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LA-1304

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THE NICKEL-PLUTONIUM SYSTEM

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AEC RESEARCH AND DEVELOPMENT REPORT

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ABSTRACT

A tentative nickel-plutonium constitutional diagram has been based on data obtained by thermal analysis, metallography, and X-ray diffraction techniques.

The system is a complex one with the following important features:

1. Nickel is soluble in epsilon plutonium, extending the epsilon field to 4.3 atomic per cent nickel at 465°C.
2. Nickel and plutonium form six intermetallic compounds, PuNi, PuNi₂, PuNi₃, PuNi₄, PuNi₅, and PuNi₉. The compound PuNi₅ forms congruently from the melt at approximately 1300°C, whereas the other compounds form peritectically.
3. The extended epsilon field terminates in a eutectoid reaction at 415°C and 1.5 atomic per cent nickel.
4. Epsilon plutonium and the compound PuNi form a eutectic system at 465°C with a eutectic composition of 12.5 atomic per cent nickel.
5. Nickel and the compound PuNi₉ form a eutectic system at 1210°C with a eutectic composition of 92 atomic per cent nickel.
6. Plutonium forms a limited solid solution with nickel.

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EXPERIMENTAL DETAILS

Raw Materials

The nickel employed in this investigation was one of the purest grades available and was obtained from the International Nickel Company. Precision lattice constant measurements made on two lots of the above nickel, which had been vacuum melted, gave an average unit cell determination of $a_0 = 3.5183 \text{ kX}$ at 25°C . This is slightly higher than the value reported by Jette and Foote¹ and may be due to the carbon impurity found in the nickel used in this investigation, as shown in Table I.

The plutonium used in this investigation came from three different plutonium reductions, designated as A-672, A-674, and A-675. The chemical compositions of the plutonium stocks after vacuum remelting (R), are given in Table I.

The occasional differences noted between reported chemical analyses and weighed-out alloy compositions have, for the most part, been inexplicable. A comparison of alloy charge weights before and after melting indicated that the average melting losses were approximately 0.30 per cent by weight. Consequently, where the chemical analysis disagrees with the nominal weighed-out composition, the chemical determination may be more reliable.

Table I

COMPOSITION OF RAW MATERIALS

(In parts per million)

	Plutonium			Nickel
	RA-672	RA-674	RA-675	
Mg	5	5	10	Trace
Al	15	50	50	N.D.
Si	300	300	25	N.D.
K	10	10	50	--
Ca	10	10	10	Trace
Mn	30	200	35	N.D.
Ni	10	50	120	--
Co	N.D.	N.D.	N.D.	N.D.
Cu	5	5	15	Trace
La	65	200	200	--
Pb	5	5	2	N.D.
C	179*	168*	133*	125*

N.D. Not detected.

* Carbon determined by combustion method;² other elements determined by spectrographic methods.

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Apparatus and Procedure

The first alloys produced were prepared in a resistance type furnace and were very clean as the static condition of the liquid melt contributed to the coalescence of impurity phases and their subsequent flotation. However, the maintenance of the resistance furnace was excessive, so two methods of induction heating were investigated.

The first method of induction heating used a 15-kw Tocco unit with a frequency of 10 kc/sec. The use of this unit reduced the maintenance but produced alloys which contained inclusions. The vigorous stirring action in the melt produced by the electromagnetic flux of 10 kc/sec prevented the inclusions from coalescing and floating to the top of the liquid charge.³

The results obtained by the second method of induction heating, which utilized a Thermonic induction unit of 10 kw capacity at 5 Mc/sec frequency, proved more successful since it provided rapid heating with good control and produced a clean alloy.

The operating frequency of the Thermonic induction unit is of such high magnitude (5 Mc/sec) that little stirring occurs³ and as a result the melt is very clean; furthermore, these alloys solidify with no apparent segregation.

The specimens were melted in a vacuum of better than 1×10^{-4} mm Hg. The induction coil, which transmitted the varying electromagnetic flux to the metallic charge, surrounded a vitreous silica cylinder which contained the specimen within a refractory crucible. The design of such a furnace is relatively simple and has been previously described by Brewer.⁴

Crucibles of magnesia, alumina, and thoria were used. Thoria did not prove successful because of its poor thermal shock characteristics. Magnesia and alumina were successful as crucible refractories and were used interchangeably in this investigation. These crucibles were made by the refractory section of CMR-6.

The alloys produced and their attendant chemical compositions and densities are listed in Table II. The as-cast weights of these alloys varied from 0.3 to 4.0 gm when prepared for metallographic and X-ray studies; larger specimens (25 to 50 gm) were used for thermal analysis. The alloy solidification cooling rates were undetermined but were probably rapid.

The liquidus, solidus, and solid-state reaction temperatures were determined by inverse-rate and time-temperature curves. Alloys of approximately 2.5 cc volume were contained in specially-designed magnesia crucibles in which the thermocouple protection tube was an integral part of the crucible. Such a crucible design had been previously used by Gayler.⁶

Heat was supplied to the crucible containing the thermal analysis specimen by a molybdenum resistance element furnace wound on a 2-in. alundum core. The furnace was

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Table II

ALLOY COMPOSITIONS AND DENSITIES

Specimen Number	Nominal Composition Atomic % Ni	Chemical Analysis Atomic % Ni	Density gm/cc	Specimen Number	Nominal Composition Atomic % Ni	Chemical Analysis Atomic % Ni	Density gm/cc
514*	1.0	0.8	18.92	550	75.0	76.2	11.24
471*	2.0	4.6	18.56	448	75.0	74.9	11.60
429*	4.9	3.1	18.53	406	75.0	75.0	11.31
435	5.0	3.5	none	526	76.0	75.9	11.45
434*	10.0	12.4	18.03	588	77.0	79.8	11.15
428*	10.0	8.4	17.88	551	77.8	79.2	11.02
427	14.7	12.3	17.17	490	78.7	79.0	11.41
441	15.0	15.0	18.99	496	79.3	85.2	9.49
426	20.1	18.6	15.91	405	80.0	84.9	10.66
425	25.1	27.2	15.60	554	80.0	80.6	11.21
446	29.8	31.1	none	587	80.1	80.0	11.16
451	35.0	24.0	none	470	81.8	81.8	11.12
419	35.0	34.4	13.73	586	82.0	83.5	10.81
420	35.0	34.8	14.11	440	82.5	84.6, 82.1	10.92
522	36.1	34.2	14.38	552	84.3	85.0	10.45
424	40.0	45.9	13.70	512	85.0	86.3	10.63
456	41.0	42.4	none	404	85.0	89.7	10.28
423	45.0	42.0	13.00	556	86.5	87.4	10.47
458	49.0	55.3	none	492	87.0	87.6	10.47
457	50.0	50.2	12.85	585	87.1	87.2	10.37
422	50.0	40.2	12.84	559	87.8	88.2	10.30
421	55.0	54.8	12.78	560	88.9	90.0	10.14
493	55.0	52.4	12.72	529	90.0	89.9	10.14
465	55.8	52.1	12.72	447	90.0	89.9	10.24
491	60.0	58.9	12.90	403	90.0	89.8	9.83
409	60.1	67.2	12.32	546	95.0	96.5	9.49
499	60.3	60.6	none	495	95.0	92.3	9.64
408	65.0	71.1	12.07	401	95.0	95.2	8.97
525	66.0	70.8	10.38	402	98.3	98.2	8.64
509	69.8	74.3	11.78	548	99.4	98.6	8.91
589	66.7	69.0	12.18				
407	70.0	77.4	11.38				
528	70.0	71.0	12.46				
547	72.5	73.5	12.21				

* Nickel was determined colorimetrically,⁵ the weight per cent plutonium of the other alloys was determined by oxidation-reduction methods,¹⁴ and nickel by difference.

Since the phase fields in this system are relatively narrow, small errors in alloy composition result in large changes in the amounts of phases present.

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enclosed by a water-cooled, vacuum-tight, brass jacket so that a pressure of less than 10^{-3} mm of mercury could be maintained.

Electrical power for the furnace was provided by a 10-kw direct-current generator whose output voltage was controlled by an electronic voltage regulator (servo furnace control). The purpose of this power unit was to provide either a constant or continuously (linear with time) increasing or decreasing direct voltage with isolation from ground. The servo furnace voltage control is described in detail elsewhere.⁷

Although fully annealed, certified, platinum-platinum 10 per cent rhodium thermocouples were used for all thermal analysis determinations, subsequent calibration with Bureau of Standards melting point metals indicated that the mean error of the equipment was $\pm 2.5^{\circ}\text{C}$ in the range from 0 to 1063°C . The error at higher temperatures did not appear constant, but an accuracy of $\pm 5^{\circ}\text{C}$ seems likely. The decrease of the thermoelectromotive force with time, when used at high temperatures in vacuum, has been noted before⁸ and is probably due to the evaporation of rhodium from the rhodium-rich thermocouple.

Following thermal analyses, some specimens were examined microscopically and all specimens were analyzed chemically.

X-ray powder techniques were used to resolve the phase fields of the system and to determine the structures of the intermetallic compounds wherever possible. Single crystal methods of X-ray diffraction analysis were applied where single crystals were available in order to determine the structures of those intermetallic compounds which could not be readily identified by X-ray powder techniques.

Specimens used for obtaining Debye patterns were made by filing the heat-treated samples and placing the filings in clear silica capillaries. The filled capillaries were then evacuated to a pressure of 10^{-5} mm Hg and sealed. Patterns were obtained on all specimens in the as-cast condition and after heat treatments. The Straumanis⁹ technique was used with a 114.7 mm diameter powder camera for the production of room temperature Debye patterns. A Unicam high-temperature 19.0-mm powder camera was used to obtain Debye patterns above room temperature. In order to obtain precision lattice measurements, stress-relieved filings were mounted between layers of Scotch tape and exposed in a back-reflection focusing camera. Resulting patterns were analyzed by Cohen's method.¹⁰

Single crystal specimens were sealed in vitreous silica capillaries as in the preparation of the powder specimens. Oscillation and Weissenberg methods of X-ray diffraction analysis were used. Because of the lack of good single crystals of the nickel-plutonium compounds, the resulting patterns were not particularly good.

Specimens for metallographic examination were mounted in prefabricated methacrylate mounts. Then they were hand-lapped from 1 through 4/0 metallographic papers, using

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carbon tetrachloride as the lubricant. When excessive surface pitting was not encountered, a preliminary polish was carried out by hand-lapping the specimens on a billiard cloth with No. 600 alumina and carbon tetrachloride.

Alloys containing 40 to 99 atomic per cent nickel were mechanically polished with No. 3 Micropolish on Microcloth laps rotating at 250 rpm. Since these alloys were free from staining, they were usually wiped dry with cheesecloth and transferred from the polishing dry box to a hood for etching.

Alloys containing less than 40 atomic per cent nickel were polished by hand-lapping on Microcloth with AB Micropolish using carbon tetrachloride as the lubricant. Since these alloys contained appreciable quantities of alpha plutonium, the use of a water suspension of abrasive resulted in the formation of a gray adherent film that masked the true microstructure. The formation of this gray pseudomicrostructure is characteristic of plutonium-rich phases and was eliminated by using carbon tetrachloride for the abrasive suspension instead of using an aqueous abrasive suspension.

All alloys were etched electrolytically. Those containing from 85 to 99 atomic per cent nickel were etched in a solution of 53 parts of 85 per cent phosphoric acid and 100 parts distilled water, with a current density of 15 ma/cm^2 for 10 to 60 seconds.¹¹

Alloys containing 50 to 84 atomic per cent nickel were electro-etched in a solution of 7 parts of tetraphosphoric acid, 57 parts 2-ethoxyethanol (glycol monoethyl ether) and 36 parts distilled water with a current density of 15 ma/cm^2 for 1 to 2 min. With nickel contents of less than 50 atomic per cent, the alloys were etched in the same electrolyte from 3 to 5 sec, with a current density of 80 ma/cm^2 . After being etched, the specimens were swabbed with cotton and distilled water, rinsed in distilled water, and blown dry.

Following metallographic examination, the specimens were submitted for X-ray diffraction analyses and, where applicable, for chemical analyses.

The phases in the various alloys were identified by both their microstructural habits and respective Diamond Pyramid Hardness (DPH) Numbers at 25-gm loads. The initial phase identification was the result of collaboration between metallography and X-ray diffraction analysis. Some metallographic phase identification characteristics are given in Table III.

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Table III
DPH NUMBERS OF NICKEL-PLUTONIUM PHASES

Phase	DPH Number	Remarks
alpha Pu	285	Slight ductility
PuNi	250	Slight ductility
PuNi ₂	505 to 634	Brittle
PuNi ₃	388 to 550 (as-cast)	Brittle
	499 to 575 (heat-treated)	
PuNi ₄	196 to 292	Probably brittle
PuNi ₅	442 to 580 (as-cast)	Brittle
	516 to 641 (heat-treated)	--
PuNi ₉	416 to 560 (as-cast)	Brittle
	499 to 616 (heat-treated)	--
zeta Nickel	138 to 224	Ductile
Pure Nickel	97	Ductile

EXPERIMENTAL RESULTS

The individual solid phases are first discussed, starting with plutonium and proceeding in the direction of nickel. Following this, the thermal, X-ray, and metallographic data leading up to the diagram itself are presented. All compositions are expressed in atomic per cent.

Plutonium

The melting point of the plutonium used in the majority of the alloys was $635 \pm 2^{\circ}\text{C}$. This melting point temperature seems somewhat high in view of previous melting point determinations. Further work is now being conducted in order to evaluate the effects of normal impurities on the melting point temperature.

Nickel is soluble in epsilon plutonium and extends the epsilon plutonium field to approximately 4.3 atomic per cent nickel at the eutectic temperature of 465°C .

The epsilon field terminates in an invariant point at 415°C in an allotropic, eutectoid inversion reaction ($\epsilon \rightleftharpoons \delta + \text{PuNi}$) which was confirmed by thermal analysis, X-ray (see Figure 1), and metallographic data. Areal analyses indicated that the eutectoid composition was 1.5 atomic per cent nickel. A photomicrograph of a heat-treated alloy is shown in Figure 2 in which the characteristic microstructure of a eutectoid can be observed.

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Precision unit cell measurements of delta plutonium in a 2 atomic per cent nickel alloy indicated that the solubility of nickel in delta plutonium is essentially zero at 415°C and lower.

A comparison of the interplanar spacing of the highest angle reflection ($\theta = 81^\circ$) for alpha plutonium, and the alpha plutonium phase in a 2 atomic per cent nickel alloy, indicated that there is no solubility of nickel in alpha plutonium. Metallographic evidence did not indicate any significant solubility of nickel in either beta or gamma plutonium.

The (Epsilon Plutonium plus PuNi) Eutectic

Epsilon plutonium forms a eutectic with the compound PuNi. The eutectic composition was placed at 12.3 atomic per cent nickel by areal analyses. An alloy of 12.3 atomic per cent nickel was examined metallographically and revealed a eutectic microstructure like that shown in Figure 3. The eutectic reaction temperature was 465°C as determined by thermal analysis.

PuNi

This compound forms peritectically at 800°C from the reaction between PuNi₂ and the melt. Primary PuNi forms in the composition range 12.3 to 45.9 atomic per cent nickel. However, the presence of PuNi₂ in the latter alloy indicates that the liquidus-terminal end of the peritectic isothermal is somewhat less than 45.9 atomic per cent nickel. A reasonable approximation would be 45 atomic per cent nickel.

A combination of powder and single crystal X-ray data revealed evidence which indexed an orthorhombic lattice with constants $a = 3.62$, $b = 4.19$, $c = 10.22$ kX and $Z = 4$.

PuNi₂

This compound forms at 1210°C as a result of the peritectic reaction, PuNi₃ + liquid $\rightleftharpoons$ PuNi₂. PuNi₂ was found as a primary constituent in the composition range from 45.9 to about 67 atomic per cent nickel. An as-cast alloy of 42.0 atomic per cent nickel did not reveal the presence of PuNi₂, whereas both as-cast or heat-treated alloys of 45.9 atomic per cent nickel disclosed small amounts of PuNi₂ as a primary constituent (compare Figures 4 and 5). Consequently, the composition range for primary crystallization of PuNi₂ is placed between 45 and 66 atomic per cent nickel.

Metallographic and X-ray data indicated that a slight homogeneity range exists in this phase. Hardness increased with increase in plutonium and a precipitation of PuNi occurred when the 71.1 per cent alloy was held at 600°C (Figures 6 and 7). According to the precision lattice cell measurements, the unit cell dimension is 7.1268 kX on the plutonium-rich side of the homogeneity range and 7.1010 kX on the nickel-rich side at a temperature of 600°C. Additional lattice constant measurements of the compound after heat-treating at 800°C have revealed no differences from those determined at 600°C. Atomic and molecular volume calculations indicate that the homogeneity range of PuNi₂ extends from 66.2 to 67.2 atomic

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per cent nickel at 800 and 600°C. PuNi₂ is cubic and isomorphous with PuAl₂, having eight molecules per unit cell.

PuNi₃

This intermetallic compound is believed to form at 1230°C as a result of the peritectic reaction, PuNi₄ + liquid ⇌ PuNi₃. The liquidus-terminal end of the peritectic isothermal has been placed metallographically at approximately 67 atomic per cent nickel. An alloy of the PuNi₃ composition has the microstructure shown in Figure 8.

Fragments from a 70 atomic per cent nickel alloy were analyzed by oscillation and Weissenberg techniques. The structure of PuNi₃ was found to be orthorhombic, with unit cell constants of 4.26, 4.98, and 8.16 kX, and with 3 molecules per unit cell.

PuNi₄

The intermediate phase, PuNi₄, is believed to form at 1260°C as a result of the peritectic reaction, PuNi₅ + liquid ⇌ PuNi₄. The liquidus-terminal end of the peritectic isothermal has been qualitatively placed at 75 atomic per cent nickel by the examination of metallographic data.

Although PuNi₄ and PuNi₃ are believed to be peritectic reaction products, they did not exhibit typical peritectic microstructures (Figures 8 and 9). Since considerable supercooling (approximately 90°C) was encountered in the solidification of the alloys containing the compound, the effect of supercooling could easily produce a microstructure unrepresentative of a normal equilibrium reaction.¹²

The structure of PuNi₄ has not yet been determined.

PuNi₅

This compound forms at an open maximum with a melting point of approximately 1300°C. This melting point agrees well with the melting points of other isomorphous compounds, viz.,

CeNi ₅	1310°C M. P.
LaNi ₅	1315°C M. P.
PrNi ₅	1370°C M. P. ¹³

The binary systems of cerium, lanthanum, praseodymium, and plutonium with nickel have certain features in common (compare Figures 10 and 19).

A homogeneity range was indicated by the microscopic observation of heat-treated specimens containing an excess of nickel over the composition PuNi₅. A photomicrograph of a slowly cooled alloy slightly richer in plutonium than the PuNi₅ composition is shown in Figure 11 in which primary PuNi₅ is associated with PuNi₄. For comparison, a photomicrograph of a slowly cooled alloy containing more nickel than the PuNi₅ composition is exhibited in Figure 12. Here primary PuNi₅ is associated with a precipitate of PuNi₉ and peritectic PuNi₉.

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This compound has a hexagonal space lattice with $a_0 = 4.862 \pm 0.001$ kX, $c_0 = 3.972 \pm 0.001$ kX, and $c/a = 0.817$, and contains 1 molecule per unit cell. The calculated density was 10.81 gm/cc. As stated previously, it is isomorphous with $CeNi_5$, $LaNi_5$, $CaNi_5$, and $PrNi_5$, and belongs to the space group $c6/mmm - D_{6h}$.

The atomic positions in a unit cell are given below:

1. Pu in 1(a), 000
2. Ni_I in 2(c), $1/3 \ 2/3 \ 0$, $2/3 \ 1/3 \ 0$
3. Ni_{II} in 3(g), $1/2 \ 0 \ 1/2$, $0 \ 1/2 \ 1/2$, $1/2 \ 1/2 \ 1/2$

Precision unit cell measurements confirmed the homogeneity range found by metallographic evidence. Unit cell determinations at 800 and 980°C of an alloy containing a small excess of $PuNi_9$ are given below.

<u>Temperature, °C</u>	<u>a_0</u>	<u>c_0</u>
800	4.851 kX	3.974 kX
980	4.833 kX	3.986 kX

If one assumes that the change in lattice parameter is due to a change in chemical composition with change in temperature, the homogeneity range of $PuNi_5$ is approximately 2 atomic per cent nickel. However, if the chemical composition remains constant, then the lattice parameter change may be due to a negative volumetric coefficient of expansion. Insufficient data exist to answer this question. $PuNi_5$ is ferromagnetic.

$PuNi_9$

The designated stoichiometric composition of this intermetallic compound is uncertain. However, in view of the calculated and experimental densities, and assuming that 4 molecules are in a unit cell, the ratio of one plutonium atom to nine nickel atoms seems probable, but metallographic evidence failed to confirm this ratio.

This phase forms at 1235°C as a result of the peritectic reaction, $PuNi_5 + \text{liquid} \rightleftharpoons PuNi_9$. It was impossible to make an alloy comprising only the compound. However, a photomicrograph of an alloy approaching the $PuNi_9$ composition is shown in Figure 13. Although this alloy had a nominal composition of 90.0 and an analyzed composition of 89.9 atomic per cent nickel, a small amount of zeta nickel was observed in the microstructure.

X-ray high angle line positions of $PuNi_9$ on both its nickel-rich and plutonium-rich sides were essentially the same, indicating no measurable range of homogeneity for the compound. It is hexagonal with 4 molecules per unit cell; the cell constants are $a_0 = 8.27$, $c_0 = 7.99$ and $c/a = 0.966$, and it is ferromagnetic.

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The Eutectic (PuNi₉ + zeta nickel)

The compound PuNi₉ and zeta nickel solidify as a eutectic at 1210°C. By areal analysis the eutectic composition was found to be 92 atomic per cent nickel. A photomicrograph of an alloy of eutectic composition is shown in Figure 14.

Zeta Nickel

On the basis of metallography, more than 1.4 atomic per cent plutonium was found to dissolve in nickel at temperatures from 375 to 980°C. In the as-cast condition, a fine precipitate of PuNi₉ was observed as a decreasing solid solubility product (Figure 15). By solution treatment, however, the precipitate was redissolved by the zeta nickel and held in solution (Figure 16).

A microscopic examination of another alloy containing 1.9 atomic per cent plutonium, in both the as-cast and solution-treated condition, revealed that the compound PuNi₉ was present. Assuming that the errors in chemical analyses were small, then the solvus may be placed between 1.4 and 1.9 atomic per cent plutonium. A realistic assumption is to place the solvus at 1.6 atomic per cent nickel, and to estimate conservatively that the zeta field is increasing slowly with increase in temperature until the eutectic isothermal is reached (1210°C). This is not a rash assumption since the precipitation of PuNi₉ from zeta nickel denoted a negative solvus below the eutectic isothermal. The maximum plutonium solubility in zeta nickel has been deduced from Figure 17 as being less than 1.9 atomic per cent, say, 1.8 atomic per cent. Precision lattice constant measurements confirmed the solid solubility of plutonium in nickel.

A resumé of the various solid phase fields is shown by corresponding reproductions of the X-ray powder patterns in Figure 18.

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SUMMARY

A critique of the experimental evidence indicates that nickel and plutonium form six compounds: PuNi, PuNi₂, PuNi₃, PuNi₄, PuNi₅, and PuNi₉. The stoichiometric composition of PuNi₉ is uncertain, but may approach the designated composition. The compounds PuNi₄, PuNi₅, and PuNi₉ are ferromagnetic.

Plutonium and nickel form a solid solution containing approximately 1.8 atomic per cent plutonium at 1210°C. Epsilon plutonium and nickel form a solid solution extending the epsilon plutonium field to approximately 4.3 atomic per cent nickel. Delta plutonium probably dissolves a small amount of nickel, but nickel is insoluble in gamma, beta, and alpha plutonium.

Although the mechanical properties of the alloys were not formally determined, alloys containing up to 25 atomic per cent nickel were hot-extruded. The compounds were brittle, but the zeta nickel appeared to be ductile.

Experience obtained in preparing the alloys for microscopic examination indicates that PuNi is reactive with laboratory air and water, whereas the other compounds are relatively inert to these conditions. Zeta nickel demonstrated good corrosion resistance, but less than that of nickel.

An observation of the tentative nickel-plutonium constitutional diagram, as illustrated in Figures 19a and 19b, shows several features of interest to reactor engineers:

1. The low temperature eutectic (465°C) existing between plutonium and PuNi may be suitable as a liquid fuel.
2. The solid solubility of plutonium in nickel would eliminate use of nickel as the container material for plutonium slugs.
3. Zeta nickel may be a suitable reactor material since it exhibits favorable ductility and corrosion resistance.

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Fig. 1. Phases as determined by Debye patterns at temperature. The indicated temperatures are low because of errors in temperature measurements.

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Fig. 2. Specimen number 514b, 1 atomic per cent nickel alloy which had been annealed for 715 hr at 480°C and quenched, followed by 280 hr at 410°C and quenched. The four dark grey spherical grains are PuNi, the lighter matrix is alpha plutonium, and the pearlitic microconstituent is the eutectoid mixture of alpha plutonium and PuNi. 500X.

Fig. 3. Specimen number 927, as-cast 12.3 atomic per cent nickel alloy, exhibiting the eutectic microstructure of alpha plutonium and PuNi. 100X.

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Fig. 4. Specimen number 423b, as-cast 42.0 atomic per cent nickel alloy. The lighter grains are primary PuNi and the intergranular material is the "divorced" eutectic (plutonium and PuNi) with some plutonium oxide from polishing. 500X.

Fig. 5. Specimen number 424b, as-cast 45.9 atomic per cent nickel alloy. The light grains are primary PuNi; the intergranular material is the "divorced" eutectic (plutonium + PuNi); and the dendritic material is unreacted PuNi₂. 500X.

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Fig. 6. Specimen number 409a, 67.2+ atomic per cent nickel alloy in the as-cast condition, showing the development of Widmanstatten areas. The lighter phase is primary PuNi₃ and the other phase is peritectic PuNi₂. 250X.

Fig. 7. Specimen number 409a, 67.2+ atomic per cent nickel alloy which had been annealed for 525 hours at 600°C and quenched. The PuNi₂ exhibits a Widmanstatten structure and was associated with primary and precipitated PuNi₃. 250X.

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Fig. 8. Specimen number 406b, as-cast 75.0 atomic per cent nickel alloy consisting of PuNi_3 . The minute inclusions are particles of polishing abrasive which were embedded in the PuNi_3 during the polishing operation. 250X.

Fig. 9. Specimen number 587, as-cast 79 atomic per cent nickel alloy consisting of PuNi_4 . The inclusions are Pu_2O_3 . 250X.

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Fig. 10. Constitutional diagrams of cerium-nickel, lanthanum-nickel, and praseodymium-nickel. ¹³

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Fig. 11. Specimen number 586, 82.0 atomic per cent nickel alloy in a slowly cooled as-cast condition which shows primary PuNi_5 associated with PuNi_4 (the darker acicular constituent). Microcracks are visible in the PuNi_4 . 250X.

Fig. 12. Specimen number 552, 85.0 atomic per cent nickel alloy in a slowly cooled as-cast condition which shows primary PuNi_5 associated with PuNi_9 . 250X.

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Fig. 13. Specimen number 447a, 89.9 atomic per cent nickel alloy in the solution-treated state (230 hours at 800°C, quenched, followed by 70 hours at 980°C, quenched.) showing the presence of fine zeta nickel in a matrix of PuNi₉. 500X.

Fig. 14. Specimen number 495b, 92.0 atomic per cent nickel alloy in the as-cast condition which reveals the eutectic (PuNi₉ + zeta) associated with a small amount of primary nickel. 500X.

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Fig. 15. Specimen number 548, 1.38 atomic per cent plutonium alloy in the as-cast condition. The zeta nickel contains a fine precipitate of PuNi_9 . 500X.

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Fig. 16. Specimen number 548, 1.38 atomic per cent plutonium alloy after heat-treating at 980°C for 50 hours, followed by quenching. The absence of PuNi₉ clearly indicates that 1.38 atomic per cent plutonium is soluble in nickel at this temperature to form zeta nickel. 500X.

Fig. 17. Specimen number 402B, 1.9 atomic per cent plutonium alloy in the as-cast condition. The primary grains are zeta nickel and the grain boundary material is PuNi₉. The latter is a product of the "divorced" eutectic (Liquid $\rightleftharpoons$ PuNi₉ + zeta), with possible coalescence of precipitated PuNi₉. 250X.

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Cu K-Alpha Radiation

	Atomic PerCent Nickel	Phases
A	0.	ALPHA Pu
B	34.8	PuNi + ALPHA Pu
C	67.2	PuNi ₂
D	74.9	PuNi ₂ + PuNi ₃
E	77.4	PuNi ₄
F	80.1	PuNi ₄ + PuNi ₅
G	84.6	PuNi ₅
H	89.8	PuNi ₉ + Zeta
I	100.0	Ni

Fig. 18. Debye patterns of various phases of the Pu-Ni system.

Fig. 19a. Tentative constitutional diagram for the system Pu-Ni.

Fig. 19b. Tentative constitutional diagram for the system Pu-Ni.

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REFERENCES

- 1 E. Jette and F. Foote, J. Chem. Phys. 3, 605 (1935).
- 2 W. G. Smiley, "A New Micro-Combustion Method for Carbon in Plutonium," Los Alamos Scientific Laboratory Report, LA-1128. Confidential.
- 3 P. C. L. Pfeil, "The Constitution of Uranium-Molybdenum Alloys," J. Inst. Metals 77, 555 (1950).
- 4 Leo Brewer, "A High Temperature High-Vacuum Apparatus," CT-2139. Restricted.
- 5 A. L. Henicksman, "The Spectrophotometric Determination of Gallium in Plutonium," Los Alamos Scientific Laboratory Report (at press).
- 6 M. L. V. Gayler, J. Iron Steel Inst. 128, 303 (1933).
- 7 J. Buchen, "Servo Furnace Control," Los Alamos Scientific Laboratory Report (at press).
- 8 American Institute of Physics et al., Temperature Its Measurement and Control in Science and Industry, Reinhold Publishing Co., New York, 1941, p. 1270.
- 9 M. Straumanis and A. Ievins, Naturwissenschaften, 23, 833 (1935).
- 10 M. Cohen, Rev. Sci. Instr. 6, 68 (1935); 7, 155 (1936).
- 11 G. Wensch, "Electrolyte Polishing of Nickel," Metal Progress, 57, 488 (1950).
- 12 H. Carpenter and J. Robertson, Metals, Oxford University Press, New York, 1939, p. 234-245.
- 13 R. Vogel, "Uber die Systeme Cer-Nickel, Lanthan-Nickel, Praseodym-Nickel und Cer-Cobalt," Metallforschung 2, 97-103 (1947).
- 14 H. E. Boaz et al., "Chemical and Spectrochemical Analysis of Uranium and Plutonium Materials," Los Alamos Scientific Laboratory Report, LA-416A. Secret.

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