Nickel – Palladium – Silicon

Elena L. Semenova

Introduction

Data on the Ni-Pd-Si phase equilibria, obtained from the investigation of bulk alloys, are restricted to [1976Wop] and [2004Loo]. [1976Wop] studied the ternary alloys of about 60 compositions in the region of 20-75 at.% Si with powder diffraction method using Guinier camera. The alloys were prepared from components of 99.9% purity by induction melting under argon atmosphere (those with less than 40 at.% Si) or in arc furnace (those with more than 40 at.% Si). Their homogenization at 980-700°C for 16 h - 4 d was followed by water quenching. Isothermal section at 800°C was constructed. Two ternary phases were found to exist - $NiPd_2Si$ and $Ni_{18}Pd_7Si_9$. They are in equilibrium and they take part in a number of equilibria with some binary phases. The powder diffraction pattern of the $NiPd_2Si$ phase was not analyzed (it was supposed that the crystal structure of the phase is similar to that of Pd_3Si, of Fe_3C type) whereas the crystal structure of the $Ni_{18}Pd_7Si_9$ phase was determined as of $Pd_{25}Ge_9$ type. Equiatomic intermetallics, NiSi and PdSi, were shown to be completely dissolved while a miscibility gap was observed at this temperature between Ni_2Si and Pd_2Si phases. The isothermal section at 800°C demonstrates an equilibrium of the monosilicide solid solution, $NiSi_2$ phase and (Si); a vertex of the tie-triangle for the first phase is placed at about 12 at.% Pd. An evidence of this value was not given in [1976Wop] as well as of other concentration points.
Some recent experimental works on the phase equilibria of the Ni-Pd-Si system were carried out in order to provide a necessary basis for understanding of the processes connected with destabilizing of $NiSi_2$ in ternary system [2004Loo, 2003Wan]. The processes are important for technology of the Ni-Pd-Si films. [2004Loo] studied the Ni-Pd-Si alloys in the region of 50 to 100 at.% Si with the methods presented in Table 1. The concentration of Pd in the monosilicide phase that can effect the decomposition of the disilicide phase was determined. It was shown that this quantity increases with the rising of temperature. The thermal stability of NiSi phase in the presence of Pd, intercalated between Ni and Si in the film was investigated in [2003Wan]. Using of the Pd layer contributed in enhancing of the thermal stability of the monosilicide phase.
A number of studies were devoted to the investigation of the Ni-Pd-Si amorphous alloys as prospective basis for development of modern amorphous materials [1990Rab, 1988Ino, 1985Ino, 1966Tsu] that can be used in production of solders. They searched for the regions where the ternary alloys could be amorphizied easily, studied the techniques of the preparing of glasses, processes of their crystallization and the properties of the amorphous samples. In the study of the glass forming ability characteristics of the Ni-Pd-Si amorphous alloys by the methods pointed out in Table 1, [1990Rab] determined some constitutional data on rapidly solidified samples such as solidus and liquidus temperatures as well as the temperature of glass transition and crystallization for some compositions.
The influence of hydrogen on physical and chemical properties of the amorphous alloys was discussed by [1984Fil, 1991Yos].

Binary Systems

The binary phase diagrams of Ni-Pd and Ni-Si [1991Nas1, 1991Nas2] as well as Pd-Si [1993Oka] were accepted.

Solid Phases

[1993Mas] using DTA, EMPA and XRD methods analyses showed many new phases in the Pd-Si system. The determination of their crystal structures was not carried out. [1993Oka] questioned the existence of some phases, especially four of them, related to Pd_2Si. Data on solid phases are given in Table 2 including all the phases listed in [1993Oka].

Ni_2Si dissolves nickel up to about 50 at.%. Both lattice parameters of the hexagonal solid solution decrease appreciably with increasing of nickel content along the section 33 at.% Si. On extending of the NiSi based solid solution into the Ni-Pd-Si ternary system, its lattice parameters measured at 800 and 700°C increase (Table 2).

Quasibinary Systems

Based on the new version of the Pd-Si system [1993Oka], where the PdSi monosilicide exists in the very restricted temperature interval, 908 - 888°C, it can be accepted that complete solubility of the PdSi and NiSi phases exists in the narrow interval at subsolidus area. Here the section between monosilicides will be quasibinary.

Liquidus and Solidus Surfaces

According to DTA data of [1990Rab] obtained on amorphous samples of the Ni-Pd-Si system the liquidus and solidus temperature of the samples belonging to the section between the alloys Ni-85Pd-15Si (at.%) and 78Ni-Pd-22Si (at.%) drops with increased nickel content in the alloys, that are close to the Pd-Si side of the ternary phase diagram (5-10 at.% Ni).

Isothermal Sections

To make an agreement with the last version of the Pd-Si phase diagram [1993Oka], showing a lack of the PdSi phase at 800°C, the isothermal section constructed by [1976Wop] had to be corrected. Taking into account that the ternary alloy with 20Ni - 12Pd - 68Si (at.%) is a two-phase one, (Ni,Pd)Si + (Si), at 800°C [1976Wop], it can be assumed that the monosilicide solid solution exists at this temperature at least up to this alloy and the composition of the monosilicide that is in equilibrium with Pd_2Si and Si phases should be somewhat richer in Pd. An arrangement of other three-phase fields at the isothermal section at 800°C is given in Fig. 1 according to [1976Wop]. Mentioned in [1993Mas, 1993Oka] a group of phases close to the hexagonal Pd_2Si phase is not shown here. A series of three phase equilibria observed by [1976Wop] is the following: $Ni_{18}Pd_7Si_9 + \beta_1 + \gamma$; $\gamma + \delta + Pd_2Si$; $Pd_2Si + \gamma + Ni_{18}Pd_7Si_9$; $Pd_2Si + Pd_3Si + NiPd_2Si$; $\delta + Pd_2Si + \varepsilon$; $Pd_2Si + \varepsilon$ +(Ni,Pd)Si; $Pd_2Si + NiPd_2Si + Ni_{18}Pd_7Si_9$; (Ni,Pd)Si + $\alpha NiSi_2$ + (Si). Considering that the compositions of the (Ni,Pd) solid solution in equilibria with the Pd_3Si and $NiPd_2Si$, $NiPd_2Si$ and $Ni_{18}Pd_7Si_9$; $Ni_{18}Pd_7Si_9$ and Ni_3Si phases are unknown, the equilibria are shown tentatively by three triangles.

Temperature – Composition Sections

Figure 2 demonstrates the vertical section passing through binary alloys 85Pd-15Si and 78Ni-22Si (at.%) in the temperature range of the alloy crystallization. The alloys of the section in the composition range of 5-10 at.% Ni have the lowest melting temperature and the narrowest melting interval [1990Rab].
Below 888°C, the temperature of eutectoid decomposition of the PdSi phase, PdSi $\rightleftharpoons$ (Si) + Pd_2Si, the section through the monosilicides cannot be quasibinary one because the compositions of conjunctive phases, Pd_2Si and (Si), and their tie lines are off the plane of the section. Since the (Ni,Pd)Si phase was observed at 800°C in the alloy with 20 at.% Pd [1976Wop] the decomposition temperature of it should be lower than 800°C. With considering this the section through the monosilicides is built as a general guide (Fig 3).

Notes on Materials Properties and Applications

The amorphous $(Ni,Pd)_{82}Si_{18}$ alloys with 29-82 at.% Pd revealed a high ability to form wire of circular cross section, as well as high strength combined with good ductility, and good corrosion resistance and can be used in practice as the tip material in various kinds of brushes and pens [1985Ino]. [1988Ino] managed to prepare the amorphous spherical particles with diameters of 0.5 to 2 mm by injection of molten Ni-Pd-Si alloy containing 1 at.% B into stirred cold water. So large-scale amorphous balls are important for various

practical use including the soldering balls for a connection, for which a high dimensional accuracy is required, while in a ball-point pen the balls in bearing as well. The hardness, crystallization parameters for large particles found to retain practically the same as for the thick ribbons. A number of the ternary alloys compositions containing 22 at.% Si may be used as materials for step brazing because their melting range fits precisely any particular temperature interval between 770 and 1000°C. Vacuum tube brazing is the first successful application where this advantage of Ni-Pd base alloys has been used [1990Rab]. Due to oxidation resistance, ductility, relatively high melting points the Ni-Pd based alloys were recommended to use in brazing ceramics (SiN) to metals [1992Sel].
The Ni-Pd-Si system is considered as a prospective base for production of materials for integrated circuits [2004Loo, 2003Wan, 2000Tsa]. [2004Loo] found that an addition of Pd as an interlayer enhanced thermal stability of the Ni-Si system, where Ni is a film and Si - substrate. [2000Tsa] studied the processes occurring in the Ni-Pd-Si films, where Pd is an interlayer, by measuring the total force per unit width of the film during isochronal annealing. It was shown, that introduction of Pd layer retarded the formation of Ni_2Si and NiSi phases due to the increase of the formation temperature.

Miscellaneous

The resistance and thermoelectric power of the Ni-Pd-Si amorphous hydrogenized alloys were increased monotonously towards positive value with increasing the hydrogen pressure. It points out that sites accessible for hydrogen exist even at hydrogen pressure of about 2 GPa. Superconductivity at temperatures down to 1.5 K in the Ni-Pd-Si alloys was absent [1984Fil].
The solubility of hydrogen in the amorphous ternary 8.8Ni - Pd - 18Si alloy is decreased in comparison with the $Pd_{82}Si_{18}$ amorphous binary alloy [1991Yos].
The crystallization process in the amorphous Ni-Pd-Si alloys with 10-30 at.% Ni and 50-70 at.% Pd is greatly influenced by nickel: the onset time of crystallization retarded on increasing of nickel content [1980Uts].
Amorphous structure was obtained in the alloy 15Ni-65Pd-20Si (at.%) by quenching from the liquid using “piston and anvil” technique [1966Tsu].
[1978Chu] studied angular correlations of both electron irradiated and quenched amorphous alloy with 6Ni-77.5Pd-16.5Si (at.%) and concluded that the electron irradiation does not induce vacancies in the material.

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Table 1: Investigation of the Ni-Pd-Si Phase Relations, Structures and Thermodynamics

Reference	Experimental Technique	Temperature/Composition/Phase Range Studied
[1976Wop]	Induction melting and arc furnace melting, powder diffraction with using Guinier camera	20-75 at.% Si
[1990Rab]	Jet cast and planar flow cast to obtain amorphous foils; DSC, DTA, XRD, plasma emission spectroscopy	5-68 at.% Ni-10-79.5 at.% Pd-10-22 at.% Si
[2004Loo]	Arc melting with following vacuum casting Annealing at 730-902°C for 28 - 11 days EDS, optical microscopy, SEM	Ni-2.83Pd-65.6Si Ni-1.57Pd-66.9Si

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ni,Pd)	*cF*4 $Fm\bar{3}m$		
(Ni) < 1455	Cu	*a* = 352.40	pure Ni at 25°C [Mas2]
(Pd) < 1555		*a* = 389.03	pure Pd at 25°C [Mas2]
(Si) < 1414	*cF*8 $Fd\bar{3}m$ C	*a* = 543.06	at 25°C [Mas2]
β_1, Ni_4Si < 1035	*cP*4 $Pm\bar{3}m$ $AuCu_3$	*a* = 350.6	22.8 to 24.5 at.% Si [Mas2] [V-C2]
β_2, Ni_3Si 1115 - 990	*mC*16 *C*2/*m* $GePt_3$		~24.5 to 25.5 at.% Si [Mas2]
β_3, Ni_3Si 1170 - 1115	*mC*16 *C*2/*m* $GePt_3$		~24.5 to 25.5 at.% Si [Mas2]
γ, $Ni_{31}Si_{12}$ < 1242	*hP*43 *P*321 $Ni_{31}Si_2$	*a* = 666.7 ± 0.2 *c* = 1227.7 ± 0.2	[V-C2], *hP*14 in [Mas2] at 27.9 at.% Si [Mas2] dissolves ~7 at.% Pd at 800°C [1976Wop]
θ, Ni_2Si 1306 - 825	*hP*6 $P6_322$ Ni_2Si	*a* = 383.6 ± 0.1 *c* = 494.8 ± 0.1	[V-C2] 33.4 to 41 at.% Si [Mas2]
δ, Ni_2Si < 1255	*oP*12 *Pnma* Co_2Si	*a* = 502.2 ± 0.1 *b* = 374.1 ± 0.1 *c* = 708.8 ± 0.1	[V-C2] at 33.3 at.% Si [Mas2]
ε', Ni_3Si_2(h) 845 - 800	-	-	39.2 to 41 at.% Si [Mas2]
ε, Ni_3Si_2(r) < 830	*oC*80 $Cmc2_1$ Ni_3Si_2		*oP*80 in [Mas2] 39.0 to 41 at.% Si [Mas2] dissolves ~7 at.% Pd at 800°C [1976Wop]
$\beta NiSi_2$ 993 - 981	-	-	[Mas2], [1991Nas2]
$\alpha NiSi_2$ < 981	*cF*12 $Fm\bar{3}m$ CaF_2	*a* = 538.3	[V-C2] dissolves 1.43 at.% Pd at 882°C; 1.39 at.% Pd at 854°C; 1.18 at.% Pd at 801°C; 1.07 at.% Pd at 759°C; [2004Loo]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$Pd_{21}Si_5$ < 811	-	-	at 16 to 16.3 at.% Si, forms by peritectoid reaction [1993Oka]
Pd_5Si 856 - 809	*mP*24 $P2_1$ Pd_5P	 *a* = 846.5 *b* = 748.5 *c* = 555.5 β = 100.7°	at 16.7 at.% Si [1993Oka] [V-C2] prototype from [Mas2]
$Pd_{14}Si_3$ < 795	-	-	at 17.6 at.% Si, forms by peritectoid reaction [1993Oka]
Pd_9Si_2 819 - 764	*oP*44 *Pnma* Pd_9Si_2	 *a* = 941.4 *b* = 741.88 *c* = 905.48	at 18.2 at.% Si [1993Oka] [V-C2]
$Pd_{15}Si_4$ 792 - 753	*aP*20 $P\overline{1}$?		at 21.1 at.% Si, forms by peritectoid reaction [1993Oka]
Pd_3Si < 1074	*oP*16 *Pnma* Fe_3C	 *a* = 574.0 ± 0.1 *b* = 755.6 ± 0.1 *c* = 526.1 ± 0.1	[1993Oka] dissolves ~8 at.% Ni at 800°C at 25 at.% Si [1976Wop]
Pd_2Si < 1404	*hP*9 $P\overline{6}2m$ Fe_2P	 *a* = 649.3 ± 0.5 *c* = 342.7 ± 0.5 *a* = 647.7 ± 0.1 *c* = 343.2 ± 0.1 *a* = 619.6 ± 0.1 *c* = 325.0 ± 0.1	at 33.5 at.% Si [1993Oka] dissolves ~50 at.% Ni at 800°C [1976Wop] at 33.3 at.% Si [1953And] at 2.7 at.% Ni at 49.2 at.% Ni at 790°C [1976Wop]
Pd_2Si' < 1053	-	-	at 33.3 at.% Si by peritectoid reaction [1993Oka]
Pd_2Si'' < 1080	-	-	at 33.9 at.% Si by peritectoid reaction [1993Oka]
Pd_2Si''' < 1072	-	-	at 34.5 at.% Si by peritectic reaction [1993Oka]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ni,Pd)Si	*oP*8 *Pnma*		
PdSi 908 - 888	MnP	*a* = 561.7 ± 0.3 *b* = 338.6 ± 0.2 *c* = 614.9 ± 0.4	[1993Oka] [1976Wop]
NiSi < 992		*a* = 562.8 ± 0.2 *b* = 519.0 ± 0.1 *c* = 333.0 ± 0.1	at 50 at.% Si at 800°C complete solid solution with PdSi at temperature >888°C dissolves >20 at.% Pd at 800°C
		a = 584.3 ± 0.6 *b* = 538.1 ± 0.5 *c* = 332.1 ± 0.3	at 20 at.% Pd at 800°C
		a = 562.4 ± 0.1 *b* = 519.2 ± 0.1 *c* = 333.1 ± 0.1	at 20 at.% Pd at 700°C [1976Wop]
* $Ni_{18}Pd_7Si_9$	? ? $Pd_{25}Ge_9$	*a* = 683.5 ± 0.1 *c* = 991.6 ± 0.1	quenched from 800°C [1976Wop]
* $NiPd_2Si$	?	?	~69-75 at.% Ni [1976Wop]

Fig. 1: Ni-Pd-Si.
Isothermal section at 800°C

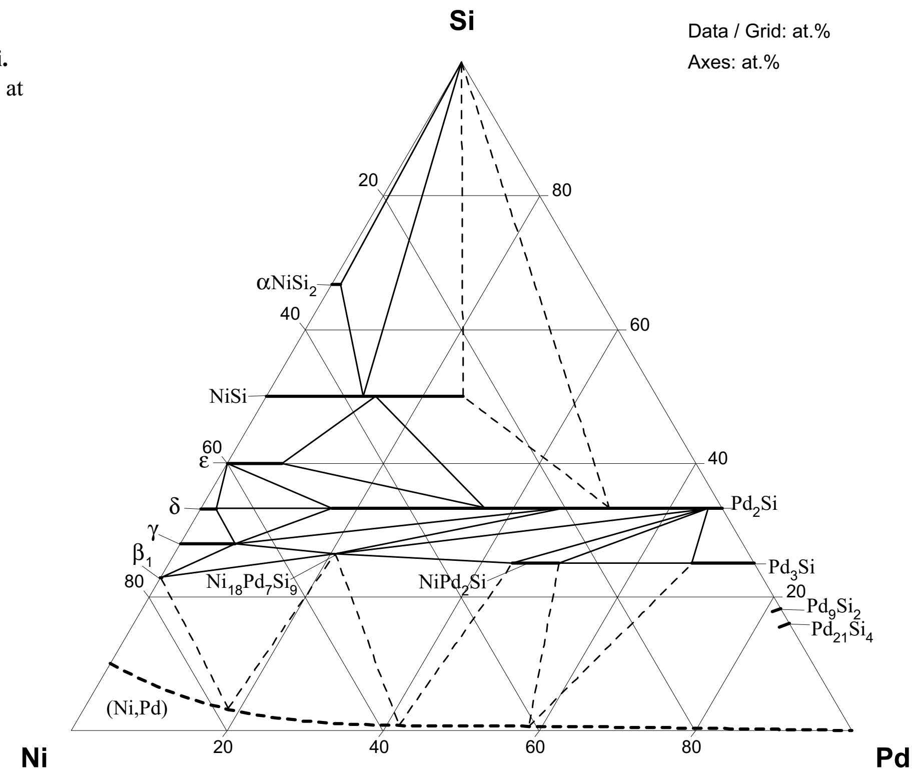

Fig. 2: Ni-Pd-Si. Liquidus and solidus temperature of the alloys along the vertical section 85Pd15Si - 78Ni22Si

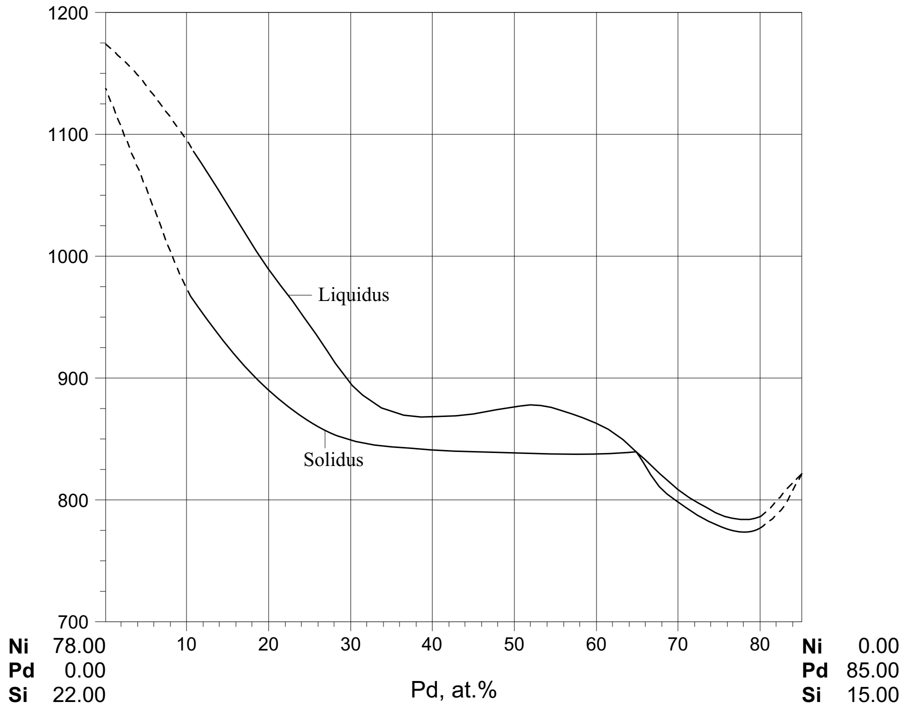

Fig. 3: Ni-Pd-Si. Vertical section NiSi-PdSi