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Ni + Pd + Ga AND Ni + Pd + In LIQUID ALLOYS: ENTHALPIES OF FORMATION

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In order to fill the evident gap in the thermodynamic data of nickel-palladium-gallium and nickel-palladium-indium ternary alloys, the enthalpies of formation of these systems in the liquid state have been determined. This was achieved by means of a very high temperature calorimeter (T < 1800 K), using the direct drop method, and based on analogous measurements of the respective binary alloys previously published. Complete automation of the calorimeter led to a good precision even at the highest temperatures. The enthalpies of formation of the ternary liquid alloys were measured between 1400 and 1600 K on the whole composition range. As in the limiting binary systems, enthalpies of formation are negative and non temperature dependent at any composition.

Introduction

Very few high temperature thermodynamic data exist on the nickel–palladium–gallium and nickel–palladium–indium ternary alloys, and their equilibrium phase diagrams are also unexplored.

For the limiting binary alloys constituted with nickel, palladium, gallium and indium, experimental values of enthalpy and free energy of formation are scarce and often contradictory. Only the equilibrium phase diagrams are available.

This lack of data makes it impossible to propose recommended thermodynamic values for all these alloys. Therefore and in order to fill this gap, as a first step, we undertook the determination of the enthalpies of formation of the Ni–Pd, Ni–Ga, Ni–In, Pd–Ga and Pd–In liquid alloys, by high temperature calorimetry [1]. Strongly exothermic enthalpies were observed which are indicative of strong interactions in the liquid; this is related to the several high melting definite compounds in the binary phase diagrams.

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From this experimental basis, and using the same calorimetric technique, the enthalpies of formation of Ni–Pd–Ga and Ni–Pd–In ternary alloys were determined. The operation method and the obtained results are given in the following.

Experimental

Experimental procedure

Using a very high temperature calorimeter ($T < 1800$ K) previously described [2, 3], the enthalpy of formation of liquid alloys has been determined; all measurements were performed by the direct drop method. This apparatus (introduction of samples and data acquisition) is completely automated [4].

In the field of very high temperature calorimetry, an important role is played by the parasitic reactions involved by interactions between alloy and atmosphere, crucible and alloy, crucible and atmosphere. Accordingly, all the chemicals used in the present study were of high purity. Crucibles were made either of nuclear grade graphite or boron nitride.

All experiments were conducted under argon flux purified by passing through titanium sponge at 850°. Prior to argon introduction, the furnace and experimental chamber were degasified at high temperature under vacuum.

The metals used to make the alloys had the following grade (in % at.): palladium: 99.995; nickel: 99.999; gallium and indium: 99.9999.

Calibration

During each experiment, the calorimeter was calibrated first by drops of weighed amounts of the pure metal in the empty crucible, then by drops of NIST α -alumina. Heat capacities and, if required, enthalpies of fusion involved in the calibration constant were taken either from Hultgren *et al.* [5] or from NIST [6].

Precision

It depends on the alloys under investigation and on the experimental temperature. For the ternary alloys examined here at the average temperature 1600 K, enthalpies of formation were obtained with a precision of about ±6%.

Results

Palladium-nickel-gallium system

All the enthalpies of formation of this liquid alloys were obtained from drops of palladium and nickel, at temperatures ranging between 1500 and 1660 K. Measurements were conducted along the following sections:

x_{Pd}/x_{Ga} = 0.301/0.699, 0.305/0.695, 0.495/0.505, 0.589/0.421 and 0.599/0.401 (Table 1–(Ni)).

x_{Ni}/x_{Ga} = 0.401/0.599, 0.409/0.591, 0.598/0.402, 0.599/0.401, 0.800/0.200 and 0.804/0.196 (Table 1–(Pd)).

The mole fractions of the third added component, the experimental temperature and the corresponding enthalpies of formation are given in tables. The enthalpies of formation (in $kJ \cdot mol^{-1}$) of the ternary alloys were calculated from the data obtained from preliminary measurements on the binary systems; those binary values are given in the first line of each $\Delta mix\,H_m$ column, at the zero mole fraction of the third component added. It should be noted that the enthalpy of formation is non temperature dependent as already observed for the limiting binary mixtures.

The values of the ternary formation enthalpy obtained either by nickel drop or palladium drop are in good agreement ($\pm 0.5\ kJ \cdot mol^{-1}$). Figure 1 shows isoenthalpic sections obtained from these results.

Palladium-nickel-indium system

Similar experiments were conducted on this system and the ternary alloys were also obtained by addition of nickel and palladium, on the whole composition range between 1400 and 1520 K.

The investigated isotheph sections were:

x_{Ni}/x_{In} = 0.240/0.760, 0.381/0.619, 0.388/0.612, 0.400/0.600, 0.423/0.577, 0.599/0.401 and 0.600/0.400 (Table 2–(Pd))

x_{Pd}/x_{In} = 0.299/0.701, 0.336/0.664, 0.400/0.600 and 0.662/0.338 (Table 2–(Ni))

The formation of these alloys is exothermic on the whole composition range.

Figure 2 shows the isoenthalpic curves corresponding to the formation of this ternary system.

Table 1 (Ni) The values in the first line of the table correspond to x_{Pd}/x_{Ga}

0.305 / 0.695		0.589 / 0.411		0.495 / 0.505		0.599 / 0.401		0.301 / 0.699	
xNi	$-\Delta_{mix}H_m$	xNi	$-\Delta_{mix}H_m$	xNi	$-\Delta_{mix}H_m$	xNi	$-\Delta_{mix}H_m$	xNi	$-\Delta_{mix}H_m$
1519 K		1517 K		1517 K		1516 K		1516 K	
0.000	44.199	0.000	73.142	0.000	68.101	0.000	72.618	0.000	44.031
0.047	45.644	0.044	69.899	0.064	65.890	0.034	69.909	0.061	45.641
0.091	46.914	0.132	62.082	0.122	63.296	0.071	66.843	0.116	47.017
0.135	47.939	0.182	57.683	0.179	60.250	0.108	63.854	0.166	48.087
0.177	48.785	0.227	53.674	0.234	56.675	0.147	60.589	0.213	48.968
0.217	49.270	0.269	49.963	0.282	52.922	0.186	57.154	0.257	49.481
0.254	49.340	0.307	46.560	0.326	49.502	0.225	53.592	0.297	49.603
0.289	16 680	0.345	43.239	0.367	46.131	0.261	50.333	0.334	49.324
0.323	48.336	0.379	40.188	0.405	42.908	0.296	47.323	0.367	48.716
0.355	47.456	0.412	37.453	0.440	39.908	0.329	44.591	0.397	47.889
0.385	46.274	0.440	34.958	0.471	37.204	0.359	42.065	0.425	46.768
0.414	44.928	0.467	32.699	0.498	34.845	0.388	39.719	0.452	45.512
0.441	43.171	0.491	30.626	0.523	32.584	0.439	35.488	0.478	43.889
0.465	41.509	0.514	28.688	0.546	30.498	0.465	33.394	0.502	42.357
0.488	39.784	0.535	26.925	0.569	28.656	0.489	31.519	0.523	40.767
0.509	37.871	0.556	24.904	0.590	26.758	0.512	29.709	0.544	38.999
0.530	36.000	0.579	23.066	0.597	26.013	0.534	28.222	0.568	37.450
0.550	34.446			0.610	24.942			0.590	36.226
0.570	31.970			0.624	24.273				
0.587	30.603								

Table 1 (Pd)

$xNi/xGa = 0.804/0.196$		$xNi/xGa = 0.800/0.200$		$xNi/xGa = 0.599/0.401$		$xNi/xGa = 0.409/0.591$		$xNi/xGa = 0.598/0.402$		$xNi/xGa = 0.401/0.599$	
xPd	$-\Delta_{mix}H_m$	xPd	$-\Delta_{mix}H_m$	xPd	$-\Delta_{mix}H_m$	xPd	$-\Delta_{mix}H_m$	xPd	$-\Delta_{mix}H_m$	xPd	$-\Delta_{mix}H_m$
1662 K		1518 K		1517 K		1516 K		1516 K		1508 K	
0.000	19.000	0.000	21.586	0.000	33.791	0.000	32.671	0.000	33.668	0.000	32.767
0.050	19.387	0.043	21.728	0.042	35.632	0.036	36.019	0.041	35.000	0.044	36.824
0.096	19.768	0.083	20.995	0.084	37.030	0.074	39.232	0.084	36.696	0.085	40.178
0.140	20.163	0.119	20.278	0.169	39.064	0.121	42.799	0.125	37.747	0.124	43.211
0.180	20.429	0.155	20.798	0.209	39.713	0.166	46.223	0.167	38.689	0.161	45.860
0.221	20.833	0.189	21.065	0.246	40.168	0.211	48.909	0.207	39.523	0.196	48.165
0.258	21.233	0.221	21.111	0.280	40.458	0.251	51.145	0.247	40.040	0.229	50.162
0.294	21.402	0.251	21.273	0.312	40.618	0.288	52.767	0.322	40.310	0.261	51.768
0.328	21.595	0.280	21.402	0.343	40.609	0.321	53.881	0.354	40.262	0.292	53.091
0.359	21.709	0.308	21.443	0.374	40.342	0.353	54.890	0.384	40.092	0.321	54.162
0.392	21.750	0.337	21.441	0.403	39.863	0.384	55.453	0.414	39.754	0.348	54.942
0.421	21.681	0.363	21.407	0.431	39.411	0.412	55.671	0.443	39.271	0.374	55.475
0.448	21.455	0.388	21.395	0.457	38.882	0.440	55.565	0.469	38.603	0.400	55.759
0.473	21.250	0.413	21.216	0.481	38.325	0.466	55.227	0.495	37.872	0.424	55.852
0.497	20.842	0.435	20.995	0.505	37.613	0.489	54.766	0.518	37.177	0.447	55.702
0.519	20.519	0.457	20.789	0.527	36.737	0.512	54.163	0.541	36.374	0.470	55.413
0.540	20.212	0.476	20.540	0.547	35.934	0.532	53.416	0.562	35.626	0.492	54.905
		0.495	20.305	0.567	35.140	0.551	52.556	0.586	34.353	0.512	54.327
				0.586	34.167	0.572	51.606			0.538	53.353
				0.604	33.196						

Table 2 (Pd) The values in the first line of the table correspond to x_{Ni}/x_{In}

0.240 / 0.760		0.423 / 0.577		0.381 / 0.619		0.388 / 0.612	
1520 K x(Pd)	$-\Delta_{mix}Hm$	1519 K x(Pd)	$-\Delta_{mix}Hm$	1519 K x(Pd)	$-\Delta_{mix}Hm$	1519 K x(Pd)	$-\Delta_{mix}Hm$
0.000	6.535	0.000	11.309	0.000	10.115	0.000	9.669
0.078	15.418	0.055	16.480	0.014	11.592	0.019	11.806
0.146	22.743	0.153	24.885	0.029	13.109	0.040	14.145
0.207	29.051	0.198	28.345	0.047	14.895	0.062	16.394
0.262	34.459	0.241	31.212	0.064	16.599	0.083	18.523
0.312	38.954	0.279	33.552	0.081	18.215	0.103	20.618
0.359	42.557	0.313	35.411	0.097	19.797	0.123	22.649
0.401	45.314	0.381	38.262	0.114	21.326	0.142	24.604
0.439	47.152	0.411	39.098	0.131	22.886	0.163	26.566
0.473	48.481	0.467	40.192	0.149	24.481	0.182	28.439
0.504	49.258	0.491	40.354	0.166	26.049	0.202	30.225
0.532	49.457			0.184	27.601	0.221	31.839
0.558	49.269			0.202	29.118	0.239	33.370
0.581	48.123						

0.240 / 0.760		0.400 / 0.600		0.599 / 0.401		0.600 / 0.400	
1518 K x(Pd)	$-\Delta_{mix}Hm$	1516 K x(Pd)	$-\Delta_{mix}Hm$	1515 K x(Pd)	$-\Delta_{mix}Hm$	1513 K x(Pd)	$-\Delta_{mix}Hm$
0.000	6.925	0.000	10.890	0.000	9.886	0.000	10.060
0.054	12.950	0.041	14.851	0.087	16.000	0.056	14.089
0.106	18.682	0.085	19.000	0.161	20.486	0.110	17.540
0.154	23.806	0.126	22.585	0.227	23.944	0.160	20.745
0.199	28.444	0.164	25.752	0.283	26.385	0.211	23.520
0.241	32.570	0.199	28.632	0.333	27.944	0.257	25.714
0.278	36.227	0.234	31.169	0.377	28.894	0.300	27.340
0.315	39.469	0.270	33.521	0.416	29.437	0.339	28.567
0.355	42.466	0.309	35.887	0.451	29.582	0.374	29.262
0.391	44.769	0.344	37.701	0.482	29.574	0.405	29.689
0.422	46.590	0.376	39.143	0.510	29.421	0.435	29.887
0.455	47.923	0.406	40.131	0.537	29.038	0.462	29.931
0.485	48.795	0.434	40.840	0.560	28.651	0.487	29.846
0.513	49.335	0.461	41.292	0.602	26.737	0.510	29.579
0.540	49.343	0.486	41.462			0.531	29.208
0.569	49.058	0.509	41.542			0.552	28.837
		0.530	41.526			0.571	28.452
		0.551	41.239			0.589	27.927
		0.571	40.884				
		0.589	40.459				

Table 2 (Ni) The values in the first line of the table correspond to x_{Pd} / x_{In}

0.400 / 0.600		0.336 / 0.664		0.400 / 0.600		0.299 / 0.701		0.662 / 0.338	
xNi	$-\Delta_{mix}H_m$	xNi	$-\Delta_{mix}H_m$	xNi	$-\Delta_{mix}H_m$	xNi	$-\Delta_{mix}H_m$	xNi	$-\Delta_{mix}H_m$
1514 K		1513 K		1513 K		1511 K		1408 K	
0.000	48.111	0.000	41.378	0.000	47.295	0.000	36.468	0.000	58.967
0.071	45.287	0,079	39.314	0.069	44.666	0.073	35.366	0.061	53.250
0.136	42.206	0.148	37.290	0.135	41.729	0.139	34.290	0.115	48.156
0.195	39.292	0.208	35.126	0.195	38.817	0.202	32.614	0.168	43.322
0.249	36.469	0.261	32.913	0.251	36.031	0.256	30.977	0.234	37.662
0.296	33.997	0.351	29.048	0.299	33.468	0.303	29.338		
0.338	31.629	0.387	27.198	0.342	31.116	0.346	27.718		
0.376	29.503	0.420	25.485	0.381	28.992	0.384	26.276		
0.409	27.595	0.451	23.783	0.415	27.031	0.420	24.705		
0.442	25.750	0.478	22.253	0.446	25.293	0.483	21.902		
0.471	24.135	0.503	20.856	0.474	23.708	0.510	20.638		
0.497	22.630	0.527	19.563	0.499	22.278	0.535	19.511		
0.522	21.228	0.547	18.314	0.523	20.982	0.558	18.391		
0.546	19.935	0.567	17.143	0.545	19.808				
0.567	18.726	0.586	15.928	0.565	18.647				
0.587	17.470	0.605	14.904						
0.606	16.394	0.621	13.895						
0.623	15.477								

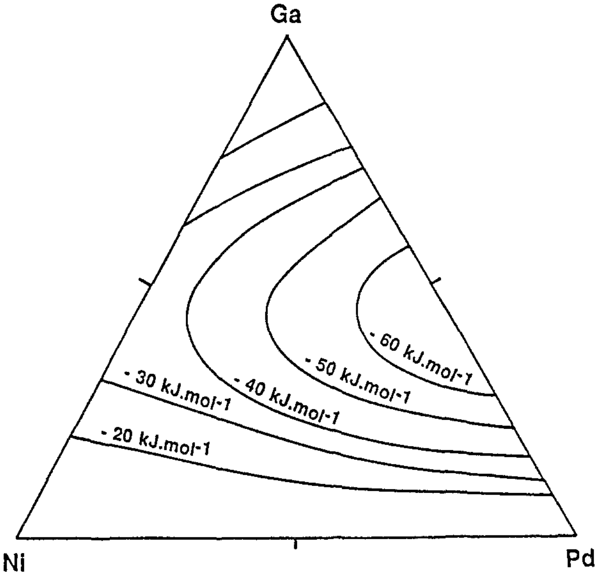

Fig. 1 $\Delta_{mix}H_m$,(Pd–Ni–Ga, liquid) = $f(x_{Pd}, x_{Ni}, x_{Ga})$. Isoenthalpic sections of the liquid Pd–Ni–Ga system determined on the temperature range 1400–1600 K

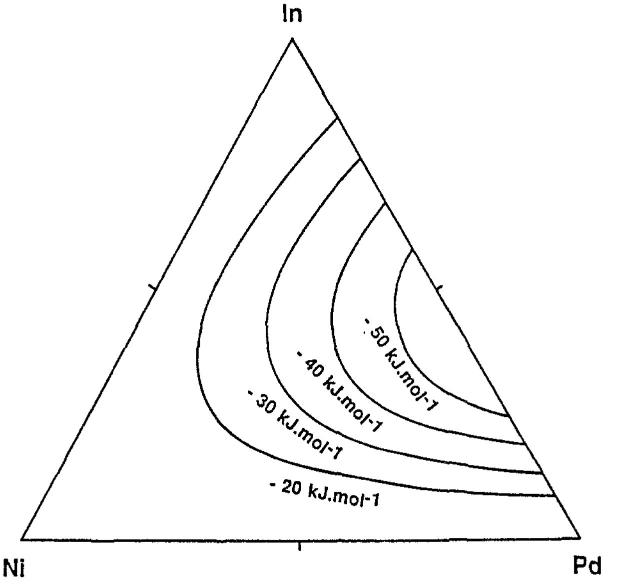

Fig. 2 $\Delta_{mix}H_m$,(Pd–Ni–In, liquid) = $f(x_{Pd}, x_{Ni}, x_{In})$. Isoenthalpic sections of the liquid Pd–Ni–In system determined on the temperature range 1400–1600 K

Conclusion

By calorimetry at very high temperature, it has been possible to determine the enthalpies of formation of the Pd–Ni–Ga and Pd–Ni–In ternary liquid alloys between 1400 and 1600 K, on the whole composition range. The complete automation of the calorimeter led to a good precision even at the highest temperatures. As in the limiting binary systems, enthalpies of formation are negative and non temperature dependent ay any composition.

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Zusammenfassung — Um die Lücke hinsichtlich thermodynamischer Daten von Nickel–Palladium–Gallium und Nickel–Palladium–Indium Legierungen zu füllen, wurden die Bildungsenthalpien dieser ternären Systeme im flüssigen Zustand bestimmt. Dies erfolgte mittels eines Kalorimeters für sehr hohe Termperaturen (T < 1800 K), unter Verwendung der direkten Einwurfmethode auf der Basis früher veröffentlichter Messungen an den entsprechenden binären Systemen. Die Bildungsenthalpien der flüssigen ternären Legierungen wurden zwischen 1400 und 1600 K über den gesamten Zusammensetzungsbereich bestimmt. Vollständige Automation des Kalorimeters bewirkte hohe Präzision selbst bei den höchsten Temperaturen. Wie in den begrenzenden binären Systemen sind die Bildungsenthalpien negativ und bei allen Zusammensetzungen nicht temperaturabhängig.