Chromium – Nickel – Phosphorus

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Introduction

Electroless Ni-P has been widely used as an excellent protective coating in versatile applications due to its mechanical and chemical properties. Amorphous interlayer of Ni-Cr-P can be also used by transient liquid phase (TLP) metallic bonding for joining. The first investigation in the Cr-Ni-P system was carried out by Nowotny and Henglein [1948Now] who melted samples from pure powder of the elements up to 1200°C for 70 h. They assumed continuous solution between Cr_2P and Ni_2P but mentioned not complete reaction of the samples. [1962Lun] reported a ternary σ phase in the system Cr-Ni-P with a solubility range of ~3 at.% P. The samples were prepared by dropping pellets of red phosphorus into a melt of nickel. The resulting master alloys were arc-melted with Cr powder and heat treated at 1050°C for 20 to 30 d. An isothermal section at 797°C is given by [1984Ori]. The samples were prepared from element powders by press molding in steel crucibles at a pressure of 4.9 MPa. The resulting briquets were heat treated twice for 500 h at 797°C, in between re-melted in arc furnace under argon atmosphere and afterwards quenched in cold water. The samples were characterized by Debye-Scherrer powder method. One ternary phase with the composition $Cr_{1.2}Ni_{0.8}P$ (τ_1) and large ternary solid solubilities of the phases CrP, $Cr_{12}P_7$, Cr_3P and Ni_2P were found. The ternary Sigma phase (σ) reported by [1962Lun] was not confirmed by [1984Ori] at 797°C. [1990Muc] described the phase formation under combustion conditions and gave an isothermal section similar to [1984Ori].

Binary Systems

The binary systems are accepted as given by [Mas2].

Solid Phases

The solid phases are given in Table 1. The dependence of lattice parameters of the Cr_3P, $Cr_{12}P_7$, and Ni_2P phases after [1984Ori] is given in Figs. 1 to 3. Lattice parameters up to the maximal solubility of 0.7 mole fraction NiP in the CrP phase at 20°C by [1986Fje] is given in Fig. 4.

Isothermal Sections

The isothermal section at 797°C given in Fig. 5 is based on the data of [1984Ori]. Modifications have been introduced to the diagram of [1984Ori] to remove artificial homogeneity ranges of the binary phases (along the axis) which where not established experimentally and do not correspond to the accepted binary diagrams. At this temperature the binary phases CrP, $Cr_{12}P_7$, Cr_3P and Ni_2P dissolve large amounts of the third element (see Table 1). Cr is replaced by Ni on the same site in the crystal lattice and forms line compounds between the binary Cr-P and the corresponding Ni-P phases. A partial isothermal section at 1050°C by [1962Lun] is given in Fig. 6. The ternary Sigma phase (σ) reported by [1962Lun] is most probably part of a ternary solid solution of the binary Ni_3P phase, since both phases crystallize in the same crystal structure.

Notes on Materials Properties and Applications

[1997Yeh] describes transient liquid phase (TLP) metallic bonding for joining Inconel superalloy by amorphous interlayer of Ni-Cr-P at 1100°C. The structure and thermal stabilities of Ni-P-based ternary coating by RF magnetron sputtering were studied by [2003Wu], [2004Che1] and [2004Che2].

References

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α'Cr)	*tI*2 *I*4/*mmm* α'Cr	*a* = 288.2 *c* = 288.7	at 25°C, HP [Mas2]
(αCr) < 1863	*cI*2 $Im\bar{3}m$ W	*a* = 288.48	at 25°C [Mas2]
(Ni) < 1455	*cF*4 $Fm\bar{3}m$ Cu	*a* = 352.40	at 25°C [Mas2]
(P) (red) < 417	*c**66	 *a* = 1131	sublimation at 1 bar triple point at 576°C, > 36.3 bar; triple point at 589.6 at 1 atm [Mas2] [V-C2]
(P) (white) < 44.14	*c*** ? P (white)	*a* = 718	at 25°C [Mas2] common form of elemental P, probably less stable than P (red) at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(P) (black)	*oC*8 *Cmca* P (black)	*a* = 331.36 *b* = 1047.8 *c* = 437.63	at 25°C [Mas2]
γ', $CrNi_2$ < 590	*oP*6 *Immm* $MoPt_2$	-	[Mas2]
$(Cr_{1-x}Ni_x)_3P$ < 1510	*tI*32 $I\bar{4}$ Ni_3P	 *a* = 918.87 *c* = 455.93 *a* = 913.1 *c* = 453.9	0.8 ≤ *x* ≤ 1 [1984Ori] *x* = 1 [V-C2] *x* = 0.8 [1984Ori]
Cr_2P(HT) ≲ 1640	*hP*9 $P\bar{6}2m$ Fe_2P	-	[Mas2]
Cr_2P(LT)	*oP*18 *Pmmm* ?	-	[Mas2]
$(Cr_{1-x}Ni_x)_{12}P_7$ $Cr_{12}P_7$	*hP*26 $P6_3/m$ $Cr_{12}P_7$	 *a* = 877.0 *c* = 342.7 *a* = 898.1 *c* = 331.3	0 ≤ *x* ≤ 0.16 [1984Ori] *x* = 0.16 [1984Ori] *x* = 0 [V-C2]
$(Cr_{1-x}Ni_x)P$ CrP	*oP*8 *Pnma* MnP	 *a* = 516.8 *b* = 327.8 *c* = 585.7 *a* = 523 *b* = 334 *c* = 595 *a* = 534.6 *b* = 310.7 *c* = 599.9	0 ≤ *x* ≤ 0.7 [1984Ori] *x* = 0.7 at 27°C [1984Ori] and [1986Fje] *x* = 0.7 at 1027°C [1986Fje] *x* = 0 [V-C2]
Cr_2P_3	?	-	[Mas2]
CrP_2 1000 - 850	*mC*12 *C*2/*m* Ge_2Os	*a* = 821.3 *b* = 303.4 *c* = 709.8 β = 119.47°	[V-C2]
CrP_4 1200 - 900	*mC*20 *C*2/*c* MoP_4	*a* = 519.14 *b* = 1076.0 *c* = 577.12 β = 110.65°	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Ni_3P < 970	*tI*32 $I\bar{4}$ Ni_3P	*a* = 881.2 *c* = 437.3	[V-C2]
αNi_5P_2 < 1025	*hP*168 $P\bar{3}$?	*a* = 1322.0 *c* = 2463.2	[V-C2]
βNi_5P_2 1170 - 1025	-	-	[Mas2]
$Ni_{12}P_5$ < 1025	*tI*34 *I*4/*m* $Ni_{12}P_5$	*a* = 864.6 *c* = 507.0	[V-C2]
$\delta Ni_{12}P_5$ 1125 - 1000	-	-	[Mas2]
$(Cr_{1-x}Ni_x)_2P$	*hP*9 or $P3_21$ $P\bar{6}2m$ Fe_2P or Ni_2P	 *a* = 584.0 *c* = 351.4	$0.5 \leq x \leq 1$ [1984Ori] $x = 0.5$ [1984Ori]
Ni_2P < 1100		*a* = 585.9 *c* = 338.2	$x = 1$ [V-C2]
Ni_5P_4	*hP*36 $P6_3mc$ Ni_5P_4	*a* = 678.9 *c* = 1098.6	[V-C2]
$Ni_{1.22}P$ ~825 - 770	-	-	[Mas2]
NiP ≥ 850	*oP*16 *Pcba* NiP	*a* = 605.0 *b* = 488.1 *c* = 689.0	[V-C2]
NiP_2	*mC*12 *C*2/*c* NiP_2	*a* = 636.6 *b* = 561.5 *c* = 607.2 β = 126.22°	[V-C2]
NiP_3 ≥ 700	*cI*32 $Im\bar{3}$ $CoAs_3$	*a* = 781.92	[V-C2]
* τ_1, $Cr_{1.2}Ni_{0.8}P$	*oP*12 *Pnma* Co_2Si	*a* = 589.4 *b* = 349.3 *c* = 676.2	[1984Ori]
* σ, Cr_5NiP_2 (σ phase)	*tI*32 $I\bar{4}$ Ni_3P	*a* = 913.1 *c* = 452.9	[1962Lun] at 1050°C Not confirmed by [1984Ori] at 797°C Probably solution of Ni_3P

Fig. 1: Cr-Ni-P. Lattice parameters of the Cr_3P phase at 797°C as function of composition at constant P content

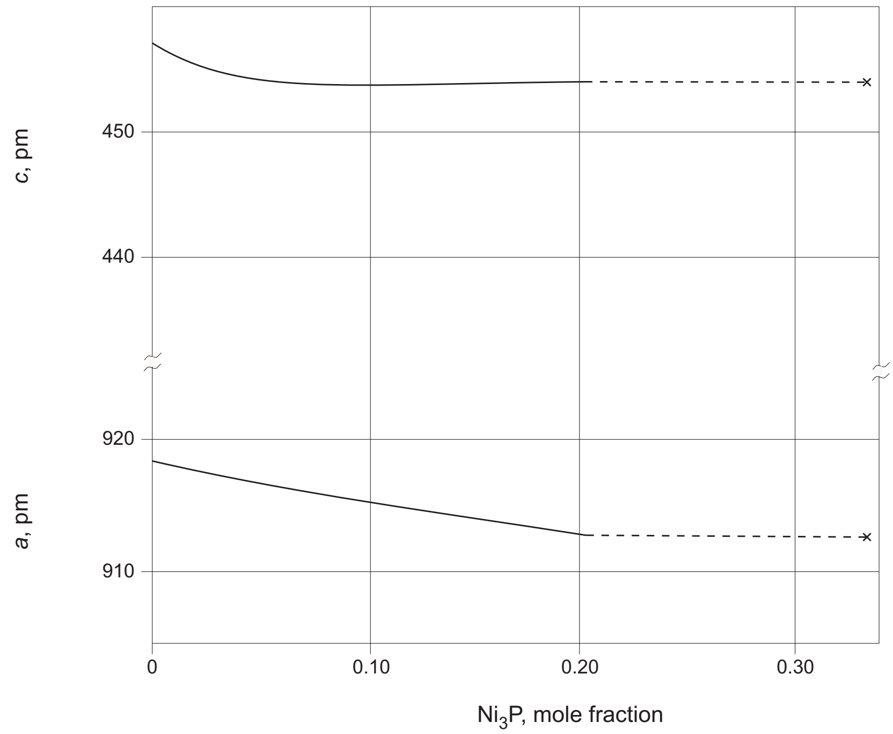

Fig. 2: Cr-Ni-P. Lattice parameters of the $Cr_{12}P_7$ phase at 797°C as function of composition at constant P content

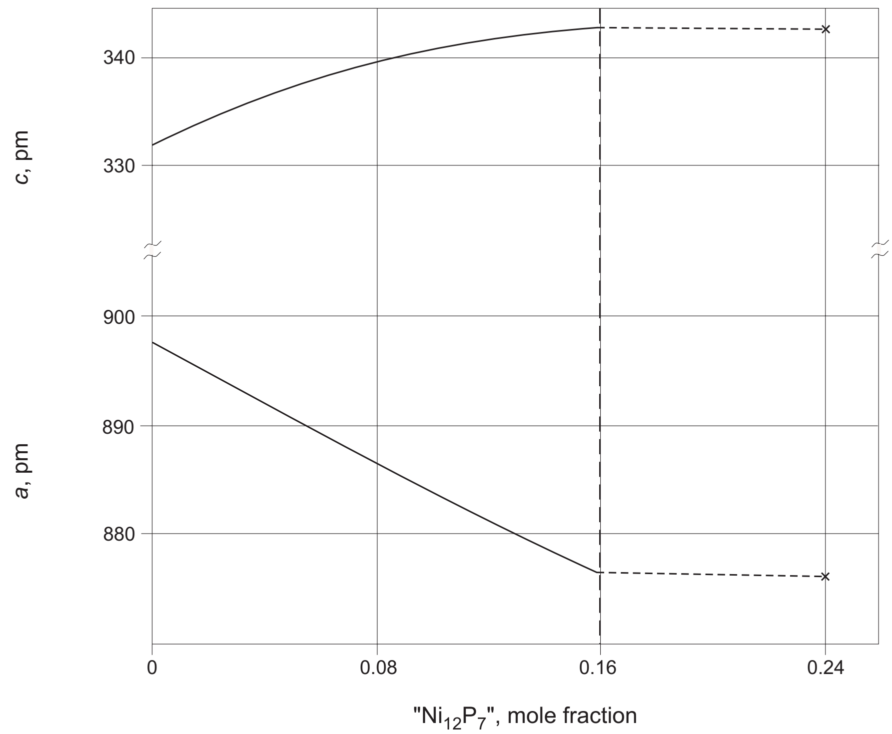

Fig. 3: Cr-Ni-P. Lattice parameters of the Ni_2P phase at 797°C as function of composition at constant P content

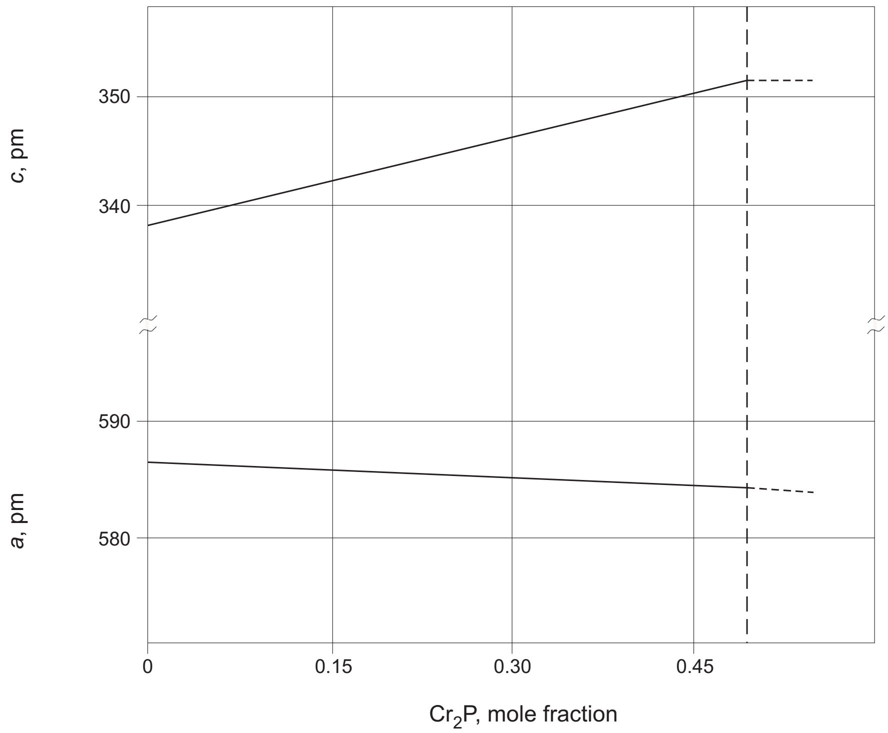

Fig. 4: Cr-Ni-P. Lattice parameters of the CrP phase at 20°C as function of composition at constant P content

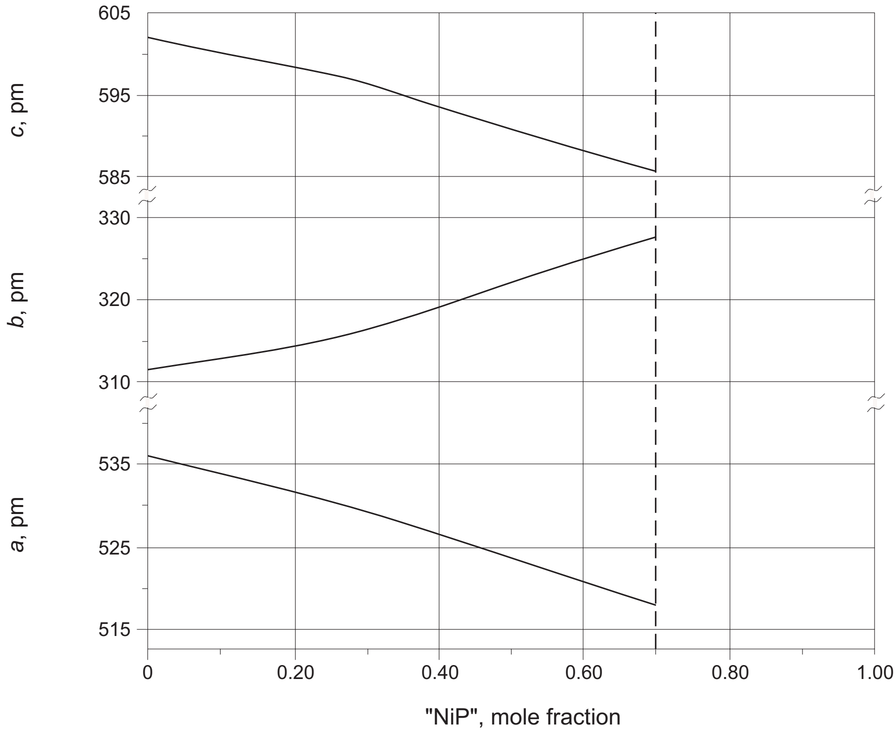

Fig. 5: Cr-Ni-P.
Partial isothermal section at 797°C

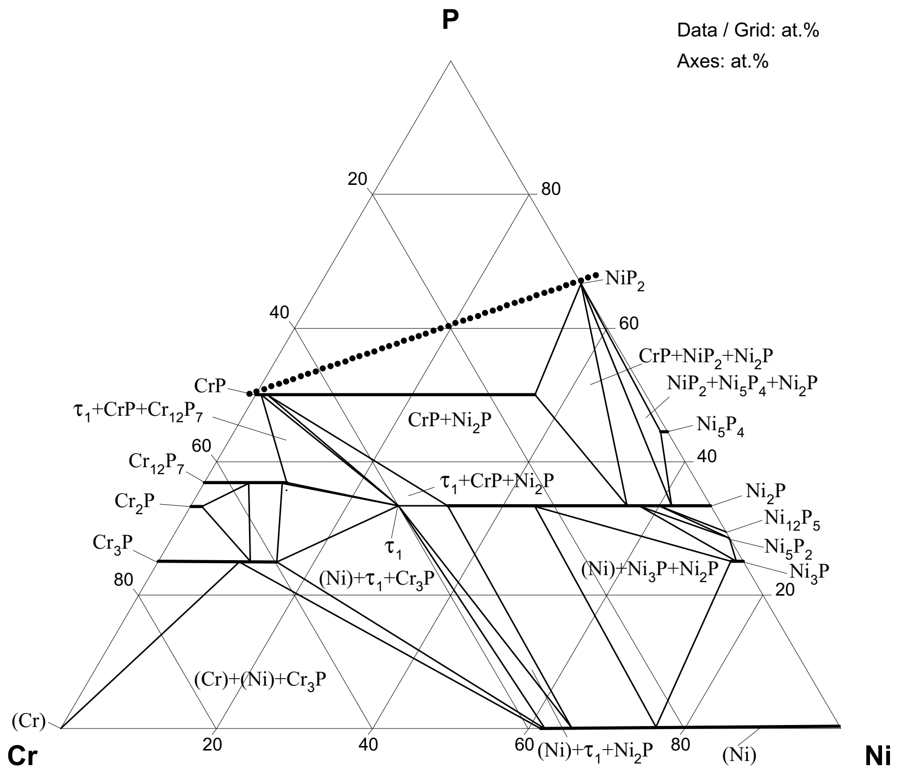

Fig. 6: Cr-Ni-P.
Partial tentative isothermal section at 1050°C