precision of an l.p. measurement is estimated to be $\pm 0.02 \%$, while the absolute accuracy is probably not better than $\pm 0.04 \%$.

Chemical analysis. Some of the Cr-Ni-P samples were chemically analyzed in the Department of Analytical Chemistry at this Institute.

Five samples from, or close to, the sigma phase region were analyzed for phosphorus and silicon. The samples were dissolved in HCl + Br₂, followed by treatment in HNO₃ + HClO₄ for complete oxidation of phosphorus and chromium. The residue was treated with HNO₃ + H₂SO₄ and then with HClO₄. The phosphorus was weighed as P₂O₅ · 24MoO₃ according to Nydahl¹⁴. The phosphorus content obtained from this chemical analysis deviated very little from the nominal composition (the deviation was in all cases less than 2 % of the total phosphorus content).

For the determination of silicon the samples were dissolved in HCl + Br₂. This treatment was followed by boiling with HClO₄ to evaporate chromium as chromylchloride. The amount of silicon dioxide was determined from the weight loss, produced by treating the precipitate with hydrofluoric and sulfuric acids. The analysis of the five samples gave an average value of 0.1 % silicon. The accuracy of this value is a little uncertain, owing to the presence of a very small amount of residue which could be observed after the solution procedure, and because the silicon dioxide content in the precipitate was unusually small. However, not more than 0.2 % silicon was estimated to be present in the samples.

The samples were not analyzed for chromium and nickel, as previous experience has not given any reason to expect departure from nominal composition. The concentration values for chromium and nickel given below are nominal.

RESULTS

Cr-Ni-P system at 1050°C. The metal-rich part of this system is outlined in Fig. 1. The diagram is characterized by a ternary sigma phase, the phase boundaries of which have an estimated accuracy of $\pm 0.5 \%$ for each component. One phase (X), coexisting with the sigma phase, has not been identified,

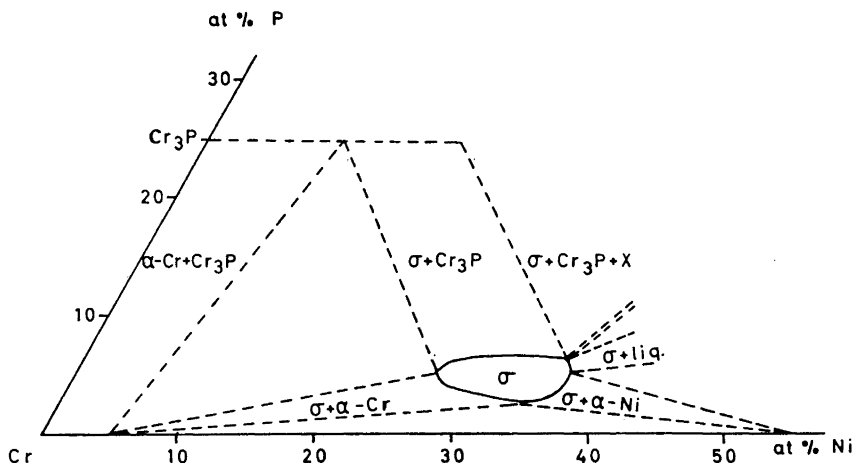


Fig. 1. The sigma field in the Cr-Ni-P system at 1050°C.

but it seems probable that it is a ternary Cr-Ni-P phase. The solid solubility of nickel in Cr_3P has been determined using the l.p. variation method. The binary Cr_3P phase was found to have $a = 9.186 \text{ \AA}$ and $c = 4.558 \text{ \AA}$, while the smallest l.p.'s observed were $a = 9.131 \text{ \AA}$ and $c = 4.529 \text{ \AA}$ for the $(\text{Cr,Ni})_3\text{P}$ phase. This corresponds to an interchange of 18.5 % of the chromium atoms with nickel atoms. This value is considerably larger than that given by Nowotny and Henglein¹⁵.

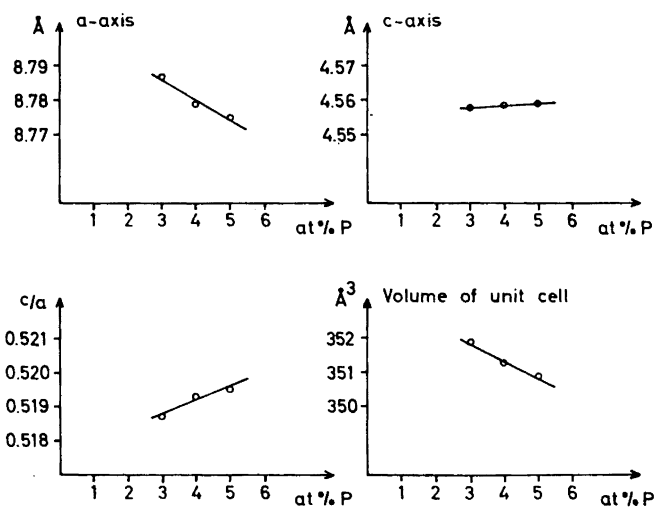


Fig. 2. Lattice parameters of the sigma phase CrNiP as functions of phosphorus content at 1050°C and with Cr/Ni ratio 65/35.

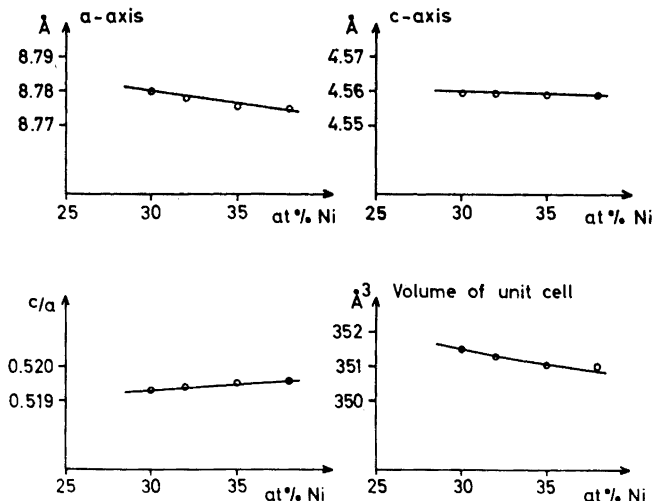


Fig. 3. Lattice parameters of the sigma phase CrNiP with 5 at% P as functions of Ni content at 1050°C.

The measured lattice parameters for the sigma phase in the Cr-Ni-P system are given in Figs. 2 and 3. It is found that for a constant Cr/Ni ratio, an increase in phosphorus content causes a decrease in the a -dimension, while within the limits of experimental error, the c -dimension is unaltered. As shown earlier⁴ the introduction of silicon in the FeCr sigma phase causes a decrease in the a -dimension and an increase in the c -dimension. In both cases the introduction of phosphorus or silicon causes a contraction of the unit cell. The l.p. and cell volume variations of the Cr-Fe-Si sigma phase are typical of those of a number of Me_1 - Me_2 -Si systems described by Stüwe¹⁶.

Fig. 3 shows no unexpected features. Both cell dimensions decrease when the larger chromium atom is replaced by the smaller nickel atom.

The Fe-V-P system. In this system the sigma single-phase field has been found to include phosphorus concentrations as high as 4 at% at 1050°C.

The systems Cr-Ni-X (X = Al, Si, Ge, Sn, As). A sigma phase was observed in the system Cr-Ni-Si only, and in this instance the results are in agreement with those of Gupta, Rajan and Beck⁴. The absence of a sigma phase in the Cr-Ni-Al system is in accordance with the ability of Al to suppress sigma phase formation in the related systems V-Fe-Al and Cr-Co-Al⁴. Although the data, presented here, are insufficient to permit any definite conclusion to be drawn, it is quite clear that aluminium, germanium, tin and arsenic do not stabilize the sigma phase as effectively as do silicon and phosphorus.

The systems Mo-Pd-Si and W-Pt-Si. Silicon has a stabilizing influence on sigma phases formed between $3d$ elements. Accordingly it was thought possible that in the systems Mo-Pd and W-Pt in which sigma phases do not occur¹⁷⁻¹⁹, the addition of silicon might promote their formation. Fifteen

samples in each system were therefore prepared with the silicon content ranging from 2 at % to 12 at % and the Mo-Pd (or W-Pt) ratio ranging from 9:1 to 1:1. No sigma phase could be detected after heat-treatment at 1150°C for 30 days.

DISCUSSION

In connection with the ternary sigma phase Cr-Ni-P comment may be made concerning the Cr-Ni system. In an electron-microscopic study, Schüller and Schwab²⁰ demonstrated the existence of a binary Cr-Ni sigma phase. However, in view of the great stabilizing power of silicon it is not unlikely that the sigma phase observed may be stabilized by silicon impurities. Furthermore, the existence of a phase in a foil sufficiently thin for electron microscopy does not necessarily mean that it is also stable in bulk material.

In discussing the stabilizing of binary sigma phases by a third component, two factors are often considered to be important, namely the size factor and the "electronic" factor. The importance of the first has been particularly stressed by Stüwe¹⁶, who from the assumption of closest packing of the atoms calculated the l.p. variations in binary sigma phases produced by the addition of a third element. These calculations agree fairly well with observed values, (though perhaps not quite convincingly), for sigma phases, where the added third element is a transition element. However, when the third element is silicon the calculations are unsatisfactory, even on a qualitative basis.

The investigation shows that in this respect phosphorus is similar to silicon. The l.p. variations at constant phosphorus content show qualitative agreement with the calculations. Calculated variations in the *a*- and *c*-dimensions of -0.041 \AA and -0.021 \AA respectively are matched by the measured values of -0.006 \AA and -0.001 \AA .

On the addition of silicon (and phosphorus) the cell volume and *a*-dimension decrease. This is a surprising result in view of the Goldschmidt radius of 1.34 Å for silicon in twelve coordination²¹. However, results obtained from structure determination of silicides and from the solid solubility of silicon in transition metals (with unfilled *d*-shells), indicate²² an apparent silicon "radius" of 1.20 Å. Similar experience obtained from studies of phosphides and the solid solubility of phosphorus in iron²³ points to an apparent phosphorus "radius" of less than 1.2 Å. This value is in agreement with the observation that phosphorus has a more pronounced effect on the l.p.'s than silicon. If these revised estimates of atomic radius are used, the cell shrinkage is quite understandable, and the cell volume variation is perhaps the most significant from the point of view of the size factor.

In the Fe-Cr-Si sigma phase it was shown³ that the silicon atoms prefer the IV (or D) position in the main layers of the sigma structure (not the V (or E) position as was wrongly quoted by Stüwe¹⁶). If any similar ordering exists in the Cr-Ni-P sigma phase, it may perhaps explain the absence of variation in the *c*-dimension.

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